The physical and chemical characteristics of the porphyrin metallo complexes coupled with their presence in mineral oils in small amounts, has rendered their removal from oils containing them extremely difficult. Porphyrin metallo complexes occur in crude oils obtained from many geographic locations. On preparation of distillates from such crude oils a portion of these complexes passes into the products. It has been ascertained that the porphyrin metallo complexes possess sufficient volatility and thermal stability to distill over with petroleum fractions without decomposition. Regardless of whether the porphyrin metallo complexes are introduced into the distillates by distillation or entrainment their presence is highly undesirable. Because of their neutral and oil-soluble character, the porphyrin metallo complexes of the type occurring in crude oil, particularly the vanadium complexes, can not be removed from petroleum stocks by conventional procedures including extraction, acid-treating, caustic washing, and the like. Since the porphyrin metal bonds are usually non-ionic, ion-exchange methods of removal are ineffective. The porphyrin complexes of vanadium and nickel are so stable thermally that their destruction without substantial modification of the oils in which they occur is difficult. The resinous and aromatic portions of crude oil are adsorbed more readily than the porphyrin metallo complexes on polar adsorbents such as clay thus preventing removal of the complexes in this manner.

Attempts have been made to reduce the porphyrin metallo complexes in catalytic cracking charge stocks by cutting the crude at temperatures below which the metallo complexes pass into the distillate. While such attempts to control the porphyrin metallo complexes in the distillates have been at least partially successful, the amount of cracking charge stock obtained from a crude oil is materially reduced.

We have now discovered that porphyrin metallo complexes can be destroyed by subjecting them to ionizing radiation with high energy particles or with high energy photons. We have found that the porphyrin metallo complexes can be destroyed by irradiating either a crude oil or distillates containing them. We have found, for example, that porphyrin metallo complexes in o-xylene or in mineral oils including crude oils, and petroleum fractions such as fuel oils, and catalytic cracking charge stocks can be decomposed without substantial modification of the hydrocarbons containing them by subjecting the respective solutions to ionizing radiation.

When the porphyrin metallo complexes have been completely destroyed in an oil solution, a distillate substantially reduced in metal content can be obtained by distilling the volatile hydrocarbons away from the metal or metal-containing fragments. Other means of separating the oil and metal or metal-containing fragments including separation by extraction, adsorption or ion exchange can be employed after the porphyrin metallo complexes have been destroyed. For extraction, an aqueous acid solution, an aqueous base solution where the vanadium is oxidized, or an aqueous solution of a sequestering agent such ethylenediamine tetracetic acid can be used. A further separating means is a modified extraction process, i.e., partition where the aqueous phase is spread as a film on a polar solid such as clay, alumina and silica gel. Where distillates are to be treated, ion exchange resins can be used whereby hydrogen or an alkali metal ion is exchanged for the heavy metal.

Ionizing radiation can be obtained using radio isotopes, nuclear reactors and high energy particle accelerators. Examples of the radio isotopes which can be used are cobalt 60 for gamma and strontium 90 for beta. Operating nuclear reactors of intermediate or full power size may be used as a source for either gamma rays or neutrons or both. Particle accelerators such as the cyclotron, Van de Graaff, or X-ray machines can also be used but large scale industrial application of these machines may be less practical.

In order to effect substantial destruction of the porphyrin metallo complexes, the total energy absorption should be between about 0.1 and about 1000 megarads. While the energy absorption can be greater than 1000 megarads, such high dosages are usually not warranted. While a dosage less than 0.1 megarad can be employed in some instances the degree of porphyrin metallo complex destruction obtained with such a dosage may be insufficient in many instances. Substantial destruction of the porphyrin metallo complexes can be obtained in some instances with a dosage of 50 to 150 megarads. In other instances, the increased destruction obtained by employing dosages above about 60 to 70 megarads does not justify the added cost involved. A megarad is a unit of energy equal to $10^9$ ergs per gram of material.

