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NEW DIRECTIONS FOR USING LIQUID SECONDARY HEXANES

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Abstract: The composition of asphalt-tar-paraffin sediments in local oil fields and their solubility in hexane-based composite solvents that preserve compounds consisting of concentrates of nonionic surfactants and aromatic hydrocarbons have been studied. According to the research results, it has been determined that neonol AF-9-10 and liquid pyrolysis products have high efficiency. The use of such additives makes it possible to increase the efficiency of decomposition and dissolution of asphalt-tar-paraffin sediments by 1.3-1.6 times compared to the main solvent. It was found that the effectiveness of detergent compositions decreases when the concentration of individual additives increases from 0.5 to 3%.

Keywords: hexane solution, solvents, asphalt-resin-paraffin deposits, asphaltenes, butylbenzene.

The oil and gas industry covers all oil and gas operations, from oil and gas exploration, drilling, extraction, hydrocarbon processing, production of petroleum products, production of petrochemical and chemical equipment to the provision of petroleum products to consumers. The investment policy of the oil and gas industry is urgent, first of all, diversification of the sector, identification of new oil fields and their operation, introduction of high technologies to ensure deep processing of oil and gas resources, and drilling out product from old oil wells, where oil production is a problem.

There are huge reserves of natural gas, gas condensate, oil, coal and mineral raw materials in the the Republic of Uzbekistan. Every year about 60 billion cubic meters of gas, 8 million tons of oil and gas condensate are extracted and refined. At the same time, in recent years, a number of difficulties have arisen, including in oil extraction, and these problems are related to long-term exploitation of oil wells and oil extraction mainly from old wells. The formation of organic and inorganic layers during oil production leads to the formation of asphalt paraffin resins (ARP) of different composition in downhole and surface devices, which in turn leads to a decrease in the technological performance of the devices and their premature failure. The formation of ARP is mainly related to the generation of organic crystal layers on the metal surface of the structural device.

The purpose of the work is to evaluate the effectiveness of hexane-based hydrocarbon solvents for breaking down asphalt-tar-paraffin deposits in local oil fields and to develop a solvent production technology.

The formation of ARP in oil wells is mainly related to sudden changes in temperature and pressure (the temperature in the well is lower than the saturation temperature of crude oil with paraffins due to the effect of cold water transferred to the plastic layer to increase the activity of oil transfer and the pressure in the well decreases). Due to this condition, paraffin crystals generate and accumulate in oil production facilities. In addition to paraffins, heavy hydrocarbons stored in oil, including asphaltenes, resins, inorganic and mechanical compounds, stick to the walls of the devices, give strength and stability to the sludges, and this, in turn, causes a number of difficulties in their elimination.

There are many ways to eliminate ARP in oil wells, such as stabilizing the temperature of wells using water as a heat carrier, transferring water vapor, washing the well with heated oil and oil products, using various types of heating devices, carrying out chemical reactions with heat release at the bottom of the well, surfactant loading, washing using organic and inorganic solvents, etc.

The composition and stability of ARP depends on the composition and nature of oil, the location and conditions of oil wells. Usually, in oil wells, 50-70% high paraffins, 10-15% crystalline paraffins, 10-40% tar and asphaltenes, water, sand and mineral salts are stored in the tar of ARP. For liquefaction of ARP with such a composition, the composition of solvents is selected only empirically, due to the fact that there are no clear indicators about the composition of oil lumps and the mechanism of the effect of solvents on the solids has not been fully studied [1].

Technical and economic indicators have been calculated, and guidelines for solving the problem have been developed studying the negative effects of asphalt-resin-paraffin formation in the oil production, transportation and processing industry. The main influence on the transition of ARP from the solvent to the liquid phase has been shown by the concentration of lower alkanes (mainly methane) in the oil and the cryoconstant for methane has been calculated. Equilibrium temperatures of the transition phase for various gases in oil have been proposed [2].

A new solvent TPMDS composition to dissolve ARP under static and dynamic conditions have been proposed by researchers in the field [3,4]. TPMDS solvent consists of toluene, pyridine, methanol, surfactant dodecylbenzenesulfonyl acid and sodium hydroxide. The optimal concentration of TPMDS components is determined, and the highest efficiency of ARP dissolution (98 %) is achieved when kept in the solvent for 6 hours. Four different oil samples have been studied in the presence of TPMDS solvent, and the asphaltene dissolution efficiency is greater than 97.5%. The permeability due to asphaltene precipitation is 51% of the original core sample permeability before any solvent injection. The permeability after injection of toluene and TPMDS solvent reached about 94 and 71 %, respectively. The reduction of oil viscosity with the use of TPMDS solvent is more effective than with the use of toluene. TPMDS solvent oil extraction rate can be increased 3.3 times. Authors of the literature [5,6] also recommended modern methods of preventing and eliminating the formation of ARP clots, along with studying the processes of oil extraction, transportation and processing. In particular, the mechanism of formation, composition and effect on the properties of ARPD were shown, and chemical methods related to the use of various additives, reagents and cleaning agents were recommended. In this source, it is stated that according to the characteristics of ARPD, it is a complex mixture of soluble and insoluble organic compounds interacting with inorganic substances of various types and amounts, and it is divided into three main groups depending on the relative proportions of the components: organic, inorganic and their mixture.

