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RADIOACTIVE SOLID PARTICLES FOR USE IN WELL LOGGING

Cassius R. McEwen, Fullerton, Calif., assignor to Union Oil Company of California, Los Angeles, Calif., a corporation of California

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This invention relates to radioactive solid particles suitable for use in certain well logging operations, and to a method for preparing the same. It further relates to a well logging method in which such particles are obtained.

The use of radioactive substances in determining the variations in the permeabilities of subterranean strata traversed by a well bore is well known. According to one embodiment of such methods, a fluid such as crude oil or brine carrying suspended radioactive solid particles is pumped down the borehole under a pressure sufficient to force the fluid out into the strata traversed by the bore. The various strata act as filters to remove the suspended solids from the suspending liquid. Since the quantity of fluid which is forced into any one stratum is directly proportional to the permeability of that stratum with respect to the suspending liquid, the quantity of radioactive solids which is filtered out and deposited as a filter cake on the wall of the borehole opposite such stratum is likewise directly proportional to such permeability. Accordingly, after a brine suspension of radioactive solid particles has been forced down the bore under the aforesaid pressure the walls of the bore will bear a coating of radioactive solids, and the thickness of such coating at any point will be a measure of the permeability with respect to the brine of the particular stratum which underlies the coating at that point. Since the intensity of radiation from said coating is directly proportional to the thickness of the coating, a log of the thickness of the coating (and hence of the brine permeabilities of the strata which underlie the coating) can readily be obtained by passing a radiation detector, e.g., a Geiger-Müller counter, through the bore and plotting the radiation intensity versus depth. When it is desired to determined the permeabilities of the strata with respect to a fluid other than brine, such fluid is employed for suspending the radioactive particles.

As will readily be appreciated, the success and accuracy of the logging method described above will depend upon the radioactive solid particles possessing certain requisite characteristics. Thus, they must be relatively light in weight, ideally having the same density as the suspending liquid, so that they may readily be maintained uniformly suspended in the suspending liquid. Also, they must be inert with respect to the suspending liquid and the environment in which it is employed; that is, the radioactive element in the solid particles should be of such nature and should be so combined with the particles that it is not leached out by the suspending liquid or replaced by ions or other entities contained in such liquid, and is not absorbed by or in the subterranean strata. Furthermore, the particles should be of such nature that they are readily filterable, i.e., they should not swell or otherwise change physical form so as to clog the strata and impede the filtering action. At the present time the radioactive solid most widely employed is obtained by treating an anion-exchange resin with a radioactive iodide and thereafter treating the exchanged resin with silver nitrate to precipitate radioactive silver iodide on the resin particles. Such material, however, is not satisfactory for use where the suspending liquid is an oil field brine containing sulfide ion since the latter chemically replaces

the iodine in the silver iodide and the radioactive iodine is carried into the strata by the brine.

I have now found that a highly superior radioactive solid suitable for use in logging well bores by the method described above can be prepared by treating a solid polyolefine or a solid vinyl polymer with a radioactive halogen. The latter becomes firmly bound to the solid polymer (possibly by addition at sites of unsaturation) and cannot be removed therefrom by any of the ions present in aqueous suspending liquids or by oil or other organic liquids or by any of the minerals in subterranean formations. Furthermore, polyolefine and vinyl polymers are of relatively low density and can readily be maintained uniformly suspended in the conventional suspending liquids over relatively long periods of time. Also, the method by which the new products are prepared is very simple and inexpensive, and requires no special equipment or procedure. If necessary, they can be prepared at the well site.

The polymeric solid which is treated with a radioactive halogen in accordance with the invention is preferably solid polyethylene, e.g., ordinary commercial polyethylene such as is widely employed for electrical insulating purposes and for the manufacture of flexible containers such as the familiar "squeeze" bottle. Alternatively, other polyolefines such as polypropylene and vinyl polymers such as polystyrene, the polyacrylates and methacrylates, the polyvinyl halides and polyvinyl esters, and the like may be employed although it is to be understood that polyvinyl compounds which contain ion-exchanging functional groups are excluded. The term "non-ion exchanging polyvinyl resin" is herein employed to designate the present class of vinyl polymers and to distinguish over the prior art use of ion-exchanging polyvinyl resins such as the sulfonated polystyrenes.

Since the logging method to which the invention pertains operates on the principle of the radioactive solids being filtered out of the suspending liquid and forming a filter cake of varying thickness on the walls of the bore, the size of such particles will depend upon the nature of the subterranean strata traversed by the bore, i.e., such size should be larger than the interstices or pores of the strata to be logged in order to avoid the particles being carried into such interstices or pores. In general, such particle size will correspond to between about 30- and about 300-mesh, although particles of larger or smaller sizes may be employed where the strata have unusually large or unusually small pores. In order to attain good filtering action and to avoid clogging the pores of the strata it is desirable to employ as large a particle size as is consistent with accurate results and the maintenance of a relatively uniform and stable suspension in the suspending liquid.

