STORAGE OF HIGH BOILING DISTILLATE FRACTIONS

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21 Claims. (Cl. 21—60.5)

The present invention is directed to the storage of distillate fractions boiling in the range from about 300° to about 900° F. More particularly, the invention is directed to the storage of middle distillate fractions which have a tendency to form severe corrosion on metal surfaces on contact therewith in the presence of water.

The present invention may be described briefly as involving the storage of a distillate fraction boiling in the range from about 300° to 900° F. in which the fraction is maintained in contact with a ferrous metal surface and a body of water. The distillate fraction and the body of water have added to them, respectively, an oxidation inhibitor and a corrosion inhibitor, the distillate being maintained during storage in contact with a ferrous metal surface. By adding and/or maintaining in the distillate an oxidation inhibitor and in the body of water a corrosion inhibitor it is possible to eliminate substantially sediment formation in the distillate and corrosion of the ferrous metal in contact with the distillate and the body of water.

The fraction stored in accordance with the present invention may be a distillate fraction boiling in the range from about 300° to 900° F. which has a tendency to form sediment and corrodé ferrous metal in the presence of water on storage in contact therewith. The distillate may be either a gas oil or a heating oil fraction and consist of substantial amounts of cracked petroleum products. The cracked petroleum may make up as much as 100% of the distillate fraction on storage. The cracked fraction may be either thermally cracked or a catalytically cracked product and by virtue of the cracking operations may contain olefins and other materials which contribute to instability on storage.

The oxidation inhibitor finding employment in the practice of the present invention may be any of a large number of well-known oxidation inhibitors. For example, it may be an oxidation inhibitor, such as set out in the Downing et al. Patent 2,181,121 and which may be represented by the formula:

\[ \text{HO—A—CH=N—R—N=CH—A—OH} \]

wherein A represents an aromatic ring or an unsaturated heterocyclic ring of 5 to 6 atoms in which the hetero atom is nitrogen, the OH radical being attached directly to a ring carbon atom ortho to the —CH=N— group, and R represents an aliphatic radical having the two N atoms attached directly to different carbon atoms of the same open chain. R in the formula may also represent an aromatic group, a cyclo-aliphatic group containing 6 carbon atoms in the ring or a heterocyclic group containing a heterocyclic ring of six atoms in which the hetero atom is nitrogen, the two N atoms being separately attached directly to adjacent carbon atoms or to the most closely positioned ring carbon atoms of different rings, other than carbon atoms forming part of the linkage between the two rings. As exemplnary of this type of compound may be mentioned N,N'-disallyldienylidenone-1,2-diamino-propane. Other oxidation inhibitors finding use in the practice of the present invention are triti-butyln phenol, 2,4-buty1.4-methoxyphenol, 2,2-bis(2-hydroxy-3-5-buty1-methoxyphenyl) propane, petroleum phenols, nitro aromatics, 4,4-isopropyliden-bis(2-isopropyl)phenol, polyethenol resin amine, and many others.

The corrosion inhibitors finding usage in the present invention are the well-known aqueous corrosion inhibitors, such as sodium nitrite and sodium chromate. The oxidation inhibitor may be used in the petroleum distillate in an amount in the range from about 1 to about 15 lbs. of oxidation inhibitor per 1000 bbls. of petroleum distillate. The corrosion inhibitor may be used in the body of water in an amount in the range from about 100 to 2000 parts per million. When an alkali metal nitrite solution is used, a preferred amount is in the range between 400 and 2000 parts per million. When using an alkali metal nitrite corrosion inhibitor it is desirable to employ it in an alkaline solution having a pH in the range from about 8 to about 12. The pH may suitably be adjusted by addition to the body of water containing alkali metal nitrate a suitable amount of sodium hydroxide to bring the pH in the range given.

