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FORMING SEALING DEPOSITS IN WELLS

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The invention relates to the treatment of wells, particularly those drilled for oil and gas. It more specially concerns forming a cementitious solid seal either or both in and adjacent to the formation penetrated by the well bore.

In boring into the earth for any one of the many purposes for which such borings are made, such as for obtaining oil and gas, a variety of earth strata are usually penetrated before reaching the desired earth stratum. The strata thus penetrated may be loose and tend to cave into the bore, or tend to swell on being exposed to water, or may be permeable to fluids and either absorb fluid from the bore or discharge fluid thereinto as when a water, oil, or gas-bearing stratum is penetrated. These encounterings, in general, cause difficulties not only in carrying out the boring operation but, in many cases, also adversely affect the use of the bore after it is made. Many of these effects are well known and methods have been proposed which have had for their object their amelioration.

Numerous difficulties, however, arise when it is attempted to apply the methods heretofore suggested for coping with these difficulties.

As an illustration of a method of treating well bores to counteract some of the effects of undesirable fluid permeability of the adjacent formations, the application of resin-forming liquids may be cited. Under certain conditions, these liquids spontaneously change into a more or less solid mass which is usually quite inert and moderately strong, so that by injecting the resin-forming liquid into the earth formation at the desired place transformation into a solid resin occurs producing sealing, plugging, and consolidation provided conditions in the well are favorable for the transformation of the liquid into a solid. However, complete success with such method is not always assured and oftentimes cannot be had due to the fact that the liquids heretofore available do not solidify rapidly enough and some not at all under prevailing well conditions.

I have now found that one of the important factors which militates against the effective use of conventional synthetic resin-forming liquids in wells is that their rates of setting are too slow at the temperatures often encountered in the formations in which setting is to take place. In

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some instances, also, the chemical action of certain constituents of the earth or rock formations also adversely affect the setting of the resin-forming liquid.

It is an object of the present invention to provide an improved method of forming a sealing deposit either in or adjacent to an earth formation penetrated by a bore hole in which a resin-forming liquid is employed that readily spontaneously solidifies in situ without an excessive time lag at even the moderate temperatures usually encountered deep in the earth. Other objects and advantages will appear as the description proceeds.

My invention is predicated upon the discovery that by mixing a first liquid comprising the resinous partial condensation product of an aldehyde and an alkylated phenol with a second liquid comprising the resinous partial condensation product of an aldehyde, a phenol, and a polyhydroxy benzene selected from the group consisting of phloroglucinol and resorcinol, a mobile resinous liquid mixture is obtained which when introduced into the earth boring readily and rapidly undergoes further condensation, thereby becoming transformed without significant loss of volume into a strong solid mass unaffected by oil and water in contact with the earth formations without the necessity for increasing the temperature above that usually encountered in wells. In addition, the rate of setting is susceptible of control and is adjusted to meet the specific temperature of the well to be treated by suitable proportioning of the constituents of the first and second liquids as hereinafter set forth so as to preclude excessive time lag in setting. As a result, earth voids are sealed, loose particles bound together, and a solid plug is readily produced under a wide variety of conditions in well bores. The sealing deposits thus produced resist the chemical and physical disintegration tendency of the earth fluids and strongly resist displacement by fluid pressure.

The invention, then, consists of the method hereinafter fully described and particularly pointed out in the claims.

In carrying out the invention, a quantity of each of the two partial liquid condensation products referred to above as first and second liquid, respectively, is prepared so that a stock of each

is maintained in storage for future use when required as the sealing mixture itself which is made by mixing the two stock solutions cannot be kept for long under ordinary conditions without spontaneous solidification. The preparation of the sealing mixture is deferred, therefore, until just before it is to be used in the well. The preparation of a stock of each of the partial liquid condensation products for use in forming the sealing mixture will now be described in detail. The first of the two liquid partial condensation products, briefly described above, is formed by partially condensing an alkylated phenol with an aldehyde in the presence of an alkaline catalyst, the temperature and duration of the condensation being controlled and limited so as to avoid over condensation. The partially condensed aqueous phenolic liquid is then treated with an acid, thereby obtaining a stabilized slightly acid partially condensed resinous aqueous liquid having a moderate viscosity.

