METHOD OF COMBATTING THE OBSTRUCTION OF GAS CIRCULATION IN GAS DRILLING

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Filed July 1, 1959, Ser. No. 824,263

10 Claims. (Cl. 166—5)

This invention relates to improvements in a method using gas as a circulation medium in the drilling of wells. It is particularly concerned with a method for expeditiously and economically combating the effect of a reduction or cessation of gas circulation when gas drilling wells through permeable formations, i.e., those containing gas, liquid or loosely consolidated strata. A method of this type is described in a pending application Serial No. 686,198 filed September 25, 1957, now Patent No. 3,011,547, hereby incorporated by reference.

As described in that application, when an obstruction of air circulation, i.e., a reduction or cessation thereof, is experienced during an air drilling operation and the obstruction is attributed to the ingress of gas, liquid or loosely consolidated earth particles into the bore from an adjacent stratum, resin-forming material is introduced into the well. This material that will harden at temperatures encountered in the well bore, which in many cases are between about 50 to 200° F. The quantity of resin-forming material used must be adequate to extend horizontally into the formation of ingress for a distance sufficient to secure this form and for the material to prevent further ingress of unwanted extraneous materials. This distance usually extends at least about 6 inches into the formation. Moreover, in this method it is imperative that the resin-forming material occupy the well bore adjacent the formation of ingress when the hardened resin is formed. Accordingly, after the introduction of the resin-forming material into the well bore, detection means are employed to track the upper level of the resin-forming material; gas or liquid, e.g. air or water pressure, is applied to bring this upper level approximately adjacent the upper level of the strata of ingress, and the resin material is maintained in this position until it solidifies. Following solidification of the resinous material, air drilling is resumed.

In the practice of the method described in the above-mentioned application, the resinous material is introduced into the well bore, forming a column above the upper level of the permeable formation, the drill pipe is raised and the resinous material is displaced downwardly in the well bore and into the formation to seal the portion of the formation exposed in the well bore. Frequently, when following this procedure formations exhibiting high areas of permeability, e.g. crevices, are encountered, for instance crevices 108 and 109 as shown in the drawings. These crevices, in addition to consuming large quantities of expensive resinous material, prolong the sealing operation. For instance, during the sealing operation considerable quantities of expensive resinous material are consumed in the crevices located above the permeable formation to be sealed and particularly the crevices located in the formation to be sealed due to the pressure applied on the resinous material column extending above the upper level of the permeable formation. During the displacement operation significant quantities of resinous material can be lost unfortunately, in either of these types of crevices. In connection with the crevices located in the formation, as pressure is applied to the upper level of the resinous material, greater quantities of this material are displaced into the upper portions of the formation as the material is generally displaced into the upper levels and progressively down to the lower levels of the formation. The resin displaced in and sealing the formation takes the form of an inverted pyramid as shown in the drawings of the cited application. If the permeable formation to be plugged contains a crevice, large quantities of resinous material can be lost in the crevice before the lower portion of the formation is sealed when the procedure is followed. Thus this results in an inefficient use of the expensive resinous material. Additionally, as the resinous material is usually precatalyzed with polymerization catalyst prior to its introduction into the well bore, sufficient quantities of the resinous material must be available to insure proper sealing of the exposed formation. Accordingly, when formations exhibiting high areas of permeability are encountered, the use of a bogey run in which an inexpensive solution, e.g. sugar-water solution, is substituted for the expensive resinous material. The data provided by such a run include an estimation of the quantities of resinous material required to seal the exposed formations as well as an estimation of the time required for displacing the resinous material into the formation. The time required for the displacement operation is used in determining the amount of catalyst necessary to provide ample working time before polymerization of the resinous material causes a change from a mobile liquid to a solid mass.

An object of the present invention is the provision of a method for expeditiously combating the effect of a reduction or cessation of gas circulation when gas drilling wells through permeable formations. Another object of the present invention is the provision of a method for the efficient employment of resinous material in a method for expeditiously combating the effect of a reduction or cessation of gas circulation when gas drilling wells through permeable formations. These objects are accomplished when using the method of the present invention which is designed to obviate the use of a bogey run and provide for simultaneous injection of the resinous material over the entire portion of the permeable formation exposed in the well bore with the use of a string of tubing.