In effecting irradiation of the porphyrin metallo complexes, the complexes can be introduced into a well in a nuclear reactor or through a tube which traverses the
reactor. In some instances where it is desirable to expose the porphyrin metallo complexes to fast or high energy neutrons only, and in the substantial absence of beta or gamma radiation, the irradiation can be conducted outside of the reactor using a collimated beam of fast neutrons. Such a collimated beam of fast neutrons can be secured as described in U.S. Patent No. 2,708,656 to Enrico Fermi and Leo Szilard, by inserting a hollow shaft or tube into the central portion of the reactor. Gamma rays can be screened from the fast neutron beam by means of a sheet of bismuth metal extending across the path of the beam.

A neutron-free radiation source may be obtained directly from a homogeneous reactor by separating the radio active fission gases, xenon and krypton, from the reactor core by conventional or modified gas-liquid separating means. A continuous supply of the radio active fission gases could be obtained from such a reactor. The fission gases have a very high intensity of beta and gamma radiation but a very short half life. These gases possess about one percent of the total fission energy. The gases are chemically inert and therefore would not form undesired side reaction products.

The porphyrin metallo complexes or the mineral oil containing the complexes can be introduced into the reactor or into the path of a fast or high energy beam in a continuous flow through a conduit, or they may be placed in a receptacle in the reactor or in the path of the beam and subjected to irradiation while in a quiescent state.

Irradiation of the porphyrin metallo complexes or oils containing them can be carried out at subatmospheric, atmospheric or superatmospheric pressures while maintaining the bulk of the material being irradiated at any desired practical temperature. The process is thus advantageous for treating oils in that the porphyrin metallo complexes can be destroyed without materially altering the oils with which the complexes are associated. When desired, however, irradiation can be conducted simultaneously with one or more other processes. For example, the ionizing radiation whether obtained from a radio isotope, a nuclear reactor or a high energy particle accelerator can be employed both to heat and to irradiate an oil. Thus, ionizing radiations can be employed to irradiate an oil while simultaneously supplying a portion of the necessary heat to produce a metals-free vapor.

The process of the invention will hereinafter be illustrated in connection with embodiments wherein hydrocarbons containing porphyrin metallo complexes are subjected to irradiation in a cyclotron and a Van de Graaff machine. The examples will clearly demonstrate how the porphyrin metallo complexes content of hydrocarbons containing them is effectively reduced.

The process of the invention can be applied to crude oil, other bitumens, or to selected fractions thereof obtained by distillation, solvent refining, propane deasphalting or other means of refining. The invention will be illustrated by the treatment of crude oil and catalytic charge stock as well as xylene solutions containing porphyrin metallo complexes.

**EXAMPLE 1**

An o-xylene solution of etioporphyrin I vanadium complex was subjected to 15 million electron volt (mev.) deuteron radiation by a cyclotron. The bulk temperature of the solution was maintained between about 30° and 60° C. during irradiation. The concentration of the complex in the solution was 63.0 mg. per liter. The vanadium content of the complex is 9.4 weight percent. A fifteen gram sample of the solution was irradiated for a total energy absorption of 61.3 megarads. The concentration of the complex in the irradiated solution was 2.5 mg. per liter, thus indicating that 95 percent (50.5 mg. per liter) of the etioporphyrin I vanadium complex had been destroyed.

**EXAMPLE 2**

The process of Example 1 was repeated increasing the total energy absorption to 613 megarads. In this instance the concentration of the complex in the irradiated solution was 1.0 mg. per liter, thus indicating that 98 percent (52 mg. per liter) of the etioporphyrin I vanadium complex had been destroyed. Spectral examination of the irradiated products of this example and the products of Example 1 indicated that fragmentation of the porphyrin ring extends beyond the pyrrole rings.