In order to illustrate the invention, a sample of heating oil was divided into five portions which were stored under the following conditions: One portion of oil was stored over water with no inhibitor being added either to the water or to the oil. A second portion had no inhibitor added to the oil, but 500 parts per million of sodium nitrite were added to the water. A third portion was stored with no inhibitor added to the oil and 500 parts per million of sodium chromate were added to the water. A fourth portion had N,N'-disallyldienylidenone-1,2-diaminopropane added to the oil in the amount of 10 pounds per 1000 barrels, and 500 parts per million of sodium nitrite added to the water. A fifth portion had N,N'-disallyldienylidenone-1,2-diaminopropane added to the oil in the amount of 10 pounds per 1000 barrels and the water had added with an iron strip across the interface. The results of inspection tests of all the samples both before storage and after 10 weeks of storage at 125° F. are shown in Table I.

<table>
<thead>
<tr>
<th>Oil Inhibitor</th>
<th>Water Inhibitor</th>
<th>Storage Tests After 10 Weeks</th>
<th>Metal Loss, Mgm. per 100 MIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>None</td>
<td>13.6</td>
<td>8.7</td>
</tr>
<tr>
<td>NaNO₂</td>
<td>NaCO₃</td>
<td>10</td>
<td>7.7</td>
</tr>
<tr>
<td>None</td>
<td>NaNO₂</td>
<td>9.4</td>
<td>7.7</td>
</tr>
<tr>
<td>10 lbs. per 1000 bbls</td>
<td>10 lbs. per 1000 bbls</td>
<td>10 lbs. per 1000 bbls</td>
<td>10 lbs. per 1000 bbls</td>
</tr>
</tbody>
</table>

1 N,N'-disallyldienylidenone-1,2-diamino-propane.

These data show that, when the heating oil was stored in the absence of any inhibitor, the deterioration was caused by total sediment and metal loss was quite severe, and that adding a corrosion inhibitor to the aqueous phase alone, although improving storage stability somewhat, still caused severe total sediment formation and metal loss. Storage with the inhibitor in the oil phase alone improved the metal loss appreciably, but caused nearly as bad a sediment as the entire absence of an inhibitor. Only the storage of the oil with inhibitor present both in the oil phase and in the aqueous phase produced satisfactory results as shown by no measurable metal loss and a total sediment of only 10 lbs. per 1000 bbls.

In order to illustrate the invention further a gas oil fraction was stored in a 55,000 bbl storage tank. This gas oil fraction was stored in the tank over a body of water. The gas oil fraction had added to it N,N'-disallyldienylidenone-1,2-diamino-propane in an amount of 10 lbs. per 1000 bbls. of gas oil. A second 55,000 bbl storage tank had stored in it gas oil which was also stored over a body of water. This gas oil had N,N'-disallyldienylidenone-1,2-diamino-propane added to it in an amount of 10 lbs. per 1000 bbls. of gas oil and the water had added

...
to it sodium nitrite in an amount of 0.2%. A third
55,000 bbl. tank of gas oil had N:N'-disalicylidene-1,2-
diamino-propane added in an amount of 10 lbs. per 1000
bbls. of gas oil and like the other tanks was also stored
over a body of water. This body of water had sodium
chromate added to it in an amount of 0.2%. These
tanks were left on storage for one month and then
sampled. In the following table comparative tests are
given for the total sediment content of the gas oil in the
several tanks after one month's storage.

**TABLE II**

<table>
<thead>
<tr>
<th>Plant storage in 55,000 barrel tanks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil Inhibitor</td>
</tr>
<tr>
<td>Amount, Lbs./1,000 Bbls.</td>
</tr>
<tr>
<td>Water Inhibitor</td>
</tr>
<tr>
<td>Amount, Percent</td>
</tr>
<tr>
<td>Tests: Total Sediment, After 1 Month</td>
</tr>
<tr>
<td>Storage, mgs./100 ml.</td>
</tr>
</tbody>
</table>

1 N:N'-disalicylidene-1,2-diamino propane.
2 Sodium Nitrite.
3 Sodium Chromate.

It will be seen from the foregoing results that the
N:N'-disalicylidene-1,2-diamino propane alone did not
reduce the total sediment but the N:N'-disalicylidene-1,2-
diamino propane and sodium nitrite and the N:N'-disali-
cyldene-1,2-diamino propane and sodium chromate both
reduced the total sediment substantially after one
month's storage. From these results it may be con-
cluded that the N:N'-disalicylidene-1,2-diamino pro-
pane and the corrosion inhibitor effect an improved
result over the N:N'-disalicylidene-1,2-diamino propane
alone.

