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STABILITY OF FUEL OIL EMULSIONS CONTROLLED BY RESIN ASPHALTENE RATIO

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This invention relates to a method of reducing the tendency of liquid hydrocarbon oils such as crude petroleum oils or petroleum fuel oils therefrom, and the like to form stable emulsion with water.

Emulsions which form between liquid petroleum oils and water make difficult and undesirable problems. Emulsion sludges which form when water becomes mixed with petroleum oils are difficult to handle and to dispose of. Mechanical precautionary measures such as the use of centrifuges to remove and dispose of emulsion sludges are costly and have proven ineffective since such equipment requires frequent cleaning and even replacement of parts.

For example, the emulsion sludges formed when water becomes mixed with the petroleum fuel oil in ships' bunkers causes inconvenience in handling the fuel oil and also necessitates removing the sludge therefrom prior to burning the fuel oil. The conditions on board ships are such that some contamination of bunkers with sea water is, in practice, unavoidable, and this leads to the formation of emulsion sludge.

In those cases where the petroleum fuel oil is to be burned in diesel engines, the presence of excessive emulsion sludge in the said fuel oil causes the centrifuges, by means of which the oil is purified, to become overloaded. In extreme cases a ship may have to stop on the high seas during the cleaning of these centrifuges and associated equipment, and serious contamination of coastal waters occurs when these very stable emulsion sludges are jettisoned. Furthermore, in cases where petroleum fuel oils are used under boilers, the presence of excessive emulsion sludge in such oils often necessitates frequent cleaning of the pumping and atomizing equipment which is employed.

The reason for the formation of stable emulsions which are formed between water or other aqueous compositions and liquid petroleums such as crude petroleum oils or petroleum fuel oils, is not clearly understood. However, it has been observed that the weight ratio of petroleum resins to asphaltenes present in liquid petroleums is an important factor in controlling the formation of emulsions between oils and water.

It has now been discovered that the tendency of emulsion formation between water and oil can be substantially reduced or prevented by adjusting the weight ratio of petroleum resins to asphaltenes, so that the weight ratio of petroleum resins to asphaltenes in the oil does not lie between 1:1 and 4:1.

Throughout this specification, the term "petroleum resins" refers to those constituents of oils, such as crude petroleum oils or petroleum fuel oils, which are soluble in a mixture of n-octane and iso-octane at 100° C., and which are capable of being adsorbed upon magnesia at 100° C. from the resulting solution. The term "asphaltenes" refers to those constituents of crude petroleum oils or petroleum fuel oils which are precipitated from

the said oils when a mixture of n-octane and iso-octane is added thereto at 100° C., and which are soluble in hot benzene.

Thus, although petroleum resins and asphaltenes can be obtained for addition to an oil or removed therefrom by various means, such as will be hereinafter described, only those petroleum resins and asphaltenes which come within the scope of the above definition are to be considered as determining whether the weight ratio of petroleum resins to asphaltenes is outside the range of between 1:1 and 4:1.

The present invention provides a method of preparing a crude petroleum oil or petroleum fuel oil having a reduced tendency to form stable emulsions with water, which comprises altering the weight ratio of petroleum resins to asphaltenes in solution in a crude petroleum oil or petroleum fuel oil, which has originally a weight ratio of petroleum resins to asphaltenes of between 1:1 and 4:1, in such a way that the aforesaid weight ratio falls outside the range of between 1:1 and 4:1.

Adjustment of the weight ratio of petroleum resins to asphaltenes as described, in order to reduce the tendency toward emulsion formation, can be made to any liquid petroleum products such as crude oils, various fractions and mixtures thereof including heavy fuel oils, such as high ash residual fuel oils, diesel oils containing residual components, or mixtures of said oils with other liquid fuel oils such as distilled or cracked hydrocarbon fuel oils.

One method of effecting the aforesaid alteration comprises adding to the crude petroleum oil or petroleum fuel oil such an amount of either a petroleum resin or an asphaltene that the weight ratio of petroleum resins to asphaltenes in the product does not lie between 1:1 and 4:1.

The petroleum resin or the asphaltene which is added to the crude petroleum oil or petroleum fuel oil may be a substantially pure resin or asphaltene, but may also be a resin or asphaltene mixed with heavy oils or other contaminants.

