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The Nanostructuring of the Functional Surface of the Oil Pipelines

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Abstract: The current state of oil pipelines is characterized by decrease of operational reliability and efficiency which are caused by intensive corrosion processes and accumulation of asphaltens-resinous-wax formations on internal surfaces. Formation of accumulations is the reason of essential increase in hydraulic resistance of pipeline. The most suitable way for decrease of hydraulic resistance of oil pipelines is the modifying of internal surfaces at the expense of formation of molecular fluorine SAS layers. Nano-structural modification of internal surfaces is carried out at the expense of the focused adsorption of fluorine SAS molecules from the transported environment and formation so-called «a paling of Lengmjura». It is established that updating of internal surfaces of the pipeline at the expense of formation on them of molecular fluorine SAS layers leads to reduction of their hydraulic resistance on $30 \div 23$ %. Molecular fluorine SAS layers, generated on a metal surface, considerably improves its hydraulic characteristics without dependence from roughness size. This peculiarity of molecular fluorine SAS layers allows not only to restore hydraulic resistance of the oil pipelines which have grown during of operating process, but also to improve their initial hydraulic characteristics. Characteristics of interaction of a stream of oil and an internal surface are optimized by nano-structural processing. The given technology allows to lower hydraulic resistance by changing the roughness of the internal surface of the pipeline, to lower power expenses for transportation of hydrocarbons raw materials, to raise operational reliability and to extend the between-repairs period.

1. Introduction

The current state of oil pipelines is characterized by decrease of operational reliability and efficiency which are caused by intensive   corrosion processes and accumulation of asphaltens-resinous-wax formations on internal surfaces. Formation of accumulations   is the reason of essential increase in hydraulic resistance of pipeline [1].

One of the basic ways for the decrease of hydraulic resistance is mechanical ways of cleaning. However, the relief and geometrical characteristics of the oil pipeline do not always allow to clean devices. Cleaning of devices leads to deterioration   of pipe wall   which reduces a residual resource of oil pipelines.

Other direction of decrease of the hydraulic resistance increasing in result of deterioration of oil rheology and changing in current parameters is using of chemical reagents [2]. Application of anti-turbulent additives at oil transport is ineffective. The currently applied depressor additives and inhibitors differ in a complex production technology are scarce and expensive [3].

The most perspective method of decrease is the hydrophobization of internal surface of the oil pipeline on a basis fluorine containing surface-active substances. Characteristics of interaction of a stream of oil and an internal surface are optimized by nano-structural processing [4.

2. Experimental Section

2.1. Materials

For modification of surfaces have been used fluorine SAS, the epilame compositions of different marks, such as « Efren 1», «Zonyl® 9027» and «Foleoks 1». «Efren-1» represents 0,05-0,5 %-s' solution of perfluorine-acid in hladone-350. «Foleoks 1» represents the 0,1-2 %-s' solution of perfluorine-ether with acid group; as solvent is used aliphatic ozone safe hydro-chlorine-fluorine-hydrocarbons of formulas $H(CF_2)nCl$. Hladon-350 is one of the most effective and universal solvents for fluorine SAS. «Zonyl® 9027» is the water solution of fluorine-chemical anion for surfaces processing.

The solution of fluorine surface-active substances (SAS) is colorless nonflammable mobile liquid, which is nontoxical and has density in a range of 1,22-1,74 g/cm ³.

2.2. Test method and Equipment

The researches of influence of the modifier on the thickness of adsorption layer are based on modeling of oil stream condition in pipelines in an initial condition and after formation of molecular fluorine SAS layers on an internal surface and comparison of parameters of a stream. The principle scheme of experimental installation is presented in figure 1. Internal surface of steel pipes in diameter of 159 mm was pumped preliminarily by oil to determine the initial hydraulic resistance of a working piece of the pipeline. After that the injection of epilame structures of «Efren 1», «Zonyl® 9027» and «by Foleoks 1»was made. From a tank the oil was pumped over in an expenditure tank by means of the pump with adjustable frequency of rotation.