The sediment test is determined by filtering the oil
and weighing the sediment recovered from the oil.
In order to show the effect of a corrosion inhibitor and an
oxidation inhibitor on sediment formation and corro-
sion, samples of gas oil were stored in the laboratory at
125° F. over a body of water with an iron strip main-
tained in the oil-water interface. One portion of oil
was stored over water and had no inhibitor added either
to the water or to the oil. A second portion had N:N'-
disalicylidene-1,2-diamino propane added to the oil but
nothing added to the water. A third portion had N:N'-
disalicylidene-1,2-diamino propane added to the oil and
sodium nitrite added to the water while the fourth por-
tion had N:N'-disalicylidene-1,2-diamino propane added
to the oil and sodium chromate added to the water.
These results are shown in Table III.

**TABLE III**

<table>
<thead>
<tr>
<th>Oil Inhibitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount, Lbs./1,000 Bbls.</td>
</tr>
<tr>
<td>Water Inhibitor</td>
</tr>
<tr>
<td>Amount, Percent</td>
</tr>
<tr>
<td>Tests: Total Sediment, mgs./100 ml.</td>
</tr>
<tr>
<td>After 4 weeks' storage, mgs.</td>
</tr>
<tr>
<td>Metal Loss, mgs./metal/100 ml. of oil,</td>
</tr>
<tr>
<td>after 4 weeks' storage.</td>
</tr>
</tbody>
</table>

1 N:N'-disalicylidene-1,2-diamino propane.
2 Sodium Nitrite.
3 Sodium Chromate.

It will be seen from the data in Table III that in the
oil which had been stored over water, and where the oil
contained an oxidation inhibitor and the water a corro-
sion inhibitor, the sediment was substantially reduced
after 4 weeks’ storage, whereas with N:N'-disalicylidene-
1,2-diamino propane alone the sediment was substan-
tially the same as in the sample without the inhibitor.

It will be noted also that the corrosion as determined as
loss of weight of the metal strip immersed in the oil-
water interface had been reduced to an immeasurable
quantity.

In this particular test the sediment test was determined
in the same manner as set out before.

Additional tests were made where a heating oil was
stored in a laboratory at 125° F. over a body of water.
Various portions of the heating oil which had a total
sediment of 5.0 milligrams per 100 milliliters and had a
metal loss of 5.37 milligrams of metal per milliliter of oil
was divided into 6 portions. To two of the portions
was added 2,4,6-tri-t-butylphenol in the amount of 10
lb./1000 bbls. The first of these portions was stored
over a body of water to which no corrosion inhibitor was
added. The second of these portions was stored over a
body of water to which 0.2% by weight of sodium nitrite
was added. A third and fourth portion had added to it
2,4-t-butyl-4-methoxyphenol in the amount of 10
lb./1000 bbls. The first portions having 2,4-t-butyl-4-
methoxyphenol added to it was stored over a body of
water which contained no corrosion inhibitor while
the second of the portions to which 2-t-butyl-4-methoxy-
phenol was added was stored over a body of water which
contained 0.2% by weight sodium nitrite.

A fifth and sixth portion had added to it 2,2-bis(2-
hydroxy-3,5-4-t-butyl-1-methoxyphenyl) propane in the
amount of 10 lb./1000 bbls. The fifth portion was then
stored over a body of water to which no corrosion in-
hibitor had been added while the sixth portion was stored
over a body of water which contained sodium nitrite in
an amount of 0.20 weight percent. In each case the
various portions were stored in contact with a forming
metal strip which was arranged to project into the oil
and into the water. In other words, it passed through the
oil-water interface. These several portions were then
placed on storage and samples withdrawn after 10 weeks'
storage and tested for total sediment formation.

