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COMPOSITION OF AND METHOD FOR THE TREATMENT OF HYDROCARBON COMPOUNDS

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This invention relates to material for and the method of treating hydrocarbon compounds for the purpose of increasing the fuel value thereof, and for recovering fuel oil from waste hydrocarbon materials, or for increasing the fuel oil yield of various hydrocarbon compounds.

The invention is especially applicable to the treatment of fuel oil, bottom sediment, residuums from batch stills and heavy pressure stills, sludges, emulsions of petroleum, petroleum, slop oils and various hydrocarbon compounds which are at present considered to be largely waste materials or from which fuel oil is at present only recovered in small quantities with considerable expense.

Fuel oil is the residue of crude oil after the removal therefrom of the lighter distillates, and is therefore highly charged with carbon. The heavier hydrocarbon compounds in fuel oil have a tendency to separate out from the lighter oil and emulsify. They form permanent emulsions with water and will not permanently mix with the lighter compounds in the fuel oil. Ordinary facilities are inadequate for the proper atomization of such fuel oil, and hence much difficulty is experienced in its use due to the fact that these heavier hydrocarbon compounds cause carbon deposits on burner tips, furnace walls, grates, in stacks, and on boiler tubes. Further trouble is experienced by reason of the tendency of these heavier compounds to settle out in tank cars and in oil lines. They tend to coagulate and obstruct strainers and meters. If fuel oil is allowed to stand for any considerable time, these heavy masses will form a semi-solid mass in the bottom of a tank. Furthermore, the water content of fuel oil, which ranges from 2% to 7%, utilizes a considerable portion of the heat energy of the oil when the oil is being burned, thereby lowering the flame temperature and consuming some of the available heat of the oil.

The coagulated mass which forms in the bottoms of the storage tanks is commonly referred to as bottom sediment. Heretofore most of this bottom sediment has been waste product. It has heretofore been an expensive operation to recover any of the available fuel oil contained therein. The coagulated particles which form this bottom sediment distributed through the mass of fuel oil are not properly atomized in oil burners and are the cause of the carbon deposits, as hereinbefore pointed out.

The hot residuums from batch stills and high pressure stills contain considerable fuel oil, but heretofore it has only been with considerable difficulty and expense that the oil could be removed or these residuums be consumed by being mixed with other oil. Some of these residuums are solid or semi-solid masses and are frequently referred to as coke or floating carbon, and to be consumed advantageously must be mixed with heavy oil and after being mixed with oil, the mixture must be immediately burned or the residuums will settle out. Various hydrocarbon refuse in a refinery is emptied into sewers. These waste hydrocarbons are generally termed "slop oils." The available fuel oil content in this slop oil has heretofore been so difficult to extract that the slop oils are considered a waste product.

By the process of the present invention, I treat the hydrocarbon materials with a relatively small quantity of a material which, through some action, possibly catalytic in its nature, functions as a dispersing medium, breaks up the emulsified formations and deflocculates the minute particles of the heavier hydrocarbon compounds, thereby bringing the oil into a homogeneous state and preventing the further formation of emulsions therein. In breaking up the emulsions the water and dirt, such as oil silt, is released and is free to precipitate or rise to the top, depending upon the specific gravity of the hydrocarbon material being treated. The oil treated or recovered by the present process is permanently stable.

When fuel oil is treated according to the present invention, its vapor tension is decreased so that there is less loss due to evaporation. Because of the homogeneous nature of the oil and its being largely free of bottom sediment, the oil may be atomized to

better advantage with less steam or air, whereby more thorough and efficient combustion is secured. The treated oil will also clean the oil lines, strainers, meters, and burners of any coagulated formations and will keep them clean. This treatment of the oil, because it effects the removal of substantially all of the contained moisture, leaves a dry, snappy fuel.

The material which I use for the treatment of the hydrocarbon compounds consists of naphthalene in a powdered granular form, purified and treated with relatively small quantities of other substances which have the effect of holding it in its granular form and preventing the naphthalene from becoming crystallized or otherwise deteriorating.

According to this invention, seventy pounds of naphthalene are ground into powdered granular form and simultaneously subjected to the purifying action of air. This may be done for instance, by allowing the powdered naphthalene to fall through a column of air whereby it is brought into intimate contact with the air. The powdered naphthalene is then screened, preferably in an eighteen to twenty-two mesh screen, after which approximately one gallon of nitro-benzol or lemon colored oil of mirbane are thoroughly mixed therewith for a period of about twenty minutes. Then approximately three pints of white medicinal paraffine, or medicinal paraffine oil, and approximately two and one-half ounces of oil soluble red aniline are added thereto and mixed therewith until the various substances are thoroughly commingled. After the mixture has stood for approximately twenty-four hours, it is ready for use in the treatment of hydrocarbon compounds. It is desirable that the mixture should stand for at least twenty-four hours before it is used, but it is not injured by standing longer. As a matter of fact, it is improved by standing, so that it can be stored indefinitely until such time as it is needed in the treatment of hydrocarbon materials.

