International Journal of Applied Engineering Research ISSN 0973-4562 Volume 10, Number 24 (2015) pp 45075-45081
© Research India Publications. http://www.ripublication.com

Estimation Of Bitumen Adhesion To The Mineral Material On The Basis Of Its Wetting Properties

Irek I. Mukhamatdinov [1], Alim F. Kemalov [1], Pavel S. Fakhretdinov [1], Svetlana A. Bogdanova [2]
[1] Kazan (Volga Region) Federal University
[2] Kazan National Research Technological University

Abstract- Wetting and adhesive properties are essential characteristics of bitumen as they exert determining effect on performance of composite materials on the basis thereof, for example, bitumen-concrete mixes. As a consequence, ability of bitumen to wet the mineral material surface to the fullest extent is the necessary condition for asphalt pavement durability. As is known, wetting depends on the nature of the contacting phases. On the basis of the concept of non-classic cationic surface-active agents the new adhesive additive 'Adhesoline' for bitumen modification that allows improving bitumen adhesion to the mineral materials surface has been developed. The paper presents experimental data on identification of bitumen wetting properties in respect of the mineral material surface. It was established that the adhesive additive 'Adhesoline' promotes to better wetting of the mineral material surface with the modified bitumen. At the same time the contact wetting angle θ is reduced, the spreading coefficient with the maximum by dosing 0,8 % wt. is increased, cohesion function is decreased. Also, growth of relative adhesion function Z_a the values of which approximate to one is observed. Therefore, cohesive forces between bitumen and mineral materials approximate in their magnitude to the cohesive forces of bitumen itself which promotes to formation of material with homogenous defectless structure.

Keywords: bitumen, mineral material, adhesion, wetting.

1. INTRODUCTION

Asphalt concrete pavements include two basic components: bitumen and mineral material. At that bitumen fulfills the functions of the substance binding the particles of the mineral material into a single bitumen-concrete coating.

Wetting and adhesive properties are essential characteristics of bitumen as they exert determining effect on performance of composite materials, in particular, bitumen-concrete mixes. As a consequence, ability of bitumen to wet the mineral material surface to the fullest extent is the necessary condition for asphalt pavement durability [1].

The quantitative measure of the process of bitumen adhesion to the mineral material surface is adhesion function. The source of adhesion is molecular attraction of contacting phases or their chemical interaction. It shall also be noted that adhesion phenomenon forms the basis of the strong contact (adhesion) between the solid matter – substrate and the adhesive agent being the main components of adhesive bonding [2].

In order to increase adhesive strength the substrate or adhesive may be modified as the result of which the reactive groups appear that are able to interact [3].

Wetting is a surface phenomenon consisting in interaction of the fluid with a solid or liquid body upon presence of the simultaneous contact of the three immiscible phases, one of which is a gas (air). The degree of wetting is quantitatively characterized by cosine of the contact angle θ (wetting angle) with respect to a fluid droplet on a solid surface (Fig.1) [4]. Interfacial tension at the point of contact of three phases is denoted as follows: σ_{lv} – between fluid and gas; σ_{sl} – between solid body and fluid; σ_{sv} – between solid body and gas [5].

