United States Patent Office

3,302,733
Patented Feb. 7, 1967

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3,302,733

METHOD OF SEALING A PERMEABLE POROUS MEDIUM

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No Drawing. Filed July 1, 1963, Ser. No. 292,107
8 Claims. (Cl. 175—59)

The present invention is generally concerned with the sampling of underground formations. The invention particularly relates to a method for obtaining samples of subterranean strata from wellbores which have been drilled into the earth's crust. It is especially directed to a method for obtaining samples of essentially unaltered fluid content by a rotary core drilling technique which involves the use of a non-invading coring fluid to seal the surfaces of the core samples essentially as drilled.

The stock-tank volume of petroleum contained in a porous underground reservoir is normally calculated in terms of the reservoir volume, the formation volume factor, the average reservoir porosity and the average oil saturation within the pore volume. In reservoirs wherein a number of development wells have been drilled, the reservoir volume and the formation volume factor can usually be determined with reasonable accuracy by comparing structural maps and by measuring the gravity, temperature, pressure and gas content of the oil under reservoir conditions. The average porosity of the reservoir is generally determined by analyzing cores recovered from a number of development wells. Experience has demonstrated, however, that volumetric oil content in the cores as determined from core analysis is usually not an accurate indication of the actual quantity of oil present in a reservoir.

Reliable values for volumeric oil content, together with the other data, are extremely desirable to forecast the productive life of oil and gas reservoirs, to select the primary recovery techniques most suitable for particular reservoirs, and to assess the susceptibility of such reservoirs to later secondary and tertiary recovery processes. It is a principal object of the invention to obtain samples from a reservoir, the analysis of which will provide reliable values for volumetric oil content.

Conventional core drilling systems include an annular bit and core barrel which are rotated from the earth's surface by means of a rotary drill string. A coring fluid is circulated downwardly through passages in the drill string, barrel, and bit in order to maintain pressure on the formation and thus prevent the escape of fluids contained therein. Cuttings produced by the bit are entrained in the coring fluid and returned to the surface through the annulus surrounding the drill string. As the bit cuts away the formation the central core which remains is encased in the barrel. The core barrel is provided with means for breaking off the core once the barrel has been filled. Pressure core barrels which can be sealed against changes in pressure are also used. After the core has been cut the drill string is withdrawn from the borehole and the core recovered therefrom.

Studies have shown that the pressure maintained at the bottom of a borehole during a coring operation has a profound effect on the fluid content of the cores subsequently recovered. If this pressure is less than the formation pressure, fluids contained in the formation will tend

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to flow out of the core into the borehole until equilibrium is established. If on the other hand the bottom hole pressure exceeds the formation pressure, the coring fluid will tend to flow into the interstices of the formation and displace any oil, gas or water contained therein. In either case the result is a change in the fluid content of the core such that subsequent measurements of the amount of fluids present will not accurately reflect the original fluid content of the cored formation. Since this change in fluid content occurs continuously as the core is cut, the use of a pressure core barrel does not prevent it.

Several methods for avoiding the difficulty outlined above have been proposed in the past. The most obvious of these involves carrying out coring operations without any pressure differential between the coring fluid and the formation. This is impractical, if not impossible, because the formation pressure cannot be conveniently measured during core drilling, and moreover, because the coring fluid pressure cannot be controlled with sufficient accuracy.

The use of coring fluids which will not invade the formation under pressures well in excess of the formation pressure has been suggested, but efforts to develop a satisfactory non-invading fluid have not been entirely successful. Mercury, molten metal and other materials advocated in the past all invade the formation to an appreciable extent and hence cause changes in the fluid content. In addition, the materials proposed for this purpose have generally been costly and difficult to use and in many cases require highly specialized core bits and core barrels. Other systems including the use of tracers which permit determination of the extent to which core invasion has occurred, and systems for freezing the core have been proposed but have not been found to be generally effective.

The most promising of the non-invading coring fluids which have been developed heretofore are the polymeric elastomer latices. These materials are aqueous colloidal dispersions of polymeric elastomers, including natural and synthetic rubber latices.

It has now been found that aqueous dispersions or suspensions of finely divided, oil-extended reclaimed rubber are unexpectedly superior to the natural and synthetic rubber latices, in their ability to seal a permeable porous medium. Specifically, a field-scale rotary coring operation in which an oil-extended reclaimed rubber dispersion is used as the coring fluid has been found capable of recovering a core sample in which the original fluids content is altered by less than 3% by volume, even when the operation is conducted with as much as 500 p.s.i. pressure differential between the coring fluid and the fluids of the formation being cored.

