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DEVELOPMENT OF NEW COMPOUNDS WITH ASPHALTENE DEPOSITION DEPRESSANT PROPERTIES

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Abstract

By transporting oil under conditions of minimal thermal gradient in the pipeline, it is possible to reduce the activity of paraffin formation. A promising method of preventing paraffin formation is to cool the oil to a temperature slightly lower than it would have been during its journey through the pipeline. Increasing the thermal treatment temperature has a positive effect on reducing temperature characteristics. Reducing the cooling rate allows the onset of crystallisation and freezing temperatures to be lowered. Reducing the crystallization onset and freezing temperatures reduces the temperature of the waxing process in the transport pipes and production plant communications.

Keywords: paraffin deposit, depressant, aromatic solvent, alcohol

I.Introduction

The negative consequences of the formation of asphaltene deposits, as well as the difficulties associated with their prevention and removal, are related to the specific rheological, structural-mechanical, chemical, and colloid-chemical properties of the deposits. These difficulties are exacerbated by the very wide diversity of sediment composition and properties. They contain mainly organic materials that are practically insoluble and do not disperse in crude oil under extraction and transportation conditions. A characteristic feature of the movement of highly viscous oils in pipelines and also during their preparation for transportation is that as a result of their significantly high viscosity, mechanical energy dissipation occurs in the friction of the liquid layers. In pipelines and also in the process of preparing highly viscous oils for transportation, the non-isothermal movement of the additional temperature released from the dissipation of mechanical energy along the length of the pipe is studied. The dissipation of mechanical energy during the movement of viscous oils in pipes is studied, and then the results obtained are solved for fluids that obey the superordinate law between the friction stress and the velocity gradient, in the special case of highly viscous oils. The study of the effect of the heat generated by the friction of the fluid layers during the movement of liquids heated to a certain temperature in the initial area of cylindrical pipelines, which are not subject to Newton's law, on the flow parameters is important from the point of view of saving energy consumption in heat exchange issues [1].

In the oil industry, a depressant additive is used to reduce the freezing point and dynamic viscosity of oils during transportation and storage, as a depressant additive made of a copolymer of ethylene with vinyl acetate modified with diphenylamine. When the depressant is added to oil and fuel oil with freezing points of +10^{0}C and +18^{0}C, respectively, their depression reaches 32 and 34^{0}C.

A mixture of aromatic hydrocarbons with diesel fuel is used as the solvent for the additive. Its disadvantage is the limited application of the depressant additive. Thus, for each oil product, a co-polymer with a qualitatively different composition or the same composition, but with different monomer chains, should be used.

Depressant additives of various compositions are known for paraffinic, asphaltene and tarry oil products. Known polymer additives include ethylene-acrylonitrile copolymers and terpolymers of ethylene with acrylonitrile, from the monomer group vinyl acetate, acrylic acrylates, alkyl vinyl ethers, vinyl chloride, acrylic acid. The maximum depression is 20^{0}C at a concentration of 0.15% of the EAN 18 depressant, and 23.5^{0}C at a concentration of 0.025%.

An EAN 18 depressant is an ethylene-acrylonitrile copolymer containing 17% acrylonitrile by mass. In order for the depressant additive to dissolve, the oil product is heated to 60^{0}C. The limited range of applications of the depressant additive is its disadvantage. In addition, heating a large amount of fuel for the introduction of the depressant is not considered economically feasible.

The DT-1 additive, which is a copolymer of methacrylic acid and vinyl acetate esters, is known for diesel fuel. More often, additives based on a copolymer of ethylene with vinyl acetate are used. When such an additive is introduced into oil and oil products in small quantities (up to approximately 0.2%), their freezing point decreases by 25-35^{0}C. The disadvantages of the mentioned additives are their insufficient solubility in oil and oil products, limited spectrum of action, high cost, as well as high requirements for storage and operation.

