Sept. 25, 1956 G. H. ROHRBACK ET AL 2,764,242

PREVENTION OF CASING CORROSION

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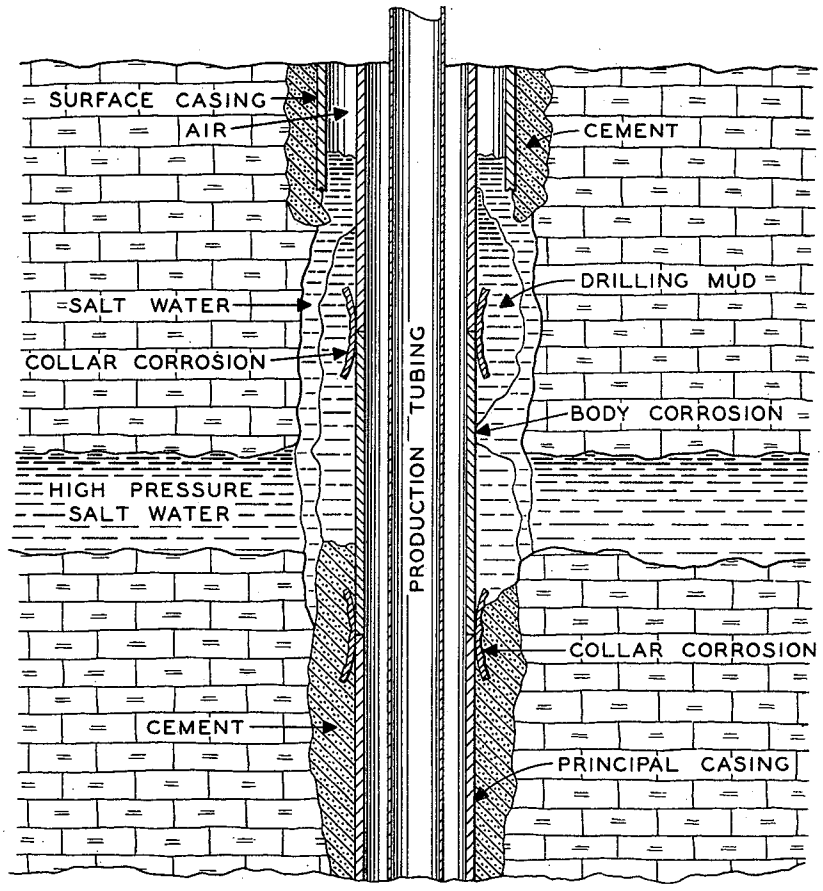


FIG. 1

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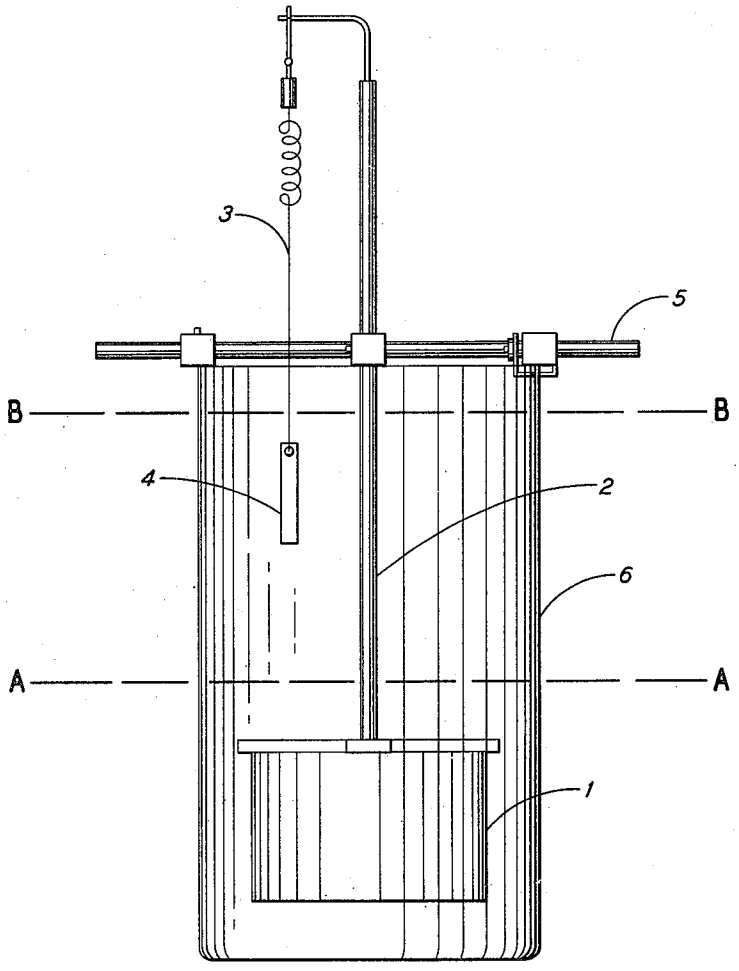


