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RADIOACTIVE TRACERS FOR PIPE LINES

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This invention relates to liquid radioactive tracers and methods for their preparation, and particularly refers to those prepared from isotopes of cesium that are of specific utility in tracing the flow of liquid hydrocarbons through pipe lines.

In the operation of long pipe lines through which successive batches of liquid hydrocarbon products are passed, it is essential to be able to distinguish the interfaces between different products so that they may be separated at their points of take-off or delivery. A suitable method that has been developed consists in the introduction into the interface between successive different products of a small quantity of an oil-soluble liquid carrying a radioisotope that can be detected outside of the pipe line at any point along the length. Usually the isotope is chosen to be a gamma-emitter, and compounds of radioactive antimony and the like have been employed, as described in the Patent No. 2,706,254 of R. C. Mithoff and D. E. Hull.

This invention is particularly directed to improve long-lived liquid radioactive tracers, particularly but not necessarily exclusively suited for such pipe line operations, and employing radioisotopes of cesium, namely, Cs^{134} having a 2.3 year half-life and emitting gamma radiation in the 0.57–0.79 m. e. v. range, and Cs^{137} having a 37 year half-life which does not emit gamma radiation but is in equilibrium with a 2.6 minute Ba^{137} daughter emitting 0.66 m. e. v. gamma radiation. A given number of millicuries of the Cs^{134} isotope is about twice as specifically effective as the Cs^{137}. The radioactive tracer composition containing either isotope may be prepared by the procedures which will be described below. The Cs^{137} isotope has the advantage of a longer effective life, which can be of substantial importance in certain tracer applications. The earlier-used antimony isotopes, having a 60-day half-life, required frequent preparation in small quantities, due to their rapid decay, and were accordingly more expensive to prepare and to store.

It is an object of this invention to provide an improved oil-soluble and water-insoluble radioactive liquid tracer composition which is simply prepared and conveniently used, and which has a longer effective useful life than certain of those tracers heretofore available, and which may be prepared at a much lower cost.

Another object is to provide an improved method of preparing a radioactive tracer composition that may be carried out conveniently and with safety to the operator.

Another object is to provide an improved method of purifying a sulfonate component of a radioactive liquid tracer to produce a product having desirable characteristics.

These and other objects and advantages will be further apparent from the following specification, which describes the improved product and an exemplary procedure for producing it.

The cesium isotopes Cs^{134} and Cs^{137} are available to qualified users from Oak Ridge National Laboratory

of the United States Atomic Energy Commission as a chloride solution having a very high specific radioactivity, requiring shielded handling, as is well known in this art. The final product also requires suitable equipment for safe storage and utilization.

In this example, an 0.5 ml. (milliliter) aliquot of cesium^{134} chloride containing 9 mc. (millicuries) of Cs^{134} activity and 0.5 mg. cesium in 0.5 N HCl was evaporated to dryness and then redissolved in 0.5 ml. of water to which 2.0 ml. of 95% ethanol was added. To this solution was added 15 ml. of sodium sulfonate which had been prepared by sulfonation of a petroleum distillate stock followed by conversion to free sulfonic acid and neutralization with NaOH. It is considered that the radioactive cesium chloride reacts to form cesium sulfonate.

This mixture was heated to 150° C. with stirring to remove water and alcohol. The cooled mixture was then dissolved in a low boiling hydrocarbon diluent, in this case xylene, and made up to 100 ml. volume. The yield of activity was greater than 99%, resulting in 100 ml. having 9 mc. activity or about 0.1 mc./ml. of product. The specific activity of the sulfonate-cesium mixture and the final diluted tracer may be chosen to suit the particular use to which the product may be put. In the usual pipe line operation, about 3 to 12 millicuries of the cesium isotope may be used for each injection, diluted to a convenient quantity to suit the injection equipment.

