PROCESS FOR PREVENTING EMULSION FORMATION BY ACIDIFYING WAS WATER

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This invention relates to stabilization of distillate fuel oils. More particularly, the invention relates to stabilization of fuel oils by acid treatment, neutralization and washing.

It has been found that sulfonic acid treatment of distillate fuel oils that normally tend to darken and/or deposit sludge during storage will substantially improve the stability of the oils. In order to render the acid treated or “sour” distillate fuel oils non-corrosive they are neutralized, following acid treatment and separation of acid sludge, with an excess of aqueous alkali. The oil and aqueous alkali phases are separated and the neutralized oil is subjected to an aqueous wash. The washed oil is then separated from the wash water and dried to the extent desired to produce a finished oil of improved stability. The treated distillate oil can also be redistilled to further improve its quality, if desired.

In the course of stabilizing distillate fuel oils as described above, it has been found that inadequate washing of the neutralized oils, caused either by inadequate admixture of oil and wash water or by the use of insufficient wash water, often results in reduced stability in the finished oils. Attempts to overcome this difficulty merely by the use of larger proportions of water during washing, with vigorous intimate admixture of oil and water, have generally resulted in excessive losses of oil due to emulsification. While washing losses can be avoided to some extent, when intimately admixing oil and water, by the use of relatively small water:oil ratios and a large number of washing stages, or by using a very large volume of wash water and a low degree of admixture of oil and water, these solutions to the problem are less than fully satisfactory for obvious reasons.

The present invention relates to an improved process for stabilizing distillate fuel oils that normally tend to darken in color and/or to deposit sludge during storage. We have discovered that distillates of good color stability and having reduced sludging tendencies can be produced without excessive washing losses, without the use of a large number of washing stages, and without the use of excessive volumes of wash water by the process of this invention. Briefly, this process involves treating a distillate fuel oil that is normally unstable on storage with sulfonic acid of a strength and in a proportion sufficient to improve the storage stability characteristics of the oil. Sour oil is separated from acid sludge and neutralized with an aqueous alkali in an amount in excess of that required to neutralize the acidity of the sour oil. Neutralized oil is separated from the aqueous alkali phase and subjected to intimate admixture with water that has been acidified with a minor proportion of a strong mineral acid. The water:oil proportion is at least 0.25:1 by volume. The washed oil is then separated from wash water to produce a distillate fuel oil of improved stability characteristics.

Referring briefly to the drawing, there is shown a simplified flow diagram of suitable apparatus in which our process can be practiced. A detailed description of the illustrated apparatus and its functioning will be found elsewhere herein.

The acid treating phase of the herein disclosed process can be accomplished by treating a normally unstable distillate fuel oil with sulfuric acid of sufficient strength and in sufficient proportion to effect a substantial improvement in the storage stability characteristics of the distillate oil. Fully satisfactory results have been obtained with 86 percent sulfuric acid, but acid of greater or lesser strength can be used. Normally, good results will be obtained with about 80 to 93 percent sulfuric acid. When treating times and temperatures are sufficiently low, even stronger acid, for example, 98 percent acid and fuming sulfuric acid can be used. It is not necessary that the acid be fresh; excellent results have been obtained with partially spent sulfuric acid that has been used in alkylation of olefins to produce “alkylate” gasoline. The proportion of acid with respect to the distillate fuel oil will normally vary with the nature of the oil. When treating distillate fuel oils that are very unstable either with respect to coloration and separation of acid sludge, or cracked distillate oils, it may be necessary to use up to forty pounds or more of acid per barrel of oil to obtain a high degree of improvement. Conversely, when treating oils that naturally possess fairly good stability characteristics, acid dosages of as little as 0.5 or 1 pound of acid per barrel can be sufficient to effect an improvement in the oil. For most distillate fuel oils acid dosages of about 3 to 30 pounds of acid per barrel of oil will be found to produce a substantial improvement in stability.