Figure 1. Scheme of experimental installation : 1 – a pressure tank; 2 – an expenditure tank; 3 – preparation knot of epilame structure; 4 – the dosing pump; 5 – the pump with adjustable frequency of rotation; 6 – the device for measuring of expenditure; 7 – replaceable pieces of the working pipeline; 8 – a differential manometer; 9 – a point of taking of sample; 10,11,12,13,14,15,16,17,18 – slide-valves
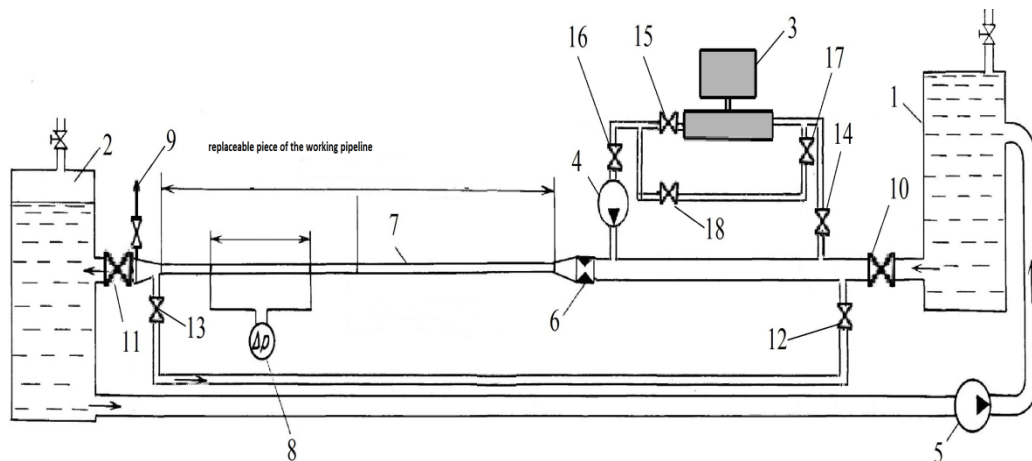
The expenditure of oil was measured with help of expenditure device. The replaceable working piece of a pipe of 3 meter long is located between tanks. This piece includes the system of measurement of pressure drop and a point of taking of sample. Process of updating of an internal surface occurs as follows. Dehydrated solution of perfluorine-acid is added in preparation knot of epilame structure. Then the received solution with the help of the dosing pump moved in the working pipeline. Thus the slide-valve 11 is closed.

Several samples were taken in order to measure the concentration of fluorine SAS molecules during the course of circulation of epilame structure with a certain intervals. After pumping over of fluorine SAS solution on pipelines oil pumping was carried out again. It was done for the purpose of comparison of initial hydraulic characteristics of the pipeline with the modified molecular fluorine SAS layers. Thus slide-valves 12,13,14 – are closed, and 10,11 – are opened.

3. Results and Discussion

3.1. Optimization of technological parameters of nano-structural hydrophobization of an internal surface of the oil pipeline

The speed of an oil stream is the key parameter influencing hydraulic resistance of pipelines. The researches have been carried out to find out the influence of speed of fluoride SAS pumping in solvent on the formation of adsorption layers. The thickness of molecular fluorine SAS layers were measured on equilibrium concentration of fluorine SAS molecules at various speeds of a stream. At small speeds of pumping the adsorption process occurs much more strongly. So, at speed of 1 m/c «Efren 1» creates of adsorption layers 1000 microns, whereas at speed of 3 m/s only 200 microns. It is possible to assume that adsorption process in general will stop at higher speeds.

Results of calculation of hydraulic resistance coefficient on various speed of oil in a working pipe are presented in figure 2.

Figure 2. The dependence of hydraulic resistance from speed of oil pumping : 1 - in an initial pipe; 2 - in a pipe modified by epilame structure «Efren 1»; 3 - epilame structure «Zonyl® 9027»; 4 - epilame structure «Foleoks 1»
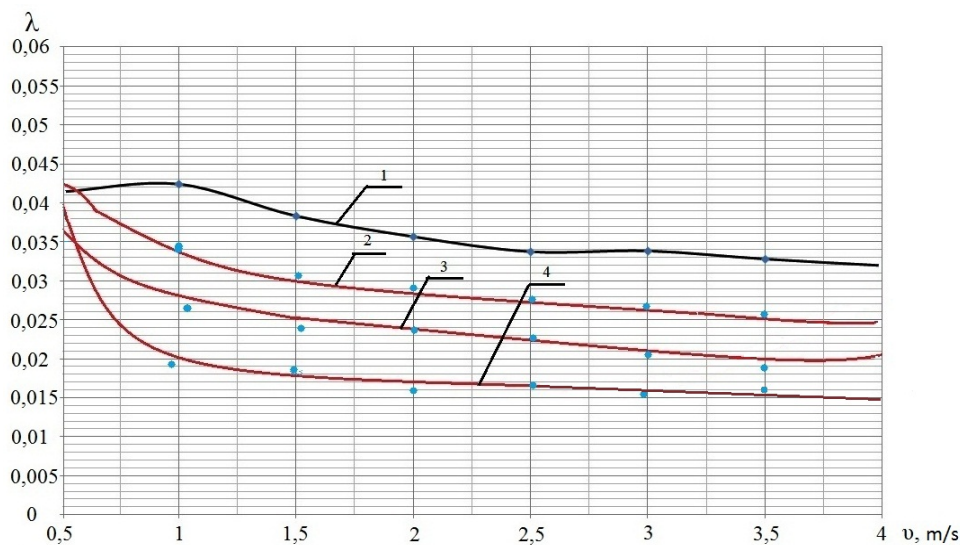
From a schedule it is clear that in the beginning of tests there was a washout of surpluses of epilame structures, and the friction coefficient was closed to the level corresponding to a pipe without a covering (a line 1). In the subsequent the hydraulic resistance coefficient decreased in 1,2-2,2 times as compared with an initial pipe ; only at speed above 3,5 – 4 m/s the covering is gradually washed off, and the hydraulic resistance coefficient aspires to the initial level.

