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IRRADIATION OF HYDROCARBON OILS

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This invention relates to irradiation of hydrocarbon distillates and more particularly relates to a process for improving the stability of hydrocarbon distillates containing selected additives by subjecting the same to gamma radiation.

Distillate fuels treated in accordance with the present invention include generally fuels having boiling ranges between about 100 and about 1200° F. and may include gasolene, kerosene, diesel fuels, heating fuels, jet fuels and the like. Such distillates may be obtained from any suitable source such as by fractionation from crude oils or may be obtained from any of the various hydrocarbon conversion processes commonly used in the treatment of hydrocarbon oils, such as catalytic or thermal cracking, or reforming, coking, alkylation, polymerization and the like.

Distillates such as those described above and especially distillates boiling in the ordinary fuel oil boiling range such as between about 400 and about 700° F. have a strong tendency to form gums and sediments especially after prolonged periods of storage. Such gums and sediments are highly undesirable and may clog fuel lines, valves, meters, filters, etc., as well as form deposits in internal combustion engines or fuel burners. In order to prevent the formation of such sediment and gums for as long a period as possible, various additives or inhibitors are commonly added to distillate fuels. While the use of such additives has proved effective in substantially increasing the stability of distillate fuels by preventing the formation of sediment or gums for substantial periods of time even under adverse conditions or elevated temperatures, such additives are not as effective as might be desired and considerable difficulty is still experienced in the storage and use of distillate fuels due to lack of sufficient stability with respect to the formation of sediment and gums.

It is therefore, an object of the present invention to provide a method of treating hydrocarbon distillate fuels containing selected additives to improve the stability thereof.

It is another object of the invention to provide an improved process for the treatment of hydrocarbon fuel oils.

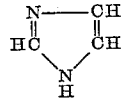
In accordance with a preferred embodiment of the present invention hydrocarbon distillate fuel containing an additive selected from the group consisting of imidazole, acetonitrile, o-benzyl phenol and 2,6-ditertiary-butyl p-cresol is treated for improvement of stability by being subjected to gamma radiation.

It has been found quite unexpectedly that when hydrocarbon distillate containing one of the above mentioned additives is subjected to gamma radiation the stability of the fuel is thereby substantially increased. This increased stability is far in excess of the stability achieved either by radiation alone or by the addition of any of the above mentioned additives without irradiation. These results, which are set forth in more detail below, are especially surprising since irradiation of distillate fuels containing other additives, some having chemical structures very similar to those of the additives mentioned above, did not produce this marked increase in stability.

While the invention is generally applicable to a wide range of distillate fuels as mentioned above, it is especially

applicable to distillate fuels boiling in the fuel oil range such as fuel oils boiling between about 400 and about 700° F. at atmospheric pressure. The additives contained in these distillate fuels in accordance with the invention have the structures indicated below.

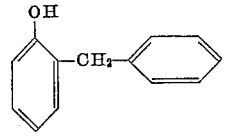
Imidazole:



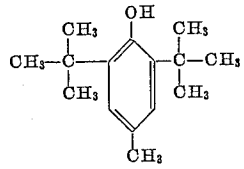
Acetonitrile:

$$CH_3—C{\equiv}N$$

o-Benzyl phenol:



2,6-ditertiary-butyl p-cresol:



These additives may be present in any suitable amounts in the distillate fuels treated in accordance with the invention. In typical distillate fuels these additives are present in quantities between about 0.001 and about 1.0 weight percent, preferably between about 0.001 and about 0.1 weight percent of the total distillate fuel. In addition to these sediment and gum inhibiting additives distillate fuels treated in accordance with the invention may contain minor amounts of other additives designed for this or other purposes.

In subjecting distillate fuels containing selected additives to gamma radiation in accordance with the invention the distillate may be subjected to any suitable amount of gamma radiation with dosages on the order of between about 10^7 and about 10^9 roentgens being preferred. The total gamma radiation received by the distillate may be received at any suitable rate, but relatively high rates of dosage such as about 10^5 or 10^6 roentgens per hour are usually preferred in order to make efficient use of the relatively expensive materials and facilities required for radiation treatments. It should be understood, however, that insofar as is known, the rate at which the total radiation dosage is applied to the distillate fuel does not effect the end result of increased stability.