Similar runs were made with other inhibitors such as a
polyethylene resin amine type, a nitro aromatic type, 4,4-
isopropylenide-bis (2-isopropyl)phenol, distilled petro-
leum phenols, and an unidentifed commercial inhibitor
sold under the trade name "Sustane" by the Universal
Oil Products Company. In each case a marked reduction
in the formation of sediment with total elimination of
measurable corrosion was effected.

From the foregoing data it will be seen that by the
practice of the present invention it is possible to store
middle distillates, such as gas oil and heating oil frac-
tions, in metal tanks in contact with a body of water so
that deterioration of the gas oil or heating oil does not
occur. In short the presence of unstable materials in
the gas oil or heating oil when practicing our invention
will not result in formation of corrosion inhibitors which
left to form may clog burner tips or result in corrosion
of metal surfaces with which the gas oil or heating oil
comes in contact. Thus the presence of an oxidation
inhibitor and a corrosion inhibitor is necessary only to
temporarily to obtain the beneficial results of our inven-
vention. Furthermore, it may be seen that the gas oil or
heating oil or other middle distillate may be stored at at-
mospheric temperatures, such as a range ranging from
about 40° up to about 100° F. or may be stored at even
higher temperatures, such as 125° F. or higher. This lat-
ter is important especially when considering the fact that
the air lubricating oil may be obtained at a low temper-
atures engines as a means for propulsion. Thus it is entirely
possible that middle distillates boiling in the range from
350° to 900° F. may be stored at high temperatures for
By adding an oxidation inhibitor to the oil and a corrosion inhibitor to the water over which the oil is ordinarily stored it is possible to alleviate the sediment problem and to eliminate the corrosion problem.

By way of explanation, the water which is found in the storage tanks in which gas oil and heating oil are stored, results from atmospheric moisture condensation and from processing operations by which the oil becomes substantially saturated with water which drops out on storage.

The nature and objects of the present invention having been completely described and illustrated, what we wish to claim as new and useful and to secure by Letters Patent is:

1. In the storage of a distillate fraction boiling in the range from about 300° to about 900° F. having a tendency to form sediment and corrode ferrous metals in the presence of water on storage in which said fraction is maintained in contact with a ferrous metal surface and a body of water, the step of maintaining simultaneously in said distillate a phenolic oxidation inhibitor in an amount in the range from 1 to 15 pounds per 1000 barrels of said distillate and in said body of water a water soluble corrosion inhibitor selected from the group consisting of the alkali metal nitrates and the alkali metal chromates in an amount in the range between 100 and 5000 p.p.m., whereby sediment formation in said distillate and corrosion of said surface is substantially eliminated.

2. A method in accordance with claim 1 in which said inhibitor is a petroleum phenol.

3. A method in accordance with claim 1 in which the corrosion inhibitor is an alkali metal chromate.

4. A method in accordance with claim 1 in which the corrosion inhibitor is an alkali metal nitrate.

5. A method in accordance with claim 1 in which the corrosion inhibitor is an alkali metal chromate.

6. A method in accordance with claim 1 in which the oxidation inhibitor is 2,4-6-tri-t-butyl phenol.

7. A method in accordance with claim 1 in which the oxidation inhibitor is 2,2-bis(2-hydroxy-3,5-butyl-t-methoxyphenyl) propane.

8. A method in accordance with claim 1 in which the oxidation inhibitor is 4,4-isopropylidenebis(2-isopropyl) phenol.

9. A method in accordance with claim 1 in which the oxidation inhibitor is N,N'-disalicylidene-1,2-diamino propane.

10. In the storage of a gas oil fraction having a tendency to form sediment and to corrode ferrous metals in the presence of water on storage in contact therewith in which the gas oil is maintained in contact with a ferrous metal surface and a body of water, the step of maintaining simultaneously in said gas oil a phenolic oxidation inhibitor in an amount in the range from 1 to 15 pounds per 1000 barrels of gas oil and in said body of water a water soluble corrosion inhibitor selected from the group consisting of the alkali metal nitrates and the alkali metal chromates in an amount in the range between 100 and 5000 p.p.m. whereby sediment formation in said fraction and corrosion of said surface is substantially eliminated.

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