FIG. 2

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PREVENTION OF CASING CORROSION

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4 Claims. (Cl. 166—1)

This invention relates to a composition and method for inhibiting the corrosion of oil well casings.

Although relatively little attention has been given to corrosion failure of oil well casings in the literature, this problem is rather wide-spread. A number of theories have been proposed to account for casing corrosion and some attempts to control it have been made on the basis of the theories. Among the theories heretofore advanced to explain casing corrosion have been suggestions that the corrosion was due to bacterial action; due to electric currents flowing through the casing; due to localized corrosion at metal flaws; due to particular compositions of formation water; due to corrosion by self-potential currents, and due to interzonal migration of salt water. So far as is known, no successful method of controlling casing corrosion has been developed on the basis of any of these theories. Meantime, casing failure due to corrosion continues to be a serious problem in many oil fields. Repair of casing failure is difficult at best and if the failure escapes detection for an appreciable period of time, the well ceases to produce and production may not be resumed, even though the casing be repaired, necessitating abandonment of the well.

Thirty instances of casing failure due to corrosion in a California field were carefully studied. The average time of failure was about five years, but failures occurred at times ranging from less than one year to about sixteen years from completion of the well. In the large majority of these cases the failure occurred in the salt water zone above the cemented zone. Corrosion of the casing in all instances was highly localized and from an overall study of the circumstances attending these casing failures it was concluded that the corrosion was electrochemical in character and occurred when a part of the casing was in contact with low (7–8) pH formation water and a part of the casing was in contact with higher (8 to 12) pH mud or with higher (8–12) pH washing solutions. The situation existing in the well when serious corrosion is encountered will be better understood by reference to Fig. 1 of the appended drawings, which is a diagrammatic illustration of a section of a typical well casing and formation. The portion of the casing in contact with formation water of relatively low pH is the area at which rapid corrosive attack appears to occur.

It has now been found that casing corrosion can be very markedly inhibited by filling the annular space above the cemented zone and between the casing and the formation with an aqueous clay drilling mud containing .001 to 2.5% by weight of ferrous chloride or stannous chloride. When a well has been drilled to the desired depth and is ready for a cementing operation, the casing is full of drilling mud. Cementing of the casing is commonly accomplished by forcing a cement slurry (optionally preceded by an aqueous washing solution) downwardly through the casing, causing the mud contained in the casing to flow around the lower circumference of the casing and upwardly through the annulus between the outer casing wall and the formation. When the desired amount

of cement slurry has been introduced into the casing, the cement is forced into position between the outer casing wall and the formation by pushing it down the casing with additional mud. When the cement is in place it is allowed to set and that portion of the annulus between the outer casing wall and the formation and above the cemented zone is filled with drilling mud which was pushed ahead of the cement slurry. This drilling mud should have a substantial content of either ferrous chloride or stannous chloride in order to prevent casing corrosion. Similarly, it is desirable that the mud introduced into the casing to force the cement into position and which is ultimately resident in the annulus between the casing and the formation below the cemented zone should also be treated so as to have an appreciable content of either ferrous chloride or stannous chloride.

While ferrous chloride and stannous chloride are the preferred ferrous and stannous compounds for use pursuant to the invention, it is the ferrous and stannous ions which are the effective inhibiting additives. Accordingly, other ferrous and stannous compounds which are soluble or dispersible in aqueous fluids such as the sulfates, the nitrates, the hydroxides, can be used instead of the chlorides in equivalent amounts and are found essentially equally effective.

