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PROCESS FOR THE TREATMENT OF OIL OR GAS WELLS

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This invention relates to a process for increasing or restoring the production of oil or gas wells by means of a treatment with a washing liquid, the present application being a continuation-in-part of my application Serial No. 77,550, filed May 2, 1936.

In many cases, the decrease in production of oil and gas wells is due not to actual exhaustion of the well reservoir, but to various other causes: for example, a considerable portion of the original oil may remain adhering to the sands of the formation; the pores, crevices, and flow channels of the producing formation may become clogged due to the precipitation of mineral deposits from the formation water or the mud fluid; gummy resinous, asphaltic or other organic solid matter may accumulate on the walls of the borehole, or in the pores, crevices and flow channels of the adjoining formation, blocking or reducing the flow of oil or gas to the well; finally, connate water, or water forced into the formation during the drilling period, may tenaciously adhere to the sand particles and decrease the permeability of the formation to the flow of oil.

Various methods have been developed to remedy these conditions, such as acidizing methods, flooding methods, treatments with heat-generating mixtures, treatments with solvents such as benzol, etc.

All of these methods are, however, subject to inherent limitations, and can therefore be successfully used only to attain limited objectives. Thus, treatment with acids is not effective in formations devoid of calcareous matter; flooding requires a plurality of suitably located wells; washing solvents such as carbon disulphide, carbon tetrachloride, benzol or gasoline are ineffective in cases where the low permeability of the formation is due, for example, to the presence therein of connate waters, etc.

The object of the present invention is to provide a process for treating oil wells passing through non-calcareous formations whose permeability is decreased by the presence therein of water and of asphaltic or gummy deposits, and, more specifically, to provide a method whereby the well and the adjacent formations are treated with a solvent capable at once to dissolve said organic deposits and the water held in the small capillary spaces of the sand.

Briefly stated, the present process consists in introducing into a well, preferably under pressure, a washing liquid which does not chemically attack the rock, causing it to penetrate into the formation, dissolving therein the gummy and resinous deposits and the water held between the sand grains by virtue of its surface tension, and withdrawing, after a desired time, the washing liquid from the same well together with the dissolved organic deposits and connate waters, for example, by releasing the pressure.

The washing liquid may be introduced into the oil formation in various ways. The desired amount of liquid, that is, an amount sufficient to impregnate the oil-bearing formation over its entire depth and to a desired radius around the well, may be run into the well through the tubing with the casing head open during this process. Another liquid, which may be immiscible with the washing liquid, such as water, oil, etc. may then be pumped into the casing and tubing simultaneously to force the washing liquid into the formation. Likewise, air or gas pressure may be applied in the same way and for the same purpose to the washing liquid charge. After the washing liquid has penetrated into the formation and remained therein for a desired period of time, the pressure on the well may be released, the formation pressure forcing the washing liquid, together with the dissolved water and gummy or resinous materials, back into the well, from which it may be withdrawn by pumping or swabbing.

It has been found that the following substances are particularly suitable for the purposes of this invention: heterocyclic nitrogen base compounds of the type of pyridine or quinoline, their homologues and derivatives, such as picolines, lutidines, alpha-collidines, pyridine-carboxylic acids, pyridine-sulphonic acids, hydroxy-pyridines, amino- and di-amino-pyridines, piperidine, quinoline-carboxylic acids, hydroxy-quinoline, and, in general, nitrogen bases obtained from coal tar and cracked petroleum products by various processes such, for example, as extraction with mineral acids. The nitrogen bases may be used for the purposes of this invention in such form as they are obtained in commercial processes, that is, in the form of mixtures containing various impurities, or they may be subjected to a preliminary purification to increase the percentage of the effective compounds contained therein.

These compounds may further be used either in pure form, or in any mixture with each other, or in admixture with suitable solvents, such as ketones, for example, methyl ethyl ketone, methyl propyl ketone, diethyl ketone; alcohols, for example, methyl alcohol, isopropyl alcohol, secondary butyl alcohol; ethers, for example, dioxane, tetra methylene oxide, furan; ether alcohols, for example, ethyl ether of ethylene glycol and diethylene glycol-monethylether; esters, for example, butyl lactate, glycol diacetate, carbitol or cellosolve acetates; acetone tops; benzol, gasoline, etc. The solvent is selected in each case depending on the particular nitrogen base compound used. Thus, for example, pyridine which is miscible in any proportions with water, can be used either alone, or with any of the above sol-

vents, including the water-immiscible solvents such as benzol or gasoline, since it is in itself effective in dissolving the water within the formation. Other agents, such as quinoline, which have only a limited solubility in water, but are miscible in all proportions with alcohol and ether, should preferably be used in combination with the latter as solvent, and will operate to dissolve the asphaltic deposits, while the alcohol or ether solvent will dissolve and act to remove the connate water.

