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# RADIOACTIVE TRACER

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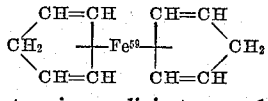
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This invention relates to radioactive tracers and more particularly relates to oil-soluble cyclopentadienyl compounds of radioactive iron. The invention also relates to methods of tracing hydrocarbons and related organic compositions using such compounds of iron as radioactive tracers.

The importance of radioactive tracers is well known. Such materials have been used heretofore, for example, in medical, agricultural and industrial research. A number of radioactive materials have been suggested heretofore for tracing hydrocarbons and related organic compositions in order to determine location, flow patterns, rates of mixing, etc. However, these tracers have not been entirely satisfactory. Thus a large number of the tracer elements having desirable radioactivity characteristics form compounds which are only slightly soluble in hydrocarbons and thus cannot be used in the concentrations desired or else tend to separate out of the hydrocarbons after a short period of time. One of the most serious drawbacks to those radioactive materials used heretofore as oil-soluble tracers for hydrocarbons has arisen from the fact that such compounds are chemically unstable; or readily dissolved out of (or leached from) the hydrocarbon by materials such as water, acids and the like. This represents a serious problem in refineries. For example, petroleum oils are frequently stored in refineries in contact with water. Also due to changes in ambient humidity (combined with the slight solubility of water in oil) it is difficult, if not impossible, to exclude water completely from the oil in many cases where the use of a tracer might be desired—e.g., in following the mixing or dilution of plant blends, or in the proof of contamination of branded products. In addition, many of the prior art radioactive tracers are strongly adsorbed on the surfaces of metal equipment, thus making the use of such tracers ineffective. There has thus been a need for an effective tracer material for labeling hydrocarbons, which tracer material is readily soluble in hydrocarbons, is not destroyed or leached out of the hydrocarbon when in contact with water, acids and the like, and is not adsorbed on the surfaces of metal equipment.

A novel class of compounds has now been found which are extremely effective as radioactive tracers for labeling hydrocarbons and related organic compositions. More particularly, these new compounds are oil-soluble cyclopentadienyl compounds of radioactive iron. It has been found that such radioactive compounds are readily soluble in hydrocarbons and related organic compositions, are highly resistant to extraction by hot water and strong acids and are not adsorbed on the surfaces of metals. The radioactive tracers of the present invention are particularly useful for labeling hydrocarbons and related organic compositions in order to determine location, flow patterns, rates of mixing, etc.

The preferred radioactive compound of the present invention is bis-cyclopentadienyl iron which may be represented by the following structural formula:




where the iron atom is a radioisotope and preferably $Fe^{59}$ as indicated. The methyl derivative may also be used to advantage in the present invention. Other substituted



compounds of bis-cyclopentadienyl iron may also be employed in certain specific instances although it will be understood that they are generally much less desirable for the general purposes of the present invention. The preparation of bis-cyclopentadienyl iron and its substituted compounds is well known in the art. For example, bis-cyclopentadienyl iron can be readily prepared by reacting cyclopentadienyl magnesium bromide with an ether solution of anhydrous ferric chloride at a temperature of about 20° to 40° C. for about 2 to 6 hours. It will be understood that the radioactive iron compounds of the present invention may be prepared by the same methods as have been employed heretofore to prepare similar compounds of naturally-occuring iron.

The radioactive compounds of the present invention may be prepared employing any of the radioisotopes of iron such as, for example, iron 59, iron 55, iron 52 and iron 53. However, iron 59 is particularly preferred in that it is a gamma ray emitter, the gamma rays being sufficiently energetic to be detected through thick metal walls of equipment containing the isotope solution. Iron 55 is second choice. Iron 59 has a half life of about 46 days and decays by emitting 1.1 and 1.3 mev. (million electron volts) gamma rays and, in addition, 0.46 and 0.26 mev. beta rays to produce cobalt 59 as the ultimate product of decay. Iron 55 decays by K capture giving an X-ray of 6 kev. (thousand electron volts) to produce manganese 55 as the ultimate product of decay. These radioisotopes of iron may be prepared by bombarding naturally-occurring iron with neutrons in an atomic pile. It will be understood that mixtures of various iron radioisotopes may be employed and, further, that the mixture may also contain some non-radioactive isotopes of iron. The radioactive isotopes should be present in sufficient proportion to contribute at least 0.001 microcurie per gram of compound and preferably at least 0.1 microcurie per gram. Specific examples of radioactive tracers of the present invention include bis-cyclopentadienyl iron 59, bis-cyclopentadienyl iron 55, bis-cyclopentadienyl iron 53, bis-cyclopentadienyl iron 52, bis-methyl-cyclopentadienyl iron 59 and bis-methyl-cyclopentadienyl iron 55. Bis-cyclopentadienyl iron 59 or mixtures containing substantial proportions of this material are particularly preferred in the present invention.

