

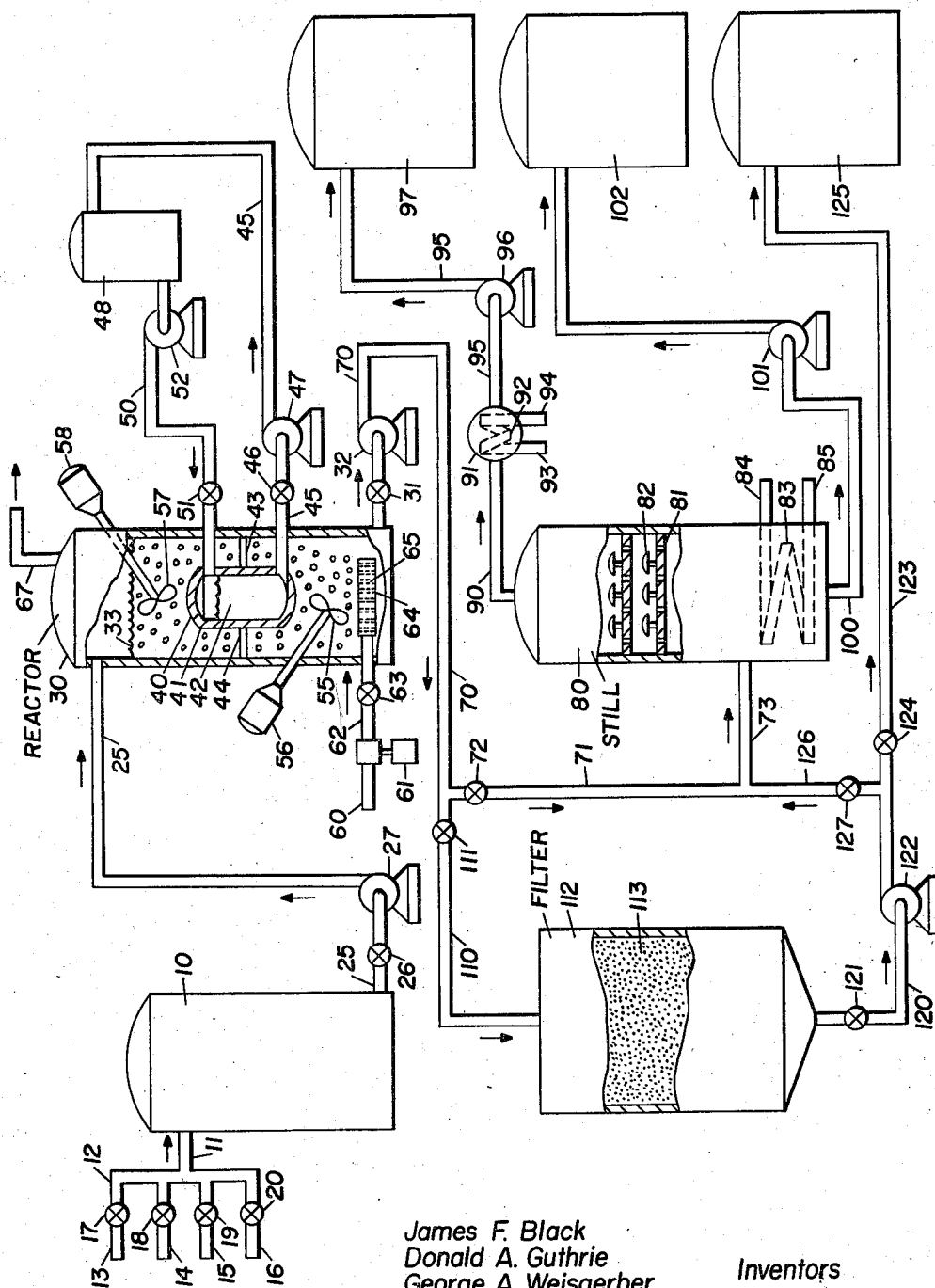
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STABILIZATION OF PETROLEUM DISTILLATES

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STABILIZATION OF PETROLEUM DISTILLATES

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This invention relates to radioactivity and more particularly relates to a method for stabilizing petroleum distillates by exposure to radiation emitted by radioactive materials, preferably in the presence of an oxygen-containing gas. The invention also relates to a method for determining the stability of petroleum distillates. The invention further relates to apparatus useful for carrying out the present method and to the stabilized products so produced.

Petroleum distillates irradiated in accordance with the present invention include fuels for internal combustion engines such as Diesel engines, automotive engines, aviation engines and the like, heating oils for the home and industry, as well as solvents, lubricating oils, flushing oils and the like. These petroleum distillates generally boil within the range of about 100° to 650° F. at atmospheric pressure and are derived from petroleum crude oils. By use of vacuum distillation, distillates with normal atmospheric boiling points as high as 1200° F. may be obtained. The distillates referred to above may be virgin stocks derived directly from petroleum crude oils by distillation, or may be obtained from any of the various hydrocarbon conversion processes employed in refineries such as, for example, catalytic cracking, thermal cracking, thermal reforming, steam cracking, coking, alkylation, polymerization, hydroforming and the like.

In general, all of these petroleum distillates under certain conditions of storage and/or use can form sediment and/or oil-soluble high boiling gums. Such sediment and gums (which are sediment precursors) are undesirable as they clog filters, valves, meters, etc., and, in addition, form deposits in internal combustion engines and fuel burners, thereby substantially decreasing the efficiency of such machines. The use of certain additives and treating processes has alleviated this problem to a certain extent. However, there remains a need for a low-cost and effective means for substantially reducing or eliminating the sediment and gum formation in petroleum distillates.