Especially good results are obtained, by using the treating agents and compositions shown in Table I.

Table I

	Treating Agent	Percent	Solvent	Percent
1	Pyridine	100		0
2	Nitrogen bases (fraction boiling 160–230° C.)	40	Acetone	60
3	Nitrogen bases	50	Acetone Methyl propyl ketone.	30 20
4	do	50	Acetone tops	50

In general, water-soluble agents, such as pyridine, may be used in any concentration, preferably between 100–40% limits. Agents which are only partially water-soluble, such as quinoline or the commercial nitrogen bases, can be used preferably in 60–40% concentrations.

The treating agents listed above possess the following properties which are essential for the purposes of this invention:

(1) They quickly and completely dissolve the organic deposits plugging a formation. Pyridine, its derivatives, and nitrogen bases, in general, have a preferential solvent power for asphalt and are therefore especially effective against organic deposits of a gummy or asphaltic nature.

(2) They are capable of releasing the connate water held in the capillary spaces of the sand by lowering its surface tension and also the interfacial tension between the water and the oil. For example, the addition of 20% by volume of pyridine reduces the surface tension of water by 51%, and its interfacial tension with oil by 89%. These agents are further capable of dissolving or absorbing the released connate water, whereby the latter may subsequently be removed from the formation together with the treating agent.

(3) They have further a favorable effect on oil sand, and particularly on silicious sand, in that they do not increase its wetting properties for water. The connate water removed from said sand is not therefore immediately replaced by edgewater flowing through the formation, and the permeability of said sand to oil flow is increased.

These agents are therefore considerably more effective in treating formations whose permeability is decreased by the presence of connate waters and of asphaltic deposits than any of the agents hitherto used for this purpose.

Thus, solvents like carbon disulphide, carbon tetrachloride, benzol, gasoline, etc., besides having a somewhat smaller solvent power for the asphaltic deposits, are not substantially miscible with water at ordinary temperatures, and can therefore neither release, nor dissolve the connate water held between sand particles.

Solutions such as used in flooding processes, for example, aqueous sulfate or sulfonate solutions, which are capable of lowering the surface tension of water, but are poor solvents for asphaltic deposits, are relatively ineffective for the purposes of this invention. These solutions tend, moreover, to form emulsions whereby the permeability of the formation is sometimes decreased instead of being increased.

Table II shows the greater effectiveness of the present method as compared to methods hitherto used in treating formations plugged by asphaltic deposits and connate waters. The results shown in Table II were obtained by treating under identical conditions virgin cores obtained from suitable formations.

Table II

Core No.	Treating agent	Permeability before treatment (in millidarcys)	Permeability after treatment (in millidarcys)	Increase in permeability in percent
1	Carbon disulphide	3.05	4.8	57
	Pyridine	3.05	5.4	77
2	Carbon tetrachloride	1.96	2.47	26
	Methyl alcohol	1.96	3.10	58
	Pyridine	1.96	4.28	118
3	1% solution of alkyl sulfates (C_{10}–C_{12})	1.73	1.56	[1] −9.8
	Nitrogen bases (boiling range 150°-215° C.)	1.73	2.08	+20
	Pyridine	1.73	2.15	+24

[1] Decrease.

As has been stated above, the present method is especially useful in non-calcareous formations, where ordinary acid treatment cannot be applied with success. The present method can, however, be applied to any formations, including calcareous formations, and may, if desired, be preceded or followed by an acid treatment. In such cases, however, care should be taken to secure a complete removal from the ground of the treating agent used first, before applying the second treatment, since a reaction within the formation between, for example, hydrochloric acid and the nitrogen bases of the present reaction may cause a precipitation of undesirable salts and lead to a serious plugging of the formation.

I claim as my invention:

1. In the process of treating wells passing through formations obstructed by the presence therein of organic deposits and water, the steps of introducing into the well an acid free treating liquid comprising pyridine, forcing said liquid into the formation, allowing said liquid to dissolve said organic deposits and water, and withdrawing the treating liquid together with the dissolved matter from the well.

2. In the process of treating wells passing through formations obstructed by the presence therein of organic deposits and water, the steps of introducing into the well an acid-free treating liquid comprising a fraction of heterocyclic nitrogen base compounds obtained in cracking coal-tar and petroleum products, said fraction having a boiling range from 150 to 230° C., forcing said liquid into the formation, allowing said liquid to dissolve said organic deposits and said water, and withdrawing the treating liquid together with the dissolved matter from the well.

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