Development of boring solutions produced from using compositions of clay minerals and surface-active substances from raw fatty acids of cotton soap stock

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Abstract. The article studies the physical and chemical properties of water glycerin to obtain various types of surface-active substances for use as additives to boring solutions. The addition of technical glycerin to the composition of surface-active substances obtained from raw fatty acids of cotton soap stock at oil and fat enterprises contributes to a significant improvement in their surface-active properties. A water solution of glycerin to a certain extent increases the surface-active properties of the developed soap-like surface-active substances. The qualitative indicators of the composition of surfactants obtained with different ratios of a water solution of glycerol of liquid and ointment fractions of raw fatty acids of cotton soap stock were studied for their use in the process of drilling oil and gas wells. Analyzes of the developed compositions of were carried out in the preparation of drilling fluids from alkaline bentonite, alkaline earth bentonite and carbonate palygorskite, as well as double and triple compositions. A comparative analysis of the main indicators of drilling fluids, as well as surface-active substances synthesized from the greasy fraction of raw fatty acids of cotton soap stock, showed the greatest stability of boring solutions at high temperatures and salinity of formation waters.

1 Introduction

Effective drilling solutions must combine the multifunctionality of actions that follow from the structural and mechanical features of boreholes. In Uzbekistan, there are such hard-to-reach wells that require the use of special-purpose boring solutions. High temperature and salinity of formation waters in wells, as well as the presence of hard formation rocks complicate the drilling process, greatly increase the drilling time and are accompanied by emergencies [1-3]. Currently, in the chemical, oil-fat and other industries, a significant amount of glycerol of various compositions obtained by synthetic and natural methods is produced. Glycerin as a trihydric alcohol has certain specific properties that can change the surface-active and other physical and chemical properties of liquids with a certain chemical

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composition. For the production of distilled glycerin, raw glycerin or glycerin water must be used in accordance with the current regulatory documentation of enterprises [4].

At oil and fat enterprises, when producing raw fatty acids, water solutions of glycerin are formed - a valuable raw material for the production of various types of surface-active substances (SAS), plasticizers and other products, pharmaceutical, food, cosmetic and other industries.

In recent years, many SAS for boring solutions have been developed on the basis of waste from the secondary raw materials of the oil and fat industry, considering them cheap and accessible.

The low concentration of glycerin in the wash water does not allow its effective use in the above-mentioned areas of its application. The high cost of thermal and energy resources contributes to the disposal of such water into sewers or water sources. Despite such problems, we propose to concentrate the resulting aqueous solution of glycerol using a less energy- and heat-intensive method for obtaining this product.

2 Methods

As trial tests have shown, the addition of technical glycerin to the composition of SAS obtained from raw fatty acids of cotton soap stock (RFA CS) contributes to a significant improvement in their surface-active properties, which is explained by a decrease in viscosity and surface tension of the resulting products [5].

Table 1. Physical and chemical parameters of produced glycerol.

Name of indicator	**Norm for marks**			
	D-98	**PK-94**	**T-94**	**T-88**
Color number, mg J2/100 cm^3, no more	5	0	5	10
Relative density d at 20°C relative to water of the same temperature, not less than	1.2584	1.2481	1.2481	1.2322
Density ρ at 20°C, g/cm^3, not less than	1.255	1.244	1.244	-
Glycerol reaction, 0.1 mol/dm^3 of HCI or KOH solution, cm3, not more	1.5	1.5	1.5	1.5
Mass fraction of pure glycerin, %, not less than	98	94	94	88
Mass fraction of ash, %, no more	0.14	0.01	0.02	0.25
Saponification coefficient (esters), mg KOH per 1 g of glycerol, not more than	0.7	0.7	2.0	-
Chlorides	Presence	Absence	Presence	-
Sulfuric compounds (sulfates)	Presence	Absence	Presence	-
Carbohydrates	Absence			

The second table presents the main indicators of the composition of SAS obtained with different ratios of a water solution of glycerol and liquid and ointment fractions of RFA cholesterol.

Table 2. Qualitative indicators of the composition of SAS obtained with different ratios of a water solution of glycerol, liquid and ointment-like fractions of RFA CS.

The ratio of components in the composition of SAS RFA CS with a solution of glycerin %	Qualitative indicators of the compositions of SAS RFA CS			
	Viscosity at 20°C, %	pH 1% - water solution	Pour point, °C	Specific gravity, at 20°C, g/cm^3
SAS, produced from liquid fraction of RFA CS				
at 95:5	79.6	8.6	31.4	0.9839
at 90:10	76.4	9.0	30.2	0.9835
at 85:15	72.8	9.4	29.3	0.9830
at 80:20	69.3	9.7	28.3	0.9827
SAS, produced from ointment-like fractions of RFA CS				
at 95:5	96.6	9.2	40.7	0.9860
at 90:10	93.2	9.5	39.2	0.9857
at 85:15	89.8	9.7	38.3	0.9855
at 80:20	86.5	9.8	37.0	0.9852

The second table shows that with an increase in the amount (from 5 to 20%) of a liquid solution of glycerol in the composition of SAS, their viscosity for the liquid fraction decreases from 79.6 to 69.3%, and for the greasy fraction, from 96.6 to 86.5%. In this case, the pH of a 1% water solution increases for the liquid fraction from 8.6 to 9.7 con. units, and for ointment - from 9.2 to 9.8 con. units. Moreover, the pour point for surfactants obtained from the liquid and ointment fractions of RFA CS decreased from 31.4 to 28.3°C, and from 40.7 to 37.0°C, respectively, and the specific gravity at 20°C decreases from 0.9839 to 0.9827 g/cm^3 for the liquid fraction, and for the greasy fraction, this indicator decreases from 0.9860 to 0.9852 g/cm^3.