It has now been found that a petroleum distillate may be stabilized with respect to sediment and gum formation by exposing it to high energy ionizing radiation emitted by radioactive materials and separating the resultant oil-insoluble sediment from the irradiated composition. Preferably, the radiation comprises gamma rays or the combination of gamma rays and neutrons. The oil-insoluble sediment may be separated from the irradiated petroleum distillate composition by filtration, centrifuging, and/or distillation. Preferably the separation is effected by distillation since this process also separates the high boiling oil-soluble gums as well as the sediment from the bulk of the irradiated petroleum distillate composition. Filtration, employing clay or alumina as a filtering medium, will also remove a considerable amount of the high boiling oil-soluble gums as well as the oil-insoluble sediment. In the preferred method of this invention, the irradiation is carried out in the presence of an oxygen-containing gas,

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preferably air and preferably employing sufficient air to saturate the petroleum distillate being treated. It has also been found that the stability of a petroleum distillate with respect to its sediment and gum-forming tendencies may be readily determined by exposing a sample of the petroleum distillate to radiation emitted by radioactive materials. The amount of sediment and/or high boiling oil-soluble gum produced upon such irradiation is an indication of the stability of the petroleum distillate in normal storage and use.

SOURCES OF RADIATION

Radioactive materials providing high energy ionizing radiation are useful in the present invention. The preferred radioactive materials are those emitting gamma rays. Materials emitting only beta rays may be employed but are less effective than materials emitting radiation comprising gamma rays. Also, if desired, neutrons may be employed alone or in combination particularly with gamma rays, the latter being a preferred combination.

One source of radioactive materials is an atomic pile. Large quantities of radioactive by-products or waste materials from these atomic piles are now available. The present invention provides a practical utilization of such by-product or waste materials which at present represent a disposal problem due to their steady accumulation. These fission by-products of atomic piles include radioactive elements with atomic numbers ranging from 30 (zinc) to 63 (europium). These waste materials are formed in the course of converting uranium, plutonium or other fissionable material in atomic reactors.

In addition, various materials made radioactive by exposure to neutron radiation, such as radioactive cobalt (Co^{60}), europium¹⁵², europium¹⁵⁴, etc., may also be used for the purposes of the present invention. Also, the gamma radiation and the neutron flux existing in an atomic reactor may be employed if desired. This latter method is an especially desirable method when an atomic reactor is readily available.

THE PETROLEUM DISTILLATES

In general, petroleum distillates boiling within the range of about 100° to 1200° F. may be stabilized in accordance with the method of the present invention. More specifically, the following is a partial list of petroleum distillates which may be stabilized in accordance with this invention:

Distillate	ASTM Boiling Range, °F. at 760 mm. Hg	
	General	Specific
Motor Gasoline	80-400	90-325
Aviation Gasoline	100-375	100-350
Solvent Naphtha, Mineral Spirits	300-410	310-380
Kerosene	300-600	325-550
Turbo Jet Fuels	150-650	300-500
Diesel Fuel	300-600	325-600
Heating Oil	300-700	325-650
Lubricating Oil	600-1300	650-1200

The present invention is particularly useful in stabilizing (1) low-boiling distillate fuels boiling within the range of about 100° to 375° F. such as those employed as motor gasolines and aviation gasolines and (2) petroleum middle distillates boiling generally within the range of about 300° to 750° F. such as those employed as Diesel fuels, jet fuels and heating oils.

The petroleum distillates referred to herein include the virgin stocks derived from petroleum crude oils generally, such as Gulf Coast crude oils, Mid-Continent crude oils, California crude oils, Pennsylvania crude oils, South

American crude oils, Middle East crude oils and the like. It will be understood that the present invention is applicable not only to these virgin petroleum distillates but also to distillates obtained from the various hydrocarbon conversion processes conventionally employed in refineries. More particularly, the present invention is also applicable to distillates obtained from such petroleum hydrocarbon conversion processes as catalytic cracking (either fixed bed, fluid bed or transfer line reactor), thermal cracking, thermal reforming, steam cracking, coking, hydroforming and the like. The present invention is also directed to synthetic hydrocarbon oils prepared, for example, by the polymerization or alkylation of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. Also, shale oil distillates may be stabilized in accordance with the present invention. Petroleum distillates which have been treated by such conventional processes as acid treating, caustic washing, etc. may be also improved in accordance with this invention. However, it will be understood that one of the purposes of the present invention is to eliminate the need for such treating processes.

TREATING CONDITIONS

The stabilization of petroleum distillates in accordance with the present invention is carried out generally by exposing the petroleum distillates to radiation emitted by radioactive materials. This exposure of the distillate to the radiation may be carried out by a variety of procedures. For example, radioactive materials disposed in a container may be placed into the petroleum distillate. This procedure may be employed either on a batch or continuous basis. Thus, more particularly, the radioactive source may be placed in a tank containing the petroleum distillate to carry out a batch operation or the radioactive source may be placed into a stream of the petroleum distillate to carry out a continuous process. Also, if desired, the petroleum distillate may be piped through an atomic reactor or pile as a continuous stream wherein the stream of petroleum distillate is exposed to neutrons and gamma rays present in the atomic reactor or pile. It will be obvious that many modifications of these procedures will be apparent to those skilled in the art. The utilization of radiation emitted by radioactive materials of course necessitates the provision of adequate radiation shielding means and techniques. Such means and techniques are well known in the art and need not be described herein in detail.