According to the method of the present invention, when an obstruction of air circulation, i.e., a reduction or cessation thereof, is experienced during an air drilling operation and the obstruction is attributed to the ingress of gas, liquid or loosely consolidated earth particles, particularly salt water, into the bore from an adjacent stratum, resin-forming material is introduced into a string of tubing, for instance the drill string, extending downwardly below the permeable formation. The resinous material is conducted downwardly in the tubing. A first portion of the resinous material is conducted through the lower extremity of the tubing and forms a column in the annular space between the tubing and the wall of the well bore which column at least a portion of the formation to be sealed. The level of this annular column is maintained while the upper level of the remaining or secondary portion of the resinous material in the tubing is pressured to force permeable formation sealing amounts of resinous material into the permeable formation. The resinous material is maintained in this position until it substantially solidifies. The solid resin is drilled through and drilling is continued with gas circulation to remove cuttings from the well.

The method of this invention can best be described with reference to a specific example and the drawing, FIGURES 1 through 10, in which several distinct phases of the method are illustrated.

Referring to the drawing, FIGURE 1, the numeral 10 represents the earth's surface through which a well bore 12 is being drilled to an oil-producing formation with
rotary drill pipe 14 containing a rotary bit 16 at the lower end. Pressurized air is introduced into drill pipe 14 at the surface of the earth, is conducted downward therewith, exits through opening 15 of rotary drill bit 16 at the site of the earth's surface, and penetrates upwardly through annulus 20, surrounding drill pipe 14, carrying relatively small as well as larger rock particles from the site of drilling to the earth's surface.

In FIGURE 2 rotary drill bit 16 passes through crevice 101, and penetrates a salt water formation 22 at its upper level 24 as indicated by a reduction in air circulation rate as well as the muddy nature of the particles recovered from the site of drilling. The depth of the drill bit is noted and thus the position of upper level 24 of salt water formation 22 is known. In FIGURE 3 drilling is continued through the salt water-bearing formation containing crevice 101, air circulation eventually ceases due to the back pressure of the salt water, a column of salt water 28 rises in the well bore and drill pipe to level 30 in annulus 20 and upper level 31 in drill pipe 14, the lower level 26 of salt water formation 22 is penetrated by rotary drill bit 16 and drilling is discontinued. Occasionally, in cases where the water formation is of considerable depth, it may not be possible to penetrate the lower level of the formation before water production stops further drilling.

A small amount, e.g. 10 gallons, of radioactive fluid, e.g. aqueous iodine 131 solution, is injected into drill pipe 14 at position 42. A detecting device 32, consisting essentially of a Geiger-counter is inserted to locate the radioactive fluid.

In FIGURE 4 gas pressure is applied to the liquid column in drill pipe 14 to move the upper level 44 of the column of radioactive liquid 43 downwardly in the drill pipe to the position shown. As the column moves downward salt water exits through openings 15 of rotary drill bit 16 and forms annular salt water column 48 with an upper level 50 in the annular space formed between the drill pipe and the walls of the well bore. An amount of resins material at least sufficient to cover the portions of formation 22 exposed to well bore 12, for instance, fifty gallons of resinous material, weighted, e.g. with 25% CaCO₃, to be heavier than the salt water in the well bore, consisting essentially of 20 weight percent of a mixture of 5% N,N'-methylene-bis-acrylamide and 95% acrylamide in water along with 0.3 weight percent of ammonium persulfate and 0.6 weight percent of nitro-tris-pro-pionamide is injected down drill pipe 14 at a rate of 2 gallons per minute and positioned in tubular area 36 located above upper level 44 of the radioactive liquid. Detecting device 32 is used to locate the position of radioactive liquid 42. A second radioactive isotope layer 45, e.g. of iodine 131, is added on top of the resinous material which thus has a leading radioactive edge 42 and a rear radioactive edge 43.