Results of experimental researches of influence of the modifier on hydraulic resistance are presented in the form of dependence of relative hydraulic resistance of the pipeline (ΔP_{rel}) from relative value of a thickness of molecular fluorine SAS layers on a surface (b_{rel}) (figure 3).

$$\Delta P_{REL} = \frac{\Delta P_{SAS}}{\Delta P_{INT}} \qquad (1)$$

where: ΔP_{sas} - hydraulic resistance of the pipeline with molecular fluorine SAS layers , generated on its internal surface;

ΔP_{int} - initial hydraulic resistance of the pipeline.

$$b_{REL} = \frac{b_{SAS}}{\Delta r} \qquad (2)$$

where: b_{sas} - total thickness of molecular fluorine SAS layers;

Δr - an average roughness of a surface of the pipeline

Figure 3. Influence of a relative thickness of adsorption molecular layers of "Efren 1" on a hydraulic resistance of the pipeline
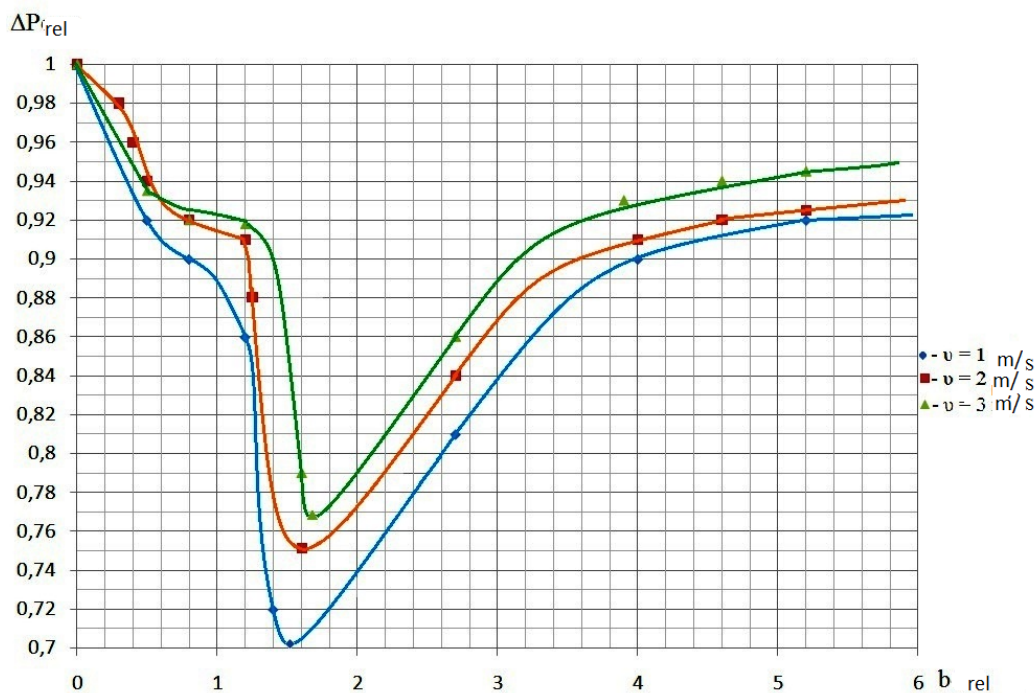
The maximum level of decrease of hydraulic resistance of the pipeline is reached at a relative thickness of molecular fluorine SAS layers, being in an interval $1,3 \div 2$. Thus the maximum fixed decrease of hydraulic resistance concerning a initial level has made 23 % at speed of 3 m/s and 28 % at speed of 1 m/s. Similar dependences of influence of a relative thickness of the molecular layers adsorbed on an internal surface on hydraulic resistance of the pipeline at various speeds of a current of oil are received after updating of «Zonyl® 9027» and « Foleoks 1».