Reclaimed rubber is a staple item of commerce, produced by any one of various processes, each of which involves the application of heat and chemical agents to waste vulcanized rubber, whereby a substantial "devulcanization" or regeneration of the rubber to a plastic state is achieved. It may then be processed, compounded, and again vulcanized, similarly as is true of new rubber.

The reclaiming process, from a chemical viewpoint, is not an exact reversal of the reactions which occur during the vulcanization of natural rubber or synthetic rubber; hence, the term "devulcanization" has been criticized as misleading and inaccurate. However, the term persists in the literature and is considered to be a valid description

of the reclaiming process, inasmuch as a reversal of physical properties does occur. That is, vulcanized rubber is characterized by elasticity and a resistance to compression, stretching and swelling, whereas the devulcanized product is restored to a state of plasticity, more nearly like that of unvulcanized new rubber.

Nevertheless, reclaimed rubber has many unique properties which distinguish it from new rubber. For example, in the processing of a rubber compound, the presence of reclaim in the recipe enhances working properties in all primary stages. Mixing times have been halved and calender speeds doubled. Calender temperatures become less critical, and the gauge of a calendered sheet can be increased without blistering. The uncured stock possesses better dimensional stability and is less susceptible to overmilling. Friction and skim-coating operations are expedited.

Reclaim stocks possess a high rate of cure. They often exhibit improved moulding properties. They possess low thermoplasticity and are less affected by continuous milling.

Suitable oil-extended reclaimed rubber dispersions for use in accordance with the invention are prepared by first mechanically milling or grinding reclaimed rubber with any of the art-recognized plasticizers and softeners, including various oils of vegetable and mineral origin, waxes, coal tar and petroleum residues, pitches and resins. Examples include pine tar, rosin oil and paraffin wax. Paraffinic petroleum oils of a boiling range between 130° and 300° C. are particularly suitable. Useful proportions of oil or other extender range from 5 to 35 parts by weight in each 100 parts of reclaim. The Mooney plasticity of the softened reclaim at 212° F. and a stirring time of four minutes should be less than 50 and preferably less than 20.

An emulsifying agent is then blended into the rubber, after which water is slowly added with continued milling. Once the correct amount of water has been added, a change of phase takes place, whereby the water becomes the continuous phase, and the rubber becomes the discontinuous, or dispersed phase. Dispersions containing from about 20 to about 75% oil-extended reclaim by weight are generally suitable for purposes of the invention. Those containing from about 35% to about 70% are preferred.

Core drilling operations utilizing the coring fluid of the invention may be carried out with conventional apparatus familiar to those skilled in the art. A variety of commercially available core bits and core barrels may be used. The coring fluid is circulated down the drill string through channels in the core barrel and bit so that it emerges adjacent the cutting surfaces of the bit. The fluid contacts the core surfaces as the surrounding rock is cut away and continuously forms a film on the surface which is impermeable to oil, gas and water, thus preventing any significant alteration of the original fluid saturations in the core. Once a coated core of sufficient length has been cut, it is separated from the formation, and lifted to the surface inside the core barrel.

fully understood by reference to the following experimental work, conducted to demonstrate the effectiveness of reclaimed rubber dispersions as coring fluids.

In each of the following operations a core sample, or series of core samples, was drilled with conventional field-scale rotary core-drilling equipment from an octagonal block of Berea sandstone measuring four feet in length and ten inches between parallel sides. Each block was first cemented inside a length of 11¾ inch diameter steel casing which was equipped with suitable fittings to permit the simulation of high formation pressures while drilling.

In Table I comparative data is shown which illustrates the sharply reduced core invasion attributable to the use of an aqueous dispersion of oil-extended reclaimed rubber as the drilling fluid.

TABLE I

	Drilling Fluid	
	Dispersite D–735	Water-base Clay-starch Mud
Core Diameter, Inches	2⅜	2⅜
Differential Pressure, p.s.i.g.	500	500
Original Oil Saturation, Percent Pore Vol	40.5	40.8
	Oil Saturations of Core Samples Recovered	
Average Depth from Top of Block, Inches:		
1	35.5	(*)
5	40.8	(*)
8	34.2	26.0
12	32.9	29.1
16	35.7	26.0
21	36.7	24.4
26	35.8	24.4
29	38.7	(*)
33	37.9	(*)
37	37.1	25.4
41	36.5	(*)
Weighted Averages (Percent of Pore Volume):		
Oil Saturation in the Core	36.6	25.6
Change in Oil Saturation by Drilling Fluid Invasion	3.9	15.2

*Core Samples recovered at these points were not large enough to analyze in the usual manner.

"Dispersite" is a trademark of Naugatuck Chemical Company, a division of the U.S. Rubber Company, Naugatuck, Connecticut. The D–735 product is a rubber-in-water dispersion containing about 65% by weight of oil-extended first quality whole tire reclaim, containing 20 parts of a paraffinic hydrocarbon oil extender per 100 parts of reclaim. The average particle size of the dispersed phase is slightly less than one micron.

