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METHOD OF PREPARING NONAQUEOUS CARBON DISPERSIONS

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This invention relates to dispersions of amorphous forms of elemental carbon in inert organic liquids and to their preparation.

Dispersions of amorphous carbons in finely divided form in liquids are useful for many purposes and especially as high heat value fuels. The present invention is concerned with the preparation of dispersions suitable for such uses and which are characterized by their excellent stability and ease of preparation.

It is an object of the invention to provide improved fluid dispersions of finely divided amorphous, elemental carbon in inert organic liquids, particularly dispersions in hydrocarbon liquids such as mineral oils. Another object is to provide a method for preparing such dispersions in a form in which the dispersed carbon particles are stable against settling. Still further objects of the invention will be apparent from the ensuing description.

The above objects are accomplished in accordance with the invention by forming in an agitated body of the inert liquid into which the carbon is to be dispersed, an alkali metal soap of a higher fatty acid and then agitating the resulting mixture with the finely divided amorphous carbon. The carbon may be added to the inert liquid before or after the formation of the soap therein. The presence of the soap in such compositions effectively hinders or entirely prevents settling of the carbon particles.

One effective and preferred way of preparing the present compositions is to add to an agitated mixture of the inert liquid and the carbon at ordinary temperature, an alkali metal in finely dispersed form and a higher fatty acid. The metal and the acid react rapidly to form the required soap. When using finely predispersed alkali metal, the carbon dispersion can be made satisfactorily by mixing the inert liquid and carbon in an open vessel and adding the acid and metal thereto with ordinary agitation as is provided by an ordinary laboratory type stirrer.

If massive alkali metal is used, it is necessary to prepare the dispersion at a temperature above the melting point of the metal and to use much more vigorous agitation to effectively disperse the alkali metal. For this purpose equipment similar to that described and illustrated in my copending applications Serial Nos. 767,666 and 767,667, filed August 8, 1947 and issued November 3, 1949 as Patents 2,487,333 and 2,487,334, respectively, is suitable. This equipment consists of a cylindrical vessel of about 1 qt. capacity having a conical bottom and two $\frac{1}{8}$ " pipe connections near the bottom. The inlet and outlet of

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a small gear pump (Viking) are joined to these pipe connections. Inside the vessel, the pipe from the outlet of the pump is extended to about the apex of the cone and is provided at its discharge end with a nozzle having an orifice outlet of about $\frac{1}{8}$ to $\frac{1}{2}$ " in diameter. The pump is driven by an air motor through a belt and pulley system. Operation of the pump circulates material from the vessel through the pump and back into the vessel. The passage of the contents of the vessel through the orifice mentioned causes effective mixing. Circulation at a linear orifice velocity of about 100 to 1,000 ft. per second is generally satisfactory. Preferably, the stream of material from the orifice is directed against a splash plate or baffle positioned a short distance, e. g., $\frac{1}{4}$ " from the orifice, which plate functions to break up the stream. The entire pump and vessel assembly is immersed in a bath for heating and temperature control. A cover for the vessel and an inert gas blanketing system may be provided if desired, as may also heaters and controls for the surrounding bath.

In one manner of operation, the vessel is charged with the finely divided carbon and the inert liquid. Thorough mixing is accomplished by operation of the pump and then with the pump still running the reactants from which the soap is to be made are added separately so that the soap is formed in situ. Alternatively, the carbon can be added to the system after the soap has been formed, or after one of the soap-forming reactants has been added. In any case, after all the required ingredients have been added the resulting mixture after thorough agitation is withdrawn from the vessel for use or storage as desired.

Another suitable form of apparatus is that illustrated and described in my U. S. Patent 2,394,608.

The term "alkali metal" is used herein to include lithium, sodium, potassium, rubidium and cesium. The term "higher fatty acid" is used to mean a fatty acid having at least 6 carbon atoms.

The invention is further illustrated by the following examples. In Examples 1, 2 and 3 the apparatus described and illustrated in my above-identified applications was used. In all the examples, all parts and percentages stated are parts and percentages by weights unless otherwise stated.