Any suitable means may be used for subjecting hydrocarbon distillates to gamma radiation in accordance with the invention. For instance, the gamma radiation may come from suitable sources such as cobalt 60 or other natural or artificial gamma emitters. The distillate to be treated may be placed in a container in a shielded radiation chamber and subjected to radiation from a suitable gamma source for the length of time necessary to obtain the desired total dosage of radiation or the distillate may be passed continuously through radioactive source material or in the vicinity thereof.

Treatment of distillates in accordance with the present invention may be carried out under any suitable operating conditions in any suitable atmosphere such as air or nitrogen. While very satisfactory results have been obtained at ordinary room temperatures and atmospheric pressures it should be understood that any other suitable temperatures and pressures such as the relatively high temperatures and pressures commonly used in hydrocarbon treat-

ing and conversion processes may be used in treating hydrocarbons in accordance with the invention. Temperatures ranging from room temperature up to about 1200° F. and pressures up to about 200 atmospheres or higher are common in such processes. Treatment at such elevated temperatures or pressures may, for instance, be desirable if the radiation treatment immediately precedes or follows or is combined with another treating step. Radiation treatment of distillates under conditions of lower temperatures such as down to about −40° F. and under sub-atmospheric pressures is also contemplated. Where the radiation treatment is a continuous process the rate of flow of the hydrocarbon distillate will, of course, depend upon the radiation dosage rate and total desired dosage.

The following specific examples will illustrate the application of the present invention to the treatment of various fuel oils containing selected additives.

EXAMPLE 1

A suitable fuel oil for treatment in accordance with the present invention comprises a No. 2 fuel oil containing 0.005 weight percent imidazole.

This fuel oil as well as other No. 2 fuel oils discussed herein was a hydrocarbon distillate fuel meeting ASTM distillation standards of 10% distillation at 440° F. with a maximum of 90% at 600° F. This fuel also met other ASTM requirements for No. 2 fuel oil including; pour-point not more than minus 5° F., gravity 30.0° API minimum, maximum ASTM color 2½ and flash point between 125 and 185° F.

EXAMPLE 2

Another suitable distillate fuel for irradiation in accordance with the present invention is a No. 2 fuel oil containing 0.1 weight percent imidazole.

EXAMPLE 3

Another distillate fuel suitable for treatment in accordance with the invention comprises a No. 2 fuel oil containing 0.5 weight percent acetonitrile.

EXAMPLE 4

Another suitable fuel oil for treatment in accordance with the present invention comprises a No. 2 fuel oil containing 0.005 weight percent o-benzyl phenol.

EXAMPLE 5

Still another distillate fuel suitable for irradiation in accordance with the invention is a No. 2 fuel oil containing 0.05 weight percent o-benzyl phenol.

EXAMPLE 6

Yet another distillate fuel suitable for irradiation in accordance with the present invention comprises a No. 2 fuel oil containing 0.001 weight percent o-benzyl phenol.

EXAMPLE 7

Another distillate fuel siutable for treatment in accordance with the present invention comprises a No. 2 fuel oil containing 0.005 weight percent 2,6-ditertiary butyl p-cresol.

EXAMPLE 8

In order to evaluate the treatment of the present invention three 350 cc. samples of a No. 2 fuel oil of the type described above were placed in a shielded radiation chamber and irradiated with 1.0×10^8 roentgens of gamma radiation from a cobalt 60 source. As indicated in Table 1 below, one sample contained no inhibitor while a second sample contained 0.005 weight percent o-benzyl phenol and a third sample contained 0.005 weight percent 2,6-ditertiarybutyl p-cresol. Three other samples identical to those just described were also prepared but were not subjected to the radiation treatment. Following the radiation treatment all six samples were tested for stability by the optical density test described below.

In testing the fuel oils described herein for stability the sample being tested was first passed through a coarse qualitative filter paper for removal of extraneous material and was then placed in an oxidation tube and fitted with a sparger and condenser. The tube and contents were then placed in an oil bath. Filtered dry air was passed into the sparger at the rate of 5 liters per hour while the oil bath was maintained at 180° F. Air was also passed through the condenser at a suitable rate to prevent loss of volatile materials. The sample was inspected at approximately 24 hour intervals. When, as judged by the general appearance of the sample, tube and sparger, the break point was being approached, a portion of the sample was pipetted off sufficient to fill a glass stoppered test tube. The stopper was inserted and the tube permitted to cool for not less than 4 hours. The stoppered test tube was then inverted several times to insure uniformity and just over half the contents poured into a filtering crucible (5 microns) for suction filtration. Optical density measurements were then obtained at 500 millimicrons on the filtered and unfiltered samples of the aged oil, the spectrophotometer used being zeroed in on n-heptane. The optical density difference obtained in this manner served to indicate whether or not the sample had reached the break point. This sampling procedure was repeated at suitable intervals until the test sample was broken. The break point for purposes of these tests was considered to be that number of hours during which the optical density difference between filtered and unfiltered portions of the aged sample did not exceed 0.160. This served as an excellent measure of the stability of the fuel oil being treated