It is evident that the core samples were invaded much less by the reclaimed rubber dispersion than by the clay-starch mud.

The data of Table II illustrates two additional features of the invention. One, the percentage of the pore volume invaded is minimized by drilling large cores. This aspect of the method follows simply from the decreased ratio of surface area to volume, whereby the same invasion per unit of surface area is equivalent to a smaller fraction of the total pore volume.

Two, the data indicates the effect of increasing the pressure difference between the coring fluid and the fluids of the formation being cored.

TABLE II

[Coring fluid—Dispersite D–735]

Weight on Bit, lbs	6–15,000	10,000
Penetration Rate, ft./hr	7.1–15.0	4.9
Rotary Speed, r.p.m	70	70
Circulation Rate, gallons per min	73	73
Pressure Difference, p.s.i.g	100	500
Initial Oil Saturation, percent pore vol	60.6	60.7
Average Oil Saturation in Recovered Cores	60.3	58.3
Core Diameter, inches	3¾	3¾
Change in Oil Saturation Caused by Drilling Fluid Invasion, percent pore vol	0.3	2.4

Increasing the pressure difference from 100 p.s.i.g. to 500 p.s.i.g. caused the indicated increase in invasion. Moreover, by comparison with the D–735 test in Table I it is seen that the increase in core diameter has lessened the percentage of pore volume invaded.

Static invasion tests were conducted to compare the sealing ability of an oil-extended reclaimed rubber dispersion with the corresponding effectiveness of an unextended reclaimed rubber dispersion. Berea sandstone cores of about 2⅜ inches in diameter and about one inch in length, having a porosity of about 20% and a permeability ranging from 200 to 300 millidarcies, were used in testing the fluids. Each core was first saturated with a mixture of

oil and brine, to simulate field conditions, and then mounted in a core holder. As summarized in Table III, the cores were then exposed to the test fluids, under a force of 100 p.s.i. differential pressure.

TABLE III

Coring Fluid	Total Core Invasion, Milliliters	
	1.0 Min.	10 Min.
Dispersite D-735	0.58	0.75
Dispersite D-731	0.63	1.09

"Dispersite D–731" is a rubber-in-water dispersion prepared from first quality whole tire reclaim, without the oil extender of D–735. Each of the two products is composed of 60–65% by weight dispersed phase. The superiority of the oil-extended reclaim (D–735) is clearly indicated by the data of Table III.

There are many types and grades of reclaimed rubber. The most abundant source of reclaimed rubber is old tires, including passenger car and truck tires. Reclaim types produced from tires include the whole tire reclaim, the tire tread reclaim, and the tire carcass reclaim. There is also a red inner tube reclaim and a black inner tube reclaim.

Other types include the mechanical reclaim, the footwear reclaim the butyl reclaim, the neoprene reclaim and the nitrile reclaim, as well as several others.

In its broadest scope, the present invention includes the use of aqueous dispersion of oil-extended reclaimed rubber of any of the above types. It also includes the use of mixtures of two or more reclaim types, and mixtures of one or more reclaim types with one or more of the natural and synthetic elastomer latices. In the latter case, however, it is preferred that the mixture contain a major proportion of oil-extended reclaimed rubber.

What is claimed is:

1. In the recovery of core samples from a borehole in the earth by rotary core-drilling wherein a fluid is circulated downhole, the improvement which comprises circulating as the drilling fluid a composition comprising a dispersion of finely divided oil-extended reclaimed rubber in water.

2. A process as defined by claim 1 wherein said oil-extended reclaimed rubber contains from 5 to 35 parts of oil in each 100 parts of reclaim.

3. A process as defined by claim 1 wherein the oil-extended reclaim of said dispersion has a Mooney plasticity not greater than 50 at 212° F. and a stirring time of four minutes.

4. A process for the recovery of core samples from a borehole in the earth which comprises advancing a rotary core-bit into the earth at the bottom of the borehole, while circulating downhole an aqueous dispersion of finely divided oil-extended reclaimed rubber, whereby the samples recovered are sealed substantially as cut, thereby capturing the original fluids contained therein.

5. A process as defined by claim 4 wherein said rubber comprises first quality whole tire reclaim.

6. A process as defined by claim 4 wherein the dispersed phase comprises 35% to 70% by weight of said dispersion.

7. A process as defined by claim 6 wherein said dispersed phase contains 5 to 35 parts by weight of oil in each 100 parts of reclaim.

8. A process as defined by claim 4 wherein the Mooney plasticity of said dispersed phase is not greater than 20.

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