The irradiation of the petroleum distillates may generally be carried out at temperatures in the range of -20° to 400° F. or higher. However, generally, the irradiation will be carried out at a temperature in the range of about 30 to 210° F., particularly about 60° to 100° F. One of the advantages of the present process as compared to other stabilization processes of the prior art is that effective stabilization of the petroleum distillates may be realized at room temperatures, or at normal atmospheric temperatures. The irradiation may be conveniently carried out at atmospheric pressure, but it will be understood that the irradiation may be carried out under vacuum or elevated pressures, such as about 2 to 50 atmospheres, if desired.

Generally, the radiation dosage useful in the present invention will be in the range of about 100,000 to 100,000,000 roentgens, preferably about 1,000,000 to 80,000,000 roentgens. Radiation dosages below about 100,000 roentgens, in general, do not give sufficient stabilization for the purposes of the present invention. Radiation dosages in excess of about 100,000,000 roentgens may be employed if desired, but in general will not be required for effective stabilization and, in addition, are generally uneconomical.

In the preferred embodiment of this invention the petroleum distillate is irradiated until essentially all the potential sediment forming constituents have been con-

verted to higher boiling or to oil-insoluble materials. This will be indicated generally when further irradiation of the distillate produces essentially no additional oil-insoluble sediment. The radiation dose rates employed will generally be in the range of about 1,000 roentgens per hour up to about 20,000,000 roentgens per hour. Preferably the radiation dosage rate is maintained in the range of about 50,000 to 20,000,000 or more roentgens per hour. In general, it is preferred to operate with as high a radiation dose rate as possible in order to obtain a high throughput of petroleum distillate through the irradiation zone. In this way, the investment in treating facilities may be maintained at a minimum. The time of irradiation will be dependent upon the radiation dose desired as well as the dosage rate employed. In general, irradiation times in the range of about 0.1 to 50 hours or longer, usually about 1 to 24 hours, will be employed. Radiation sources having in the range of about 50 curies to 1,000 kilocuries, for example, will generally be employed although sources having lesser or greater amounts of radiation may be employed if desired.

The specific radiation dosage employed will in general depend upon the following two factors. Petroleum distillates having relatively high aromatic contents in general will require relatively higher radiation dosages. Also in general the more unstable petroleum distillates will require relatively higher radiation dosages. The amount of radiation dosage to be employed in commercial operations may be conveniently determined by carrying out a simple laboratory test to determine in general the relative stability of the petroleum distillate prior to its irradiation in a full-scale treating unit. Convenient tests for low boiling distillates, such as motor gasolines, which may be employed in this connection are carried out briefly as follows: (1) The sample (50 cc.) is oxidized in a bomb (initially filled with oxygen at 15 to 25° C. at 100 p. s. i.) by heating to 100° C. The pressure is recorded continuously until the break point is reached. The time required for the sample to reach this point is the induction period. (ASTM test D525-46.) A stable fuel has a longer induction period than an unstable fuel. (2) In ASTM D873-46T the sample is oxidized under above conditions for a specified time. The gum in the oxidized sample is determined by evaporating the sample to dryness at 160° C. with a jet of preheated air. A stable fuel will form less gum in this test than an unstable fuel. For petroleum middle distillates the following test may be conveniently carried out on a sample of the middle distillate in order to determine its relative thermal stability with respect to its tendency to form oil-insoluble sediment: A sample of the distillate for test of known weight (e. g., 600 gm.) is placed in a clean glass container and stored in a bath at 210° F. for a period of 16 hours, the oil surface being freely exposed to the air during the heating period. After the heating period the sample is removed from the bath and cooled and the amount of oil-insoluble sediment produced in the test sample is determined by a suitable means such as filtration and weighing of the sediment, turbidimetric measurement, etc. High boiling oil-soluble gum constituents in the distillate product may be determined by ASTM D381-54T which specifies a range of evaporation temperatures to be used depending upon the volatility of the test sample. For heating oil, an evaporation temperature of 500° F. is used.

The irradiation of the petroleum distillate can be most effectively carried out with intimate mixing, such as that obtained by stirring. In the preferred form of the present invention, the irradiation is carried out in the presence of an oxygen-containing gas, which generally will be air. The oxygen-containing gas is bubbled into or through, or blown through, the petroleum distillate during irradiation. This may be carried out at atmospheric or elevated pressures. This treatment with the oxygen-containing gas not only provides effective agitation, resulting in intimate mixing of the petroleum

the petroleum distillate from tank 10 may be carried out on either a batch basis or a continuous basis. In the continuous process, petroleum distillate will be continuously withdrawn from tank 10 and simultaneously additional petroleum distillate will be introduced into tank 10 by means of manifold 12. The petroleum distillate in line 25 is discharged into reactor 30 wherein the petroleum distillate is exposed to radiation emitted from radioactive materials. The rate of withdrawal of the petroleum distillate from reactor 30 is regulated by means of valve 31 and pump 32 such that a relatively large volume of the petroleum distillate is maintained in reactor 30. For example, the level of petroleum distillate in reactor 30 is indicated by the reference numeral 33.

Disposed within reactor 30 is radioactive source 40 which in this embodiment of the present invention comprises a sealed metal container 41 and an aqueous solution 42 of salts of radioactive fission products from an atomic reactor. Source 40 is maintained in a fixed position in reactor 30 by means of rigid supports 43 and 44 connecting source 40 to the walls of reactor 30. In this embodiment of the invention, when reactor 30 is emptied of petroleum distillate, solution 42 is pumped out of container 41 through line 45 by opening valve 46 and operating pump 47. Solution 42 of radioactive salts is passed through line 45 into storage tank 48 which is adequately shielded to protect personnel from harmful irradiation. Storage tank 48 may be placed underground or adequately shielded with water, lead or the like. Then when it is desired to treat petroleum distillate in reactor 30, solution 42 of radioactive salts is pumped through line 50 by opening valve 51 therein and operating pump 52.

