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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 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 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.

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, in the presence of a suitable alcohol not substantially in excess of 3% calculated on the amount of hydrocarbon present in the final product.

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 appreciable segregation of suspended particles should occur. This, as a rule, may be accomplished by agitation or by the procurement of finest dispersion of saponification agent in the hydrocarbon to be solidified and preferably with the aid of a suitable dispersion device such as a colloid mill, ball mill or the like. Alternatively, segregation of suspended particles may be avoided 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, in which case agitation may be discontinued once the viscosity of the mix and the particle size of suspended saponification agent

are thusly coordinated. In general, the product obtained when the saponification reaction is permitted to proceed in at least the last stages thereof while the reaction mix is in substantially quiescent condition possesses superior characteristics, inter alia, with respect to homogeneity and compactness, as compared with a product obtained from a reaction mix agitated during the entire saponification reaction or at least during the last stages thereof. Though the more compact product is normally preferred, special considerations and circumstances may make it desirable to procure a product of the type obtained with agitation during the last stages of the saponification reaction.

In some cases it is of advantage to initiate or expedite the saponification reaction by heating the hydrocarbon solution containing the reactants 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 higher temperatures must be resorted to. In most cases, once the saponification reaction has been satisfactorily initiated the heating may be discontinued. 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 aforementioned type in accordance with the invention may comprise either a resin acid salt or a free rosin acid, of, for instance, the type of abietic acid. If the same is a free acid, the saponification reaction is one of neutralization of the acid with the saponification agent. On the other hand, if the same is a salt, the saponification reaction is one of double decomposition between the resin acid salt and the saponification agent. In many instances, a commercial form of rosin acid may be used such as, for instance, rosin.

Wherever reference is made herein to the term "rosin acid" the same is used generically, and is intended to embrace any one or more rosin acids either as such, or in their commercial form or forms.

The saponification agent in accordance with my invention may be any agent capable of neutralizing or entering into a metathetical reaction with the rosin or rosin acid, as the case may be, present in the hydrocarbon solution. Good results are preferably obtained with hydroxides and alcoholates and suitable saponification agents of

this type are, for example, sodium hydroxide, sodium alcoholates and the like.

In some cases I prefer to suspend the saponification agent in substantially anhydrous pulverulent finely dispersed form in the solution containing the organic acid with the use of a colloid mill or other device for procuring finest dispersion. This may be accomplished by either dispersing the dry saponification agent as such in the hydrocarbon solution of the rosin acid 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 adding such dispersion to the other part of such hydrocarbon in which the rosin acid has been dissolved. It is also sometimes of advantage and desirable to initiate or expedite the saponification reaction by passing the reaction mix through a colloid mill or other device for producing finest dispersion. Such dispersion device may be also of advantage to procure finest dispersion in the case where a preliminary dispersion of the saponification agent in a hydrocarbon solution is used.

When using alcoholates they are preferably the metal salts of monohydric and polyhydric alcohols carrying the hydroxy 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.

In accordance with the invention, from .25 to 3% alcohol and preferably from .5% to 1.5% calculated on the amount of hydrocarbon present gives satisfactory results. The alcohol may be added either before or after the addition of saponification agent. The reaction mix should be well agitated while the saponification reaction takes place at least until the gel formation has reached a point as hereinabove stated at which the viscosity thereby imparted to the hydrocarbon solution is sufficient to substantially maintain the dispersed saponification agent in suspension upon discontinuing the agitation. Agitation may be continued to the point of complete saponification of the rosin acid or salt should, for any reason, such procedure be desired or should such be required to obtain a product having the characteristics peculiar to one obtained in this manner.

For practical purposes the alcohol addition may be effected by way of a portion of the hydrocarbon solution. Thus, for instance, a portion of the hydrocarbon to be solidified is admixed with the alcohol while another portion is prepared containing the reaction products as, for instance, a suitable rosin and finely dispersed saponification agent. It is then only necessary to intermix

both these hydrocarbon products to procure solidification. This, as is well understood, offers certain advantages for industrial production.

The amount of reagents used within the practical application of my invention should be preferably so adjusted that the organic compound and the hydrocarbon 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% of rosin acid or salt 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.

In the majority of cases the amount of alcohol introduced as crystal alcohol when using alcoholates is sufficient to expedite the saponification reaction to the desired extent. In some cases, however, it may be desirable to have a relatively small amount of free alcohol, i. e., alcohol not present in bound form, such as crystal alcohol, so as to at least initiate the saponification reaction whereby the further amounts of alcohol are liberated from the alcoholate to serve this purpose. In all cases, however, care should be taken that the total amount of free alcohol ultimately present in the solidified product upon completion of the saponification reaction is not substantially in excess of 3%. This is critical in view of the fact that higher percentage contents of alcohol may impair the characteristics of the finished solidified product, as such excess alcohol content may result in a liquification or partial liquification of the product upon heating or when burning. The amount of alcohol present in accordance with the invention, i. e., not appreciably in excess of about 3%, is at no time sufficient to interfere with the effective formation of insoluble soap gel and thus solidification of the hydrocarbon material.