**EXAMPLE 3**

An o-xylene solution of etioporphyrin I vanadium complex was subjected to 2 mev. electron radiation by a Van de Graaff machine. The bulk temperature of the solution was maintained between about 0° and 30° C. during irradiation. The concentration of the complex in the solution was 204.5 mg. per liter. The vanadium bound as porphyrin complex was 19.22 parts per million. A four gram sample of the solution was irradiated to a total energy absorption of about 44 megarads. The concentration of the vanadium bound as porphyrin complex in the irradiated solution was 8.17 parts per million, thus indicating that 75.5 percent of the porphyrin vanadium complex had been destroyed.

**EXAMPLE 4**

The process of Example 3 was repeated increasing the total energy absorption to about 440 megarads. In this instance the spectrum of the vanadium porphyrin complex in the irradiated solution disappeared, thus indicating that the porphyrin vanadium complex had been completely destroyed.

**EXAMPLE 5**

An o-xylene solution of etioporphyrin I nickel complex was subjected to 2 mev. electron radiation by a Van de Graaff machine. The bulk temperature of the solution was maintained between about 0° and 30° C. during irradiation. The concentration of the complex in the solution was 54.2 mg. per liter. The nickel bound as porphyrin complex was 5.94 parts per million. A four gram sample of the solution was irradiated to a total energy absorption of about 44 megarads. The concentration of the nickel bound as porphyrin complex in the irradiated solution was 3.77 parts per million, thus indicating that 36.6 percent of the porphyrin nickel complex had been destroyed.

**EXAMPLE 6**

A Mara catalytic cracking charge stock containing 23.9 parts per million of vanadium bound as porphyrin complexes was subjected to 15 mev. deuteron radiation by a cyclotron. The bulk temperature of the solution was maintained between about 30° and 60° C. during irradiation. A fifteen gram sample of the cracking charge stock was irradiated to a total energy absorption of 125 megarads. After being subjected to irradiation, the concentration of the vanadium bound as porphyrin complexes in the catalytic cracking charge stock was reduced to 5.5 parts per million, thus indicating that 77 percent of the porphyrin vanadium complexes had been destroyed.

**EXAMPLE 7**

A Mara crude oil containing 40 parts per million of vanadium bound as porphyrin complexes was subjected to 15 mev. deuteron radiation by a cyclotron. The bulk temperature of the solution was maintained between about 30° and 60° C. during irradiation. A fifteen gram sample of the crude oil was irradiated to a total energy absorption of 125 megarads. After being subjected to irradiation, the concentration of the vanadium bound as porphyrin complexes in the crude oil was reduced to 10 parts per million, thus indicating that 75 percent of the porphyrin vanadium complexes had been destroyed.
EXAMPLE 8

The process of Example 7 was repeated increasing the total energy absorption to 187 megarads. In this instance the concentration of the vanadium bound as porphyrin complexes in the irradiated solution was reduced to less than 12 parts per million, thus indicating that more than 70 percent of the porphyrin vanadium complexes had been destroyed.

EXAMPLE 9

A Mara crude oil containing 40 parts per million of vanadium present as porphyrin vanadium complexes was subjected to 15 mev. deuteron radiation by a cyclotron. The bulk temperature of the solution was maintained between about 30° and 60° C. during irradiation. Three nearly equal batches, about 15 grams each, of the crude oil were irradiated to a total energy absorption of about 245 megarads. After being irradiated, the three batches were combined and then subjected to fractional distillation using a modified alembic still. For the sake of comparison, an untreated sample of raw Mara crude oil was similarly fractioned. The concentration of the vanadium bound as porphyrin complexes in each of the fractions were spectrally determined. The results obtained are summarized in the following table.

Distribution of Distillable Material and Porphyrin Metallo Complexes in Raw Mara Crude Oil and in Irradiated Mara Crude Oil

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Boiling range, °F</th>
<th>Position in the crude volume percent</th>
<th>Concentration of vanadium as porphyrin complex, p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>448 to 560</td>
<td>0-43.2</td>
<td>0-92.2</td>
</tr>
<tr>
<td>II</td>
<td>433 to 602</td>
<td>82.7-93.1</td>
<td>82.7-73.1</td>
</tr>
<tr>
<td>III</td>
<td>560, last drop</td>
<td>81.4</td>
<td>78.5-81.4</td>
</tr>
</tbody>
</table>

1 Atmospheric pressure.
2 At a pressure of 1 micron of mercury, that is conditions for molecular distillation.

It will be noted that the concentration of vanadium as porphyrin complex in the distillate of irradiated Mara crude oil is substantially reduced over the concentration of vanadium as porphyrin complex in the corresponding distillate of untreated Mara crude oil.