Reactor 30 is provided with apparatus for effecting intimate mixing of the petroleum distillate composition contained therein. In the figure, stirrer 55 operated by motor 56 and stirrer 57 operated by motor 58 are arranged within reactor 30 to provide intimate mixing of the petroleum distillate contained therein. Other equivalent means of mixing may, of course, be employed in reactor 30.

In the preferred embodiment of the present invention, the irradiation is carried out in the presence of an oxygen-containing gas. In the embodiment of the invention shown in the figure, atmospheric air is passed through line 60 into air compressor 61 and the resultant compressed air is passed through line 62 by opening valve 63 therein into distribution plate 64 which is provided with a plurality of perforations 65 whereby the air being discharged therefrom is distributed relatively uniformly throughout the petroleum distillate contained in reactor 30. Preferably sufficient air is passed from distribution plate 64 to saturate the petroleum distillate contained in tank 30. The air passing upwardly through reactor 30 aids in providing efficient mixing of the petroleum distillate contained in reactor 30. The air passing upwardly through the petroleum distillate is removed from reactor 30 by means of vent line 67 located in the upper portion of reactor 30. The residence time of the petroleum distillate in reactor 30 is adjusted by means of valves 26 and 31 such that essentially all of the components of the petroleum distillate which may form sediment and/or oil-soluble gum are converted thereto.

The irradiated petroleum distillate composition is removed from reactor 30 through line 70 and is then preferably passed through line 71 by opening valve 72 therein and line 73 into still 80. Still 80 may be any conventional still adapted to take at least one overhead stream and a bottom stream and in this particular embodiment is a pipe still provided with a plurality of distillation trays 81 provided with a plurality of bubble caps 82. Still 80 is provided with heating coil 83 through which a heating medium such as high temperature steam, flue gas or the like is passed by means of lines 84 and 85. In still 80 the major proportion, generally at least 90 to

95% by volume, of the irradiated petroleum distillate composition is taken overhead through line 90 and passed to condenser 91 which contains cooling coil 92 through which a coolant such as water is passed by means of lines 93 and 94. The condensate, that is, the condensed petroleum distillate, is passed by means of line 95 and pump 96 into storage tank 97. A small bottoms stream, representing about 1 to 10% by volume of the irradiated petroleum distillate composition charged to still 80 is withdrawn through line 100 by operating pump 101 and passed into storage tank 102. This bottoms stream passing through line 100 into tank 102 contains substantially all of the oil-insoluble sediment formed by the treatment in reactor 30 together with all of the high boiling oil-soluble gum formed by the treatment in reactor 30. Thus still 80 separates this undesirable sediment and/or gum formed in reactor 30 from the bulk of the treated petroleum distillate so that a stable petroleum distillate product is collected in tank 97.

If desired, the irradiated petroleum distillate composition flowing through line 70 may be passed through line 110 by opening valve 111 therein and closing valve 72 in line 71 such that the irradiated petroleum distillate composition flows into and downwardly through filter 112. Arranged within filter 112 is bed 113 of an absorbent material such as bauxite, charcoal or the like. Filter 112 removes essentially all of the oil-insoluble sediment formed by the treatment in reactor 30 and may also remove a considerable amount of the high boiling oil-soluble gums. The filtrate from filter 112 may be passed through line 120 by opening valve 121 therein and operating pump 122. The filtrate flowing through line 121 may then be passed through line 123 by opening valve 124 therein and thus passed to storage tank 125. However, if desired, the filtrate passing through line 121 may be passed through line 126 by opening valve 127 therein and closing valve 124 in line 123 such that the petroleum distillate filtrate is passed through lines 121, 126 and 73 into still 80. The filtrate passing into still 80 is distilled in a manner similar to that operation previously described herein for handling the irradiated petroleum distillate composition passing through lines 70, 71 and 73 into still 80. More specifically, in the case of the filtrate the bulk thereof is taken overhead through line 90, condensed in condenser 91 and passed into storage tank 97. The remainder, representing about 1 to 10 volume percent, is withdrawn as a bottoms stream through line 100 and is passed to tank 102.

In the flow plan shown in the attached figure, it is preferred that the irradiation be carried out utilizing both mechanical stirring and air blowing. The preferred radioactive materials are those emitting gamma rays or a combination of gamma rays and neutrons. In the preferred embodiment of the invention, the irradiated petroleum distillate composition is subjected to distillation, removing the bulk of the irradiated composition overhead as a stabilized petroleum distillate fraction and removing a small amount of the irradiated petroleum distillate containing the oil-insoluble sediment and high boiling oil-soluble gum formed by irradiation as a bottoms stream.

The invention will be more fully understood by reference to the following examples. It is pointed out, however, that the examples are given for the purpose of illustration only and are not to be construed as limiting the scope of the present invention in any way.

Example I

In this example, a heating oil was subjected to gamma irradiation. The heating oil employed (hereinafter referred to as heating oil base I) consisted essentially of 50% by volume of cycle stock mixture from the products of a fluid catalytic cracking unit which had been treated by acid treatment, rerunning, sweetening and clay filtering, and about 50% by volume of virgin gas oil obtained from the distillation crude oil, followed by caustic wash-

distillate, but also increases the effectiveness of the stabilization procedure of the present invention. Preferably, sufficient oxygen-containing gas is employed to saturate the petroleum distillate with oxygen (or air). In general, about 0.1 to 100 v./v./hour (volume of oxygen-containing gas per volume of petroleum distillate per hour) will be employed. About 1 to 40 v./v./hour, particularly about 2 to 20 v./v./hour, have been found to be particularly effective in the present stabilization method. The use of the oxygen-containing gas enables the present stabilization reaction to be carried out employing lower radiation doses for a given time, or more effective stabilization for a given radiation dosage.