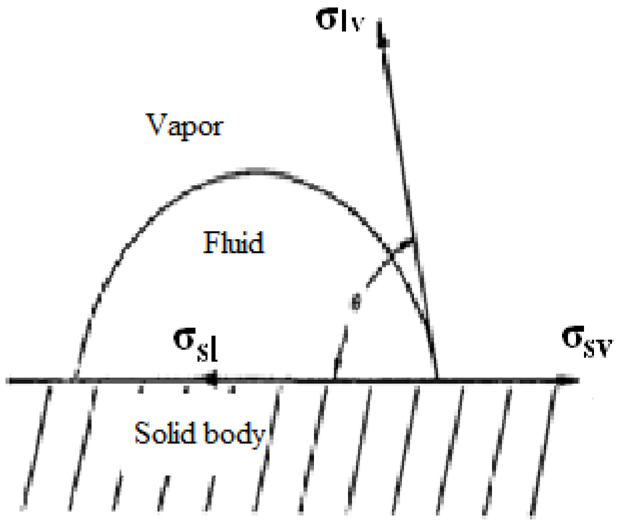

Fig. (1). – Sessile fluid droplet on the solid surface at equilibrium

Methods of wetting measurement were considered in details in the paper [6, 7]. All of them are divided into two main groups: qualitative and quantitative methods. Qualitative wetting measurements include swelling index, flotation control with the microscope, object glass method, relative permeability curves, correlation between saturation and permeability, capillary pressure curves, capillary pressure shift, nuclear magnetic resonance and dye adsorption. The quantitative methods include measurement of the contact angle, random and forced swelling (Emott) and method of contact angle estimation developed by the U. S. Bureau of Mines (USBM). The quantitative methods are used more frequently than qualitative ones. However, there is no single established procedure to be used [7, 8].

Adhesive properties may be improved by means of use of adhesive additives facilitating intensification of adsorption and chemisorptive processes at the interface 'bitumen – mineral material'. Surface active substances are most frequently as such additives [9-11]. The SAS effect on wetting is determined primarily by the chemical nature (composition) of contacting substances and SAS as such [12]. Bitumen ability to wet a mineral material is primarily determined by its fluidity as well as the nature of contacting materials. Production of a high-quality bitumen-concrete mix is only possible provided that the binder wets the mineral material well [13].

In order to formulate requirements to the structure of compounds potentially increasing the bitumen adhesion to the mineral substrate within this study the previously developed concept of non-classic cationic surface active substances (SAS) was used [14, 15]. According to this concept, cationic SAS may be classic and non-classic. Classis cationic SAS are characterized by diphilic cations with nonpolar long-chain hydrocarbon radicals with continuous hydrophobic behavior. In non-classic cationic SAS hydrophobic behavior of hydrocarbon radicals is fragmented (split) by polar heteroatomic groups. Such structure ensures their physico-chemical properties and adsorption behavior differing from the classic SAS [16]. On the basis of this concept design of the corresponding nitrogen-containing compounds was performed. As the result the adhesive additive 'Adhesoline' was created and procedure of the use thereof was designed [17, 18].

The objective of this study is estimation of effect of the 'Adhesoline' additive in modified bitumens on the wetting capacity and adhesion to surface of different mineral materials.

2. MATERIALS AND METHODS

The samples of non-modified oxidized bitumen of БНД 60/90 grade produced by JSC 'TAIF-NK' as well as those of bitumen modified with the use of 0,6, 0,8, 1,0, 1,2 % wt. of the adhesive additive were used as the source object. As a solid surface a glass substrate was used being the reference sample of polar surface [13] as well as mineral rocks of different genesis: diorite (gabbro, hornblendite) from the quarry 'Pervouralsk mining administration' and carbonate (dolomite limestone consisting of 90 % of dolomite and 10 % of calcite) from the 'Biankovsky crushed stone plant' LLC the chemical compositions of which are presented in the Tables 1 and 2.

Table 1 – Chemical composition of crushed stone from the 'Pervouralsk mining administration'

Oxide content on dry basis, %													
SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	MnO	K_2O	Na_2O	V_2O_5	P_2O_5	S	Loss on ignition
21,88	3,25	11,58	27	16,8	8,8	8,85	0,23	0,2	0,14	0,43	0,01	0,03	0,80

Table 2 - Chemical composition of crushed stone from the 'Biankovsky crushed stone plant'

Oxide content on dry basis, %												
Loss on ignition	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	$SO_{3\ общ}$	K_2O+Na_2O	Total	Insoluble residue	$CaCO_3$	$MgCO_3$
43,80	4,9	1,13	1,0	none	31,01	17,66	0,47	none	99,97	6,12	55,37	37,09

In order to get a smooth surface crushed stone was treated with the grinding-and-polishing machine MetaServ 250. For polishing the surface of the mineral material the silicon carbide powder with the particles from 50 to 200 μm was used.

