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**INFLUENCE OF MAGNETIC FIELD ON STRUCTURAL-RHEOLOGICAL PROPERTIES OF OILS**

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*Influence of a sign-variable magnetic field on structural-rheological properties of oils with various resin contents is investigated. The optical absorption spectra of oils and asphaltene fractions before and after magnetic treatment are obtained. By means of the method of laser photocorrelation spectroscopy it is shown that magnetic treatment influences sufficiently the associate sizes of continuous phase of oil systems.*

According to modern conception oil and oil residues consist of low- and highmolecular hydrocarbon and non-hydrocarbon components. By the colloid-chemical properties they are oil dispersion systems (ODS) with complex inner organization capable of changing under the action of external factors [1, 2]. Physical-chemical and structural-rheological properties of ODS are determined by structure, sizes, and composition of complex structural units formed as a result of association asphaltene-resinous components (ARC) [2]. In spite of variety of opinions on ARC nature one can state that there is a direct connection between conditions of formation and destruction of permolecular structures (associate) in ODS and ARC behaviour in different technological processes. Complex investigations of oil system behaviour carried out at different external actions showed that existence of sorption-solvate layer of asphaltene containing components is defined by the character of influence the oil systems to a considerable degree.

By the present time the nature of structure formation processes and thier connection with rheological properties of ODS has not yet been found out completely and it accounts for the absence of sufficient clearliness in the problem of control of rheological properties of high-viscous and high-solidifying oils under the conditions of mining, transporting and storing [3].

Low-energetic technologies (acoustic, vibration, magnetic and etc.) by means of which one could reconstruct its structure without noticeable external energy consumption or using internal resources of substance reconstruct its structure are the most perspective ones due to their efficiency, economy and availability. These methods find wide application in oil industry in mining, transporting and storage of high-viscous and high-solidifying oils. Their use permits to reach a significant level of structure destruction of oil associates formed by asphaltene-resinous components and crystal paraffine hydrogens within a short period of time and maintain this level during the time necessary for mass-exchange processes [4, 5].

In many fields of economical activity (including oil-mining) there is abundant positive experience of applying magneto static field (MSF) created by special devices – magnetic activator. However, industrial tests at a number of deposits revealed both positive effects and negative consequences of magnetic activator application to control asphalt-low-paraffin sediments. Scientific explanation of the results obtained in practice is limited by insufficient theoretical solution of the problem of

MSF force action owing to complexity of structural and energetic conversion taking place in the substances of different structure at micro- and macrolevel [6, 7]. Therefore all-round examination of oil behaviour of different composition in MSF permits to extend and increase our understanding of the questions dealing with influence of physical fields on different structural systems including oil colloid-dispersed systems investigated by us.

The purpose of the present work is to study the features of behaviour and structural conversion of oils with different content of resinous components after treatment of variable polarity magnetic field.

**Objects and methods of investigation**

As objects for investigation high-viscous oil of Taimurzin deposit and paraffin oil of North-Pokursk deposit were chosen. According to the data of type content the oils are high-resinous and contain 33,8 and 27,8 mass. % of ARC (table 1).

**Table 1.** Type and elemental composition of oil samples investigated

Object of investigation	ARC output, mass %	Content, mass %				
		C	H	N	S	O
Oil of Taimurzin deposit, hole 792 (1133...1145 m)						
Oil	–	82,76	11,62	0,26	4,38	0,98
ARC:						
pyrobitumens	5,80	81,52	8,18	1,96	6,15	2,19
nonpolar resin	8,64	79,65	9,97	0,70	4,01	5,67
polar resin	19,36	76,78	9,98	0,55	4,56	8,13
Oil of North-Pokursk deposit, hole 319 (2163...2175 m)						
Oil	–	85,05	12,22	0,15	1,21	1,37
ARC:						
pyrobitumens	5,25	86,10	7,57	0,66	2,53	3,14
nonpolar resin	13,97	79,72	10,23	0,62	3,45	5,98
polar resin	8,54	74,13	10,88	0,20	1,65	13,14

Magnetic treatment (MT) was carried out by means of magnetic activator MAЖ produced by Siberian chemical combine (Seversk), which is analogous to magnetic activator used in oil extraction by technical characteristics [8]. The system of six ring-type magnets permitting to obtain several zones with alternating directions of radial MSF in the gap between it and the case is used in it. Despite small overall dimensions (length – 160 mm, diameter – 40 mm), application of composite magnetically hard materials on the bases of alloys of rare-earth metals of neodymium – iron – bo-

ron provides the amplitude of magnetic induction at the internal thickener up to 0,8 T, at the external ones – 0,6 T (fig. 1).