The known depressant additive contains (0.2-1.5% by mass) and naphtha tar (the rest). Its main disadvantage is the complex catalytic synthesis of polyhexene included in the composition. In addition, the composition was tested as a depressant in oils containing 2.5-4.8% paraffin. The composition was not tested as a depressant additive in oils containing a higher amount of paraffin.

The closest to the composition, both in terms of technical nature and the effect achieved, can be written as follows as a depressor additive by mass, %

light phlegm of catalytic cracking 15-20
Flexsoil CW 288 15-25
remaining part of stable gas condensate

The amount of the known additive in oil and oil products is 0.03-0.05% (by mass, %). One of the shortcomings of the additive, which was accepted as the closest analogue, is its high freezing point, low effect on highly paraffinic oils. The use of a new effective depressor additive to lower the freezing point and viscosity properties of highly paraffinic oils during oil production, transportation and storage, as well as the expansion of the raw material base and assortment of depressants based on by-products of various hydrocarbon raw materials.

During the processing of pipelines and high-viscosity oils, we determine the average value of the mechanical energy in the thermal initial area of the pipeline and, taking into account the law of heat balance, find the temperature change along the length of the pipe. By comparing the sum of the heat released from the constant temperature of the pipe diameter and the mechanical dissipation with the initial temperature of the liquid, a temperature change graph is constructed and the effect of mechanical dissipation can be determined.

II. Methods

Asphaltene deposits (AD) are a dark brown or black, thick, jelly-like masses with high viscosity. Viscosity decreases as temperature increases. Natural polar surfactants and oil emulsions are concentrated in asphaltene deposits, which increases their strong adhesion to metal surfaces and facilitates their penetration into gaps, cracks, holes, corrosion and wear products of parts, small particles of rocks, and water on the surface of parts. Thus, substances that are poorly soluble in oil (in conditions of sediment formation) and have a high density compared to oil pass into the AD. Thus, substances that are poorly soluble in oil (in conditions of sediment formation) and have a high density compared to oil pass into the AD. Therefore, they collapse under the influence of gravitational or centrifugal forces, as well as surfactants between oil-rock, oil-metal, and oil-water boundaries.

The wide variety of AD composition makes them difficult to study and describe. Like oils, they can be characterized by the density of their structural groups. The basis of such classification is their reaction to various solvents, as well as (additionally) the amount of water and contaminations (mineral substances).

AD is a heavy component of oil that settles on the internal surface of oilfield equipment and complicates the processes of oil preparation, transportation, and storage.

As it is known, paraffinic oils in a number of large oil fields around the world are not entirely composed of paraffin hydrocarbons. Thus, the composition of the produced oil is 20-60% paraffin hydrocarbons, 20-30% asphaltenes, 5-10% tar, and the rest is light hydrocarbons. It should be noted that such deposits are often encountered in oil and gas fields in Russia and other countries.

The paper discusses the preparation of new paraffin precipitation inhibitors and their depressant effects on paraffin oils in lab conditions to prevent technological complications arising in the extraction and transportation of paraffin oils.

Depressor additive is known in the literature, the composition of which is [2] a polyethylene-co-vinil acetate modified with diphenylamine. When depressor additive is introduced into oil and fuel oil, whose freezing point is +8 ^{o}C and +15 ^{o}C, respectively, their depression reaches 37 and 35 ^{o}C.

A mixture of aromatic hydrocarbons and diesel fuel is used as the solvent for the additive. The limited application of the depressor additive is its disadvantage. Thus, for each petroleum product, a co-polymer is used that has a qualitatively different composition or the same composition but different monomer chains.

The EAN brand depressor additive for paraffinic petroleum products is also known [3]. Known polymer additives include ethylene-acrylonitrile copolymers and terpolymers of ethylene with acrylonitrile, while the monomer group includes vinyl acetate, acrylic acrylates, alkyl vinyl ethers, vinyl chloride, and propenoic acid. When the concentration of EAN 18 depressant is 0.1%, the maximum depression is 18 ^{o}C, and when density is 0.025%, it is 23.8 ^{o}C.