During the drilling of a well the mud is continually circulating and is continually in contact with the air. No advantage is obtained by adding ferrous compounds or stannous compounds to the mud used during the drilling, since the regular and intimate contact with the air in the mud pits would cause oxidation of stannous and ferrous compounds to the corresponding stannic and ferric compounds which are useless in preventing corrosion. Accordingly, the stannous compound or ferrous compound must be added to that portion of the mud which will be left between the outer casing wall and the formation when the well is completed just prior to introducing this portion of the mud into the well. Both stannous chloride and ferrous chloride, especially the latter, increase the viscosity of aqueous clay muds and increase their rate of filter loss.

It has been found that corrosion can be inhibited without adverse effect on the viscosity and water retaining properties of the mud by adding a corrosion inhibiting concentrate consisting essentially of a mixture of 4 to 20 parts by weight of stannous chloride or ferrous chloride and 2 to 10 parts by weight of a water loss reducing agent to that portion of the mud which will ultimately be resident between the casing wall and the formation immediately prior to the introduction of that mud into the well. Suitable water loss reducing agents are starch, natural gums, such as gum arabic, gum tragacanth, Indian gum, and the like, or the alkali metal salts of carboxymethylcellulose. The carboxymethylcellulose materials are especially suitable and mixtures of ferrous chloride and the carboxymethylcellulose salts containing between 1 and 10 parts by weight of ferrous chloride per part by weight of the carboxymethylcellulose compound constitute especially suitable corrosion inhibiting concentrates.

It is frequently desirable to employ a corrosion inhibiting concentrate containing a viscosity reducing agent in addition to the ferrous chloride and water loss reducing agent. For example, suitable concentrates will contain from 4 to 20 parts by weight of ferrous chloride, 2 to 10 parts by weight of a water loss reducing agent, and 3 to 30 parts by weight of a viscosity reducing agent. Mud viscosity reducing agents are well known to those skilled in the art and include the molecularly dehydrated phosphates or polyphosphates and plant tannins such as quebracho extract and chestnut extract. An especially desirable concentrate is one containing 4 to 20 parts by

weight of ferrous chloride, 2 to 10 parts by weight of an alkali metal salt of carboxymethylcellulose, 3 to 12 parts by weight of a sodium polyphosphate, such as sodium meta-phosphate, sodium tetraphosphate, sodium tripolyphosphate, tetrasodium pyrophosphate, sodium hexa-metaphosphate, and the like, and 4 to 20 parts of quebracho.

The inhibitor concentrates described above are added to the mud in amount sufficient to give the mud a ferrous chloride content in the range from 0.001% to 2.5% by weight. Compositions of typical mud treated and untreated are indicated below. The untreated mud had a density of 90 pounds per cubic foot and a pH of 11.0.

	Untreated Pounds Needed for 100 Bbls. of Mud	Treated Pounds Needed for 100 Bbls. of Mud
Clay	14,600	14,600
Barytes	6,600	6,600
Carboxymethylcellulose	None	110
Ferrous Chloride	None	220
Tetrasodium Pyrophosphate	150	150
Quebracho	250	250
Sodium Hydroxide	150	150

by the fluid of lower pH. The electrodes were then left in these relative positions for a period ordinarily of 14 days, at the end of which electrode 4 was removed and weighed to determine its loss of weight. In order to determine the weight loss of electrode 4 due to electrochemical action alone, a second small iron strip approximately identical with electrode 4 in size and shape was suspended from the wall of the jar in the same fluid which surrounded electrode 4. At the end of the test period the weight loss of electrode 4 and the weight loss of the second metal strip were determined and the difference between these two losses was the loss of weight of electrode 4 due to electrochemical action. Results of a series of experiments are set forth in Table I below. The muds employed in the tests were typical commercial drilling muds. The formation water was a typical aqueous effluent from a California well and the pyrofluid was an aqueous solution of tetrasodium pyrophosphate such as is commonly employed for washing the mud cake prior to introduction of the cement and which is commonly left in the annulus between the outer casing wall and the formation when the well is completed. The effect of various additives on the weight loss due to electrochemical corrosion is shown in the table.