The hydrocarbons in which the present radioactive tracers are incorporated (i.e., dissolved) will generally be the normally-liquid hydrocarbons such as petroleum oils and the like. The exact composition of the hydrocarbon oil is immaterial; it may contain aromatics, aliphatics and/or cycloaliphatic components. The hydrocarbons may also be pure compounds such as heptane, benzene, toluene and the like. If desired, however, the present radioactive tracers may be added to other types of hydrocarbon compositions or to related organic compositions which are fluid at one time or another during the tracing operation. Thus it will be understood that the present radioactive tracers may be advantageously added to asphalts, pitch and the like. The present tracers may also be employed advantageously in related organic compositions including those compositions containing substantial proportions of hydrocarbons (e.g., mineral oil greases and lubricating oil compositions) as well as in compositions containing substantial proportions of compounds having hydrocarbon groups in which the present compounds are soluble.

Generally, it will be desirable that the present radioactive tracers be added to fluid compositions in concentrations of about 0.001 to 1000, preferably about 0.05 to 1.0 microcurie per liter of composition, based on the total composition. Usually the amount of the iron 59 compound added will be about $1.3\times10^{-16}$ to $1.3\times10^{-10}$, preferably about $1.3\times10^{-14}$ to $1.3\times10^{-11}$ weight percent,

based on the total composition. When the compound of the present invention is one of iron 59, the amount of iron 59 activity in the iron bis-cyclopentadienyl material should be generally about 0.001 to 1000 microcuries of iron 59 per gram of iron bis-cyclopentadienyl, preferably about 0.1 to 100 microcuries of iron 59 per gram of iron bis-cyclopentadienyl, at the time when the radioactivity is to be detected. It will be understood that the intensity of radiation emitted by the radioactive tracers will decrease with time due to radioactive decay. The selection of the concentration of the radioactive tracer of the present invention is, however, well within the skill of a person skilled in the art.

The radiation emitted from the hydrocarbon compositions or related organic compositions by the present radioactive tracers may be measured by any of the conventional radiation detectors including electroscopes, vibrating reed electrometers, Geiger-Mueller counters, proportional counters, scintillation counters and the like. Such radiation detectors are well known in the art and need not be described herein in greater detail. See for example "Nuclear and Radio Chemistry" by Friedlander and Kennedy, chapter 8, pages 224 to 249 (1955).

The method of tracing hydrocarbons in accordance with the present invention comprises incorporating into the hydrocarbon or related organic composition a small amount of the present radioactive iron compound, such as bis-cyclopentadienyl iron 59, and then detecting the radioactivity emitted by the radioisotope from the hydrocarbon or related organic composition. The amount of the radioisotopic compound added should be sufficient to be detected by radiation detectors under the conditions of the tracing operation. The present invention is particularly useful for labeling hydrocarbons in order to be able to determine location, flow patterns, rates of mixing, etc. More particularly, the present radioactive tracers may be advantageously employed in the following specific applications:

(1) *Determination of flow pattern in an alkylation unit.*—Hydrocarbon and acid are injected into an alkylation unit. In order to determine whether true mixing takes place or whether the materials pass through the unit as unmixed "slugs," approximately 100 microcuries of iron 59 bis-cyclopentadienyl, previously dissolved in about one liter of the hydrocarbon, are suddenly injected into the hydrocarbon feed stream. A suitable radiation detector such as a scintillation counter is placed adjacent to the exit pipe of the alkylation unit. If the activity as recorded by the detector occurs as a sudden distinct peak, "slug" flow is taking place. If the activity appears gradually over a period of time, true mixing is taking place.

(2) *Determination of leaks in buried pipelines.*—Iron 59 bis-cyclopentadienyl is dissolved in the hydrocarbon which flows through the pipeline. At the point where a leak exists, the material collects in a pool around the pipe. By moving a suitable radiation detector over the ground above the buried pipeline, the point of increased activity where the pool has formed indicates the location of the leak.

(3) *Determination of flow rate.*—It is desired to determine the rate of flow of hydrocarbons through a pipe. Iron 59 bis-cyclopentadienyl is dissolved in a small quantity of the hydrocarbon. This tracer solution is injected under pressure into the flowing hydrocarbon in the pipe. By placing two detectors a suitable known distance apart along the pipe below the point of injection and recording the time at which each detector measures the peak of the passing activity, the rate of flow is determined.