The acid treating step is carried out under conditions such as to improve the stability of the oil. Normally, acid treating will be carried out at temperatures of between about 60° and 130° F., and at treating times of about 0.25 to about 120 minutes, which temperatures and treating times will depend primarily upon the nature and viscosity of the fuel oil, acid strength, acid:oil proportions, the nature of the mixing apparatus, and the like.

Some contacting apparatus that will produce rapid and thorough admixture of acid and oil can be used. The contacting apparatus marketed by the Stratford Engineering Company is an example of a suitable acid:oil mixing means.

The sulfonic acid reacts with substances in the distillate fuel oil which normally act as sludge and dark color precursors and removes them into the oil-immiscible acid phase in the form of acid sludge. The acid sludge and any unreacted acid are then separated from the acid treated or sour oil, utilizing the inherent immiscibility of the acid and acid sludge and the fuel oil and the difference in the densities of the respective phases to effect the separation. Normally, the quicker the acid sludge is removed from the sour oil, the better the color of the finished oil. Centrifuging can be employed to obtain rapid sludge separation but good results can also be obtained by gravity settling, especially where the settling vessel is equipped with baffles, packing or the like that are designed to accelerate agglomeration.

Neutralization of the sour oil is effected with aqueous alkali. The aqueous alkali will usually consist of a water solution of caustic soda, but this is not essential, and other aqueous alkaline materials, e.g., potassium hydroxide and lithium hydroxide, can be used. The aqueous alkali is used in excess of the amount that is required to neutralize the acidity of the sour oil. Usually, between about 0.5 and 10 percent by volume of aqueous alkali will be sufficient. The concentration of the aqueous alkali can vary widely, for example it can vary from a strength equal to that of less-than-1° to 35° Bé, i.e., about 0.3 to 30 percent, preferably 0.5 to 15 percent, sodium hydroxide. Neutralization temperatures between about 60°
and 210° F. normally will be used for convenience and/or in order to minimize the viscosity of the oil, although higher temperatures can be used if desired. The neutralization reaction proceeds rapidly and only the period of time required for thorough intermixing of sour oil and aqueous alkali must elapse before separation. Again, suitable contact between sour oil and aqueous alkali can be effected in the conventional, commercial Stratford contactor.

After neutralization, the excess of unreacted aqueous alkali, containing dissolved and/or entrained inorganic salts, such as sulfates, is separated from the neutralized oil, utilizing the immiscibility and different densities of the respective phases to effect separation. Continuous gravity settling is suitable for the purposes of this invention.

After separating the neutralized oil from excess aqueous alkali, the former is subjected to a principal aqueous wash, using wash water that has been acidified with the minor proportion of a strong mineral acid. The principal washing stage is effected by highly intimate admixture of wash water and oil. Intimate admixture is accomplished by vigorous mechanical agitation of oil and water, whereby the wash water is reduced to a very small particle or droplet size, i.e., small enough that the water particles would ordinarily be capable of remaining suspended in the oil, or in variable size, emulsifiable size. This is done in order to approach maximum interfacial contact between oil and water. We have found that the desired degree of particle size reduction and liquid/liquid interfacial contact can be obtained by effecting admixture of the oil and water in a centrifugal pump, but other apparatus designed to produce an extremely high degree of intercontact between two normally immiscible liquid phases can be used. Emulsifiable particles are usually considered to be from about 0.001 to about 1 micron in diameter.

It will be appreciated that it is by virtue of the above-described intimate admixture of oil and water that adequate washing can be obtained with a relatively small volume of wash water. However, such intimate admixture tends to promote severe emulsification difficulties.