In FIGURE 5 pressurized air is introduced downwardly in drill pipe 14 and moves the resinous material, preceded by radioactive material 42, through opening 15 up and out the annulus formed between the drill pipe and the well bore walls to form an annular column of resinous material 52 (with an upper level 54) covering the portions of salt water formation 22 exposed in the well bore. In this operation the pressure on the resinous material is insufficient to force a significant quantity into the adjacent formation and the resinous material displaces annular salt water column 48 upwardly to new level 50. As the annular resinous material column 52 is moved upwardly, radioactive material 42 is located, thus upper level 54, with its attached isotope layer 45 which is located within drill pipe 14, to insure upward movement of upper level 55 of the resinous material at least adjacent and preferably a short distance beyond the upper level 24 of salt water formation 22. By noting the depth of the device 32 the position of upper level 54 is known. Annulus 20 is sealed at the surface with casing head 21 and air pressure up to the limit of the surface casing is used to maintain upper level 54 of annular column of resinous material 52 in the position shown. Detecting device 32 is raised (not shown) to locate layer 43 thus upper level 56 of the secondary column (tubular) of resinous material 58.

In FIGURE 6 pressurized air (250 p.s.i.) is introduced downwardly in drill pipe 14 and forces resinous material through opening 15 and causes the simultaneous injection of resinous material in area 62 into the entire portion of permeable formation 22 exposed in the well bore as shown by the indicating arrows. During this phase layer 43 thus upper level 56 of resinous material tubular column 58 is tracked with device 32.

In FIGURE 7 the displacement of resinous material by air is discontinued when the upper level 56 of resinous material tubular column 58 is approximately even with upper level 54 of annular resinous material column 52 as determined by observing the depth of tracking device 32 and discontinuing the displacement when the device 32 reaches the depth priorly noted for upper level 54. In FIGURE 8 the drill pipe and bit are lifted as shown. The well is shut in and the resinous materials maintained in this position by regulating the air pressure in both the annulus and drill pipe until the resinous material commences to polymerize. However, the drill pipe can be raised above the resinous material before polymerization time and solidification of the resin as shown in FIGURE 9. The resinous material is copolymerized to a semi-solid set in about 5 minutes at 400-500 mg. of air can be controlled by changing the concentration of the catalyst or by adding small amounts of potassium ferrocyanide to delay polymerization. In FIGURE 10, following the solidification of the resinous material, air pressure is discontinued, detection device 32 is removed, the salt water is blown out, air circulation down drill pipe 14 to rotary drill bit 16 is initiated, drilling is resumed, the solidified resinous material is drilled through, and the drilling continues downwardly into the earth's surface while removing cuttings from the well bore by air circulation down the drill pipe and up the well annulus.

The above example illustrates a method designed to remove gas circulation obstructions in a rotary drilling method employing a gas as the circulating medium. The advantages in using this method are readily apparent to those skilled in the art and include, for instance economy and speed, and safety advantages result in the manner in which this method is conducted, for example, since (a) removal of the drill pipe and bit from the well bore is not mandatory, (b) a resinous material is used that will copolymerize at ambient conditions in the well bore, (c) the polymerization time of the resinous material is controllable, (d) detection means are employed in a manner to place the resinous material properly in the well bore to permit excellent air circulation when drilling is resumed, (e) a bogey run is not required and (f) the expensive resinous material is efficiently employed, since loss of the resinous material in crevices, for instance crevices 100 and 101, can be avoided or minimized. Although this invention is illustrated with a most expedient and economical method, it will be obvious to those versed in the art to use various modifications incorporating the essential features of this method such as the removal of the drill pipe and bit from the well bore completely and using packers to block off annulus 28 during the displacement of the resin from within the tubing and into the well bore.

The resin-forming material employed in the method of the present invention is catalyzed before placement in the bore and is of the type that will harden at temperatures subsequently encountered in the well bore between about 50 to 800° F. The quantity of resin-forming material used must be adequate to extend horizontally into the formation of ingress for a distance sufficient to securely seal this formation subsequent to the hardening of the resinous material to prevent further ingress of unwanted extraneous materials. This distance
usually extends at least about six inches into the formation. Moreover, in this method it is imperative that the resin-forming material occupy the well bore adjacent the formation of ingress when the hardened resin is formed.