In the treatment of hydrocarbons, the naphthalene compound is added to the hydrocarbon. Generally speaking, approximately one pound of the naphthalene compound is used for every eight hundred to one thousand gallons of hydrocarbon material at normal atmospheric temperatures. The material is introduced into the hydrocarbon to be treated while the hydrocarbon is at normal temperatures and after the introduction thereof, the hydrocarbon material may be heated to the desired temperature in order to facilitate the reaction. The reaction will take place in the hydrocarbon material at atmospheric temperature, but considerable more time is required.

In practicing the invention, I prefer to heat the hydrocarbon material to approximately 120° F. The paraffine content in some fuel oils and other hydrocarbon substances melts at 120° F. while the asphalt content in some hydrocarbon materials melts at 118° F. If the hydrocarbon material is heated sufficiently to melt the asphalt or the paraffine, the naphthalene mixture can readily permeate the mass to effect the desired reaction. At this temperature, however, the hydrocarbon material is not heated sufficiently to drive off the lighter hydrocarbons which are held in suspension.

The effect of the treatment is to break up all emulsified formations, separating the water from the hydrocarbon compounds. The heavy hydrocarbons in these emulsions are deflocculated upon the breaking down of the emulsions and are held in suspension, thus producing a permanent homogeneous body of oil. The water is precipitated to the bottom of the treating tank while the homogeneous oil rises to the top.

In the treatment of fuel oil, practically all of the moisture is precipitated and practically all of the heavier emulsified hydrocarbons are broken up, whereby the fuel oil may be effectively atomized and burned without producing carbon deposits or smoke. In the treatment of tank sediment or bottom sediment, sludge or the like, water will accumulate at the bottom of the tank. The water as it accumulates should be drawn off, for if it is allowed to remain in the treating tank, a strata of emulsion above the water and below the oil will remain. If the water is drawn off this strata will be penetrated by the compound and under the mass action of the contents of the tank will be broken up throwing down additional water which in turn must be withdrawn. The separation of the oil from the water and the coagulated mass may be easily effected.

The treatment of the hydrocarbon materials may require several days, the length of time depending on the nature of the material being treated and the temperature at which the operation is carried out. Heating the hydrocarbon material accelerates the reaction, but the reaction will occur more slowly at normal temperatures.

In reclaiming sludge or bottom sediment in storage tanks or other heavy semi-solid masses of hydrocarbon, it is desirable to introduce oil into the mass prior to the introduction of the naphthalene compound. One satisfactory procedure is to first determine the number of gallons of sludge in the tank to be treated and to then add two or more gallons of oil for each gallon of sludge. One pound of the naphthalene compound should then be added for each eight hundred

or one thousand gallons of sludge and oil to be treated. After the introduction of the naphthalene compound the sludge and oil are heated to approximately 120° F. and held at this temperature for several hours, after which the mass should be allowed to stand for several hours or perhaps several days. At the end of this time, the moisture content may be withdrawn from the bottom of the tank while the oil which is recovered will rise to the top of the tank. It is, however, not necessary to mix the oil with the bottom sediment or sludge.

As a specific example of one application of the invention, the accumulated sediment in a crude oil tank was treated in accordance with this invention. The contents of the tank were first heated to 180° F., at which time the original gauge on the tank showed a depth of eleven feet nine inches. Two feet of water were drawn off after heating, leaving nine feet nine inches of stock in the tank. Samples were caught every two feet before treating with the following results:

	Per cent
Bottom sludge and water at 2'_____	98
Bottom sludge and water at 4'_____	60
Bottom sludge and water at 6'_____	25
Bottom sludge and water at 8'_____	20
Bottom sludge and water at 10'_____	2.4

The naphthalene content was thrown into the tank when the temperature was about 172° F. The tank was then closed and left to stand for fifteen hours, after which samples were taken every two feet with the following results:

	Per cent
Bottom sludge and water at 2'_____	80
Bottom sludge and water at 4'_____	1
Bottom sludge and water at 6'_____	2.8
Bottom sludge and water at 8'_____	1.2
Bottom sludge and water at 10'_____	1

After this analysis was taken additional naphthalene compound was introduced with the temperature of the tank at approximately 138° F. After standing approximately twenty-four hours, further analysis was made with the following results:

	Per cent
Bottom sludge and water at 2'_____	17
Bottom sludge (no water) at 4'_____	.2
Bottom sludge (no water) at 6'_____	.1
Bottom sludge (no water) at 8'_____	.1

The total time consumed for the treatment of the sediment was thirty-seven hours. The original sample was taken out of the tank before treating and showed 50% of moisture and the sample taken after treating showed 2% moisture. Water drawn from the bottom of the tank showed a trace of alkali while the final sample taken in the tank four feet from the bottom showed the oil to be both free of acid and alkali. The bottom two feet in the tank were drawn off and when the final sample was taken at two feet from the bottom, it showed 2.6% of bottom sludge.