Thanks to the study of the reasons for the stability of ARPD, there have been concluded that the stable oil consists of neutral aromatic compounds, lower aromatic asphaltenes are also preserved, and unstable oils are rich in paraffin and contain high aromatic and condensed asphaltenes, the insolubility of organic materials. It depends on hydrogen content in them, in particular, low hydrogen/carbon (H/C) ratio due to the absence of the aliphatic [7].

In order to evaluate the efficiency of the effect of solvents, the experiments have been conducted in static conditions according to the methodology of “Neftkhimprom” IIB. The ARPD sample is heated until soft, mixed thoroughly and shaped into a 12×20 mm cylinder. It is then cooled and placed in a pre-weighed basket made of brass (steel) mesh with a cell size of 1.5×1.5 mm (basket size 70×15×15 mm). A basket with a sample of ARPD is weighed and placed in a hermetic glass cell, over which 100 ml of the tested solvent is poured. The temperature of the experiment is 10ºC. After four hours, the basket containing the non-degraded ARPD is removed and dried to a constant mass. The broken down but undissolved part of ARPD that fell from the basket into the cell is filtered, dried to a constant mass and weighed.

In accordance with the above methodology, the efficiency of the solvent has been evaluated according to the following main indicator:

1. The ability of the solvent to break down ARPD into smaller parts. This is the dispersing ability of the solvent. It is estimated by the amount of ARPD remaining in the filter (expressed as a percentage). This indicator should be optimal, because at a very high dispersing ability of the solvent, the probability of the formation of ARPD particles, which will get stuck in the collectors of the extraction zone, increases.

2. The ability of the solvent to form true solutions with ARPD components. This is the solubility of the solvent. It is estimated by the amount of ARPD dissolved (expressed as a percentage). The value of this indicator should be as high as possible.

3. The ability of the solvent to simultaneously dissolve and decompose ARPD components. This is the solvent's ability to wash. It is estimated by the difference between the mass of ARPD obtained for analysis and the ARPD residues in the basket (expressed in % mass.). This indicator can be considered universal. The larger this value, the higher the efficiency of the solvent.

The results of the last analysis show that the oil content is low-sulfur 0.44%, and the density at 20°C is mainly high-butane - 932 kg/m^3. The oil is distinguished by its very high viscosity 30 mPA < 35 mPa•s (Tables 1 and 2):

Table 1

Water %	Sulfur %	Asphaltenes %	Excise resin %	Coke according to Conradson %	Paraffin %	Selicogel resin %	Chlorides g/l	Ashes %
75,0	0,23	3,269	58,0	8,8	6,6	15,3968	110,0	0,61

On November 18-23, 2021, a complete analysis of formation oil was conducted in well Number 148 in the Western Palvantash field. Sampling was held on November 09, 2021. The result of the formation oil analysis is presented in Table 2.

Table 2

The results of the analysis of the formation oil sample of well Number. 148 in the Western Palvontash field

Location	№ well	Density 20°C g/sm^3	Mass fraction of water %	Mass fraction of the mech. impurities %	Total mass content of sulfur %	Kinematic viscosity 50°C, sSt	Dynamic viscosity 50 °C, cP mPa·s	Composition of chloride salts mg/l	Excise resin %
Western Palvontash field	148	0,8744	76,0	0,72	0,3	11,0	9,62	4193,0	42,0

The well Number 148 in the West Palvantash field has the following indicators:
The density of oil at -20°C is 0.8744 g/cm^3, heavy type-3 (standard 0.8701 – 0.8950 g/cm^3);
- the mass percentage of bound water is 76.0% (norm 2-3 groups is not more than 1%);
- the amount of mechanical impurities is 0.72% (the norm is not more than 0.05%);
- sulfur content 0.3%, 1st class with low sulfur, (the norm is not more than 0.60%);
- oil viscosity 9.62 mPa•s, with low viscosity, 2nd class (norm 5.1 - 10.0 mPa•s);
- the content of chlorine salts is 4193.0 mg/l, group 3 (the norm is not more than 900 mg/l);
-excise resin content 42.0%, high resin, -1 type (more than 15.0% norm).