Normally, best results will be obtained by first washing the oil in the principal washing stage and then in one or more, preferably two, auxiliary washing stages, wherein the oil is washed with the water or aqueous:oil proportions and in the degree of admixture. Where a plurality of washing stages are employed, all but the principal wash can be effected with steam condensate condensed in contact with the oil instead of water as such. When using auxiliary washes, it is not necessary that the water used therein be acidified, this being essential only in the principal washing stage, since the severest washing losses and emulsification difficulties will be encountered therein. However, the water used in auxiliary washing stages can be acidified, if desired, with good results. It is not necessary that the principal washing stage be placed first in the series, when a series of washes is used, provided any preceding washes are operated under conditions that will not result in emulsification. Emulsification can be avoided in preliminary washes by maintaining the size of the water particles or droplets above emulsifiable size. It will be understood, of course, that washing solely by such methods is inefficient and incomplete unless extremely large volumes of water are used, which is objectionable for obvious reasons.

Any strong mineral acid can be used to acidify the wash water. By way of example, excellent results have been obtained with sulfuric acid. However, the invention can be used in connection with straight run fuel oil distillates, the storage stability problem with such oils is ordinarily not severe and the benefits of the invention will be proportionately limited when using these oils. No. 2 fuel oils are defined in the ASTM Standards on Petroleum Products and Lubricants published in November, 1954, under designation D396-48T.

In a specific embodiment of the invention, with particular reference to the drawing, a blended No. 2 distillate fuel oil consisting of 32 percent by volume caustic washed West Texas straight run fuel oil distillate, 28 percent by volume Thermofar catalytically cracked light catalytic cycle oil, and 40 percent by volume of fluid catalytically cracked light cycle oil, previously stored in a jacketed vessel (not shown) containing a heat transfer medium in the jacket, is pumped into the system through the pump 2, 2, through heat exchanger 4, in which the oil is heated or cooled, as needed, to the desired contacting temperature, for example, about 90° F. From heat exchanger 4, the oil passes through line 6 into mixing vessel 8. The oil is preferably dried before admixture with the acid, for example by filtering through rock salt in a vessel, not shown. Similar to filter 6 is filter 7. Sulfuric acid, for example 86 percent acid recovered from an alkylation unit, is pumped from storage, not shown, by displacement with transformer oil, through line 10 into mixing vessel 8. Vessel 8 can be a commercial Stratford contactor, as shown, a turbo-mixer. The latter is equipped with a centrally positioned shaft having turbo-mixer rotors mounted thereon. Turbo-mixer stators are positioned at the same height as the rotors on two stationary shafts.
The rotor shaft is rotated at, for example, 1000 r.p.m. The acid dosage is sufficient to effect an improvement in the storage stability characteristics of the oil, for example, 7.5±0.2 pounds acid per barrel of oil. The oil and acid are contacted in vessel 8 for an average of 50±4 minutes.

The sour oil-acid sludge mixture is removed from vessels 14 via line 12 into vessel 14, line 29 and identical vessel 14". Vessels 14 and 14" are provided with conical distributing baffles and are packed with approximately ¾ inch diameter rock, designated by numerals 16 and 16', to assist in separation of sludge from sour oil.

Aqueous caustic soda solution (e.g., 1 percent by weight) is continuously introduced into the system via line 26 and admixed with sour oil from vessel 14' and line 22 in contactor 24 in a proportion more than sufficient to neutralize the acidity of the sour oil, for example, 0.10±0.02 volume of caustic per volume of sour oil. The neutralization temperature is conveniently the temperature of the sour oil, or in this case about 40±5°F.

The neutralized oil and aqueous caustic and water containing unreacted caustic, water, and dissolved and entrained inorganic salts, is directed out of contactor 24, through line 28, through heater 30, into line 32 and thence into jacketed caustic settler 34. The oil-caustic mixture is heated in heater 30 to a degree sufficient to facilitate separation of the oil and aqueous phases in caustic settler 34. In this embodiment, a temperature of 160°±10°F. is used. Caustic settler 34 is provided with a jacket and a heat exchange medium is circulated through the jacket to maintain the desired settling temperature. Vessel 34, similarly as cone-bottomed water settlers 50, 60 and 76, is provided with inverted conical distributor baffles. Settled, partially spent caustic solution is withdrawn from vessel 34 by way of line 38. Neutralized oil is removed from vessel 34 by way of line 36.