(4) *Determination of degree of mixing.*—It is desired to know how much time is required for the complete mixing of materials in a mechanically agitated grease mixer. Iron 59 cyclopentadienyl is mixed with a small quantity of grease and placed at the center of the materials in the mixer. At known time intervals, samples are taken from different points within the mixer. These samples are then counted for radioactivity with a suitable detector. When samples taken from all points in the mixer have the same amount of activity, mixing is complete. A knowledge of the time at which the samples were taken makes it possible to determine how long the mixture was agitated before complete mixing, as indicated by a homogeneous sample count, was achieved.

(5) *Degree of entrapment of one liquid phase by another.*—A hydrocarbon and an acid react together in an alkylation unit and are then separated. However a portion of the hydrocarbon remains in the acid. It is desired to discover what proportion of the hydrocarbon is removed with the acid phase. Iron 59 cyclopentadienyl is dissolved in a small quantity of the hydrocarbon and this tracer solution is mixed with the total hydrocarbon phase. With a suitable radiation detector, the activity in the acid phase is measured as it leaves the unit. The activity in this acid phase is due to entrapped hydrocarbon containing iron 59. The amount of activity measured is a measure of the amount of hydrocarbon entrapped by the acid phase.

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

### *Preparation of Bis-Cyclopentadienyl Iron 59*

A product which consisted of a mixture of bis-cyclopentadienyl iron 59 and non-radioactive bis-cyclopentadienyl iron was prepared specifically as follows:

Ethyl magnesium bromide was first synthesized in ethereal solution by reacting 27 grams of magnesium metal with 110 grams of ethyl bromide. Cyclopentadiene, 66 grams, was added dropwise to the ethyl magnesium bromide to prepare the intermediate, cyclopentadienyl magnesium bromide. The cyclopentadiene was added over a period of 1 hour and 15 minutes while maintaining the mixture at temperature to give a trace amount of reflux. The mixture was held at 34–35° C. for an additional four hours, finally heated to 38° C., and allowed to stand overnight. A total of 1.04 cubic feet of gas (uncorrected for ether and water vapors) was evolved during this phase of the synthesis.

A solution of ferric chloride in anhydrous ether was added to the above Grignard reagent. The radioactive portion of the ferric chloride was made by evaporating an aqueous solution of ferric chloride (0.8 gram of iron in 1 liter of $H_2O$), containing 56.5 microcuries of iron 59 to dryness under a stream of chlorine. The radioactive salt was dissolved in anhydrous ethyl ether and added to a solution of non-radioactive ferric chloride which was made by dissolving 40 grams of non-radioactive ferric chloride in 300 cc. ether and filtering. The combined ethereal solutions were added to the cyclopentadienyl magnesium bromide over a period of about 1 hour during which time the temperature was maintained in the range of 20 to 30° C. The mixture, after standing overnight, was refluxed for 1 hour and decomposed in an aqueous solution of ammonium chloride containing ice. The product was extracted with benzene. Final purification was made by crystallizing from methyl alcohol at Dry Ice temperature. A total of 18 grams of purified product was recovered which contained $4.4\times10^{-3}$ microcuries of $Fe^{59}$ per gram of purified bis-cyclopentadienyl iron. The product was orange in color and sublimed readily.

## EXAMPLE II

### *Stability of Bis-Cyclopentadienyl Iron 59 in Benzene*

The product of Example I (a mixture of iron 59 and non-radioactive iron bis-cyclopentadienyl compounds) was then tested for its stability in benzene. More par-

ticularly, the benzene solution in separate experiments was mixed with (1) distilled water, (2) aqueous sulfuric acid, (3) aqueous hydrochloric acid, and (4) iron filings in order to determine whether any of the radioactive tracer was extracted. The benzene solutions contained a total of 7 grams per liter of the product of Example I, this 7 grams being composed of radioactive and non-radioactive iron bis-cyclopentadienyl. Of this 7 grams, approximately $6\times10^{-15}$ grams was iron 59 bis-cyclopentadienyl, the remainder being mainly the stable, non-radioactive iron bis-cyclopentadienyl. The concentration of the benzene solution in terms of activity was 0.31 microcurie of iron 59 per liter of solution. The benzene solutions were contacted with equal volumes of the extracting agents mentioned above and shown in the table below. A count of the radioactivity in the extracting agent compared to the radioactivity in the original benzene solution gave the percent of iron 59 cyclopentadienyl extracted.