Discussing the obtained experimental results of analyzes of various synthesized surfactants based on RFA CS, attention should be paid to the following theoretical foundations and patterns, which make it possible to reveal the mechanisms of action of the constituent components of the products obtained.

In crude fatty acids containing more than 12 carbon atoms, the first layer is oriented perpendicular to the friction surface, and the subsequent ones are inclined, which ensures high strength of the lubricating layer with increasing load.

Moreover, crude fatty acids are not effectively combined with the liquid phase and, therefore, are practically not used individually in the preparation of clay drilling solutions. In this case, the delivery of fatty acid molecules to the metal surface is carried out mainly by convection, which does not ensure the proper uniformity of the lubricating layer.

Therefore, to increase the solubility of fatty acids in the composition of the lubricant additive, neutralizing agents are usually introduced, which are used as inorganic or organic bases.

In this case, salts that are well compatible with water are formed, the molecules of which, under the action of the concentration gradient arising due to adsorption, quickly diffuse to the friction surfaces.

It is known that salts of crude fatty acids, being anionic SAS, contribute to the intensive dispersion of the lubricant additive and its uniform distribution in the volume of the drilling fluid. Therefore, the effectiveness of the resulting lyophilic miscellar system depends both on the degree of neutralization of fatty acids and on the nature of the alkaline agent used [6].

Therefore, the most effective lubricating systems are mixtures of free and neutralized fatty acids. However, in such lubricant compositions, the degree of neutralization of fatty acids usually does not exceed 0.45%, which does not provide satisfactory compatibility of free acids with clay drilling fluids. Because of which they are unevenly distributed in the volume of the drilling fluid and form a fragmentary “pitting” lubricating layer on the metal surface, inefficient under conditions of tangential stresses arising from the movement of pipe strings in the well. In addition, such a rarefied lubricating layer does not sufficiently reduce the adhesive component of the friction force that opposes the translational movement of the column. An increase in the content of the neutralizing agent provides a significant quantitative neutralization of crude fatty acids, inevitably leads to a decrease in the percentage of fatty acids in the lubricant additive, thereby reducing its effectiveness. On the other hand, a decrease in the proportion of crude fatty acids leads to an overall decrease in lubricity, since the action of ready-made soaps is less effective than non-neutralized fatty acids, which form organo-metallic soaps directly in the friction zone [7].

As you can see, a vicious circle is obtained, which can only be broken by solving the problem of the cornerstone of fatty acid lubricant additives - ensuring the best dispersibility of crude fatty acids in the aqueous phase of the boring solution while maintaining a low degree of neutralization, not exceeding 0.3-0.45%.

Methods for improving dispersibility according to the nature of the interaction of the dispersant with fatty acids can be divided into two types: chemical and physico-chemical. Chemical methods, in particular, include the introduction of alkalis into the composition of the lubricant additive, which neutralizes fatty acids and leads to the appearance of soaps, the action of which was discussed in detail above.

The field of application of physicochemical methods, which are based on the use of SAS as dispersants, has been relatively poorly studied. Such SAS, according to the mechanism of dispersion of fatty acids, are divided into two groups [8]:

Micellar formers, which are non-ionic SAS (NSAS) with high values of hydrophilic-lipophilic balance (HLB) (HLB=15÷16);

Emulsifiers, which are non-ionic SAS (NSAS) with low HLB values (HLB=3÷8).

3 Results

The SAS compositions developed by us (CSAS-1, 2 and 3) to a certain extent approach the requirements of the above-described drilling fluid stabilizers. This is primarily due to the presence of a significant amount of pre-saponified soap, residues of crude fatty acids and alkalis, as well as presence of an aqueous solution of glycerol.

Table 3. The main indicators of boring solutions obtained using various local clays and their composition, as well as the composition of SAS-1.

№	**Boring solution composition**	**Component ratio %**	**Solution density (ρ), g/cm^3**	**Viscosity (T), s**	**Water yield (V), cm^3/30 min**	**pH**
1	AB NF: CSAS-1:NaOH:H_2O	10:2:0.2: remains	1.21	30	40	9.2
2	AEB NF: CSAS-1:NaOH:H_2O	10:2:0.2: remains	1.17	31	45	8.4
3	CP NF: CSAS-1:NaOH:H_2O	10:2:0.2: remains	1.25	33	34	7.6
4	AB NF: CP NF:	5:5:2:0.2: remains	1.22	31	38	8.7

	CSAS-1:NaOH:H_2O					
5	AEB NF: CP NF: CSAS-1:NaOH:H_2O	5:5:2:0.2: remains	1.22	32	36	8.6
6	AB NF: AEB NF: CP NF: CSAS-1:NaOH:H_2O	3.3:3.3:3.3:2: 0.2: remains	1.20	31	43	8.3

As noted earlier, a water solution of glycerol to a certain extent increases the surface-active properties of the developed soap-like surfactants by reducing their viscosity, tension surface, etc.