Wash water that has been acidified by the addition of a strong acid in an amount more than sufficient to neutralize the residual basicity of the oil, for example, 0.01 percent sulfuric acid, is introduced into the principal washing stage of the system by way of line 86 and manifold line 90. The acidified wash water is preheated in heater 88, ordinarily to about the same degree as the oil from caustic settler 34, so as to facilitate separation of oil and wash water. In the present embodiment acidified wash water is passed through valve 92 into line 46 where it is intermingled with neutralized oil from line 36. Introduction of acidified wash water solely into the first washing stage is not essential, and if desired acidified wash water can be introduced into any or all additional washing stages, by way of valves 94 and 96 in the present embodiment. From line 46, the mixture of acidified wash water and oil is passed through a centrifugal pump mixer 48 to obtain a high degree of interfacial contact between oil and wash water and thence through the settler 50, which is similarly constructed as caustic settler 34. Wash water containing extracted impurities is settled out of the oil in settler 50 and withdrawn from the system through line 52. Once-washed and settled oil is passed overhead through line 54. The washed oil is then admixed either with additional acidified wash water from line 90 and valve 94, or as in the presently described embodiment, with non-acidified wash water which is introduced into the auxiliary washing stages of the system by way of line 40, heater 42, manifold 44 and valve 47. The water from line 40 is preheated to about the same degree as the acidified wash water. The oil and water are vigorously admixed in globe valve 56 and the mixture passes into vessel 60 for settling. In the present described embodiment vessels 60 and 70 and valves 45, 66, 72 and 96 function similarly as their counterparts in the previous stage.

The thrice-washed and settled oil is passed out of the last settler 70 through line 74, into salt filter chamber 76, filled with ¾ inch to ½ inch rock salt supported by a ¼ inch wire grid. Any entrained water in the fuel oil is settled out in the form of salt water in vessel 76, from which it can be drained periodically through line 78. Bright fuel oil having a light color and good stability characteristics is passed overhead through line 86, through cooler 82, and into line 84 to storage facilities not shown.

Distinct fuel oils obtained as described in the foregoing specific embodiment were tested for stability by a standard accelerated stability test. The accelerated storage stability test referred to in the description of this invention is carried out by heating 600 gram samples of the fuel oil composition being tested for periods varying from 16 to 64 hours at 210°F. in loosely stoppered, one-quart clear glass bottles. Following each heating period each test sample is cooled to room temperature and filtered by suction through tared, medium porosity tared glass Gooch-type crucibles. The sludge in each crucible is washed with heptane. The respective crucibles are then dried in an oven maintained at 210°F. for one hour, cooled in a desiccator and reweighed. The increase in weight is recorded as milligrams of sludge per 600 grams of oil. The color of the oil filtrates is recorded as ASTM Union color units. Using a rough rule of thumb based on experience, one hour of storage under the conditions of the accelerated test is equivalent to about ten days of storage under actual field conditions.

The results of the foregoing runs are presented below together with comparative test results obtained with the untreated No. 2 fuel oil stock and with two similar runs wherein non-acidified wash water was used.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Wash Charge Stock</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wash Water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>Water to First Washing Stage: Vol./Vol. Oil</td>
<td>1</td>
<td>1</td>
<td>0.3</td>
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<tr>
<td></td>
<td>Water to Second Washing Stage: Vol./Vol. Oil</td>
<td>0.2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Water to Third Washing Stage: Vol./Vol. Oil</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Yellow Vol. Percent of Charge</td>
<td>98.5</td>
<td>Emulsion</td>
<td>Emulsion</td>
</tr>
<tr>
<td>45</td>
<td>Finished Oil</td>
<td>0.4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Washing Loss</td>
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<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Oil to Sludge</td>
<td>1.0</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Inspection</th>
<th>Stability at 210°F.</th>
<th>Color</th>
<th>ASTM Union: Initial Filterate</th>
<th>After Aging</th>
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<tbody>
<tr>
<td>40</td>
<td>1.75</td>
<td>1.25</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>45</td>
<td>1.75</td>
<td>1.5</td>
<td>1.5</td>
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<tr>
<td>46</td>
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<td>47</td>
<td>1.75</td>
<td>2</td>
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<td>2</td>
</tr>
<tr>
<td>48</td>
<td>1.75</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>

* Acid water (0.02% H₂SO₄).