Accordingly, after the introduction of the resin-forming material, which has a specific gravity higher than the ingressing well fluid, into the well bore tubing, detection means are employed to track the upper level of the annular column of resin-forming material; and gas or liquid, e.g., air or water pressure, is applied to maintain this upper level approximately adjacent the upper level of the strata of ingress. Gas or liquid is also applied to the upper level of the secondary portion of resinous material in the tubing to force permeable formation sealing amounts of this material into the permeable formation. The resinous material is maintained in this position until it solidifies. Although gas or liquid pressure can be employed in this method, gas is preferable to liquid since (a) it permits better control of the resinous material and (b) the well bore hole is drier following the polymerization of the resin-forming materials and no time must be spent drying the hole before drilling. The gas pressure will depend upon the nature of the obstruction encountered and the depth of the permeable formation and is generally from 0 to 500 pounds up to about 150 to 1000 p.s.i. Since tremendous pressures can be required, it may be desirable to produce such pressures by employing liquid and gas in combination, e.g. provide a liquid column above the resin-forming material and exert air pressure on the liquid column. Following solidification of the resinous material, air-drilling is resumed.

In the practice of this method, it may be desirable to place in the tubing a small volume of liquid or primary buffer before the resin-forming material to prevent contact of the resinous material with the materials in the lower portion of the well bore, e.g., salt water and generally radioactive material to facilitate tracking the upper level of the annular column of resinous material. This primary buffer should have a density in between that of the well bore fluid and the resinous material so that the buffer will have a tendency to float or remain between the well fluid and resinous material. Examples of suitable buffers are radioactive fluids, e.g., iodine 131 solution in mixtures of 60% by volume of kerosene and 40% by volume of carbon tetrachloride with a specific gravity heavier than the well fluid and lighter than the resinous material or mixtures of 82% by volume of kerosene and 18% by volume of tetrabromoethylene.

It is also desirable to place on the resin-forming material a volume of liquid or secondary buffer possessing radioactive characteristics appreciably different from that, if any, of the resin-forming material to facilitate tracking of the resin-forming material; the density of the secondary buffer should be less than that of the resinous material and preferably greater than that of any fluid, liquid, or gas, used to pressure the resinous material to its position of hardening. Suitable secondary buffers are radioactive fluids, e.g. iodine 131, in 2% by weight of calcium chloride in water with specific gravity lower than the resinous material.

The detection means employed for tracking the position of the upper level of the annular column of resinous material in the well bore as well as the upper level of the secondary portion of the resinous material (tubular column) in the tubing can vary as long as it can detect the upper level of the resinous material in the well annulus. In one method, a soluble radioactive tracer, e.g. iodine 131, may be injected into the polymerizable material and a Geiger-counter attached to a line can be employed to locate the upper level of the annular and tubular columns of polymerizable material and thus by checking the depth of the Geiger-counter, these positions of the polymerizable material are known. In the preferred method primary and secondary radioactive buffers are employed as described in the above example.

Among the resin-forming materials which are utilized are those affording modified polyester-type resins, and U.S. Patents Nos. 2,255,313; 2,443,735 and 2,443,741 give examples of these materials. The first of these patents describes resin-forming materials containing a resin which is a substantially linear polyhydric alcohol ester of an unsaturated polybasic acid material of the maleic type mixed with a liquid substituted-ethylene body of resin-forming characteristics which is copolymerizable and miscible with the resinous material, for instance a vinyl compound. Thus the resin or plastic obtained from this mixture can be a reaction product of a maleic type polybasic acid, a polyhydric alcohol and a compound. This patent lists a number of suitable reactants; for instance, the polybasic acid may be maleic anhydride, maleic acid, fumaric acid, etc. and the preferred acid materials contain a single double bond and up to about 5 carbon atoms. The polyhydric alcohols are preferably dihydric of the type which react with dibasic acids to yield linear molecules or linear polymers. Various of the dihydric alcohols are listed in the patent, for instance diethylene glycol, ethylene glycol, triethylene glycol, propylene glycol, etc., and the preferred alcohols are the glycol and glycols having about 12 carbon atoms. In the resin-forming material the polyester resin formed from the dibasic acid and the glycol is mixed with an ethylene polymerizable body, preferably a vinyl compound such as vinyl esters, vinyl ethers, styrene, etc. The mixtures containing the polyester resin and ethylene compound, for instance styrene, are sold commercially and at least one material containing the CH2=CHC=C linkage. The resin component of this mixture is produced by the esterification of an alpha, beta unsaturated polycarboxylic acid with a polyhydric alcohol, such as a glycol, while the CH2=CHC=C body can, for instance, styrene. Thus, the ingredients of this resin-forming material can be generally the same as those described with reference to U.S. Patent No. 2,255,313. In Patent No. 2,443,741 similar resin-forming materials are disclosed. However, the CH2=CHC=C body is of the polyallyl type, for instance a polyallyl ether, and a number of these are mentioned in this patent.