During laboratory experiment oils involved passed through magnetic activator along Teflon tube of 4,5 mm diameter at temperature 20 °C with weight hour space velocity 3  $\text{m}^3/\text{min}$  (time of oil being in the working zone of magnetic activator amounted 4s). Rheological characteristics of oil before and after MT were defined by rotary viscosimeter «Reotest 2.1». At shift velocity  $\dot{\gamma}$  from 3 to 80  $\text{s}^{-1}$  the values of shift stress limit  $\tau_c$ , dynamic viscosity  $\eta$  and energy of viscous flow activation characterizing binding strength in associates in each structural state were calculated. Values of  $E_a$  were calculated by the dependence curves of viscosity on temperature (in the range of 20...60 °C) in hydrogen coordinates  $\lg \eta - 1/T$ .

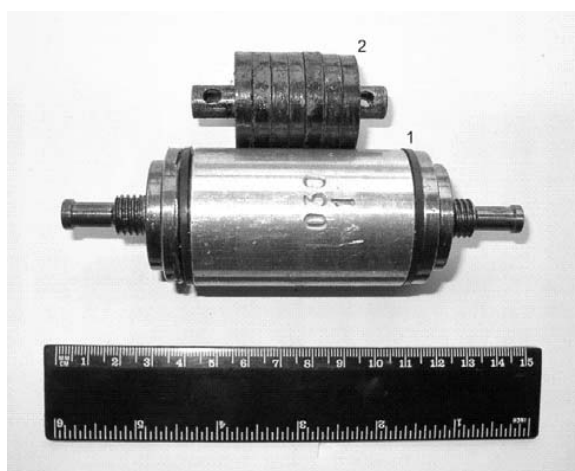


Fig. 1. Scheme of magnetic activator MAЖ: 1) case, 2) magnetic system

Spectra of optical absorption of oils and asphaltene fractions before and after MT were read by spectrometer «Uvikon 943» in the range of wave length 200...800 nm.

By means of method of laser photocorrelation spectroscopy average radii  $R$  of associates forming at diluting oils with n-hexane were determined. Measurements were carried out by the device consisting of optic-mechanic unit, system of thermal stabilization and change of temperature, system of photon calculation ФЭУ-136. At operation of laser photon correlation spectrometer He-Ne laser beam (ЛГ-38, wave length  $\lambda=0,6328$   $\mu\text{m}$ , radiation power  $\sim 50$  mW, vertical polarization) was focused by lens into the centre of cylindrical cavity with the sample. Geometrical axis of the cavity coincided with axis of rotator and is perpendicular to the scattering plane. Picture of scattering volume on photocathode was formed with the help of diaphragm and lens installed at double focus distance from the centre of scattering volume and photocathode. Change of average radii  $R$  of oil associates forming in hexane oil solutions (sample volume – 1  $\text{cm}^3$ ) was made at 20 °C for relations oil : hexane – 1 : 100, 1 : 200 and 1 : 400 (fig. 4). During the experiment reagents of ЧДА sort were used. Time of one series of changes after dilu-

ting oil accounted from 10 to 600 s, inaccuracy of measurements – up to 6 %.

### Experiment

Investigated oils of Taimurzin and North-Pokursk deposits are similar enough in content of paraffin hydrogens (2,4 and 3,2 mass. %) and asphaltenes (5,8 and 5,3 mass. %), but are sufficiently different in relation of nonpolar and polar (neutral and acid) resins (0,47 and 1,64 correspondingly), table 1. Content of heteroelements in oil asphaltenes and resins are also sufficiently different. In Taimurzin oil characterized by high content of polar resins maximum of nitrogen is concentrated in asphaltenes, but polar and nonpolar resins are similar in content of sulphur and oxygen atoms. In North-Pokursk oil with high content of nonpolar resins in asphaltenes and nonpolar resins nitrogen and sulphur concentration is maximum, but in polar resins high content of oxygen is stated (more than 13 mass. %).