The results of these tests are summarized in Table 1 below:

Table I

EFFECT OF GAMMA RADIATION ON A NO. 2 FUEL OIL CONTAINING SELECTED ADDITIVES

Inhibitor	Radiation Dose (Roentgens)	Stability (Hours)	
		before irradiation	after irradiation
None	1.0×10^8	13	42
o-benzyl phenol (0.005 wt. %)	1.0×10^8	16	234
2,6 ditertiary butyl p-cresol (0.005 wt. %)	1.0×10^8	11	59

EXAMPLE 9

Samples of another No. 2 fuel oil were prepared for testing as outlined in Example 8 above. In this case, as in Example 8, 3 samples were irradiated with 1.0×10^8 roentgens of gamma radiation and 3 other identical samples were not irradiated. One of the irradiated set of samples and one of the non-irradiated set contained no inhibitor while one sample of each set contained 0.005 weight percent imidazole and the other sample of each set contained 0.5 weight percent acetonitrile. These samples were all tested for stability in accordance with the procedures outlined in Example 8 above with the following results:

Table II

EFFECT OF GAMMA RADIATION ON ANOTHER NO. 2 FUEL OIL CONTAINING SELECTED ADDITIVES

Inhibitor	Radiation Dose (Roentgens)	Stability (Hours)	
		before irradiation	after irradiation
None	1.0×10^8	less than 22	less than 18
Imidazole (0.005 wt. %)	1.0×10^8	do	240.
Acetonitrile (0.5 wt. %)	1.0×10^8	do	168.

From Tables 1 and 2 above it is clear that distillate fuels containing the selected additives mentioned above which are irradiated with gamma radiation achieve re-

markable stabilities while neither the additives nor the radiation alone achieves anything even aproaching these results. For example, from Table 2 it can be seen that while radiation was actually harmful to the stability of the sample of fuel oil containing no additive and while the use of the selected additives alone did not appreciably effect the stability of the fuel oil, the radiation treatment of the fuel oil samples containing these selected additives increased the stability of the fuel oil many fold and created an entirely satisfactory fuel oil from a stability standpoint. In this connection it may be noted that the stability tests employed herein were aceclerated tests at elevated temperatures in order to bring about breakdown of the oil sooner than might be expected under normal storage conditions.

Likewise, Table 1 shows that the irradiation with gamma radiation of fuel oil containing the selected additives produces extremely surprising results in the form of high stability oils. For instance, irradiation of the sample containing o-benzyl phenol produced an oil with a stability of 234 hours under the test conditions described above while irradiation of the oil containing no inhibitor produced a fuel oil having a stability of only 42 hours under these conditions.

It is especially worthy of note that the selected additives used in accordance with the present invention are not particularly good gum and sediment inhibitors under ordinary conditions of use. In fact, of the 4 inhibitors used, only one showed any signs of increasing the stability of the oil by itself and this was such a small increase as to be insignificant. The present invention therefore provides as effective means of utilizing otherwise impotent inhibitors in conjunction with gamma radiation to provide fuel oils having extremely high stability in comparison with untreated oils. This of course, means that these oils can be stored for relatively long periods of time under conditions of adverse high temperatures without the usual formation of sludge and sediment.

While the invention has been described above with respect to a preferred embodiment thereof, it will be understood by those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the invention and it is intended to cover all such changes and modifications in the appended claim.

We claim:

The process for treating hydrocarbon fuel oil containing between about 0.001 and about 1.0 weight percent imidazole for the improvement of the stability thereof which comprises subjecting said fuel oil to between about 10^7 and about 10^9 roentgens of gamma radiation.

References Cited in the file of this patent

UNITED STATES PATENTS

2,357,547	Proell	Sept. 5, 1944
2,560,489	Smith et al.	July 10, 1951
2,845,388	Black et al.	July 10, 1958
2,906,680	Ruskin	Sept. 29, 1959
2,990,350	Natkin et al.	June 27, 1961