The alcohol to be used in accordance with the invention for expediting the saponification reaction or bringing the same to the desired completion is preferably a primary aliphatic alcohol. The amount of this alcohol to be used may vary with the particular alcohol and depends, inter alia, upon considerations of solubility. The alcohol should be one in which the saponification agent is at least limitedly soluble. I prefer to use a substantially water soluble alcohol of the aliphatic series such as methyl or ethyl alcohol. The procedure in accordance with the invention is exemplified in the following example.

Example

A 5% rosin solution in a petroleum hydrocarbon cut of a boiling range of 145 to 210° F. was prepared. 1.88% by weight of methyl alcohol and 1.5% by weight of substantially anhydrous sodium hydroxide were added to the rosin solution. The sodium hydroxide was added in finely pulverized form and kept in fine suspension in the rosin solution by means of agitation. Pulverization was carried out mechanically in a mortar in the presence of a portion of the hydrocarbon. Agitation was maintained until the gel formation had proceeded to a point of desired viscosity to prevent segregation of particles of saponification agent. The reaction mass was then poured into fuel containers within which it solidified without

any further manipulation. Solidification proceeded rapidly.

In a further example the same procedure was followed as hereinabove described. In this case, however, agitation was continued until the end of the saponification reaction. The resulting product was of somewhat slushy consistency but when left quiescent solidified to form a substantially solid cake. This product, as compared with the one obtained permitting the saponification to go to completion with the mix in a substantially quiescent state, is softer, less homogeneous and compact. Instead of adding, as set forth in the hereinabove recited example, the alcohol to the rosin solution, it is possible and sometimes of advantage to add the alcohol to the rosin solution after the saponification agent has been dispersed therein. This practice is particularly recommended in cases, where, as hereinabove outlined, the viscosity of the rosin solution is so coordinated to the particle size of suspended saponification agent that a substantially stable dispersion maintains. Such a rosin solution containing dispersed saponification agent may be left quiescent or may even be stored for lesser or greater periods of time depending upon its stability, to be drawn upon as required. Thus such a solution may serve as a stock solution. The addition of the required amount of alcohol to such solution, with or without heating as may be necessary, will then cause relative speedy reaction between the reactants in the solution and resultant solidification. In a majority of cases, however, when using rosin and NaOH as the reactants the reaction will proceed without the necessity of heating the reaction mix.

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 liquefy when subject to raised temperatures and will burn without melting. The products are further characterized by the fact that the normally liquid hydrocarbon materials which they contain may be recovered in substantially unadulterated form by the application of pressure, centrifugal manipulations, 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 hydrocarbon is but limitedly soluble or substantially insoluble and in which the metallic soap is substantially soluble.

The products in accordance with the invention are further characterized by a considerable density and represent essentially a solid system predominantly composed of the hydrocarbon material 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, of 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.

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

I claim:

1. Method for solidifying normally liquid inflammable hydrocarbons which comprises reacting a rosin solution 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 rosin to thereby form a voluminous metallic soap gel from limitedly soluble to insoluble in said hydrocarbon, in the presence of an aliphatic substantially water-soluble alcohol in amount not substantially in excess of 3% of the hydrocarbon.

2. Method for solidifying normally liquid inflammable hydrocarbons which comprises reacting a rosin solution in said hydrocarbon, in the presence of a substantially water soluble aliphatic alcohol, with sodium hydroxide suspended in said hydrocarbon in substantially dry pulverulent form, said alcohol being present not substantially in excess of 3% of the hydrocarbon.

3. Method for solidifying normally liquid inflammable hydrocarbons which comprises reacting a rosin solution in said hydrocarbon, in the presence of a substantially water soluble aliphatic alcohol of substantially not more than two carbon atoms, with sodium hydroxide, suspended in said hydrocarbon in substantially dry pulverulent form, agitating the mix at least until the viscosity imparted thereto by a portion of the rosin soap gel formed is sufficient to maintain the sodium hydroxide 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 alcohol being present in amount not substantially in excess of 3% of the hydrocarbon.

4. Method according to claim 3 in which said alcohol is methyl alcohol present in amount substantially from 0.25 to 1.5% of the hydrocarbon.

5. Method for solidifying normally liquid inflammable hydrocarbons which comprises reacting a rosin solution in said hydrocarbon, in the presence of a substantially water soluble aliphatic alcohol having substantially not in excess of two carbon atoms, with sodium hydroxide, suspended in said hydrocarbon in substantially dry pulverulent form and agitating the mix at least until the substantial completion of the saponification reaction, said alcohol being present in amount not substantially in excess of 3% of the hydrocarbon.

6. Method according to claim 5 in which said alcohol is methyl alcohol present in amount substantially from 0.25 to 1.5% of the hydrocarbon.

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