Rheological dependencies of dynamic viscosity  $\eta$  of oils with different content of resin components on shift velocity  $\dot{\gamma}$  are presented in fig. 2.

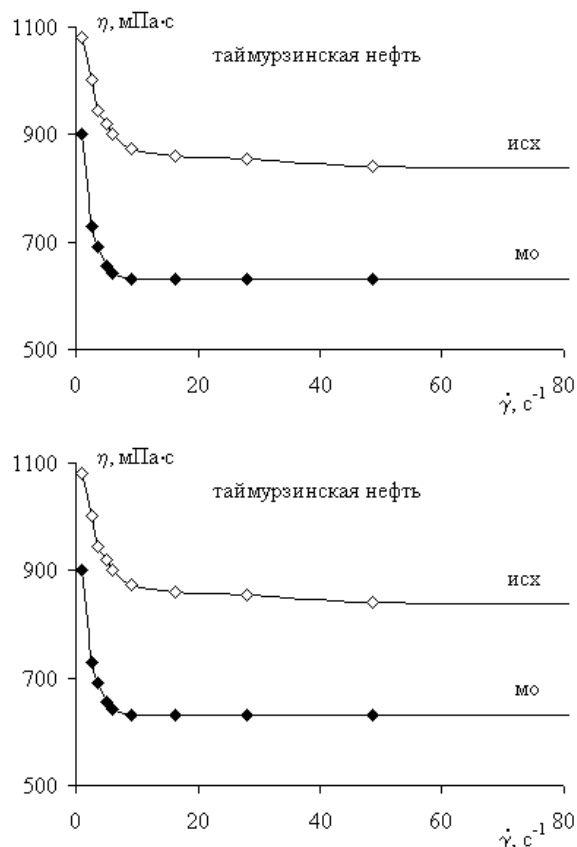


Fig. 2. Dependence of dynamic viscosity of oils on shift velocity: ИСК – before magnetic treatment; МО – after

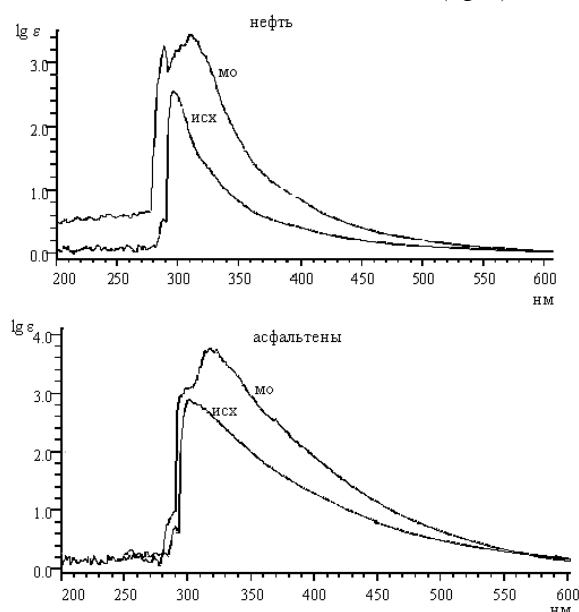
Before and after MT at shift velocity up to 50  $\text{s}^{-1}$  oils possess properties of non-Newtonian liquids, in this case MSF affects them differently. For Taimurzin oil there is 28 % decrease of viscosity  $\eta$ , 13 % that of static shift voltage  $\tau_c$ , 56 % that of activation energy of viscous flow (table 2).