The following example is illustrative of this procedure:

600 pounds of commercial cresylic acid, 500 pounds of paraformaldehyde and 25 pounds of aqueous caustic soda solution containing 50 per cent of sodium hydroxide by weight are mixed together in a reaction vessel provided with cooling means and the mixture allowed to react while maintaining the temperature at about 130° F. for about 30 minutes or until the paraformaldehyde has dissolved. The partially condensed liquid resinous mass thus obtained is then stabilized against further substantial change by treating it with enough hydrochloric acid to reduce the pH value of the mass to between about 3.5 and 6, a value of about 4 being preferred. This can be accomplished by mixing with it about 3.2 gallons of a 32 per cent aqueous solution of hydrochloric acid. The partially condensed resinous liquid mass is allowed to settle, whereupon a small proportion of aqueous sodium chloride solution separates from the resinous product and settles to the bottom. This is discarded. The amount discarded is about 4 gallons per 100 gallons of the separated resinous liquid product. The partially condensed resinous acidified liquid product thus obtained has a viscosity of about 400 centipoises and its specific gravity is 1.18. It can be kept in stock for as long as 6 to 8 weeks at room temperature before use if desired. This partially condensed alkylated phenolic aldehyde resinous liquid contains about 3 moles of aldehyde (—CHO) per mole of phenol and is termed for convenience the first liquid.

The second of the two liquid partial condensation products referred to above is prepared by partially condensing phenol and formaldehyde in the presence of an alkaline catalyst in aqueous solution at a controlled temperature. After partial condensation, the reaction mass is slightly acidified and allowed to settle whereby two liquid layers are obtained. These are separated by decantation, or otherwise, the upper layer consisting largely of water is rejected. The lower layer is an aqueous resinous liquid consisting essentially of partially condensed phenol-formaldehyde resin. This reaction product is cooled to room temperature and mixed with resorcinol which dissolves in it forming a liquid resinous solution termed for convenience the second liquid. It has a viscosity somewhat less than the first liquid.

The following example is illustrative of this procedure:

390 pounds of phenol, 506 pounds of 40 per cent (by volume or 37 per cent weight) aqueous formaldehyde solution, and 50 pounds of a 50 per cent (by weight) solution of caustic soda in water are mixed together in a reaction vessel. These mixed materials are maintained at about 175° F. for about two and one-half hours following which the aqueous reaction mass is acidified to a pH between about 4 and 6, a pH of 4 being preferable. This usually requires about 6.4 gallons of 32 per cent hydrochloric acid. As the acid is added, the mixture separates into two layers, the upper layer constituting about 38 per cent of the total volume is largely salt water, and, after cooling to room temperature, is separated and discarded. The lower layer has a volume about 62 per cent of the original total volume and comprises a slightly acid partially condensed aqueous phenol-formaldehyde resin. To this is added about 410 pounds of resorcinol which is stirred into it and thereby dissolved forming an aqueous partially condensed phenol-formaldehyde-polyhydroxy benzene resinous solution termed the second liquid. It has a viscosity of about 150 centipoises and its specific gravity is 1.23. It can be kept in stock at room temperature for as long as 6 to 8 weeks before use if desired. The molecular ratios of the constituents are about 1.11 moles of phenol and 1.665 moles of formaldehyde per mole of resorcinol.

Having prepared stocks of each of the two partially condensed resinous liquids, respectively, equal volumes of each are drawn upon in sufficient amount and mixed together to prepare the desired quantity of liquid sealing mixture for the contemplated well treatment. This mixing operation is performed just prior to the time the well is to be treated as the mixture is unstable and will sooner or later become a solid mass. In most cases, especially for low temperature wells, a suitable amount of catalyst is added to promote the desired degree of rapidity of solidification.