Example 1

300 parts of refined kerosene and 60 parts of sodium were charged into the vessel of the ap-

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paratus. The sodium was dispersed in finely divided form by operation of the pump while maintaining the charge at a temperature slightly above the melting point of sodium. 300 parts of petroleum coke of particle size ranging from 1 to 60 microns were added. There resulted a thin fluid suspension from which the coke particles tended to settle rapidly on standing. While continuing operation of the pump, 6 parts of oleic acid were added which immediately changed the mixture to a somewhat pasty consistency. Addition of 20 grams of kerosene gave a thick fluid mixture which contained 38.7% of suspended coke particles. The charge withdrawn from the vessel was thixotropic and could be poured readily upon shaking. The suspended particles exhibited substantially no tendency to settle upon standing, for about 6 months.

Example 2

37 parts of freshly cut sodium and 496 parts of straight-run Venezuelan gas oil were charged to the vessel of the equipment and circulated at 105° C. to effect dispersion of the sodium. With continued circulation 243 parts of petroleum coke having a particle size of 1 to 60 microns were added in small increments. The carbon distributed easily but settled readily as soon as circulation was discontinued. 12 parts of lauric acid were then added in small amounts with continuous circulation to facilitate completion of the soap-forming reaction and distribute the soap uniformly as formed. The charge upon withdrawal was fluid and of uniform consistency, contained about 31% dispersed carbon and showed no tendency to settle after standing unmolested for 3 days.

Example 3

14 parts of ground petroleum coke particles of size ranging from less than 1 micron in diameter to irregularly shaped particles about 30 x 90 microns and 665 parts of an industrial white oil were charged to the vessel of the apparatus and the mixture circulated for 15 minutes at 105° C. A sample was withdrawn and allowed to stand at room temperature. After 24 hours, the larger carbon particles had settled to the bottom of the container and after three days substantially all of the particles had settled to the bottom.

To the remainder of the charge in the vessel, an amount of sodium equal to 1% of the weight of the contents of the vessel was added in the form of a 33% suspension of finely divided sodium in white oil. The charge was circulated during this addition and during the remainder of the run. 10.2 parts of lauric acid were then gradually added and the resulting soap was thoroughly distributed by the circulation. Withdrawal of the charge gave a mixture having a uniform and fluid consistency resembling that of the white oil used. The dispersed carbon showed no tendency to settle after 3 days of standing.

Example 4

460 parts of industrial white oil and 20 parts of oleic acid were placed into a metal beaker. While agitating the mixture moderately with an ordinary laboratory mechanical stirrer, 500 parts of petroleum coke finer than 120 mesh were added in 10 minutes. 3.6 parts of metallic sodium dispersed in finely divided form in about an equal amount of white oil were then added in two increments. The sodium dispersion used was prepared by the method of my co-pending application Serial Number 767,666, employing as a dispersing

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agent for the sodium a carbon-soap adsorption binary prepared using an industrial colloidal carbon of 10-35 millimicrons particle size. 20 parts more of oleic acid were then added. The contents of the beaker were subjected to moderate agitation by means of the stirrer during all of these additions and for a short time thereafter. The entire operation was carried out at ordinary temperature. The resulting dispersion had a thick consistency but could be poured. It appeared to be completely stable towards settling.

Any of the higher fatty acids, whether saturated or unsaturated, and having either a straight or branched chain structure, can be used effectively for the preparation of the alkali metal soap in practicing the present invention. Examples of such acids are: hexoic, diethyl acetic, heptoic, octoic, nonoic, capric, undecylic, lauric, myristic, palmitic, margaric, stearic, arachidic, cerotic, melissic, oleic and erucic acids.

The alkali metal soap required in practicing the present invention can be formed in situ by reaction of an acid of the above type with an alkali metal or an alloy of two or more alkali metals, or with an alkali metal derivative such as an alkali metal alcoholate or amide or the like. Any alkali metal derivative which is reactive with such an acid under the conditions of use to produce an alkali metal soap in situ can be employed in practicing the present invention. The use of an alkali metal such as sodium is preferred.