As a more specific example, a resin-forming material suitable for use is provided by mixing generally about 8 to 35 percent and preferably about 20 to 35 percent by volume of an unsaturated polyester resin of the type disclosed in these patents as a solution containing about 30 to 60 percent by volume of styrene; about 80 to 65 percent by volume of an esterified, unsaturated polybasic acid; about 0.01 to 4 percent by volume of a promoter; and about 0.01 to 3 percent by volume of a polymerization catalyst. The polyester resin component can be Resolene D111, a polyethylene glycololate resinate mixed with styrene. To adjust the specific gravity of the resin-forming mixture within a desirable range, a chemically inert densifier can be added which has a low viscosity, for instance about 1 to 15 centipoises, preferably about 1 to 5, at 60° F., and a specific gravity of over about 1.5; and which is water-insoluble and water-insoluble. Among the preferred densifiers are included benzoyl chloride, dichlorobenzene and dinitrophenyl. A particularly effective densifier is tetrabromoethane.

In order to facilitate the polymerization reaction the addition of a small amount of a promoter, for example about 0.01 to 4 weight percent of benzyol or dimethyl aniline, is preferred. Apparently, the promoter acts as a linking agent and in combination with the catal-
lyst initiates a faster polymerization reaction at the relatively low polymerization temperatures encountered in a well bore. By varying the amount of promoter and catalyst the working life of the resin-forming material can be regulated. Among the promoters which can be employed in this invention are the organic acid salts of metals such as aluminum and calcium, for instance calcium stearate, aluminum stearate, aluminum napthenate and calcium napthenate.

The polymerization catalysts utilized to effect the copolymerization or condensation reactions between styrene and the modified polyester-styrene solution can be the organic peroxide catalysts such as benzoyl peroxide, methylethyl ketone peroxide, tetrabutyl hydroperoxide or cyclohexanone peroxide. Particularly effective catalysts are a 60% solution of methylethyl ketone peroxide in dimethyl phthalate or benzyl peroxide in a 50% mixture with tricresyl phosphate. As mentioned the working life of the resin-forming material is dependent upon the amounts of polymerization catalyst and promoter present as well as the temperature in the well bore, and generally polymerization starts immediately after the catalyst and promoter have been added. Consequently, at ambient temperatures within a well bore, for instance about 70 to 75° F., the amount of catalyst employed preferably is in the range of about 0.4 to 0.7 percent by volume of the resin-forming material which affords a working life of about 30 to 60 minutes. The amount of catalyst required to sustain the working life of the resin-forming material will increase as the temperature is decreased and thus at lower temperatures of about 50 to 60° F. the amount of catalyst employed may be as high as 3 percent.

Another class of desirable liquid resin-forming compositions particularly suitable for use in the method of the present invention include an aqueous solution of an alkylidene bisacylamide, an ethylenic comonomer, and calcium chloride, the bisacylamide having the formula:

$$R_{3} \overset{\text{H}}{\overset{\text{N}}{\overset{\text{O}}{\overset{\text{C}}{\overset{\text{O}}{\overset{\text{C}}{\overset{\text{H}}{\text{CH}}}}}}}}$$

in which

$$R' = \text{CH}$$

is a hydrocarbon residue of an aldehyde and R₂ is a member of the group consisting of hydrogen and a methyl radical.

The other comonomer is a solid, liquid or gaseous ethylenic (i.e. contains at least \(>\text{C}=\text{C} <\) a radical) compound with a solubility of at least about 2% by weight and preferably at least about 5%, in water and which copolymerizes with the aforesaid bisacylamide in an aqueous system. Although not essential in practicing the invention, it is preferred to select an ethylenic comonomer which is preferably soluble or at least self-dispersable in water with appropriate stirring, as such, for example, methylenebisacylamide, which is capable of polymerizing.