An ethylene-acrylonitrile copolymer containing 18% acrylonitrile by mass is used as the EAN 18 depressant. The petroleum product is heated to 50 ^{o}C to dissolve the depressor additive. The disadvantage of the depressor additive is its limited application range. In addition, it is not economically feasible to heat a large amount of fuel to add a depressant.

The additive DT-1 is known, which is a copolymer of methacrylic acid and vinyl acetate esters, and is used in diesel fuel [3]. Mainly are used additives based on a copolymer of ethylene with vinyl acetate. When such an additive is added to oil and oil products in small amounts (up to approximately 0.1%), their freezing point decreases by 20-30 °C. The disadvantages of listed additives are that they are not sufficiently soluble in oil and oil products, have a limited spectrum of action, are expensive, and require high storage and operation requirements.

Another known [4] depressant additive contains pyrolysis resin (0.1-1.0% in mass). The main drawback is the complicated catalytic synthesis of the polyhexene included in the composition. Furthermore, although the composition was tested as a depressant in oils containing 4.1-6.2% paraffin, it was not tested as a depressant additive in oils containing higher amounts of paraffin.

III. Research and analysis of results

The main issue discussed in the paper is the development of a new effective depressor additive that is superior to known depressants in order to lower the freezing point and viscosity properties of highly paraffinic oils during oil production, transportation and storage, as well as the expansion of the raw material base and assortment of depressants based on co-products of various hydrocarbon raw materials. For this purpose, a new depressor additive consisting of a solvent with aromatic hydrocarbon added has been developed and prepared. At this time, light pyrolysis resin (LPR), alcohol, and aromatic hydrocarbon reagents are added as organic solvents. The composition retains a light pyrolysis resin as a solvent with aromatic content (AZS 340-2009).

The depressor additive consists of a solvent with the addition of aromatic hydrocarbons, light pyrolysis resin as an organic solvent, alcohol and naphthalene reagent, the components are kept in the following ratio, % by mass:

- Light pyrolysis resin (LPR) - 75-85
- Naphthalene 1-3
- Alcohol balance

The composition contains light pyrolysis resin as an aromatic solvent. The parameters of LPR are given in Table 1. Information on the parameters of the naphthalene reagent is given below.

Naphthalene is an organic substance, the chemical formula is C10H8. It has a characteristic odor. It does not dissolve in water. It is well soluble in benzene, alcohol, ether and chloroform. Naphthalene is produced on the basis of coke according to technical conditions in accordance with GOST 16106-82.

Methanol or isopropyl alcohol is used as an alcohol. Alcohols must comply with GOST 2222-95 and GOST 9805-84, respectively.

Table 1: *Composition grades of E-type petroleum tars*

Brand of tar	Main properties
E-9	Products containing not less than 55% by mass of aromatic hydrocarbons (C6 – C8) and not less than 40% by mass of benzene

Table 2: *Requirements for quality indicators of E-type petroleum tars*

Name of indicators	Norm for brand	Testing methods
Appearance	Light yellow to brown (greens allowed), liquid without mechanical impurities	According to clause 7.3
Density at 20 ^{0}C, kg/m^3, not less	800	According to GOST 3900 and clause 7.4
Initial boiling point, ^{0}C, should not be lower	35	According to GOST 2177 and clause 7.5
Volume fraction of the fraction distilled up to 185 ^{0}C, %, should not be less than	85	
Final boiling temperature, ^{0}C, should not be higher	220	
Mass fraction of aromatic hydrocarbons (C6 – C8), %, should not be less than	55	According to clause 7.6
Mass fraction of benzene, %, should not be less than	40	According to clause 7.6
Copper plate test	To be continued	According to GOST6321
Mass fraction of chlorine, %, should not exceed	0,002	According to clause 7.7
Actual resin mass density, mg/100sm^3, should not exceed	200	According to clause 7.8 of GOST 8489 or GOST 1567

Mass fraction of water, %, should not exceed	0,1	According to GOST 2477 or GOST 14870, section 4 and clause 7.8
Mass fraction of total sulfur, %, should not exceed	0,5	According to GOST 19121 and clause 7.10

To prepare the depressor additive, LPR and alcohols containing methyl groups are mixed. The aromatic hydrocarbon is added to the solvent mixture and mixed at room temperature with a mechanical mixer. Mixing is continued until a homogeneous solution is formed. The results of the preparation of the compositions with the noted properties are given in Table 3.