TABLE I

Weight loss in corrosion cells for different combinations of treated and untreated fluids

Test No.	Electrode 1			Electrode 4			Measured Weight Loss from Electrode 4 Due to Current (Milligrams)
	Fluid	Additive	pH	Fluid	Additive	pH	
1	Mud	None	12.0	Formation Water	None	7.1	120
2	do	Quebracho	12.3	do	do	7.3	139
3	do	Sodium Chromate	12.3	do	do	7.2	132
4	do	$SnCl_2$	12.2	do	do	7.1	5
5	do	$FeCl_2$	12.1	do	do	7.1	0
6	Pyro	None	12.3	Mud	do	8.5	968
7	do	do	12.2	do	Sodium Chromate	8.4	522
8*	Mud	do	8.5	Pyro	$SnCl_2$	12.1	0
9	Formation Water	do	7.1	do	$SnCl_2$	12.2	0
10	Mud	$SnCl_2$	12.2	do	$SnCl_2$	12.2	0

2—Mud contained quebracho—0.42 percent.
3—Mud contained sodium chromate—0.02 percent.
4—Mud contained $SnCl_2$—0.15 percent, Pyro—0.5 percent, and quebracho—0.5 percent.
5—Mud contained $FeCl_2$—0.5 percent, Pyro—0.5 percent, and quebracho—0.5 percent.
7—Mud contained sodium chromate—0.02 percent.
8—Pyro contained $SnCl_2$—0.15 percent, and quebracho—0.5 percent.
9—Pyro contained $SnCl_2$—0.15 percent, and quebracho—0.5 percent.
10—Both mud and pyro contained $SnCl_2$—0.15 percent, and quebracho—0.05 percent.
*When pyro was treated with $SnCl_2$, the cell was set up with electrode 4 in pyro solution.

Laboratory studies of the nature of casing corrosion and of compositions and methods for controlling it were made in the apparatus diagrammatically illustrated in Fig. 2 of the drawings.

In the drawing container 6 is a glass jar having about 4 gallons' capacity. Electrode 1 was made up of three short sections of concentric pipe welded together. The weld areas were covered with a plastic paint to eliminate undesirable galvanic couples from these areas. The total area of this electrode was about 330 square inches. Electrode 4 is a small strip of iron having a surface area of approximately 2 square inches. Electrode 1 is welded to iron rod 2 which is attached to adjustable support 5 so that the position of electrode 1 in the jar can be adjusted at will. Electrode 4 is connected to rod 2 by wire 3. In making the experimental tests to fluids were introduced into jar 6. The fluids differed from each other in both pH and density. In each test, jar 6 was filled with the denser of the two fluids employed to level AA and then the less dense of the two fluids was introduced into jar 6, filling the jar to about level BB. Electrode 1 was positioned in the jar so that it was entirely surrounded by the fluid of higher pH. Electrode 4 was positioned in the jar so that it was entirely surrounded

The data in the above table was obtained employing pairs of fluids having high pH differences. Commercial drilling muds ordinarily will have pH values lying in the range from about 8.5 to 12. The electrochemical attacks of the character illustrated in the table occur wherever there is a pH differential between two fluids in contact with different areas of the casing and the rate of that attack is greater when the pH difference of the two fluids is greater. From the results shown in the table it is clear that electrochemical attack is substantially completely eliminated by the addition of either ferrous chloride or stannous chloride to the high pH fluid, which in practical effect means the addition of these materials to the mud and to the pyrowash solution if such a solution is used in completing the well.

We claim:

1. A corrosion inhibiting concentrate, suitable for addition to aqueous clay drilling mud to be left in the annular space between the casing and the formation of a completed oil well, consisting essentially of 4 to 20 parts by weight of a material selected from the group consisting of stannous chloride and ferrous chloride and 2 to 10 parts by weight of a water loss reducing agent.

2. A corrosion inhibiting concentrate suitable for ad-

dition to aqueous clay drilling mud to be left in the annular space between the casing and formation of a completed oil well consisting essentially of ferrous chloride and an alkali metal salt of carboxymethylcellulose containing 1 to 10 parts by weight of ferrous chloride to each part by weight of carboxymethylcellulose.

3. A corrosion inhibiting concentrate, suitable for addition to aqueous clay drilling mud to be left in the annular space between the casing and the formation of a completed oil well, consisting essentially of 4 to 20 parts by weight of ferrous chloride, 2 to 10 parts by weight of an alkali metal salt of carboxymethylcellulose, 3 to 12 parts by weight of an alkali metal polyphosphate and 4 to 20 parts by weight of quebracho.

4. The method of preventing external corrosion of oil well casing which comprises filling the annular space above the cemented zone and between the casing and the formation with an aqueous clay drilling mud containing

0.001 to 2.5% by weight of a material selected from the group consisting of ferrous chloride and stannous chloride.

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