Non-acidic water washing in the principal washing stage resulted in such stable emulsions in that washing stage that the runs could not be continued, and no inspections on the product could be obtained. In contrast acidification of the principal washing stage in run 1 enabled the production of light-colored fuel oil distillate that exhibited greatly improved stability characteristics. Similar improved results are obtained when treating other distillate fuel oil blends of the kind disclosed herein with the same or equivalent amounts of other disclosed acids, when using a greater or lesser number of washing stages, when using other herein disclosed washing proportions, and when using steam instead of water in washing stages other than the principal stage.

When another sample of distillate fuel oil having the same make-up as that in the foregoing table was treated similarly as in the foregoing specific embodiment, but using non-acidified water and water:oil proportions of...
0.1:1, 0.2:1 and 0.2:1, in the respective washing stages, in other words insufficient proportions to cause emulsification and large washing losses under the conditions of intimate admixture employed, the ASTM Union Oil color of the oil went from 1.75 to 3.0 after 64 hours at 210°F, and the filterable sludge went from 1 to 15 milligrams per 600 grams of oil. A washing loss of 0.4 percent, based on the volume of the oil charged, was encountered.

Thus, as demonstrated by a comparison of runs 2 and 3 in Table A and the run described in the preceding paragraph, intimate washing in the principal washing stage with unacidified water in a relatively large proportion, i.e., about 0.25:1 or higher, will result in excessive washing losses, while similar washing with a relatively small proportion of wash water, i.e., less than 0.25:1, will result in poor stability of the oil. However, as demonstrated by run 1 in Table A, intimate washing of the oil in the principal washing stage with a relatively large proportion of acidified water, i.e., more than 0.25:1, will produce a finished oil of good stability without severe washing losses.

It will be understood that many variations of the foregoing process will occur to those skilled in the art, and such modifications of the invention can be practiced without departure from the spirit or scope thereof. Accordingly, we do not intend to be limited by the above-described embodiments but only by the scope of the appended claims.

We claim:

1. A process comprising contacting a distillate fuel oil that is normally unstable during storage with sulfuric acid of a strength and in a proportion sufficient to improve the storage stability characteristics of the oil, separating acid sludge from the acid treated oil and neutralizing the latter with an excess of an aqueous alkali solution comprising about 0.3 to 30 percent sodium hydroxide, separating neutralized oil with wash water in the form of droplets of emulsifiable size, said wash water having been acidified with a strong mineral acid in a proportion sufficient to produce an acidity equivalent to 0.0075 to 0.075 percent sulfuric acid, the water:oil ratio during said intimate admixture being from about 0.25:1 to about 2:1, and separating washed oil from wash water to produce a distillate fuel oil of improved storage stability characteristics.

2. A process comprising treating a mixture of catalytically cracked and straight run fuel oil distillates that is normally unstable during storage with sulfuric acid of a strength and in a proportion sufficient to improve the storage stability characteristics of the oil, separating acid sludge from sour oil and neutralizing the latter with an excess of an aqueous alkali, separating neutralized oil from the aqueous alkali phase and intimately admixing the former with wash water in the form of droplets of emulsifiable size, said wash water being acidified with a strong mineral acid in a proportion sufficient to produce an acidity equivalent to 0.0075 to 0.075 percent sulfuric acid, the water:oil ratio during said intimate admixing being from about 0.25:1 to about 2:1, and separating the washed oil from wash water to produce a distillate fuel oil of improved storage stability characteristics.

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