Analysis of oil from Well 148 of the Western Palvantash field shows that the oil is heavy, low-sulfur, with high-resin, low-viscosity.

From Table 1 and the data presented, it can be seen that ARPD has a high content of paraffinic HC. The paraffin composition of the sediments and their low polarity indicate that the basis of the composition used to break down the ARPD structure should be aliphatic HC boiling at a low temperature, therefore, the secondary product of the Ustyurt gas chemical complex has been chosen as such a solvent.

In Ustyurt (the Republic of Karakalpakstan) gas-chemical complex, polyethylene and polypropylene are obtained by polymerization reaction in hexane solution with the presence of Zigler-Natta catalyst. In this process, in addition to the main polymer product, a liquid secondary raw material is formed. The residual product is an oligomer of used monomers, the main part of which is paraffins from C_6 to C_{20}, whose qualitative and quantitative composition has been determined by the chromatographic method (Fig. 2). Chromatographic analysis shows that the composition of spent hexane mainly consists of saturated hydrocarbons of fraction C_{14} - C_{18} of normal structure.

Separation of the mixture of liquid secondary raw materials has been carried out in a laboratory vacuum driving apparatus equipped with a cube, a reflux condenser thermometer, a Libix cooler connected to a vacuum pump: the distillation has been carried out under vacuum up to a thermometer reading of 135°C and a mercury column of 650 mm.

0.450 liters ofC_{12} - C_{20} fraction of saturated normal hydrocarbons have been obtained from one liter of spent hexane sample.

The density of the obtained liquid paraffin sample is at 20°C is 745 kg/m^3.

Solvents effectiveness has been evaluated by a number of indicators: the dispersing, dissolving and washing capabilities of the base solvent (hexane) and hydrocarbon solvents consisting of hexane and additives (a mixture of additives with different functional functions). In order to obtain additives that increase the dissolving and solvating ability of the main solvent, the secondary product called aromatic HC - TAR product is dissolved in hexane and separated by the distillation at atmospheric pressure; condensed hydrocarbon fraction CHF and gasified hydrocarbon fraction GHF (products of Fergana oil refinery) concentrates have been studied. Nonogenic surfactant (NSF) known as oxyethylated alkylphenol - Neonol AF-9-10 has been studied as additives with detergent-dispersing properties. Acid amides synthesized on the basis of cottonseed oil and diethanolamine - a nonogenic surface-active substance known as CODEA – has been studied as additives with detergent-dispersing properties. First of all, the effectiveness of the use of individual particles with a mass content of 1.0 to 3% in the main solvent has been checked (Table 2).

Table 2

Data obtained on the solubility of ARPD in the Western Palvantash field

Admixture		Dispersing ability, mass %.	ARPD residue, % масс.	Solubility, mass %.	Washing ability, mass %.
Components	Concentration in the solvent, mass %.				
Primary solvent: secondary hexane					
Hexane		13,65	3,17	76,18	89,80
Ar-TAR	1,0	14,58	3,73	74,69	89,27
	2,0	16,04	5,18	71,78	87,82
	2,5	17,50	6,63	68,87	86,37
	3,0	11,99	20,03	60,98	72,97
CHF	1,0	12,95	4,85	81,23	95,15
	2,0	11,76	5,16	76,09	87,84
	2,5	11,35	6,25	82,40	93,75
	3,0	10,56	10,41	71,78	75,66
GHF	1,0	12,22	1,75	78,99	91,21
	2,0	11,64	4,62	76,74	88,38
	2,5	11,06	7,44	74,50	83,56
	3,0	6,70	15,95	70,36	77,05

CODEA	1,0	18,23	2,41	71,96	90,59
	2,0	23,65	5,52	63,83	87,48
	2,5	28,67	8,64	55,69	84,36
	3,0	51,50	13,83	27,67	79,17

According to the research results, Ar-TAR and CODEA showed the highest efficiency. When these additives are used, the efficiency of ARPD decomposition and dissolution increases by 1.3-1.6 times compared to the main solvent. Compared to Ar-TAR, GHF and CHF, CODEA has a greater dispersing effect. When the concentration of individual additives was increased from 0.5 to 3%, the washing activity of all reagents was found to decrease. Apparently, at a concentration of more than 1.0% by mass, the particles are adsorbed on the ARPD surface, and the polymolecular layer formed in the static mode prevents the absorption of solvent molecules into the ARPD, as a result, regardless of the properties of the used particles, the washing ability of solvents deteriorates.