Thus, if the desired weight ratio of petroleum resins to asphaltenes is to be altered by addition to the oil of a petroleum resin thereto, any petroleum resin, for example those possessing a penetration value between 20 and 190 at 25° C. may be employed in this invention. Petroleum resins which may be employed may be obtained from a wide range of petroleum oils, for example aromatic distillate petroleum oils. Petroleum resins may be isolated from cracked petroleum oils such as unsaturated distillates, which distillates are obtained by cracking petroleum oils at high temperatures and low pressures and which have a specific gravity at 20° C. of from 0.84 to 0.86 and a boiling range of from 23° C. to 180° C. The petroleum resins which are employed may be obtained from petroleum oils by any known method, for example by subjecting the oils to solvent extraction with hydrocarbon solvents such as liquid propane or with aqueous phenolic solvents, followed by removal of the solvent by means of distillation. Petroleum resins which have been produced as residues from the distillation of certain crude petroleums, for example Miri, or which have been extracted from a solution of a petroleum oil in volatile petroleum spirits by adsorption on solid adsorbents such as magnesia may be used. Certain extracts from the solvent refining of lubricating oil distillates, for example furfural extracts, yield solid or semi-solid petroleum resins as residual products on straight distillation, and such petroleum resins may also be used.

If the ratio of petroleum resins to asphaltenes in an oil is to be altered to the weight ratio of this invention by addition of asphaltenes to the oil, any asphaltenes can be employed such as those obtained from petroleum oils,

from pressure tars obtained from petroleum oils or from residual asphalts by means of precipitation with suitable organic liquids. Suitable organic liquids which may be employed as precipitants are exemplified by volatile petroleum spirits such as gasoline fractions and petroleum naphthas, and by liquid propane, pentane and ethyl ether.

As an alternative to substantially pure petroleum resins and asphaltenes, petroleum fractions which have a weight ratio of petroleum resins to asphaltenes outside the range of from 1:1 to 4:1 may be employed in this invention, such as petroleum fuel oils. Thus, the method of the present invention may be applied to the blending of oils, such blending being conducted as either a batch process or as a continuous process. Thus, to a crude petroleum oil or petroleum fuel oil in which the weight ratio of petroleum resins to asphaltenes is between 1:1 and 4:1 may be added a quantity of a second crude petroleum oil or petroleum fuel oil which has an aforesaid weight ratio outside the range from 1:1 to 4:1. The said second oil is added in such an amount that the aforesaid weight ratio in the product does not lie between 1:1 and 4:1.

A further method comprises contacting the crude petroleum oil or petroleum fuel oil, in which oil the weight ratio of petroleum resins to asphaltenes is between 1:1 and 4:1, with a solid adsorbent for petroleum resins in order to adsorb petroleum resins from the oil in such an amount that the concentration of petroleum resins in solution in the said oil is reduced and the weight ratio of petroleum resins to asphaltenes in solution in the product is not greater than 1:1. Suitable solid adsorbents which may be employed in this modification of the invention include carbon, various inorganic oxides such as magnesia and bauxite, adsorbent earths and clays. Such solid adsorbents may be the activated type. Fuller's earth and acid-treated clays are very suitable.

Naturally occurring solid adsorbents which may be employed include the swelling type bentonite clays. Suitable synthetic solid adsorbents include the "synthetic zeolites," for example alumino-silicates and compounds of magnesia with silica.

The solid adsorbents which are employed may also contain small proportions of agents which assist the adsorption of petroleum resins thereon. The said adsorbents may also contain small quantities of acid or alkaline materials, for example lime.

Standard techniques may be employed to bring the solid adsorbent into intimate contact with the crude petroleum oil or petroleum fuel oil which is to be treated. For example, percolation and contact filtration techniques are generally suitable. The solid adsorbent may be added directly to the said oil, particularly when in the powdered condition, and may be allowed to remain in contact therewith until sufficient petroleum resins have been adsorbed from the oil.

From 1% to 30% of the solid adsorbent is preferably used in this method, calculated as a percentage by weight upon the weight of the crude petroleum oil or petroleum fuel oil which is subjected to treatment.

The solid adsorbent containing petroleum resins may then be removed from the resulting crude petroleum oil or petroleum fuel oil by any known method, for example by means of filtration or centrifugation.

The determination of the relative proportions of the petroleum resins and asphaltenes present in crude petroleum oils or petroleum fuel oils to which the present process may be applied, may be carried out by any one of the standard methods therefor, which methods are exemplified by the following procedure.

A quantity of the oil under examination is heated to constant weight under high vacuum at 100° C. The resulting residuum is cooled and weighed, and the petroleum resins are dissolved therefrom by digesting the residuum with a mixture of n-octane and iso-octane at 100° C. in the proportion of from 8 to 20 milliliters of said octane mixture per gram of residuum. The resulting liquid is filtered under an atmosphere of nitrogen gas to give a residue and filtrate.