In addition to the comonomer N,N'-methylene bisacylamide set out in the examples hereinafter, any of the alkylidene bisacylamides corresponding to the above formula which are described and claimed in Lundberg Patent No. 2,488,847, and similar ethylenic derivatives, or mixtures thereof may be used as cross-linking agents. Only slight solubility is required of the alkylidene bisacylamide in view of the small amount used; therefore, this component may have a water solubility as low as about 0.02% by weight at 20° C. but a solubility of at least about 0.10% is more desirable for general purposes.

A wide variety of ethylenic comonomers or mixtures thereof are copolymerizable with the alkylidene bisacylamides; those having a formula containing at least one

\(>\text{C}=\text{C}<\) group, hereinafter referred to as the ethylenoid group, and having appreciable solubility in water are suitable for use in the present invention. See U.S. Patent No. 2,801,985, hereby incorporated by reference. As more particularly set forth in this patent the unique ethylenoid group may be attached to one or more of many different atoms or radicals including hydrogen, halogens, such as chlorine and bromine, cyanide, aryl, aralkyl, alkyl, and arylamine with or without solubilizing groups attached to these hydrocarbons. In addition, the substituents on the ethylenoid group may be attached to another ethylenoid group or to other ethylenoid groups. Derivatives of the ethylenoid groups including formyl, methyl, polynoxyacylamide residues and quaternary ammonium salt radicals,

$$-\overset{\text{O}}{\overset{\text{C}}{\overset{\text{O}}{\overset{\text{C}}{\overset{\text{N}}{\overset{\text{R}}{\text{CONR}}}}}}}}$$

where each R is hydrogen, alkyl, lower alkyl or a polyoxyalkylene radical; and -CONR₁ and -CH₂CONR₂

where R is a H, NH₂, alkyl metal, alkaline earth metal, organic nitrogenous base, alkyl, lower alkyl or polyoxyalkylene radical. The large number of combinations and proportions of the various suitable substituents makes it impractical to list all compounds in this category which may be employed. The water solubility of these substances is known to depend chiefly on the number and type of hydrophilic and hydrophobic radicals therein; for example, the solubility of compounds containing an alkyl radical diminishes as the length of the alkyl chain increases and aryl groups tend to decrease water solubility whereas the aforesaid hydrophilic substituents all tend to improve the solubility of a given compound in water. Accordingly, the comonomer should be selected according to chemical practice from those containing sufficient hydrophilic radicals to balance any hydrophobic groups present in order to obtain the requisite water solubility of monomer.

Among the water-soluble ethylenoid monomers, those containing an acryl or methacryl group are especially recommended. These are exemplified by N-methyl acrylamide, calcium acrylate, methacrylamide and acrylamide. Other suitable ethylenoid compounds are acryl acid; other N-substituted acrylamides, such as N-methyl acrylamide, N - 3 - hydroxypentyloxyacrylamide, dimethylaminopropylacrylamide, N-ethyl acrylamide; acrylonitrile; saturated alkyl esters of acrylic acid, i.e. methyl acrylate, \(\beta\)-hydroxethyl acrylate and polyethylene glycol acrylates, an example being the reaction product of \(\beta\)-hydroxyethyl acrylate or acrylic acid with about 1 to about 30 mols or more of ethylene oxide; salts of acrylic acid, i.e. magnesium acrylate, sodium acrylate, ammonium acrylate, zinc acrylate, \(\beta\)-aminoethyl acrylate, \(\beta\)-methyl aminoethyl acrylate, guanidine acrylate and other organic nitrogenous base salts, such as diethylamine acrylate and ethanolamine acrylate; quaternary salts like alkyl acrylamidoethoxydimethylamino chloride; acrolein, \(\beta\)-carboxycrotonin, butenonic acid, \(\beta\)-chloracrylic acid; \(\beta\)-chloroacrylic acid; as well as methacrylic acid and its corresponding derivatives.