**Table 2.** Rheological parameters of oils before and after magnetic treatment

Oil	$\eta$ , mPa·s	$\tau_c$ , Pa	$E_a$ , kJ/mol
Taimurzin oil			
Before MT	778,1	303,2	12,8
After MT: 0 h	605,0	257,3	8,2
24 ч	754,6	284,5	10,9
North-pokursk oil			
Before MT	17,8	108,7	1,9
After MT: 0 h	23,1	120,7	2,4
24 ч	19,2	105,1	2,0

On the contrary, after MT of North-Pokursk oil there is 17 % increase of  $\eta$ , 11 % that of  $\tau_c$  and 13 % that of  $E_a$ . In 24 h during relaxation rheological properties of oils are restored up to the values close to the initial ones.

Comparison of UV spectra of oil absorption (solution concentration  $c=5,0 \text{ mkg}\cdot\text{ml}^{-1}$ ) and asphaltenes ( $c=1,5 \text{ mkg}\cdot\text{ml}^{-1}$ ) shows that MT increases absorption intensity in the range of 290...400 nm conditioned by  $n-\pi^*$ -electron transition in heteroatoms (fig. 3).

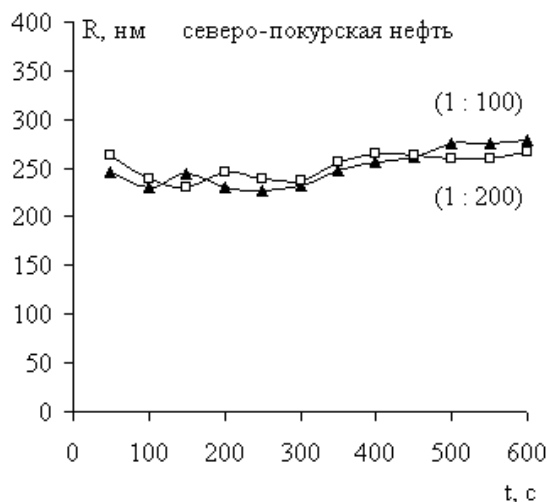
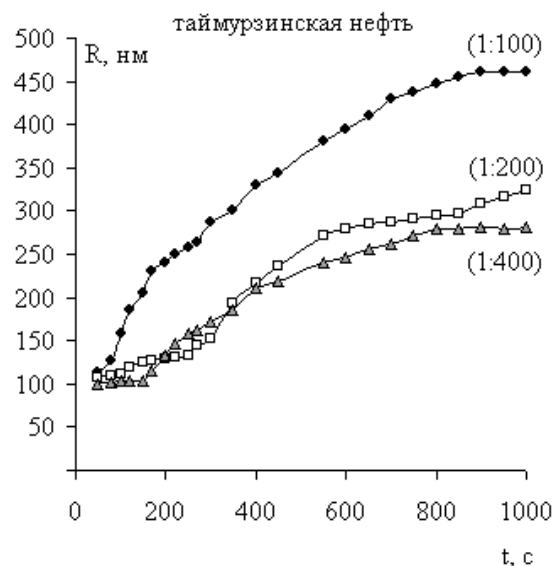

**Fig. 3.** Spectra of optical absorption of North-Pokursk oil and isolated asphaltenes before and after magnetic treatment

Along with traditional methods of investigation spectral techniques permitting to connect physico-chemical nature of structure formation processes of ODS with peculiarities of their behaviour under different external impacts are of special significance. It is known [1–3] that all widely applied spectral methods of size definition of dispersion system clear particles in white product are based on light dispersion of different wave length. Application of these methods to black products, which are oils, is complicated due to absorption, not dispersion of photons in the optical range of wave length. Using the method of laser photocorrelation spectroscopy based on definition of diffusion coefficient of colloidal particles by means of measurement of spectral composition (or correlation function) of dispersed light

permitted to examine behavior of oil colloidal dispersions in phase transitions and determine dimensions of submicron particles in low-transparent media [9].

The principle of operation of «Photocor-unicor-sp» device is based on the method of laser photocorrelation spectroscopy. The device is equipment for measuring transitional correlation function describing intensity signals of light dispersion in time region. Principle of operation consists in following. Laser beam is dispersed by particles and macromolecules, which are in Brownian motion. Photoreceiver gets dispersed light and a signal comes to detector. It is processed by digital correlator to obtain autocorrelation function. Computer calculates average radius or distribution by radii according to correlation function.