In large-scale preparations, where an appreciable weight of cesium is present, it has been found to be desirable to convert the cesium chloride to the hydroxide, using an appropriate ion-exchange column. The hydroxide may then be directly reacted with sulfonic acid to produce the sulfonate carrying the active isotope in oil-soluble form. The same procedures as just given apply also to preparation of the improved traced from the Cs^{137} isotope.

Certain commercial sulfonates contain a trace of sodium sulfate, Na_2SO_4, which precipitates when the product is dissolved in very large quantities of certain hydrocarbon thinners and solvents. In cesium sulfonate preparations made from these commercial sulfonates, no radioactivity was carried down in the precipitate, although it may be deemed advisable to remove the sulfate from the sulfonate before the cesium salt is added. This may be done conveniently by water extraction or by first diluting the sodium sulfonate with a petroleum thinner, followed by separation of the precipitate and evaporation of the excess solvent.

The radioactive and other properties of the cesium isotope products of this invention are very desirable for certain tracer applications, such as the pipe line oil interface tracer of patent No. 2,706,254 discussed above. For example, cesium sulfonate solutions which have been prepared according to this invention may be highly diluted with petroleum or other hydrocarbon solvents without separation of radioactivity. Also, it is substantially unaffected by water, as was evidenced by making up 400 ml. of petroleum thinner containing 1,25 ml. of tracer solution and shaking it successively with 25 ml. of tap water, 25 ml. of NaCl solution containing 0.7 mg./ml. NaCl, and with 25 ml. of $CaCl_2$ containing 3 mg./ml. of $CaCl_2$. No radioactivity was found in any extract. Hence, the tracer is quite stable for use in pipe lines carrying oil, but in which small amounts of water may unavoidably be present.

As stated above, the Cs^{134} isotope emits several gamma rays that are of suitable magnitude to penetrate the steel wall of a pipe line and be detected outside of the pipe by suitable single or multiple units of gamma ray

detectors. Each disintegration yields one 0.60 m. e. v. and one 0.79 m. e. v. gamma ray, and, in addition, 25% of the disintegrations yield a 0.57 m. e. v. gamma ray. As compared with radioactive tracers from Sb^{124}, with 2.7 m. e. v. gamma, a somewhat greater quantity of the cesium isotope would be required, but would still be at a lower cost per injection.

The 37-year Cs^{137} isotope does not emit any gamma rays; however, it is in equilibrium with its 2.6-minute Ba^{137} daughter, which emits one 0.66 m. e. v. gamma ray per disintegration. Accordingly, the Cs^{137} isotope product would require somewhat greater quantities per injection than the Cs^{134} product, but because of its still lower cost and much longer life, would be more economical as compared to present practices in this art.

I claim:

1. A radioactive tracer consisting essentially of an oil soluble sulfonate of an isotope of cesium selected from the group consisting of Cs^{134} and Cs^{137}.

2. A radioactive tracer consisting essentially of an oil-soluble sulfonate of Cs^{134}.

3. A radioactive tracer consisting essentially of an oil-soluble sulfonate of Cs^{137}.

4. A radioactive tracer consisting essentially of a sulfonate obtained by reacting an oil soluble sulfonate and an inorganic cesium salt, wherein the cesium is selected from the group consisting of radioactive isotopes Cs^{134} and Cs^{137}.

5. A radioactive tracer consisting essentially of the reaction product of a petroleum sulfonate and an inorganic cesium salt, wherein the cesium is a radioactive isotope selected from the group consisting of Cs^{134} and Cs^{137}.

6. A method of preparing a radioactive tracer comprising the steps of reacting an oil soluble sulfonate and a radioactive cesium isotope selected from the group consisting of Cs^{134} and Cs^{137} to produce an oil soluble radioactive tracer.

7. A method of preparing a radioactive tracer comprising the steps of reacting sodium sulfonate derived from petroleum and a radioactive cesium isotope selected from the group consisting of Cs^{134} and Cs^{137} to produce an oil soluble radioactive tracer.

8. Oil soluble Cs^{134} sulfonate.

9. Oil soluble Cs^{137} sulfonate.

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