Maleic acid and its corresponding derivatives including partial esters, partial salts, and ester salts thereof; maleic acid, chloromaleic, fumaric, itaconic, citraconic, vinyl sulfonic, and vinyl phosphonic acids and their corresponding diesters and mixtures of the kind and other suitable compounds include \(\beta\)-dichloroacrylonitrile, methacrylonitrile, potassium methacrylate, magnesium methacrylate, hydroxymethyl methacrylate, zinc \(\beta\)-chloracrylate, trimethylamine methacrylate, calcium \(\beta\)-chloromethacrylate, diethyl methylene succinate, methylene succinate dimethylmate, maleic anhydride, maleyl maleic anhydride, dimethyl maleate, methyl isopropenyl ketone, ethyl vinyl ketone, propyl vinyl ketone, vinyl formate, vinyl lactate, vinyl acetate, vinyl
brromacetate, vinyl chloroacetate, vinyl pyrrolidone, allyl levulinate, allyl alcohol, methallyl alcohol, diallyl carbonate, allyl lactate, di(methyleneaminoethyl) maleate, di(methyleneaminoethyl) maleate, di(N,N-dimethyl γ- aminoethyl) maleate, sulfonated styrene, vinyl pyridine, maleic anhydride, sodium maleate, ammonium maleate, calcium maleate, monomethylmaleate, monoaammonium maleate, monomagnesium maleate, methyl vinyl ether, N-allyl maleimide, N-allyl maleimide, N-vinyl acetamide, N-vinyl maleimide, N-vinyl maleimide, N-vinyl dimonochloride, N-vinyl dipropionamide, N-vinyl diacetamide, vinyl sulfon chloride, vinyl sulfonic acid salts, vinyl sulfonic acid amides, vinyl oxazolidone, allyl amine, di- allyl amine, vinyl methy pyridinyl chloride, and allyl trimethyl ammonium chloride to name only a few of the operative compounds.

The preferred resin-forming material which can be utilized in the method of the present invention is in an aqueous medium and has an initial viscosity approximating that of water. This material can be formed by dissolving a mixture of acrylamide and N,N'-methylene-bis-acrylamide in fresh water. Generally this mixture contains about 1 to 25 weight percent of N,N'-methylene-bis-acrylamide and about 99 to 75 weight percent of acrylamide. The aqueous solution will usually include from about 5 weight percent of this mixture to its limit of solubility and preferably this amount is about 5 to 25 percent. Although the acrylamide as such is preferred, its nitrogen atom could be substituted as with a hydroxy methyl or a hydroxy ethyl group. Ammonium persulfate is an acceptable catalyst to polymerize the aqueous mixture and it can be employed with a promoter such as sodium thiosulfate or nitro-tris-propionamidine. The amounts of each of the catalyst and promoter are about 0.1 to 2 weight percent based on the aqueous solution of resin-forming material, and these amounts can be varied to give the desired working life. For instance, a weight ratio of catalyst to promoter of 1 to 2 in an aqueous solution containing 20 weight percent of the acrylamide and N,N'-methylene-bis-acrylamide (95% acrylamide and 5% N,N'-methylene-bis-acrylamide) will give a working life at 70° F. of about 60 to 120 minutes when the catalyst plus promoter is about 0.5 to 1.5% of the aqueous solution. A specific resin-forming material found useful is an aqueous solution which contains 20 weight percent of resin-forming material, about 10 weight percent of acrylamide, about 1 weight percent of N,N'-methylene-bis-acrylamide, 0.6 weight percent of nitro-tris-propionamidine, 0.3 weight percent of ammonium persulfate, and the balance being water. The mixture has an initial viscosity (1.3 centipoises) approximating that of water (which is about 0.5 to 1.5 centipoises under the conditions in many well bores) and is not greater than about 2.0 centipoises over a working life of at least about 90 minutes to facilitate its placement in the desired well area. The mixture can be made heavier than salt water by the addition, for instance of calcium chloride or other suitable densifier. The aqueous solution of amides can advantageously be used as the resin-forming material as it has a lesser tendency to emulsify in the well than do the modified polyester-type compositions.

It is claimed:

1. A method for combating the obstruction of gas circulation in drilling wells employing gas as the circulation medium through a drill pipe tubing with a lower opening, wherein the obstruction results from the ingress of extraneous materials into the well bore from a subterranean formation, the steps comprising introducing weighted resin-forming material into the tubing extending downwardly in the well bore below the upper level of the formation of ingress, conducting a portion of the resin-forming material through the tubing to form an annular column of resin-forming material covering the formation of ingress in the annular space provided between the tubing and the portion of the formation of ingress exposed in the well bore, tracking the upper level of the annular resin-forming material column at the approximate depth of the upper level of the formation of ingress as determined by said tracking while applying pressure to the resin-forming material remaining in the tubing, forming a formation sealing amounts of resin-forming material into the formation of ingress exposed to the resin-forming material in the well bore, maintaining the resin-forming material in this position until it substantially polymerizes, drilling through the polymerized resin, and continuing drilling with gas circulation to remove cuttings from the well.