At the same time, studies have been conducted to determine the effectiveness of the composition of the particles, according to which CODEA + Ar-TAR, CODEA + GHF, CODEA + CHF and CODEA + Ar-TAR + GHF composite particles have been prepared, their total concentration in the main solvent is 1.0% did (Table 3).

Table 3

Data obtained on the solubility of ARPD in the Western Palvantash deposit
(the concentration of the precipitate in the main solvent is 0.5% by mass.)

Admixture		Dispersing ability, mass %.	ARPD residue, % масс.	Solubility, mass %.	Washing ability, mass %.
Components	The ratio of components				
Primary solvent: secondary hexane					
Hexane		13,65	3,17	76.18	89.80
CODEA		18,23	2,41	71,96	90,59
CODEA + Ar-TAR	0,9 : 0,1	13,28	13,31	66,41	79,69
	0,8 : 0,2	18,65	16,32	58,03	76,68
	0,7 : 0,3	13,12	14,61	65,27	78,39
	0,6 : 0,4	16,06	13,48	63,46	79,52
	0,5 : 0,5	19,60	12,75	60,65	80,25
	0,4 : 0,6	9,59	11,44	73,82	83,41
	0,3 : 0,7	6,03	17,04	69,94	75,96
	0,2 : 0,8	9,13	20,73	63,14	72,27
	0,1 : 0,9	9,74	10,56	72,71	82,44
	0,0 : 1,0	14,58	3,73	74,69	89,27
CODEA + CHF	0,9 : 0,1	37,83	10,22	45,00	82,78
	0,8 : 0,2	27,31	17,34	48,35	75,66
	0,7 : 0,3	27,52	13,20	52,28	79,80
	0,6 : 0,4	19,45	19,18	54,38	73,82
	0,5 : 0,5	22,98	13,02	57,00	79,98
	0,4 : 0,6	13,92	8,73	70,35	84,27
	0,3 : 0,7	13,36	14,92	64,72	78,08
	0,2 : 0,8	8,08	16,25	68,67	76,75
	0,1 : 0,9	13,09	12,16	67,75	80,83
	0,0 : 1,0	12,95	4,85	81,23	95,15
CODEA + GHF	0,9 : 0,1	12,04	6,69	74,27	86,31
	0,8 : 0,2	12,44	10,93	69,63	82,07
	0,7 : 0,3	11,11	13,65	68,23	79,35
	0,6 : 0,4	10,01	14,06	68,93	78,94
	0,5 : 0,5	10,92	19,33	62,76	73,67

	0,4 : 0,6	8,75	12,76	71,49	80,24
	0,3 : 0,7	8,51	12,53	71,96	80,47
	0,2 : 0,8	9,04	14,22	69,74	78,78
	0,1 : 0,9	6,79	15,68	70,53	77,32
	0,0 : 1,0	12,22	1,75	78,99	91,21
CODEA + Ar-TAR + GHF	0,8 : 0,1: 0,1	19,04	13,94	60,02	79,06
	0,7 : 0,2: 0,1	16,55	10,95	65,50	82,05
	0,6 : 0,3: 0,1	12,69	14,68	65,62	78,27
	0,5 : 0,4: 0,1	15,61	11,94	65,45	81,06
	0,7 : 0,1: 0,2	15,51	20,02	57,46	72,98
	0,6 : 0,1: 0,3	14,95	22,90	55,16	70,11
	0,5 : 0,1: 0,4	11,47	16,74	65,53	76,26
	0,1 : 0,8: 0,1	16,64	19,83	56,53	73,17
	0,1 : 0,7: 0,2	9,37	11,26	72,37	81,74
	0,1 : 0,6: 0,3	14,58	3,73	74,69	95,03

According to the experimental data, a positive synergistic effect is not observed for the studied compositions. Compared to individually applied admixtures and pure solvent, the detergency of composite admixtures is reduced.

Thus, the hydrocarbon solvent containing CODEA + Ar-TAR can be shown as the most effective solvent for the removal of ARPD in the West Palvantash mine (total concentration in the main solvent is 1% by mass). Compared to pure hexane, this solvent exhibits higher washing and dissolving abilities. Apparently, the solubility of certain crystals of paraffins, particles of asphaltenes and mechanical additives increases due to the increase in the solubility of the resins, which are mutually compacted by the addition of CODEA + Ar-TAR.

In conclusion, it has been determined that ARPD of the Western Palvantash field contains high amounts of paraffinic HC. T The admixture based on liquid pyrolysis product, which its total concentration in the main solvent is equal to mass 0.5 %, will have the best efficiency in the breaking down and dissolving paraffin-based ARPD. As the total concentration of individual admixtures in the main solvent increases from 1 to 3% by mass., the decrease in the efficiency of detergent compositions is observed.

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