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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 hydrocarbon herein re-
ferred to are of the inflammable type and are
preferentially 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 ordinari-
ly contain numerous hydrocarbons, the term
"hydrocarbons" as used herein includes the limit-
ing case in which only one hydrocarbon is pres-
ent. As a normally liquid hydrocarbon, for in-
stance, gasoline may be used, although a petro-
leum distillate of closer boiling point is preferred.
Also benzol or a light coal tar distillate consist-
ing predominantly of benzol homologues may be
used. The normally liquid hydrocarbons herein
mentioned are preferably for ordinary use readily
inflammable and preferentially then possess a
flash point not substantially above normal tem-
perature 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 hy-
drocarbons 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 hydrocar-
bon 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 saponi-
fication agent must be maintained substantially
stable during at least the quiescent stage of the
reaction, i. e., no appreciable segregation of sus-
pended particles should occur upon discontinu-
ance 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 qui-
escent and in the limiting case by a suspension of
particles of saponification agent of such fineness
that the same remain suspended substantially
without presence of soap gel. In any case, how-
ever, viscosity of the mix and particle size of
saponification agent must be so coordinated at

the beginning of the quiescent reaction stage that
no appreciable segregation of particles of saponi-
fication agent occur 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 obtains.

In some cases it is of advantage to initiate
or expedite the saponification reaction by heat-
ing the hydrocarbon solution containing the re-
actants for a short period of time to a tempera-
ture of above normal, or, alternatively, procure
the mixing of the reactants at such temperature.
Depending upon the reactants used, the temper-
ature 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
preferably substantially maintained at that tem-
perature 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.

In certain instances the saponification reaction
requires agitation to almost the point of com-
pletion so that the resulting product is more or
less lacking in the desired degree of homogeneity
necessary for a satisfactory solidified product.
This is particularly the case when the suspension
of saponification agent is not sufficiently fine to
be kept in suspension by the viscosity imparted to
the hydrocarbon solution with the first gel for-
mation or where the reaction between initial and
final gel formation proceeds so rapidly that no
satisfactorily quiescent state can be achieved for
the ultimate congelation. Alternatively, the agi-
tation may have been carried for other reasons
or even inadvertently by oversight too far to
permit quiescent last stage solidification.

I have discovered that from the granular prod-
uct of unsatisfactory homogeneity a satisfactory
solidified material may be obtained by the use
of a relatively small amount of alcohol.

In accordance with the invention, the granular
soap gel is heated slightly in the presence of a
relatively small amount of alcohol and there-
upon left quiescent to cool. The heating is car-
ried out at such temperature and for such time
as will serve to procure a saturated solution of

the soap gel in the amount of alcohol present. Upon cooling the thus precipitated soap gel will act as a cementitious agent cementing together the soap gel granules to form a solidified product of a high degree of homogeneity.

The alcohol used in accordance with the invention is preferably of the water soluble aliphatic type and should as such constitute at least limitedly a solvent for the metallic soap constituting the voluminous gel in the solidified hydrocarbon product. When alcohol has been introduced for instance by way of the saponification agent, as for example, when using alcoholates, or has been added by way of reaction booster, the same may suffice to produce the desired effect. Instead, however, of procuring the cementation of the granular particles, by way of heating the same in the presence of alcohol, it is possible to add a small amount of a hot separately prepared more or less saturated soap solution and have the entire mass thereupon congeal quiescent upon cooling. In any case, however, the hot granular gel should be permitted to cool in the presence of the alcohol.

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

Example

A granular solidified hydrocarbon product of unsatisfactory homogeneity and comprising substantially a solid system with about 6% sodium resinate and about 94% hydrocarbon of a boiling range of 145° to 210° F. was heated to about 125° F. in the presence of 1.0% of methyl alcohol for about 5 to 10 minutes. The mix was then permitted to cool while quiescent and a solidified product of satisfactory homogeneity was obtained. Instead of a product containing sodium resinate other granular products of unsatisfactory homogeneity such as those containing sodium stearate or a mixture of sodium stearate and sodium resinate may be substituted in the following procedure of the foregoing example.

The organic compound herein referred to is preferably an organic acid of the rosin acid, or the aliphatic acid type, the latter carrying at least one carboxyl group in aliphatic chain linkage, of preferably at least 12 carbon atoms in said chain. Aliphatic acids of this type 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 rosin or stearic acid or a mixture thereof may be used.

The saponification agent herein mentioned may be any agent capable of neutralizing the aliphatic acid 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 the saponification agent may be suspended 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 hydro-

carbon solution of the aliphatic 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 aliphatic 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 procuring 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 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, alcoholate formation is preferably obtained 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, it is preferable 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 in the preparations of the products as herein set forth and to which, when of unsatisfactory homogeneity my invention is applicable 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% in the aggregate of aliphatic acid and rosin will accomplish this result. The saponification agent should be present in amount sufficient to accomplish the saponification, which as a rule required 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. Depending upon this alcohol content, the alcohol liberated from metal alcoholate containing crystal alcohol may suffice as above pointed out for the cementation step in accordance with the invention. The amount of alcohol to be present or used for the cementation step in accordance with the invention depends at least to some extent upon the particular alcohol. In most cases, however, 5 and preferably 1 to 1.5% of alcohol give satisfactory results. Care should be taken, however, that the entire amount of free alcohol ultimately present in the solidified hydrocarbon product does not materially exceed about 3% calculated on the amount of hydrocarbon present. This is critical as alcohol contents appreciably in excess of 3% tend to deteriorate the qualities of the solidified product, particularly by way of causing partial liquefaction thereof upon heating or burning. The amount of alcohol present in accord-

ance 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. With amounts of 3% or less alcohol, however, no such liquefaction occurs.

The alcohol to be used 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. I prefer to use methyl or ethyl alcohol. In most cases from 0.5 to 1.5% of added alcohol will bring the saponification reaction to the point of desired gel formation. If alcohol is used as a reaction booster and it is desired to add additional alcohol, when proceeding in accordance with the invention, care should be taken as afore set forth that the total amount of alcohol present in the ultimate product does not appreciably exceed 3% of the hydrocarbon present.

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 liquefy when subject to raised temperatures and will burn without melting. The liquid material which they contain may be recovered in substantially unadulterated form by the application of pressure, centrifugal manipulations, distillation, or the like. Alternatively, the normally liquid 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 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 product in accordance with the invention with water.

The products in accordance with the invention are characterized by a considerable density and represent essentially a substantially solid system predominantly 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, 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 normally liquid 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 when heated but on the contrary will become increasingly more solid, 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 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 of making a substantially homogeneous solidified hydrocarbon product from a substantially granular non-homogeneous solidified hydrocarbon material which comprises heating such hydrocarbon material without substantial removal of hydrocarbon, said hydrocarbon material containing as solidificant a voluminous soap gel, being at least one member selected from the group consisting of higher aliphatic acid soaps and rosin soaps and non-melting when burning, and permitting said hydrocarbon material to cool while quiescent in the presence of a relatively small amount of alcohol not appreciably exceeding 3% by weight of the hydrocarbon present without substantial amounts of alcohol being removed during cooling.

2. Method in accordance with claim 1 in which said hydrocarbon material is heated and permitted to cool while quiescent in the presence of .5 to 1.5% of alcohol by weight, based on hydrocarbon present of the water soluble aliphatic type.

3. Method in accordance with claim 1 in which said hydrocarbon material is heated and permitted to cool while quiescent in the presence of .5 to 1.5% of alcohol by weight, based on hydrocarbon present, selected from the group consisting of methyl alcohol and ethyl alcohol.

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