2. The method of claim 1 wherein the resin-forming material contains radioactive leading and rear edges, and tracking said leading and rear edges with radioactive detection means to aid in properly positioning the resin-forming material in the well bore.

3. The method of claim 2 wherein the resin-forming material consists essentially of acrylamide and an alkylidene bisacrylamide.

4. A method for combating the obstruction of air circulation in drilling wells employing air as the circulation medium through a drill pipe tubing with a lower opening, wherein the obstruction results from the ingress of extraneous materials into the well bore from a subterranean formation, the steps comprising introducing an aqueous solution of resin-forming material consisting essentially of acrylamide and alkalidene bisacrylamide, weighted to be heavier than the extraneous material, into the tubing extending downwardly in the well bore to the approximate depth of the lower level of the formation of ingress, conducting a portion of the resin-forming material through the opening in the tubing to form an annular column of a resin-forming material covering the formation of ingress in the annular space provided between the tubing and the portion of the formation of ingress exposed in the well bore, tracking the upper level of the annular column of resin-forming material in the well bore with detection means, applying pressure to maintain the upper level of the annular resin-forming material column at the approximate depth of the upper level of the formation of ingress as determined by said tracking while applying pressure to the resin-forming material remaining in the tubing, forming a formation sealing amounts of resin-forming material into the formation of ingress exposed to the resin-forming material in the well bore, maintaining the resin-forming material in this position until it substantially polymerizes, drilling through the polymerized resin, and continuing drilling with air circulation to remove cuttings from the well.

5. The method of claim 4 wherein the resin-forming material contains radioactive leading and rear edges, and tracking said leading and rear edges with radioactive detection means to aid in properly positioning the resin-forming material in the well bore.

6. The method of claim 5 wherein the alkylidine bisacrylamide is N,N'-alkylene-bisacrylamide.

7. The method of claim 6 wherein the resin-forming material consists essentially of about 1 to 25 weight percent of N,N'-methylene-bisacrylamide and about 99 to 75 weight percent of acrylamide.

8. A method for combating the obstruction of air circulation in drilling wells employing air as the circulation medium through a drill pipe tubing with a lower opening, wherein the obstruction results from the ingress of extraneous materials into the well bore from a subterranean formation, the steps comprising introducing an aqueous solution of resin-forming material consisting essentially of acrylamide and alkylidene bisacrylamide, weighted to be heavier than the extraneous material, into the tubing ex-
tending downwardly in the well bore to the approximate depth of the lower level of the formation of ingress, conducting a portion of the resin-forming material through the opening in the tubing to form an annular column of a resin-forming material covering the formation of ingress in the annular space provided between the tubing and the portion of the formation of ingress exposed in the well bore, tracking the upper level of the annular column of resin-forming material in the well bore with detection means, applying pressure to maintain the upper level of the annular resin-forming material column at the approximate depth of the upper level of the formation of ingress as determined by said tracking while applying pressure to the resin-forming material remaining in the tubing to force formation sealing amounts of resin-forming material into the formation of ingress exposed to the resin-forming material in the well bore, raising the drill pipe above the resin-forming material, and maintaining the resin-forming material in this position and substantially polymerizing the material, drilling through the polymerized resin, and continuing drilling with air circulation to remove cuttings from the well.

9. The method of claim 8 wherein the resin-forming material contains radioactive leading and rear edges, and tracking said leading and rear edges with radioactive detection means to aid in properly positioning the resin-forming material in the well bore.

10. The method of claim 9 wherein the alkylidine bisacylamide is N,N'-alkylene-bisacylamide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,279,262 Edwards Apr. 7, 1942
2,345,611 Lerch et al. Apr. 4, 1944
2,680,595 Upham June 8, 1954
2,743,779 Brown May 1, 1956
2,801,984 Morgan et al. Aug. 6, 1957
2,801,985 Roth Aug. 6, 1957
2,837,163 Ramos et al. June 3, 1958
2,940,729 Rakowitz June 14, 1960