Examination of oil associate dimensions is based on well known properties of asphaltenes: they are substances insoluble in normal alkanes [10]. In diluting oil by n-alkanes a gradual washout of associate solvation sphere and formation of new dispersion phase presented basically by asphaltenes components take place.


**Fig. 4.** Change in time  $t$  of average radii  $R$  of associates forming in diluting oils at different oil :  $n$ -hexane proportions

Process of dispersion phase formation is continuous during 600...1000 s. At the initial and final stage (before 50 and after 1000 s) particle radii  $R$  are not calculated, which is connected with low quantity (concentration is less than  $10^{-3}$ ... $10^{-6}$  vol. %) and size of forming associates, fig. 4.

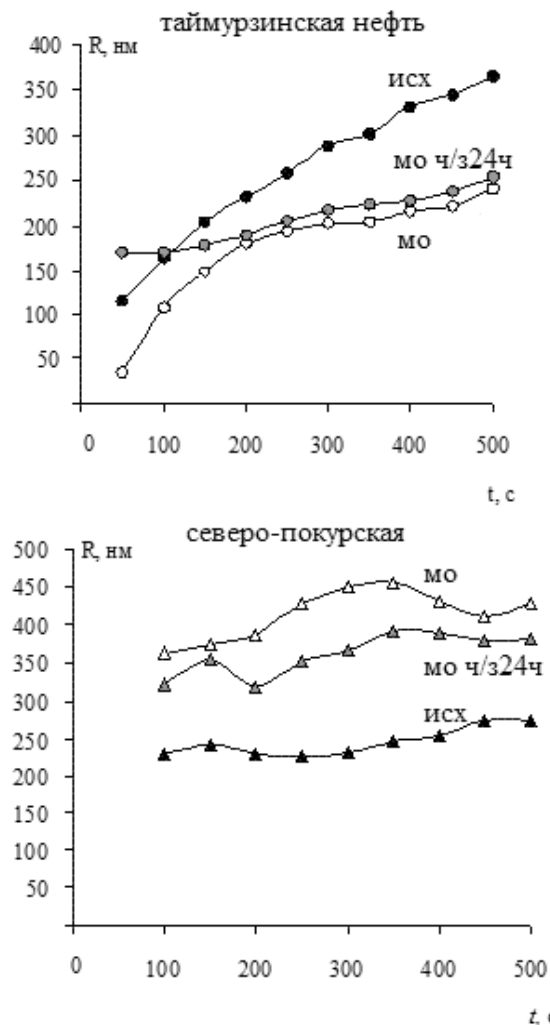


Рис. 5. Change in time of the average radii of associates forming in diluting magnetically treated oils by *n*-hexane in proportion 1 : 100

For Taimurzin oil with high content of polar resins sufficient change of dispersion degree of forming associates in diluting oil in proportion 1 : 100 was reported during 50...1000 s, average radius of particles  $R$  increases from 100 nm to 450 nm. For oil : hexane solutions – 1:200 and 1:400  $R$  decreases up to 100...270 nm (fig. 4, curves 1–3). For oil of North-Pokursk deposit with high content of nonpolar neutral resins changes of average radius  $R$  of forming associates (230...250 nm) are not

observed at diluting 1:100 and 1:200 during 600 s. In increasing the degree of diluting further (1:400) formation of associates does not take place. Thus, processes of associate formation in oil colloidal-dispersion systems are of different nature. Essential differences of oil behaviour can be explained by different qualitative and quantitative composition of resins.

Influence of MSF on the processes of oil associate formation was investigated when diluting by *n*-hexane in proportion 1:100 (fig. 5). For Taimurzin oil the 1,5 decrease of average radii  $R$  of forming particles is fixed – of the order of 35...300 nm. On the contrary, after diluting the treated North-Pokursk oil average radii  $R$  of forming associates is 1,6 times as large – up to 530 nm. For both oils relaxation of properties in time is typical, thus in 24 h both partial restoration of initial associate dimensions and restoration of rheological properties is observed (table 2). To restore structural-rheological oil characteristics completely a longer period of time is required after MT [8, 11, 12].