In accordance with the method of the present invention, the unstable components of the petroleum distillate are converted by irradiation into oil-insoluble sediment and/or high boiling oil-soluble gums which are then separated from the bulk of the petroleum distillate. In this way undesirable gum and/or sediment are not subsequently formed in the petroleum distillate upon storage and/or use. In general after the irradiation treatment (either alone or in combination with the oxygen treatment) is completed, the resultant oil-insoluble sediment is separated from the irradiated composition. Preferably the high boiling oil-soluble gums are also separated from the irradiated petroleum distillate composition after the irradiation treatment.

The oil-insoluble sediment may be separated from the remainder of the irradiated petroleum distillate composition by decantation, centrifuging or filtration. However, in the preferred form of this invention, the oil-insoluble sediment is separated from the remainder of the irradiated petroleum distillate composition by distillation. This particular technique is preferred as it removes not only the oil-insoluble sediment but also the high boiling oil-soluble gums (sludge precursors) from the irradiated petroleum distillate composition, thereby producing an effectively stabilized petroleum distillate composition. It will be understood that, if desired, combinations of decantation, centrifuging, filtration and distillation may be employed. Filtration may be very effectively carried out by passing the irradiated petroleum distillate composition through a bed of adsorbent material as for example activated clays, bauxite, silica or cellulose or carbonaceous material.

In carrying out the distillation of the irradiated petroleum distillate composition, the stabilized petroleum distillate composition will be taken overhead from a still (such as a pipe still or a fractionating column provided with distillation trays) and the oil-insoluble sediment and high boiling oil-soluble gums removed as a bottoms stream from the still. Generally about 90 to 99 volume percent, preferably about 95 to 99 volume percent, will be taken overhead and will represent the stabilized petroleum distillate composition. The remainder, representing about 1% to 10%, preferably about 1% to 5%, of the irradiated petroleum distillate composition will be removed as a bottoms stream. This bottoms stream, which contains the oil-insoluble sediment and high boiling oil-soluble gums, may be employed as a low cost heavy burner fuel component, fluid coker feed, etc.

It will be understood that the petroleum distillate which is irradiated in accordance with the present invention may contain additives such as inhibitors and the like. However, in general, any additives which are to be added to the petroleum distillate will be preferably added subsequent to the irradiation and separation steps of this invention, as the treating method of this invention may result in their removal and/or degradation in the process.

METHOD FOR DETERMINING STABILITY OF PETROLEUM DISTILLATES

The concept of the present invention may also be employed as an analytical procedure for determining the stability of a petroleum distillate, that is, the tendency of the petroleum distillate to form sediment and/or oil-

soluble gums upon storage and/or use. More particularly, in carrying out this phase of the invention, a sample of the petroleum distillate to be evaluated for stability is irradiated with radiation emitted by radioactive materials. This test can be carried out with a given volume of the petroleum distillate at room temperature and atmospheric pressure employing a given radiation dosage (most conveniently carried out using a fixed dosage rate for a fixed time). After this irradiation, the irradiated petroleum distillate sample may be filtered and the amount of the oil-insoluble sediment collected on the filter may be weighed. The amount of the oil-insoluble sediment collected on the filter is a measure of the instability of the petroleum distillate sample.

In addition, if desired, the amount of high boiling oil-soluble gum in the filtrate may be determined. This may be carried out by means of a steam jet gum test which is a modification of the method ASTM D381-54T using an evaporation temperature in that method of 580° F.

The total amount of sediment and oil-soluble gum is an effective indication of the stability of the petroleum distillate. This particular analytical method of the present invention is especially useful for evaluating the stability of petroleum distillates which are to be treated in full-scale operations in accordance with the present invention as heretofore described in the present specification. An excellent indication of the stability of the petroleum distillate and therefore the radiation dosage required in the full-scale operations will be indicated by the present analytical technique. This the present analytical technique may be employed in lieu of the other stability tests described heretofore in the present specification.

Another form of the analytical method of this invention for determining the stability of a petroleum distillate comprises exposing a sample of the petroleum distillate to radiation emitted by radioactive materials (preferably at room temperature and atmospheric pressure) until essentially no more oil-insoluble sediment is formed upon further irradiation. Then the irradiated sample is filtered, the amount of oil-insoluble sediment on the filter weighed and the amount of high boiling oil-soluble gum in the filtrate measured. The analytical method of this invention may be very effectively carried out in the presence of an oxygen-containing gas. More particularly, a given volume of air may be bubbled through the sample of petroleum distillate being irradiated in accordance with the analytical method of this invention. Air rates in the range of about 1 to 40 v./v./hour (volumes of air per volume of oil per hour), preferably about 2 to 20 v./v./hour, may be employed. The use of the oxygen-containing gas will reduce the time required for carrying out the analytical method for determining the stability of the petroleum distillate.