3.2. Discussion of results

Change of characteristics of interaction of oil stream and internal surface is the most perspective method of decrease of hydraulic resistance of the pipeline [5-8]. Nano-structurization of internal surfaces of pipeline is carried out at the expense of the focused adsorption of SAS molecules from the transported environment and formation so-called «a paling of Lengmjura» [9, 10].

The adsorbed, ordered, structured, molecular, formed layers of the SAS, which total thickness is commensurable with a surface roughness, at the expense of change of factor of a friction of oil molecules about walls reduce hydraulic resistance of a pipeline. It leads to smoothing of an initial roughness and a relief of internal surfaces of the pipeline. Conditions of flow near wall are changing [11].

The fluorine SAS is most suitable for updating of internal surfaces of oil pipelines. Epilame represents the solutions of fluorine SAS – perfluorine-polyether-acid which is unpolar part contains the fluorine-hydrocarbon radical. The compositions belong to the category of fluid liquid structures forming on firm surfaces multipurpose nano-layers, which by structure and by an organization principle concerning to nano-size films of Lengmjura-Blozhett (FLB). Fluorine SAS molecules at contact with a surface are oriented that the reaction-capable hydrophilic group to a surface of this body, and hydrophobic "tail" in outwards. Thus is carry out the communication of SAS molecules with a surface not only physical, but also the chemical nature [12].

At formation of molecular fluorine SAS layers the thickness at which the maximum decrease in hydraulic resistance of the pipeline is observed. Further, at increase in a thickness of the generated molecular fluorine SAS layers on an internal surface return process begins - the hydraulic resistance increases at the expense of narrowing of diameter of the pipeline.

The increase in hydraulic resistance doesn't reach its initial level and stabilizes at level 5 – 10 % from it, and further doesn't change. Stabilization of level of hydraulic resistance of the pipeline occurs at achievement of the greatest possible thickness of the generated molecular fluorine SAS layers.

Flowing decrease of concentration of molecules fluorine SAS occurs before stabilization at level of the established concentration which indirectly characterizes a thickness of molecular fluorine SAS layers on an internal surface. The established concentration actually reflects an equilibrium state between the SAS molecules which are in a stream and being on an internal surface. Thus speeds of adsorption processes and desorption are equal.

At increase of concentration of SAS molecules in solvent, there is an increase in a thickness of adsorption on an internal surface of SAS molecules. However, at certain concentration the process of increase in a thickness is slowed down and stabilized.

The thickness of molecular fluorine SAS layers, which have been precipitated on an internal surface indirectly measured by equilibrium concentration of fluorine SAS molecules in a stream.

Characteristic regulating of a relief of the top molecular layers is a consequence of influence on them of a stream of the liquid environment. Therefore the optimal relief from the point of view of minimization of losses in the conditions of interaction of a liquid and the changed internal surface as

any self-regulated system that to aspire to minimization of losses of energy is formed. Such formations on an internal surface are reforming a current by reducing losses at the expense of decrease in hydraulic resistance of the stream.

The basic influence on change of parameters of oil stream renders change of characteristics of an internal surface. As a result of updating of an internal surface the coefficient of a friction of oil molecules about a surface decreases and the roughness size, at the expense of its filling and smoothing by molecular fluorine SAS layers decreases. All listed leads to essential change of structure of a superficial intermediate layer of oil in which the basic part of losses on hydraulic resistance is concentrated at pipeline transport of oil.

4. Conclusions

1. The most suitable way for decrease of hydraulic resistance of oil pipelines is the modifying of internal surfaces at the expense of formation of molecular fluorine SAS layers. Updating of internal surfaces is carried out at the expense of the focused adsorption of fluorine SAS molecules from the transported environment and formation so-called «a paling of Lengmjura».

2. It is established that updating of internal surfaces of the pipeline at the expense of formation on them of molecular fluorine SAS layers leads to reduction of their hydraulic resistance on $30 \div 23$ % in a range of speeds $1 \div 3$ m/c accordingly.

3. It is shown that the greatest effect of decrease in hydraulic resistance of pipelines is reached at a relative thickness of the molecular fluorine SAS layers generated on an internal surface $1,3 \div 2$.

4. Molecular fluorine SAS layers, generated on a metal surface, considerably improves its hydraulic characteristics without dependence from roughness size. This peculiarity of molecular fluorine SAS layers allows not only to restore hydraulic resistance of the oil pipelines which have grown during of operating process,   but also to improve their initial hydraulic characteristics.

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