To be effective, the soap should be formed in situ. The soap may be prepared before, during or after the finely divided particles of carbon are added; or, the carbon may be added after either of the soap forming reactants is added. The order of addition is not critical. The concentration of soap, to be effective, should be at least 0.05% of the weight of the final mixture. A concentration of about 1 to 3% is preferred but amounts as high as about 5% may be used. In general, if amounts greater than 5% are used, non-fluid compositions result. The acid and alkali metal will generally be used in approximately stoichiometric proportions but a slight excess of either is permissible.

Dispersions containing any amount of dispersed carbon up to the point where the composition will no longer behave as a fluid, i. e., can be poured or pumped, may be readily prepared. When fluid compositions, i. e., those which may be poured upon shaking, are desired the concentration of carbon generally will not exceed about 60%. For most purposes the concentration of carbon will not be lower than about 1% although products containing smaller concentrations may be readily prepared. A carbon concentration of 20 to 50% is preferred for some purposes.

Any type of amorphous elemental carbon may be dispersed in accordance with the invention. For most uses, dispersions of carbon of particle size in excess of 200 microns and generally in excess of about 100 microns, are not desired. However, if desired, carbon particles somewhat above 200 microns in size may be dispersed by the present method. Of course, carbon of any size less than 100 microns may be readily dispersed. With very finely divided carbons, the amount that can be dispersed and still obtain fluid products is smaller than when using coarser carbon.

The present dispersions can be prepared over a wide range of temperatures, e. g., from ordi-

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nary temperature up to about 150° C. When using an alkali metal in non-dispersed form as one of the soap-forming reactants, operation at a temperature between the melting point of the alkali metal and about 150° C. gives good results. Temperatures below the melting point are entirely satisfactory when the metal is used in a finely divided predispersed form.

Any organic liquid which is inert towards the elemental carbon and towards the soap-forming reactants and which is also liquid and stable at the temperature of use, may be employed as the dispersing liquid. Mixtures of such liquids may be used. Examples of such inert liquids are: benzene, xylene, toluene, various petroleum solvents such as kerosene, straight-run gas oil, white oil and the like; and the alkali metal-stable ethers such as di-n-butyl ether and methyloleylether. Mineral oils are generally preferred.

Agitation during the formation of the dispersions is important, particularly during the soap-forming stage and thereafter, if the carbon being dispersed is added after the soap has been formed. Preferably the system is effectively agitated during the entire operation. Agitation may be effected by any desired method. The pumping systems described and illustrated in the patent and pending applications referred to above are effective and various well-known types of colloid mills, pumps and mechanical agitators may be employed.

Dispersions of carbon in mineral oils, e. g., fuel oil, prepared in accordance with the invention are valuable as fuels for various purposes due to their increased heat value per volume of material and to their stability against settling.

I claim:

1. A method of forming a fluid, non-aqueous composition comprising a dispersion of carbon particles ranging in size from 1 to 200 microns in an organic dispersing liquid, said composition containing 1 to 60% by weight of dispersed carbon particles, which method comprises reacting

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in an agitated body of said liquid a higher fatty acid with an alkali metal whereby an alkali metal soap of said higher fatty acid is formed in and uniformly distributed throughout said liquid in an amount corresponding to 0.05 to 5% of the total weight of the final mixture, and agitating a mixture of said carbon particles and said liquid containing said soap, said liquid being inert towards said carbon, said soap and said soap-forming reactants.

2. A method according to claim 1 wherein the soap is formed in the inert liquid before the addition of the carbon.

3. A method according to claim 1 wherein the soap is formed in said liquid after the addition of the carbon.

4. A method according to claim 1 wherein the alkali metal is sodium.

5. A method according to claim 1 wherein the soap-forming reagents are sodium and oleic acid.

6. A method according to claim 1 wherein the soap-forming reagents are sodium and lauric acid.

7. A method according to claim 1 wherein the inert liquid is a mineral oil.

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