The method of stabilizing petroleum distillates by exposing them to radiation emitted by radioactive materials in accordance with the present invention will be better understood by reference to the attached figure which is a showing of apparatus adapted to carry out an embodiment of the present invention. Referring now to the figure, reference character 10 designates a storage tank wherein a petroleum distillate is stored prior to treatment in accordance with the present invention. Petroleum distillate is charged to tank 10 through line 11 and manifold 12. Manifold 12 includes lines 13, 14, 15 and 16 containing, respectively, valves 17, 18, 19 and 20. These lines are adapted to carry various petroleum distillate fractions directly from operating units such as pipe stills, catalytic cracking units and the like, to tank 10. Thus it will be seen that a single petroleum distillate or blends thereof may be prepared in tank 10 for subsequent treatment employing the lines and valves of manifold 12.

The petroleum distillate contained in tank 10, which is to be treated in accordance with this invention, is withdrawn from tank 10 through line 25 by opening valve 26 therein and operating pump 27. The withdrawal of

ing, sweetening, and clay filtering. The boiling range of the catalytic cycle stock was about 406° to 620° F. and the boiling range of the virgin gas oil was about 310 to 536° F. The irradiation of a sample of heating oil base I (sample A) was carried out at room temperature (70° F.) in the following manner: Bottles with a capacity of 120 cc. were filled with 110 cc. of sample, tightly stoppered, and lowered into the center of a cylindrical cobalt 60 source. The radiation intensity in the center of this source was about 235,000 R./hr. Four samples were exposed to radiation of this intensity for 10, 15, 24 and 48 hours respectively. At the end of these times the samples were removed from the radiation field and examined.

The following results were noted in carrying out the aforesaid gamma irradiation of sample A of heating oil base I:

TABLE I.—HEATING OIL STABILITY
[Gamma irradiation (70°F.) of heating oil base I.]

Time (Hrs.)	Sediment (mg./ 100 gm.)	Filtrate Color Hold (percent)
0	0	² 100
10	2	82
15	2	81
24	2	82
48	3	80

¹ Sample A.

² Reference point, i. e., untreated oil.

The amount of sediment in the irradiated sample A was determined by filtering the irradiated composition through a sintered glass filter and weighing the sediment collected on the filter. The color hold was determined by measuring the percent transmission of white light through the sample of the filtrate relative to the original test oil set at 100%. The results reported in Table I show that sediment formation can be induced by short periods of gamma irradiation (less than 10 hours) and that the filtrate has a relatively high color hold. It has been found that the color holds of the filtrate when using the present method are substantially superior to those obtained by thermal treatment of the heating oil. Also the gamma irradiated heating oil sample (after distillation) was found to be more stable toward further degradation in terms of sediment formation, color, gum and varnish formation than was the untreated oil.

Example I

In this example, another sample (hereinafter referred to as sample B) of heating oil base I, described above in Example I, was exposed to gamma radiation in the same manner as described in Example I.

After irradiation, sample B was filtered through a sintered glass filter as in Example I and the percent color hold and Robinson color of the filtrate was determined as well as the amount of insoluble sediment collected on the filter. In addition, the amount of high boiling oil-soluble gum in the filtrate was determined in the steam jet gum test previously described.

The following is a summary of the results of these evaluations:

TABLE II.—STABILITY OF HEATING OIL BASE I

Gamma Irradiation		Insol. Sediment Formed, mg./110 ml.	Filtrate Inspections ²		
Hours' Exposure	Total Roentgen		Percent Color Hold	Robinson Color	Steam Jet Gum
0	0	0	² 100	11½	26.0
0.5	117,500	0.4	92	11½	25.4
1	235,000	0.8	83	10½	29.8
3	705,000	1.8	53	6½	28.0
5	1,175,000	2.5	50	6¼	29.2

¹ Sample B.

² Filtrate, after removal of sediment by filtration through sintered glass.

³ Reference pt., i. e., untreated oil.

It will be noted from the results shown in Table II that exposure of Sample B to gamma radiation for periods of time of 0.5 to 5 hours produced progressively greater amounts of sediment and progressively more color degradation. It will also be noted that irradiation increased the amount of steam jet gum in the filtrate.

Example III

In this example, another sample (hereinafter referred to as sample C) of heating oil base I, described above, in Example I, was subjected to gamma radiation by the same method employed in Example II except that longer irradiation times were employed, which resulted in increased radiation dosages. The results of these experiments are shown below:

TABLE III.—STABILIZATION OF HEATING OIL BASE I BY GAMMA IRRADIATION

Gamma Irradiation		Insol. Sediment Formed, mg./110 ml.	Filtrate Inspections ²		
Hours' Exposure	Total Roentgen		Percent Color Hold	Robinson Color	Steam Jet Gum
0	0	0	² 100	13¼	23.8
5	1,175,000	3	80	9½	32.8
10	2,350,000	2	82	9¼	36.4
15	3,525,000	2	81	9½	34.8
24	5,640,000	2	82	9½	38.2
48	11,280,000	3	80	9¼	41.4

¹ Sample C.

² Reference pt.

The results shown above in Table III indicate that an exposure to radiation of about 5 hours (when employing the above-described radiation conditions) gives essentially complete reaction of the oil-insoluble sludge formers. If subsequent treatment of the irradiated oil is simply filtration, then gum color hold should be maintained at as low a level as possible. We prefer, however, to use distillation after irradiation and in this case it is desirable to "degrade" the oil thoroughly prior to distillation.