As previously explained, the radioactive element with which the polyethylene or polyvinyl resins particles are treated in accordance with the invention is a radioactive halogen, e.g., chlorine 36, bromine 82, iodine 126, iodine 130, iodine 131, etc. By reason of the ease and rapidity with which the products of the invention are prepared it is possible to employ radioactive halogens having half-lives as short as several hours. However, radioactive isotopes of iodine, e.g., iodine 131, are preferred by reason of their ready availability. It should be noted that in the practice of the present invention the radioactive element is employed in elemental form rather than as a salt or other compound thereof.

The step of treating the polyethylene or polyvinyl resin particles with the radioactive halogen consists simply in contacting the solid particles with the halogen at ambient or slightly elevated temperatures until sufficient of the halogen has combined with the resin to give a

solid having the desired radiation intensity. The latter will be governed by the sensitivity of the radiation detector employed in running the log and the conditions under which the log is run. Ordinarily, the contacting time is between about 2 and about 20 hours. The radioactive halogen is most conveniently employed in the form of a solution in a solvent which is a non-solvent for the resin. Solvents such as water and paraffinic hydrocarbons are preferred, and the concentration of the halogen solution may vary over wide limits depending upon the radiation intensity of the halogen. Suitable solutions may contain from as low as 0.01 to as high as 100 millicuries/milliliter.

Upon completion of the contacting step the treated resin particles are washed, suitably with water or the pure solvent, to remove the treating solution and are dried. Depending upon the half-life of the radioactive element employed they may be stored for varying periods of time prior to use. Conventional techniques are employed in preparing suspensions of the radioactive particles for use in the logging operation, i.e., the usual suspending fluids, e.g., oil or brine, may be used (provided, of course, the particular resin which the particles comprise is not soluble therein), suspending agents such as bentonite or organic dispersing agents and weighting agents may be provided, and the suspension may contain the usual concentration of the radioactive particles.

The following example will illustrate one way in which the principle of the invention has been applied, but is not to be construed as limiting the same:

Example I

Approximately 10 parts by weight of comminuted flexible solid polyethylene, having an average particle size of about 30-mesh, were placed in a vessel containing about 100 parts by weight of solution of radioactive iodine in iso-octane. The iodine was employed in the form of mixed radioactive isotopes in admixture with an inert carrier material in a ratio of about 1000 parts of carrier material per part of iodine, and the solution was prepared by dispersing about 1 part of the iodine-carrier combination in 100 parts of iso-octane. The solution contained about 0.01 millicurie of radioactive iodine per milliliter. The resin particles were allowed to stand in the iodine solution for about 20 hours, after which the solution was filtered off and the treated resin particles were washed with hexane and dried.

When the resulting product was continuously leached with a typical oil field brine containing soluble sulfides it was found that it required 9 liters of brine to reduce the radioactivity of the product by 50%. In a similar test conducted with a product prepared by precipitating radioactive silver iodide in an ion-exchange resin it was found that only 0.7 liter of brine was required to reduce the radioactivity by 50%.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made as regards the materials or methods employed, provided the steps or the products stated by the following claims, or the equivalent of such stated steps or products, be employed or explained.

I, therefore, particularly point out and distinctly claim as my invention:

1. The method of logging boreholes which comprises introducing into the bore a fluid having suspended therein a finely-divided synthetic resin selected from the class consisting of polyethylene and non-ion-exchanging polyvinyl resins, said synthetic resin having previously been rendered radioactive by treatment with a radioactive halogen in elemental form, applying sufficient pressure to force said fluid into the strata traversed by the bore, whereby said solids are deposited on the walls of the bore, and thereafter determining variations in the intensity of radiation from said deposited solids with respect to the depth thereof.

2. The method of logging boreholes which comprises introducing into the bore a fluid having suspended therein finely-divided radioactive solids under sufficient pressure to force said fluid into the strata traversed by the bore, whereby said solids are deposited on the walls of the bore, and thereafter determining variations in the intensity of radiation from said deposited solids with respect to the depth thereof said radioactive solids being those prepared by allowing a comminuted resin selected from the class consisting of polyethylene and non-ion-exchanging polyvinyl resins having an average particle size between about 30 and about 300 mesh to remain in contact with a solution of an elemental radioactive halogen in a liquid which is a non-solvent for said resin for a period of about 2 hours at ambient temperature in the absence of a halogenation catalyst followed by washing said solution from the resin so treated and drying the washed resin.

3. The method of logging boreholes which comprises introducing into the bore a fluid having suspended therein finely-divided radioactive solids under sufficient pressure to force said fluid into the strata traversed by the bore, whereby said solids are deposited on the walls of the bore, and thereafter determining variations in the intensity of radiation from said deposited solids with respect to the depth thereof said radioactive solids being those prepared by allowing a comminuted resin selected from the class consisting of polyethylenue and non-ion-exchanging polyvinyl resins having an average particle size between about 30 and about 300 mesh to remain in contact with a solution of a radioactive isotope of iodine in a liquid which is a non-solvent for said resin for a period of at least about 2 hours at ambient temperature in the absence of a halogenation catalyst followed by washing said solution from the resin so treated and drying the washed resin.

4. A method as defined by claim 3 wherein the said resin employed in preparing said radioactive solids is polyethylene.

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