From the foregoing it will be seen how a mass of sediment consisting very largely of bottom sludge and water was reclaimed into oil where the total bottom sediment content was less than 3%. This indicates a reclamation of a very material amount of oil which ordinarily could not be reclaimed, and which, under present practice, would be mixed with fuel oil from which it would eventually settle.

The above example is merely illustrative of one application of the invention. It has been successfully used in the treatment of all types of fuel oils and in the treatment of various bottom sediments, and in the treatment of oil slop and sweetened cake and crude oils. The oil which has been treated or recovered according to the present invention remains permanently free of heavy sediment.

The invention has also been successful in the recovery of oil from tar which is obtained either as a coking plant by-product or from a gas producer. The treatment of tar of this nature is substantially the same as the treatment of fuel oil except that in the case of tar, the water rises to the top of the tar since it is the lighter element.

The invention may also be used in the treatment of various distillates of petroleum, such as gasoline or kerosene. The effect of the treatment, either on fuel oil or other petroleum is to develop the maximum B. t. u.'s and usually to lower the flash point.

Crude oil may be treated with the compound to break up the heavy hydrocarbons and effect the separation of water and salt therefrom. Bottom sediments from crude oil storage tanks may be treated the same as bottom sediments from fuel oil tanks and made to yield a large quantity of oil. Various grades of crude oils, particularly the lower and heavier grades can be advantageously treated.

When crude oil is treated according to my process, water, or salt water, is precipitated and with the precipitation of the water, such foreign matter as silt and dirt are separated out of the oil. Crude oil may be treated to good advantage at normal temperatures and heating thereof is not necessary.

I have found that by grinding the naphthalene and then exposing the powdered granular product to intimate contact with the air that more nearly uniform results are obtained than where the naphthalene is not brought into contact with the air.

I claim:

1. A material for the treatment of petroleum distillates and other hydrocarbons con-

sisting of naphthalene in powdered granular form and having relatively small quantities of lemon colored oil of mirbane, paraffine oil and oil soluble red aniline mixed therewith.

2. A composition for the treatment of hydrocarbons comprising naphthalene, nitrobenzol, white paraffine oil and oil soluble red aniline.

3. A compound for the treatment of hydrocarbons comprising powdered naphthalene to which has been added lemon colored oil of mirbane in the proportion of one gallon of oil mirbane to approximately seventy pounds of naphthalene and having white paraffine oil and oil soluble red aniline mixed therewith.

4. A compound for the treatment of hydrocarbons comprising powdered naphthalene to which has been added lemon colored oil of mirbane in the proportion of one gallon of oil mirbane to approximately seventy pounds of naphthalene and having white paraffine oil and oil soluble red aniline mixed therewith, the white paraffine oil being added in the proportion of approximately three pounds of oil to seventy pounds of naphthalene, and the oil soluble red aniline being substantially in the proportion of two and one-half ounces of aniline to seventy pounds of naphthalene.

5. A process for treating hydrocarbons which consists in adding to the hydrocarbon a relatively small amount of powdered naphthalene mixed with oil of mirbane, white paraffine oil and oil soluble red aniline.

6. A process for treating hydrocarbons which consists in adding to the hydrocarbon a relatively small amount of powdered naphthalene mixed with oil of mirbane, white paraffine oil and oil soluble red aniline, heating the mixture and then effecting a separation of hydrocarbon oils and water.

7. The method of treating hydrocarbon material which consists in adding naphthalene combined with oil of mirbane, paraffine oil and oil soluble red aniline to the hydrocarbon, heating the hydrocarbon material, and separating water therefrom.

8. The method of treating hydrocarbon materials which consists in powdering naphthalene, mixing oil of mirbane, paraffine oil and oil soluble red aniline with naphthalene and introducing the naphthalene so treated into the hydrocarbon material in the proportion of substantially one pound of naphthalene compound to each eight hundred to one thousand gallons of hydrocarbon material.

9. The method of treating hydrocarbon material which consists in powdering and aerating naphthalene, mixing the powdered and aerated naphthalene with lemon colored oil of mirbane, white paraffine oil and oil soluble red aniline, and thereafter introducing the naphthalene compound into the hydrocarbon material to be treated.

10. The method of treating hydrocarbon materials which consists in introducing naphthalene into the hydrocarbon materials, and protecting the naphthalene from crystallizing or deteriorating by adding thereto, oil of mirbane, white paraffine oil and oil soluble red aniline.

In testimony whereof I have hereunto set my hand.

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