Table 3: *Percentage of YPQ and solvent for the preparation of the additive.*

Sample serial number	Components, %		
	Solvent		Aromatic hydrocarbon
1	88	10	2
2	85	13	2
3	80	17	3
4	70	27	3
5	75	24	1
6	82	15	3
7	75	22	3
8	75	24	1
9	80	19	1
10	85	12	3

The depressant properties of the additives were determined by determining the effective viscosity (on a "Reotest-2" rotational viscometer) and freezing point. (GOST 20287-74). The depressor effect is calculated by the formula

$$\Delta T = T_{f.in} - T_{f.ad}$$

here, $T_{f.in}$-freezing temperature of the original oil, ^{0}C, $T_{f.ad.}$ –freezing temperature of the oil with the additive, ^{0}C. The additive content is 0.01-0.02% of the oil mass. The depressant properties of the prepared additives were investigated in oil samples taken from production well No. 690 of NGPD named after N. Narimanov (Azneft PU). [5,6,7,8]. First, the oil sample was heated to 60 °C and a mixture of paraffinic hydrocarbons extracted from wells that settled in the pump compressor pipes was added to it. Oil prepared in this way contains approximately 22% paraffin hydrocarbons and has a freezing point of +31°C. The results of research studies conducted to determine the depressant effect of additives are given in Table 4.

Table 4: *The concentration of the depressant effect of additives by mass percentage in oil.*

Serial number of component	Additive density in oil, % by mass fraction	$T_{f.ad.}$, ^{o}C	ΔT, ^{o}C
1	0,01	1	28
	0,02	-2	33
2	0,01	0	31
	0.02	-5	35
3	0,01	-1	32
	0.02	-7	38
4	0,01	-2	33
	0,02	-4	34
5	0,01	-3	35
	0,02	-9	41
6	0,01	-7	39
	0,02	-10	41
7	0,01	-5	35

	0,02	-13	45
8	0,01	-3	35
	0,02	-7	39
9	0,01	-2	33
	0,02	-5	35
10	0,01	-4	34
	0,02	-6	36

The effective viscosity of the original oil was set close to the freezing point (+35 ^oC and +40 ^oC). It was determined that the viscosity of oil at +35 ^oC is 18.5 mPa·s, and at +40 ^oC the viscosity of oil is 13.3 mPa·s (0.02% by mass). The results of research conducted to determine the effective viscosity of oils with depressant additives at temperatures close to the freezing point are given in Table 5.

Table 5: *Freezing point and effective viscosity of oils with depressant additives.*

Serial number of component	Temperature, 5 ^oC	Effective viscosity (η), mPa·s	$\Delta\eta$, %
1	35	10,5	43,4
	40	6,7	52,6
2	35	11,2	48,3
	40	7,3	54,2
3	35	10,3	51.4
	40	5,3	63.1
4	35	9,8	56,4
	40	7,3	60,7
5	35	9,1	56,5
	40	7,4	62,2
6	35	11,6	64,5
	40	23,7	72,5
7	35	11,6	49,6
	40	8,3	65,7
8	35	10,6	52.5
	40	7,8	63,4
9	35	9,6	57,3
	40	5,3	65,2
10	35	9,1	58,4
	40	5.3	67,2

The mechanism of action of the developed new depressor additives is explained by the increase in adsorption-desorption capacity as a result of their penetration into AD sediments. Thus, the application of depressor additives not only lowers the freezing point of highly paraffinic oils and the surface tension coefficient at the "oil-depressor additive-rock" interface, but also improves their fluidity properties.