Example IV

In this example, three different types of petroleum distillate oil bases were subjected to gamma irradiation. One of the oil bases employed in this example was heating oil base I which has been described heretofore in detail. A second oil base (hereinafter referred to as heating oil base II) was also treated and tested. Heating oil base II consisted essentially of about 40% by volume of virgin gas oil having a boiling range of about 312 to 536° F. derived from petroleum crude oil and about 60 volume percent of cycle stock from a catalytic cracking unit (cracking predominantly virgin gas oil) and having a boiling range of about 425 to 585° F. The components of base oil II were intentionally obtained to make up a "by-passed" heating oil for purposes of studying cheaper treating process for heating oil. The virgin stock was from a sweet distillate which had been caustic washed but which had not the usual clay filtering following caustic washing. The cracked stock was a raw catalytic cracking side stream distillate which received no further treatment (this stream is usually soda fined and clay filtered). The third oil base was a diesel oil (hereinafter referred to as diesel oil base I), which consisted essentially of about 40% by volume of heavy diesel base oil having a boiling range of about 367 to 650° F., about 30% by volume of catalytic cycle stock (derived from cracking of predominantly virgin gas oil) having a boiling range of about 406 to 620° F. and 30% by volume of thermal cracking gas oil (obtained by thermal cracking of predominantly virgin gas oil) having a boiling range of about 355 to 646° F. In carrying out the treatment of these oil bases, a conventional middle distillate inhibitor additive (hereinafter referred to as additive A) was added to the oil bases in certain of the evaluations.

A number of samples of the oil bases were subjected

to gamma irradiation in the same manner as that described in detail heretofore in Example I. The results of these evaluations are shown below:

TABLE IV.—GAMMA IRRADIATION OF BASE FUELS AND ADDITIVE-CONTAINING FUELS

Type of Oil Base	Sample	Gamma Irradiation		Insol. Sediment mg./110 ml.	Filtrate Inspections		
		Hrs.	Roentgen		Percent Color Hold	Robinson Color	Steam Jet Gum
Heating Oil Base I.....	Sample D.....	0	0	0	³ 100	13¼	26.0
Do.....	do.....	5	1, 175, 000	2.5	50	6¼	29.2
Do.....	Sample D + Additive ¹	5	1, 175, 000	0.8	60	8	(²)
Do.....	do. ¹	24	5, 640, 000	0.8	66	9	(²)
Heating Oil Base II.....	Sample E.....	0	0	0	³ 100	10½	16
Do.....	do.....	5	1, 175, 000	2.5	70	8½	17.4
Do.....	Sample E + Additive ¹	5	1, 175, 000	0.3	73	9¼	(²)
Diesel Oil Base I.....	Sample F.....	0	0	0	³ 100	9¼	27.6
Do.....	do.....	5	1, 175, 000	2.5	71	4¼	30.0
Do.....	Sample F + Additive ¹	5	1, 175, 000	2.3	42	3	(²)

¹ 0.0375 wt. percent of Additive A.

² Not determined.

³ Reference points for particular base oil under test.

It will be noted that the addition of additive A to the heating oil bases prior to gamma irradiation caused a reduction in the amount of insoluble sediment formed upon irradiation. Also, the additive-containing heating oil bases exhibited improved color stability. However, the addition of the inhibitor additive A to diesel oil base I did not materially affect the sludging tendency of the diesel oil base.

Results of this example show that heating oil bases and diesel oil bases may be effectively stabilized against sediment formation by gamma irradiation. The addition of a conventional middle distillate inhibitor additive such as additive A prior to irradiation may be desirable in some

substantially as described in Example I except that a bubbling tube was inserted in the sample containers and a slow stream of oxygen was passed through the oil during the irradiation period.

These five samples were then combined to give 762 cc. of irradiated, oxygen blown product which had been exposed to a total radiation dose of 1.8×10^6 roentgen. The resultant oxygen blown samples of heating oil base I were each divided into two portions which were further processed as follows: (1) The first portion was filtered and evaluated as described in Example II; (2) the second portion was distilled under vacuum in a nitrogen blanket at 7 mm. pressure to a 97% recovery. The sample which had been irradiated only was simply filtered and evaluated as described in Example II. The results of these experiments are reported in Table V.

TABLE V.—STABILIZATION OF HEATING OIL BASE I¹ BY GAMMA IRRADIATION

Treatment	Inspection after Treatment			Inspections after Treatment and Vacuum Distillation			
	Sediment (mg./600 gm.)	Filtrate		Recovery, percent	Robinson Color	Steam Jet Gum (mg./100 gm.)	Thermal Stability Test— Sediment (mg./600 gm.)
		Robinson Color	Steam Jet Gum (mg./100 gm.)				
A. None.....	0	10½	28.2	—	—	—	(³)
B. Oxygen Blown Only.....	1.1	10	27.8	97	18	3.8	22
C. Irradiated Only (in sealed bottle).....	15	9¼	35.0	(³)	(³)	(³)	(³)
D. Irradiated, while being oxygen blown.....	42	9	33.4	97	17½	0.6	5.2

¹ Sample G.

² Thermal stability test of untreated base oil gave sediment of 42.9 mg./600 gm.

³ Not determined.

cases to obtain, by the co-action of the irradiation and additive, a product which is particularly resistant to sediment formation. The desirability of using an additive in the distillate during irradiation will have to be determined for each distillate type under test.

Example V

In this example, the effect of aeration (alone as well as in combination with gamma irradiation) on the stability of heating oil base I was determined in the following comparative tests:

Oxygen blown only.—This experiment was carried out as follows: About 800 cc. of heating oil base I were placed in a one-liter cylinder and subjected to a slow stream of oxygen for 8 hours in the absence of any light or radiation.

Irradiated only.—This experiment was carried out substantially as described in Example I so as to receive a total radiation dose of 1.8×10^6 roentgen.