The said residue, which comprises precipitated asphaltenes, is washed with a mixture of n-octane and iso-octane at 100° C. and is then extracted with hot benzene. The benzene is then removed from the solution so formed by means of evaporation, and the residue, which comprises the asphaltenes originally present in the oil under examination, is heated to 100° C. under high vacuum, is cooled and is weighed.

The said filtrate is evaporated by means of distillation under an inert atmosphere in order to remove the mixture of octanes therefrom, and the resulting residue is heated at a temperature of 100° C., is weighed and is redissolved in a mixture of n-octane and iso-octane. The solution so formed is allowed to percolate through magnesia at 100° C. in order that all the petroleum resins present are adsorbed thereon, after which the percolate is distilled. The resulting residue is weighed. The petroleum resins content of the original sample of the oil under examination is equal to the difference in weight between the two last-mentioned residues.

The following example illustrates one method by which the present invention may be carried out, and demonstrates the reduced tendency of the product to form stable emulsions with water. All parts and percentages therein recorded are parts and percentages by weight.

One part of a fuel oil having a Redwood I viscosity at 140° F. of 285 seconds, which fuel oil contained 9.9% of petroleum resins and 3.1% of asphaltenes and therefore possessed a weight ratio of petroleum resins to asphaltenes of 3.2, was added to 1 part of water. The fuel oil and the water were stirred together at 80° C. at a stirring speed of 2500 revolutions per minute for 15 minutes. The resulting mixture was centrifuged, and it was found that 7.8% of emulsion sludge was formed.

One part of a fuel oil having a Redwood I viscosity at 140° F. of 1360 seconds, which fuel oil contained 23.3% of petroleum resins and 2.2% of asphaltenes and therefore possessed a weight ratio of petroleum resins to asphaltenes of 10.6 was added to 1 part of water and the mixture was subjected to the same series of operations, under the same conditions, as the first mixture of oil and water. Only 1.9% of emulsion sludge was formed.

A fuel oil was then prepared by mixing equal quantities of the two above-mentioned fuel oils. The resulting fuel oil contained 16.2% of petroleum resins and 2.6% of asphaltenes and therefore possessed a weight ratio of petroleum resins to asphaltenes of 6.2. One part of this fuel oil was added to 1 part of water and the mixture was subjected to the same series of operations, under the same conditions, as the two previous mixtures of oil and water. Only 1.8% of emulsion sludge was formed.

The present invention is illustrated by the following further example, which example also demonstrates the reduced tendency of the product to form stable emulsions with water. All parts and percentages therein recorded are by weight.

One part of a fuel oil having a Redwood I viscosity at 100° F. of 900 seconds, which fuel oil contained 9.9% of petroleum resins and 3.1% of asphaltenes and therefore possessed a weight ratio of petroleum resins to asphaltenes of 3.2, was added to 1 part of water. The fuel oil and the water were stirred together at 80° C. at a stirring speed of 2500 revolutions per minute for 15 minutes. A stable emulsion was formed.

This emulsion was then centrifuged, which centrifuge treatment caused 42% of the water present in the emulsion to separate from the emulsion.

To a second sample of the same fuel oil was added 5% of petroleum resins, which petroleum resins had been precipitated from a quantity of a petroleum fuel oil by means of iso-octane. The sample then possessed

a weight ratio of petroleum resins to asphaltenes of 4.8. An emulsion comprising 1 part of the resulting fuel oil and 1 part of water was prepared in the same manner as that employed previously.

A quantity of this second emulsion equal to the quantity of the first emulsion centrifuged, was centrifuged under the same conditions and for the same time as was used previously. It was found that this treatment caused over 95% of the water which was present in the emulsion to separate from the emulsion.

We claim as our invention:

1. A method of preparing an emulsion-resistant liquid petroleum fuel oil containing a substantial amount not exceeding about 26% of petroleum resins and asphaltenes. which comprises altering the weight ratio of octane-soluble, magnesia-adsorbable petroleum resins and octane-precipitable, benzene-soluble asphaltenes in an oil in which said ratio is between 1:1 and 4:1 so that the weight ratio of the petroleum resins to asphaltenes is outside the ratio of between 1:1 and 4:1, respectively.

2. A method of preparing an emulsion-resistant liquid petroleum fuel oil according to claim 1 wherein the fuel oil has a Redwood I viscosity at 140° F. of not greater than 1360.

3. A method of preparing an emulsion-resistant liquid petroleum fuel oil according to claim 1, wherein the fuel oil has a Redwood I viscosity at 140° F. of from about 285 to about 1360.

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