In producing the liquid sealing mixture out of the aforesaid first and second liquids by mixing them together, it is necessary to add the required amount of catalyst, if any be used, to one of them, preferably the second liquid before the two liquids are mixed. As the catalyst, an aqueous alkaline solution may be used, such as caustic soda dissolved in water in a concentration of from about 5 to 25 per cent by weight. The mixing may be done in any convenient manner as by stirring the first and second liquids together, after mixing with the second liquid, the required amount of catalyst, if used.

The rate at which the liquid sealing mixture thus prepared sets or becomes sufficiently hard to act as a cementing and sealing material depends not only upon the proportions of the phenolic and aldehyde constituents in the two partially condensed resinous liquids, i. e. the first and second liquids, but also on the amount and concentration of catalyzing solution used in the sealing mixture. In Table I, the time required to bring about hardening of the sealing mixture when maintained at 100° F. is given for various compositions of the first and second partially condensed resinous liquids, equal volumes of each being used in the sealing mixture and a fixed amount of catalyst added to each mixture, viz., 0.5 c. c. of 25 per cent aqueous caustic soda solution per 50 grams of the sealing mixture. The compositions of the first and second partially condensed resinous liquids are expressed in moles.

In the case of the first liquid, which, as aforesaid in these examples, is composed of cresylic acid and paraformaldehyde, the cresylic acid is treated as having the formula of a cresol and the paraformaldehyde, the formula 3(HCHO), in computing the number of moles of each constituent so that one mole of paraformaldehyde is equivalent stoichiometrically to three moles of formaldehyde. In determining the setting time, as shown in Table I, the weight of sealing mixture tested in each case was 50 grams.

TABLE I

Effect of variations of composition of first and second liquid on setting time of sealing mixture

SEALING MIXTURE

Composition of partially condensed resinous liquids		Setting time of mixture of first and second partially condensed resinous liquids
First liquid	Second liquid	
Number of moles of HCHO calculated from paraformaldehyde as $(HCHO)_3$, per mole of cresylic acid calculated as a cresol	Number of moles of resorcinol per 1.11 moles of phenol and 1.665 moles of formaldehyde	Hours at 100° F. to set sealing mixture of equal volumes of liquids 1 and 2 catalyzed with 0.5 c. c. 25% NaOH solution per 50 grams of sealing mixture
2.25	0.75	2¾
3	0.75	2¾
4.5	0.75	1¾
2.25	1.0	2¾
3	1.0	2¾
4.5	1.0	1¾
2.25	1.5	2¾
3	1.5	2¾
4.5	1.5	1¼
2.25	2.0	2½
3	2.0	2½

The sealing mixtures thus obtained have a moderate viscosity and are generally heavier than water. For example, a sealing mixture formed from a unit volume of first liquid composed of 3 moles of HCHO derived from paraformaldehyde per mole of cresol and a unit volume of second liquid composed of 1 mole of resorcinol per 1.11 moles of phenol and 1.665 moles of formaldehyde has a viscosity of 335 centipoises at 85° F. and its specific gravity is 1.205.

Although Table I gives examples of sealing mixtures which spontaneously harden when maintained at 100° F. using a fixed amount of catalyst in the mixture, either faster rates of setting for the same temperature or setting at lower temperatures at the same rate can be obtained by increasing the amount of alkaline catalyst added to the sealing mixture. For example, when the ratio of the number of moles of cresol to the number of moles of HCHO in the paraformaldehyde of the first liquid is about 1:1 while in the second liquid 1 mole of resorcinol is used per 1.11 moles of phenol and 1.665 moles of HCHO, the setting time of the sealing mixture formed by mixing the two partially condensed liquids together varies with the amount, if any, of catalyst (5% or 25% NaOH solution) in the sealing mixture. Similarly, for a given setting time, the setting temperature varies with the proportions of catalyst, if any is used. The data in Table II gives a number of illustrative examples of this.

In determining the setting time, 2.5 gallons of the first liquid partial condensation product was mixed with 2.5 gallons of the second liquid partial condensation product to which had previously been added the specified amount of catalyst and the mixture introduced into a length of 7-inch I. D. iron pipe surrounded by a water jacket

maintained at the aforesaid temperature of 100° F.