STABILITY OF BIS-CYCLOPENTADIENYL IRON 59 IN BENZENE

| Extracting Process | Activity Extracted percent | Appearance of Extracting Layer |
|---|---|---|
| Distilled $H_2O$, 24 hrs. at 80° F | None | Clear. |
| Distilled $H_2O$, 24 hrs. at 150° F | None | Clear. |
| Aqueous $H_2SO_4$,[1] 48 hrs. at 80° F | None | Faint blue tint. |
| Aqueous HCl,[1] 24 hrs. at 80° F | [2] 6.8 | Yellow emulsion. |
| Iron filings, 48 hrs. at 80° F | None | |

[1] Equal parts by weight of acid and water.
[2] In the form of an emulsion.

The data in the above table show the unique stability of iron 59 bis-cyclopentadienyl. From these data it is apparent that this tagging or tracer compound is not extracted from the hydrocarbon layer by extremely severe extraction conditions. It is this resistance to extraction which makes iron 59 bis-cyclopentadienyl very useful as a tracer. Other readily prepared organo-metallic salts cannot withstand all of the extraction conditions outlined above and are removed from the hydrocarbon layer thus rendering them useless under many circumstances as tracer or tagging agents.

Bis-cyclopentadienyl iron 59 may be employed as a tracer for labeling hydrocarbons in the following specific application:

*Determination of Degree of Entrapment by One Liquid Phase of Another Liquid Phase*

In an alkylation pilot plant unit an isoparaffin and an olefin are treated with concentrated sulfuric acid. The acid is then separated from the hydrocarbon phase. It is desired to determine how much of the hydrocarbon is removed with the acid. In order to determine the amount of hydrocarbon removed, iron 59 bis-cyclopentadienyl is added to the hydrocarbon phase. A count of the radioactivity in the acid phase as the acid phase is withdrawn from the alkylation unit will determine the amount of hydrocarbon removed with the acid.

The feed to the unit during a run consists of 200 liters of liquefied isobutane, butylene and propylene. Twenty grams of iron bis-cyclopentadienyl containing 10 microcuries per gram of iron 59 activity are placed in a vessel and two liters of the liquefied hydrocarbon mixture are added. The vessel is shaken to dissolve the tagged iron bis-cyclopentadienyl. The tagged solution is then injected into the hydrocarbon feed. The tagged feed is then led into a 2 inch outside diameter pipe. A scintillation detector containing a 1" diameter x 1" thick NaI crystal is then fixed so that the crystal is against the pipe containing the hydrocarbon feed. The scintillation detector is connected to a rate meter which will record the average number of counts per minute received by the scintillation detector. Under the conditions outlined above there is 1 microcurie of iron 59 activity per liter of solution. Assuming that the crystal "sees" 100 cc. of the solution and making assumptions for the attenuation through the walls of the pipe and for the efficiency of the detector, approximately 15,000 counts per minute will be received by the detector and recorded by the rate meter.

The alkylation process is then started and 98% $H_2SO_4$ is reacted with the hydrocarbon feed at approximately 40° F. As the acid becomes diluted with moisture in the liquefied gas stream, it is withdrawn and replaced. In order to obtain the same counting geometry as was used in counting the tagged feed stream, the acid being withdrawn is led through a 2" outside diameter pipe. The same scintillation detector is now placed against this pipe in the same manner as it was previously placed against the tagged hydrocarbon feed pipe. The count is recorded, as before, on a rate meter. The ratio of the count obtained on the acid pipe divided by the count obtained on the feed pipe gives the proportion of the hydrocarbon which is being withdrawn with the spent acid. For example, a count of 1,500 counts per minute on the acid stream would indicate that 0.1 liter of hydrocarbon was being removed with each liter of acid withdrawn.

With the knowledge of the amount of hydrocarbon removed with the acid, the structure and operating conditions of the alkylation unit can be altered to decrease the amount of hydrocarbon lost by withdrawal with the spent acid.

The iron 59 bis-cyclopentadienyl compound used in this application can be prepared as follows: 1 gram of iron is irradiated in a nuclear reactor for 60 days at a neutron flux of 5 x 10" neutrons/cm.$^2$/sec. resulting in an iron 59 activity of 220 microcuries/gram. This irradiated iron is dissolved in aqueous hydrochloric acid (1 part concentrated HCl, 1 part $H_2O$) and evaporated to dryness in a stream of chlorine gas. This gives as a product 2.9 grams of $FeCl_3$. To this is added 19 grams of anhydrous $FeCl_3$ as a carrier. This mixture of stable and radioactive iron chloride is then dissolved in ether and added to the cyclopentadienyl magnesium bromide Grignard reagent as shown in Example I.

What is claimed is:

In a process wherein a liquid hydrocarbon is converted and the process is monitored by dissolving a radio-tracer in said liquid hydrocarbon, the improvement wherein said radio-tracer is bis-cyclopentadienyl iron-59.

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