The table shows that when the amount of depressor additive in the composition of viscous oil increases, its viscosity decreases. Thus, at a temperature of +35 oC, when a depressor additive is added in an amount of 0.01%, the viscosity of the oil decreased by 18.5 mPa.s to 13.6 mPa.s. At a temperature of +40 oC, when a depressor additive is added in an amount of 0.02%, the viscosity of the oil decreased by 18.5 mPa.s to 9.2 mPa.s.

Studies were also conducted using the "cold finger" research method, which allows for both qualitative and quantitative assessment of the effectiveness of PCI against paraffin deposition and is closer to mining conditions. This method also provides for the development of the technology for applying this newly developed reagent. The effectiveness against paraffin deposition was tested at the minimum and maximum doses of the reagent. The main goal in this is to determine the optimal dose of the reagent. If positive results are obtained within this range, the studies are further expanded and the dependence between the amount of reagent and the effectiveness against paraffin deposition is determined. For this purpose, the dependence between the amount of PCI reagent and the effectiveness was established and is given in Fig. 1.

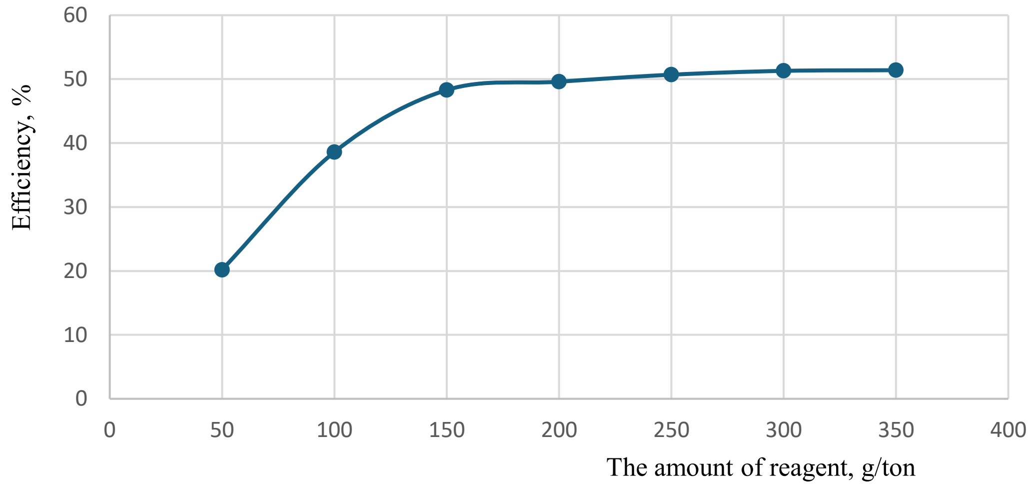

Figure 1: *Dependence of efficiency on the amount of reagent*

As can be seen from Fig.1, high efficiency against paraffin deposition was achieved at a reagent dosage of 200 g/ton. Therefore, this amount was considered the optimal dosage.

The mechanism of action of the developed new depressor additives is explained by the increase in adsorption-desorption capacity as a result of their penetration into AD sediments. Thus, the application of depressor additives not only lowers the freezing point of highly paraffinic oils and the surface tension coefficient at the "oil-depressor additive-rock" interface, but also improves their fluidity properties.

IV.Conclusion

1. The best results of the proposed depressor additive in terms of its effect on the effective viscosity and freezing point during fluid accumulation, oil preparation for transportation, and transportation were achieved at a concentration of 0.02%.

2. LPR is obtained from a mixture of aromatic hydrocarbons and alcohols to prepare the depressant additive.

3.The components in the composition, as a result of their interaction with paraffin oil, are adsorbed on its surface, affecting heavy molecular hydrocarbons and preventing the growth of paraffin crystals.

4. It reduces the viscosity of paraffin oil and increases its fluidity. It also significantly reduces the freezing point of paraffin oil.

CONFLİCT OF İNTEREST.

The authors declare that they have no conflict of interest.

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