Undoubtedly, the developed SAS compositions should be studied when obtaining drilling fluids from various clay minerals, which also determine the environment and hydrophilic-lipophilic properties of the created clay compositions.

In our work, we mainly used three types of Navbakhor clays (Navai region): alkaline bentonite (AB), alkaline earth bentonite (AEB) and carbonate palygorskite (CP), as well as double and triple compositions [9].

The third table presents the results of analyzes of boring solutions obtained on the basis of the above-mentioned local clays and surfactant -1. 30 to 33 seconds, water loss (B) from 34 to 45 cm^3/30 min and pH from 7.6 to 9.2 con. units [10].

At the same time, with the transition from individual clay minerals to their two-component or three-component compositions, the ratios of clay minerals change, where, as a result, their total content in the resulting boring solutions is preserved.

The preparation of SAS compositions based on the liquid fraction of RFA CS made it possible to study it in the preparation of drilling fluids from various clay minerals and their composition.

The fourth table presents the results of analyses of the obtained boring solutions using SAS-2.

Table 4. Technological indicators of boring solutions obtained using various local clays and their composition, as well as the composition of SAS-2.

№	Drilling solution composition	Component ratio %	Solution density (ρ), g/cm^3	Viscosity (T), s	Water yield (V), cm^3/30 min	pH
1	AB NF: CSAS-2:NaOH:H_2O	10:2:0.2: remains	1.20	28	37	9.3
2	AEB NF: CSAS-2:NaOH:H_2O	10:2:0.2: remains	1.15	31	41	8.5
3	CP NF: CSAS-2:NaOH:H_2O	10:2:0.2: remains	1.25	32	29	7.7
4	AB NF: CP NF: CSAS-2:NaOH:H_2O	5:5:2:0.2: remains	1.18	29	34	8.6
5	AEB NF: CP NF: CSAS-2:NaOH:H_2O	5:5:2:0.2: remains	1.23	31	30	8.8
6	AB NF : AEB NF: CP NF: CSAS-2:NaOH:H_2O	3.3:3.3:3.3:2: 0.2: remains	1.20	32	38	8.4

From the fourth table it can be seen that when switching from CSAS-1 to CSAS-2, the density of boring solutions decreases from 1.25 to 1.15 g/cm^3, viscosity (T) from 32 to 28 seconds, fluid loss (B) from 41 to 29 cm^3/30 min and pH from 9.3 to 7.7 con. nits.

Table 5. Technological indicators of boring solutions obtained using various local clays and their compositions, as well as the composition of SAS-3.

№	Drilling solution composition	Component ratio %	Solution density (ρ), g/cm^3	Viscosity (T), s	Water yield (V), cm^3/30 min	pH
1	AB NF: CSAS-3:NaOH:H_2O	10:2:0,2: remains	1.23	34	43	9.1
2	AEB NF: CSAS-3:NaOH:H_2O	10:2:0,2: remains	1.21	37	47	8.3
3	CP NF: CSAS-3:NaOH:H_2O	10:2:0,2: remains	1.29	38	38	7.5
4	AB NF: CP NF: CSAS-3:NaOH:H_2O	5:5:2:0,2: remains	1.22	36	42	8.6
5	AEB NF: CP NF: CSAS-3:NaOH:H_2O	5:5:2:0,2: remains	1.27	35	39	8.5
6	AB NF: AEB NF: CP NF: CSAS-3:NaOH:H_2O	3.3:3.3:3.3:2:0.2: remains	1.24	36	46	8.2

4 Discussions

As can be seen, the replacement of CSAS-1 with CSAS-2 leads to a partial decrease in the main indicators of drilling solutions. The ointment-like fraction of RFA CS compared to other fractions has a thicker mass and viscosity, which certainly affects the main indicators obtained by boring solutions from local clay minerals.

The fifth table presents the main indicators of boring solutions obtained from local clay minerals and their composition, as well as CSAS-3 synthesized from the ointment fraction of RFA CS.

From the fifth table it can be seen that when using CSAS-3, the performance of boring solutions is improved, where the mud density increases from 1.21 to 1.29 g/cm^3, viscosity (T) from 34 to 38 seconds, fluid loss (B) from 38 to 47 cm^3/30 min and pH from 7.5 to 9.1 con. units. Comparative studies carried out on three types of SAS compositions have shown that CSAS-3 is more effective than surfactant-1 and 2. This is due to a number of factors that determine the surface tension in boring solutions with various types of local clays and their composition.

5 Conclusions

Thus, it can be concluded that boring solutions obtained using SAS compositions from RFA CS have a satisfactory stability at high temperatures and salinity of formation waters, which is confirmed by the main indicators presented in the Tables 3, 4 and 5.

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