While it would appear that Fractions I, II and III of the irradiated crude oil are displaced upwards in respect to position in the crude compared to the same fractions of the raw Mara crude oil, such apparent displacement is the result of losing volatile components in handling, rather than a result of crude oil modification. The porphyrin vanadium complexes begin to distill during Fraction III and their concentration in the distillate is increasing rapidly at the upper cut point for the fraction as evidenced by the concentration of vanadium in the last drop to distill. We have determined that in the 49.1 to 81.4 percent fraction of the crude oil, which represents the catalytic cracking charge stock, irradiation resulted in a decrease in the concentration of porphyrin vanadium complexes of 65 percent, i.e., 3.46 parts per million in the irradiated distillate as compared with 9.76 parts per million in the untreated distillate.

While our invention has been described above with reference to certain specific embodiments thereof by way of illustration, it is to be understood that the invention is not limited to such embodiments except as hereinafter defined in the appended claims.

We claim:

1. A process for the destruction of porphyrin metallo complexes in solution which comprises subjecting said complexes to high energy ionizing radiation with a dosage sufficient to destroy said complexes.

2. The process of claim 1 wherein the metal of said porphyrin metallo complexes in solution is selected from the group consisting of vanadium, nickel, iron and copper.

3. A process for the destruction of porphyrin metallo complexes which comprises subjecting said complexes to high energy ionizing radiation for a time sufficient to absorb between about 0.1 and about 1000 megarads of energy.

4. The process of claim 3 wherein the porphyrin metallo complexes are present in a mineral oil.

5. The process of claim 4 wherein the mineral oil is a crude oil.

6. The process of claim 4 wherein the mineral oil is a petroleum fraction.

7. A process for reducing the porphyrin metallo complex content of a catalytic cracking charge stock which comprises subjecting a crude oil containing said complexes to high energy ionizing radiation with a dosage sufficient to reduce the complex content thereof and distilling said irradiated crude oil to obtain a catalytic cracking charge stock of reduced porphyrin metallo complex content.

8. The process of claim 7 wherein the metal of said porphyrin metallo complex is selected from the group consisting of vanadium, nickel, iron and copper.

9. The process of claim 7 wherein irradiation is conducted for a time sufficient to absorb between about 0.1 and about 1000 megarads of energy.

10. A process for reducing the porphyrin metallo complex content of petroleum oils which comprises subjecting said petroleum oils containing said porphyrin metallo complexes to high energy ionizing radiation from a nuclear reactor and with a radiation dosage sufficient to reduce the complex content, and separating a petroleum oil of reduced porphyrin metallo complex content.

11. A process for reducing the porphyrin metallo complex content of petroleum oils which comprises subjecting said petroleum oils containing said porphyrin metallo complexes to high energy ionizing radiation with a radiation dosage sufficient to reduce the complex content, and separating a petroleum oil of reduced porphyrin metallo complex content.

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UCRL 3351, AEC document, March 23, 1956; pages 4-6.
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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,100,182 August 6, 1963

John G. Erdman et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 3, for "or" read -- and --; line 68, for "63.0" read -- 53.0 --; column 5, line 40, for "41.1" read -- 41.4 --; column 6, line 8, strike out "in solution", and insert the same after "complexes", in line 9, same column 6; line 12, strike out "in solution" and insert the same before "to", in line 15, same column 6.

Signed and sealed this 4th day of February 1964.

(SEAL)
ERNEST W. SWIDER
Attesting Officer

EDWIN L. REYNOLDS
Acting Commissioner of Patents