On the basis of results of examining rheological properties, spectral and kinetic characteristics of more than 40 oils of different composition the scheme of formation of complex structural units in alternating MSF was proposed [13]. Under magnetic action in ODS the recombination processes conditioned by dissociation and associate formation occur with participation of high-molecular fragments of low-polar and polar resinous oil components. High activity of polar acid resins results in formation of additional associate centres of smaller size in MSF and, consequently, decrease or rheological parameters of oil, but partial polarization of nonpolar neutral resinous components results in interaction of associates with formation of new larger structures and increase of viscosity.

### Conclusion

The investigation carried out showed that treatment of oils with different content of resinous components by alternating magnetic field influences sufficiently sizes of particles at colloidal-dispersed phase of oil systems and, consequently, their rheological characteristics.

For oils characterised by high content of polar acid resins, after magnetic treatment the decrease in oil associate dimension, reduction of viscosity, static shift voltage and activation energy of viscous flow are observed.

For oils with high content of nonpolar neutral resins after magnetic treatment the increase of associate dimensions and values of rheological parameters are stated.

In a definite period of time partial or total restoration of initial dimensions of associates and relaxation of rheological properties of magnetically treated oils takes place.

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## ON CHOICE OF FUNCTIONAL FOR A VARIATIONAL PROBLEM OF GAS DYNAMICS

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*Numerical solution of variational problem on construction of supersonic nozzle with uniform output flow is considered. The way of choice of minimizing functional is proposed. Comparison with the results obtained by another method is carried out.*

### 1. Introduction

It is known that if numerical (programmed) solution of some problem is possible, this solution could be performed by not unique method. In this sense direct numerical methods of solving variational problems are no exception, when solution is obtained as a result of minimization of a definite functional. In this case for the class of variational problems including gas-dynamic problems some numerical realizations can result in the fact that definition domain is a holey set.

As a typical example let us consider the problem on numerical construction of supersonic nozzle with uniform output flow solved by direct method. It should be noted that the problem on nozzle of maximum draft is close to it [1]. Let flow field be calculated in some nozzle, the profile of which is defined by varied variables, but the functional characterising flow nonuniformity at nozzle output and having minimum value when the flow is uniform is calculated by the found field.

The main two approaches can be proposed as a base for numerical solution of the given problem. The former uses the fact that the flow keeps to be supersonic and it is possible to apply cruise schemes which are simple in realization and quick in calculation; the second approach supposes existence of subsonic flows and, hence, requires application of more complicated and slower numerical methods. Let the method of characteristics serve as a base of the first numerical solution [2]. It is evidently, then, that if in some contour supersonic flow would not be realized completely, and it would result in emergency stop. The consequence of it would be holey definition domain, as the functional using parameters of

flow at nozzle output cannot be calculated. The second approach taking into account appearance of subsonic flow and using, for example, pseudoviscosity method and Godunov's scheme [3] has no such disadvantage, however, intellectual and time consumption increases by the order.

In the work [4] along with method of characteristics permitting to get the solution quickly, the functional which particularly uses magnitudes of flow parameters found at each characteristic  $C^+$  is proposed. It makes possible to proceed with the functional onto simply connected domain.

In the given article, which is development of the work [4], the functional is proposed to calculate by a simpler method. To estimate the accuracy of the results obtained the solution obtained by the method [2] was used.

### 2. The problem

It is given steady nonswirling isentropic and isenergetic flow of ideal perfect gas in axial-symmetric nozzle, fig. 1. Characteristic equations and compatibility conditions have the view:

$$\frac{dy}{dx} = \operatorname{tg}(\theta \pm \alpha),$$

$$d\theta \pm \frac{\cos^2(\alpha)}{(\gamma + 1)/2 - \cos^2(\alpha)} d\alpha \pm \frac{\sin(\alpha)\sin(\theta)}{y\cos(\theta \pm \alpha)} dx = 0, \quad (1)$$

where  $\gamma$  – adiabatic exponent, further  $\gamma=1,4$ ;  $x$  and  $y$  – longitudinal and lateral coordinates referred to nozzle radius of minimum section;  $\alpha = \arcsin(1/M)$  – Mach's