Irradiated, oxygen blown.—This experiment was carried out as follows: Five samples, each of about 150 cc. of heating oil Base I, were each irradiated for 8 hours

The thermal stability test sediment reported above in Table V was determined as described heretofore in this specification. The following conclusions can be drawn from the above tests:

Oxygen blown, non-irradiated sample.—Oxygen blowing alone effects little change in the oil. Subsequent distillation effects some improvement—lowering the gum from 27.8 to 3.8 and decreasing sediment in thermal stability test from 42.9 to 22 mg. (cf. treatments A and B).

Irradiated samples.—Irradiation causes formation of sediment (42 mg. when oxygen is introduced, only 15 mg. when the system is deficient in oxygen). In both cases, however, irradiation forms oil-soluble gum, increasing the gum content from 28.2 to 33.4 or 35 mg. Excess oxygen did not increase gum over that formed with irradiation alone (cf. treatments C and D). Distillation of the irradiated, oxygen blown oil gave a sample with very low gum (0.6 mg.) and excellent thermal stability (only 5.2 mg. sediment in thermal stability test at 210° F. for 16 hours).

Example VI

In this example, samples of two jet fuel bases (hereinafter referred to as jet fuel base I and jet fuel base II) were subjected to gamma radiation. The jet fuel bases consisted essentially of petroleum distillates. Jet fuel base I was a relatively stable jet fuel base; jet fuel base II was a relatively unstable jet fuel base. The gamma irradiations of jet fuel base I and II were carried out as follows: The fuels were irradiated in a 200 cc. sample tube inserted in a Co⁶⁰ gamma radiation field which had an intensity of 235,000 roentgens/hour. During the irradiation, oxygen was bubbled through the samples at a rate of 30 cc. (standard conditions) per minute. All samples were retained under refrigeration before the experiment and after the completion of the irradiation until tested. This was done to prevent gum formation at any time other than during the irradiation period. The following results were obtained in this test:

TABLE VI.—EFFECT OF GAMMA IRRADIATION ON JET FUEL BASES

Irradiation Time (Hours)	Steam Jet Gum (mg./100 gm.)	
	Jet Fuel, Base I	Jet Fuel, Base II
0.....	0.2	2.8
1.....	1.4	2.4
3.....	2.3	4.5
8.....	5.5	22.0
24.....	34.0	(¹)

¹ Not determined.

It will be noted that gamma irradiation of jet fuel bases I and II increased the amount of oil-soluble gum in the irradiated samples. This undesirable oil-soluble gum may be removed from the irradiated jet fuel compositions by vacuum distillation. It has also been found that the results reported above in Table VI obtained by gamma irradiation can be correlated with the gum formed under desert storage conditions. This makes it possible to predict the gum-forming tendencies of jet fuel oils as well as other petroleum distillates after many months of storage by simply carrying out the above-described test which requires only a matter of a few hours.

Example VII

In this example, samples of two other jet fuel bases (hereinafter referred to as jet fuel base III and jet fuel base IV) were subjected to gamma radiation. Jet fuel base III was a relatively stable jet fuel base; jet fuel base IV was a relatively unstable jet fuel base. The two jet fuel bases consisted essentially of petroleum distillate. The gamma irradiation of jet fuel bases III and IV was carried out as described in Example VI. The following results were obtained in this test:

TABLE VII.—EFFECT OF GAMMA IRRADIATION ON JET FUEL BASES

Irradiation Time (Hours)	Steam Jet Gum (mg./100 gm.)	
	Jet Fuel, Base III	Jet Fuel, Base IV
0.....	0.8	6.0
1.....	0.4	17.0
3.....	8.4	28.0
8.....	10.0	41.0
24.....	(¹)	75.0

¹ Not determined.

The results in this example are similar to those of Example VI. Again it was found that gamma irradiation increased the amount of oil-soluble gum in jet fuel bases, which gum may be removed by distillation. The amount of oil-soluble gum formed by gamma irradiation can be correlated with the oil-soluble gum produced upon extended periods of storage such as desert conditions or cyclic storage conditions (e. g., 12 hours at 70° F., 12 hours at 100° F., etc.).

What is claimed is:

1. A method of stabilizing a petroleum middle distillate boiling within the range of about 300° to 750° F., which comprises exposing said distillate to gamma ray radiation obtained from a radio-isotope while blowing said distillate with a free oxygen-containing gas, said distillate not being in direct contact with said radio-isotope, the irradiation being carried out at a dose rate in the range of 50,000 to 20,000,000 roentgens per hour until in the range of 100,000 to 100,000,000 roentgens of radiant energy have been absorbed and until further irradiation of said distillate produces essentially no additional oil-insoluble sediment, separating the resultant oil-insoluble sediment and high boiling soluble gum from the irradiated material by distillation, and recovering a stabilized distillate.

2. The method of claim 1 wherein the temperature during the irradiation is in the range of 30° to 210° F.

3. The method of claim 1 wherein said isotope is cobalt 60 and wherein said free oxygen-containing gas is air supplied at a rate in the range of 0.1 to 100 v./v./hr.

4. A process which consists of: exposing a petroleum distillate mixture consisting essentially of 50 volume percent of an acid-treated, rerun, sweetened and clay-filtered cycle stock mixture boiling in the range of 406° to 620° F. and 50 volume percent of a caustic, washed, sweetened and clay-filtered gas oil boiling in the range of 310° to 536° F. to gamma ray irradiation from cobalt 60 at a dose rate of about 235,000 roentgens per hour while bubbling oxygen therethrough; continuing the irradiation until about 1.8×10^6 roentgens of energy have been absorbed; and distilling the material so irradiated to remove oil-insoluble sediment and oil-soluble gums, recovering thereby a distillate having less than 0.6 mg. of gum per 100 gm. as determined by the steam jet gum test.

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