TABLE II

Effect of variations of temperature and quantity of catalyst on setting time of sealing mixture

SEALING MIXTURE

Number	Composition		Setting time, hours			
	Volume of sealing mixture (less volume of catalyst solution)	Volume of catalyst solution added to sealing mixture	0.5	1	2	3
			Corresponding sealing mixture temperature, ° F.			
1	9.9 gallons	0.10 gallon [1]	124	101	78	65
2	9.8 gallons	0.25 gallon [2]	138	115	92	79
3	9.9 gallons	0.125 gallon [2]	146	124	101	87
4	10.0 gallons	0.05 gallon [2]	156	134	112	98
5	10.0 gallons	None	176	153	129	116

[1] Catalyst: 25% solution of caustic soda in water.
[2] Catalyst: 5% solution of caustic soda in water.

In general, in the preparation of the first liquid partial condensation product, the preferred alkylated phenol to use is a cresol or a mixture of them, such as cresylic acid. Other alkylated phenols may be used in similar manner. If desired, phenol itself may be substituted for a part of the alkylated phenol in the first liquid and a part of the paraformaldehyde can be replaced by formaldehyde, the amount of HCHO being not less than about 2.25 moles per mole of alkylated phenol calculated as cresol. In the second liquid, the use of the dihydroxybenzene, resorcinol, as described, gives the best results. Phloroglucinol (1,3,5-trihydroxybenzene), when substituted for resorcinol, shortens the setting time. On the other hand, resorcinol is more soluble in the phenol-formaldehyde resinous liquid than the other polyhydroxybenzenes and is generally preferred. The amount of polyhydroxybenzene used is preferably not less than about 0.67 mole per mole of phenol and the amount of formaldehyde about 1.5 moles per mole of phenol.

In forming a sealing deposit in a well hole or formation surrounding it, the sealing mixture of the first and second liquid partial condensation products and catalyst is formed by mixing these two liquids together just prior to introducing the mixture into the well. The mixture may be introduced into the well in any suitable and convenient way known in the art of treating wells as by means of a dump bailer, or by injection under pressure, if necessary, through the well tubing, casing, or other conduit in the well bore. If the well hole itself is to be plugged, as by forming in the well a solid mass occupying a portion of the well bore, a volume of the sealing mixture at least sufficient to fill the bore to the desired depth is introduced and pressure applied, if necessary, to keep it in the well until set, the length of time required for setting being determined by the temperature of the well and the composition and amount of catalyst in the sealing mixture as exemplified above. If desired, the sealing mixture can be forced into the surrounding earth by applying pressure on the sealing mixture introduced into the bore as by introducing into the bore on top of the sealing mixture therein a gas or liquid so as to drive all or part of the mixture from the bore into the surrounding earth while the sealing mixture is still in the non-set stage.

Among the advantages of the invention are that the preparation of the sealing mixture may be deferred until the moment of use, thereby

giving accurate control and advance knowledge of the setting time of the sealing mixture; the setting time of the sealing mixture is easily and readily prearranged to suit the conditions encountered in the well by simply selecting the appropriate amount of catalyst to be added to the sealing mixture; the sealing mixture has great versatility as regards those physical properties which adapt it for use in forming seals, consolidating loose sands, and penetrating and plugging earth pores in deep wells; its viscosity permits adequate but not excessive penetration into the earth pores in the absence of artificially applied pressure to give a good bond with the earth; the specific gravity is sufficiently high to permit it to displace oil, water, and most brines encountered in deep wells; the sealing liquid readily spontaneously becomes in due time a solid mass which is not practically affected by any of the fluids encountered in wells.

What is claimed is:

1. In a method of forming a sealing deposit in an earth formation penetrated by the bore of a well, the steps which comprise mixing together two partially condensed phenolic-aldehydic resinous liquids just prior to introducing the mixture into the well, bore thereby to form a sealing mixture; introducing the sealing mixture so obtained into the well bore and allowing the mixture to further condense into a solid resinous product, one of the said partially condensed phenolic-aldehydic resinous liquids being formed by partially condensing cresylic acid and paraformaldehdye in the presence of 0.056 mole of sodium hydroxide per mole of cresylic acid the sodium hydroxide being dissolved in an equal weight of water, the reaction being continued until the paraformaldehyde dissolves, the ratio of the number of moles of HCHO derived from the paraformaldehyde to the number of moles of cresylic acid being from 2.25 to 4.5, followed by acidification to a pH value between 3.5 and 6.0, the other of the said partially condensed phenolic-aldehydic resinous liquids being formed by partially condensing phenol and formaldehyde in the proportion of 1.5 and 2 moles of formaldehyde per mole of phenol in the presence of 0.15 mole of sodium hydroxide per mole of phenol the sodium hydroxide being dissolved in an equal weight of water, the reaction being continued until upon acidification two liquid layers are formed; acidifying the resulting partially condensed reaction mass to a pH value between 3.5 and 6, whereby a system of two liquid layers forms on standing; separating the lower liquid layer from the upper layer; treating the lower layer by dissolving therein a polyhydroxybenzene selected from the group consisting of resorcinol and phloroglucinol in the amount of 0.75 to 2.0 moles per 1.11 moles of phenol.

2. In a method according to claim 1, the use of resorcinol as the polyhydroxybenzene.

3. In a method according to claim 1, the use of substantially equal volumes of the two partially condensed phenolic-aldehydic resinous liquids and resorcinol as the polyhydroxybenzene.

4. A liquid composition capable of spontaneous hardening at 100° F. comprising substantially equal volumes of two partially condensed phenolic-aldehydic resinous liquids, one of the said

partially condensed phenolic-aldehydic resins being formed by partially condensing cresylic acid and paraformaldehyde in the presence of 0.056 mole of sodium hydroxide per mole of cresylic acid the sodium hydroxide being dissolved in an equal weight of water, the reaction being continued until the paraformaldehyde dissolves, the ratio of the number of moles of HCHO derived from the paraformaldehyde to the number of moles of cresylic acid being from 2.25 to 4.5, followed by acidification to a pH value between 3.5 and 6.0, the other of the said partially condensed phenolic-aldehydic resinous liquids being formed by partially condensing phenol and formaldehyde in the proportion of 1.5 and 2 moles of formaldehyde per mole of phenol in the presence of 0.15 mole of sodium hydroxide per mole of phenol the sodium hydroxide being dissolved in an equal weight of water, the reaction being continued until upon acidification two liquid layers are formed; acidifying the resulting partially condensed reaction mass to a pH value between 4 and 6, whereby a system of two liquid layers forms on standing; separating the lower liquid layer from the upper layer; and treating the lower layer by dissolving therein a polyhydroxybenzene selected from the group consisting of resorcinol and phloroglucinol in the amount of 0.75 to 2.0 moles per 1.11 moles of phenol.

5. A composition according to claim 4 in which the polyhydroxybenezene is resorcinol.

6. A liquid composition capable of spontaneous hardening at 100° F. comprising substantially equal volumes of two partially condensed phenolic-aldehydic resinous liquids, one of the said partially condensed phenolic-aldehydic resinous liquids being formed by cooking a mixture of about 6 parts by weight of cresylic acid and 5 parts of paraformaldehyde with 0.25 part of a 50 per cent aqueous solution of sodium hydroxide while maintaining the temperature at 130° F. until the paraformaldehyde has dissolved, and acidifying the resulting partially condensed resinous liquid to a pH value between 3.5 and 6, the other of the said partially condensed phenolic-aldehydic resinous liquids being formed by cooking a mixture of 3.9 parts by weight of phenol with 5.1 parts of 37 per cent by weight aqueous formaldehyde for 2½ hours at about 175° F., treating the resulting reaction mass with sufficient aqueous hydrochloric acid to reduce the pH value to 4, allowing the acidified reaction mass to settle whereby it separates into two liquid layers, separating the lower layer from the upper layer, and stirring into the lower layer 4.1 parts of resorcinol until dissolved.

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