The contact angle was determined using the 'sitting' droplet method. Bitumen was heated up to the temperature 120-130 ^{0}C. Three drops of heated bitumen were applied to the substrate. For good repeatability the droplets of the same size should have been applied so that their diameter does not exceed 2-3 mm. Upon achievement of the equilibrium form of droplets the contact angle was measured with the use of the cathetometer KM-8. Measurement was performed according to the procedure [19]. The value of cosine of the droplet contact angle was calculated according to the formula:

$$\cos\theta = \frac{r^2 - h^2}{r^2 + h^2}, \quad (1)$$

Where: r = L/2 – droplet radius, L – droplet base, h – droplet height.

As by contacting a cold surface of the mineral material a bitumen droplet hardens immediately the samples of rock materials were heated up to 40^{0}C which allowed maintaining the fluid bitumen state for a long time almost without changing the rock surface properties. Equilibrium value of the contact angle was determined on the basis of kinetic curves [20]. Heated bitumen was laid on the glass surface.

3. RESULTS

In the Fig. 2 the dependence of the contact angle of wetting the glass substrate surface on the additive content is presented. It was found that bitumen does not wet glass as cos θ takes negative values. Introduction of the proposed additive to bitumen results in insignificant increase in wetting capacity – the extreme is observed upon the additive content of 0,8 %.

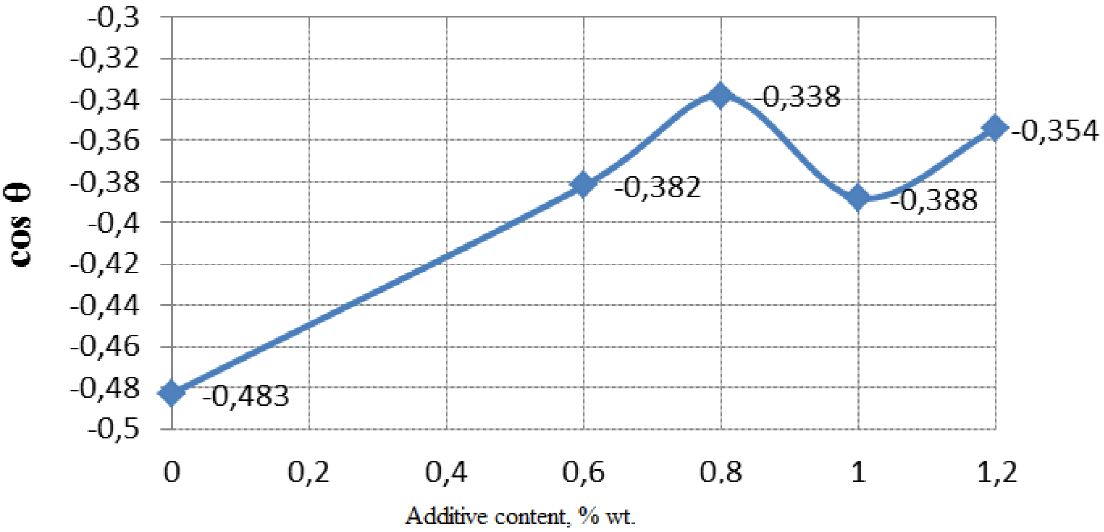

Fig. (2). - Dependence of the contact angle of wetting the glass substrate surface on the content of the 'Adhesoline' additive

The Fig. 3 represents dependence of the contact angle of wetting the mineral materials surface on the additive content. It can be seen that presence of the additive in bitumen significantly changes wetting of the mineral substrate by modified bitumen – wetting inversion is observed, cos θ increases with increase in the additive content and takes positive values. It shall also be noted that in case of the mineral materials surface the extreme is observed upon the additive content of 0,8 % wt.

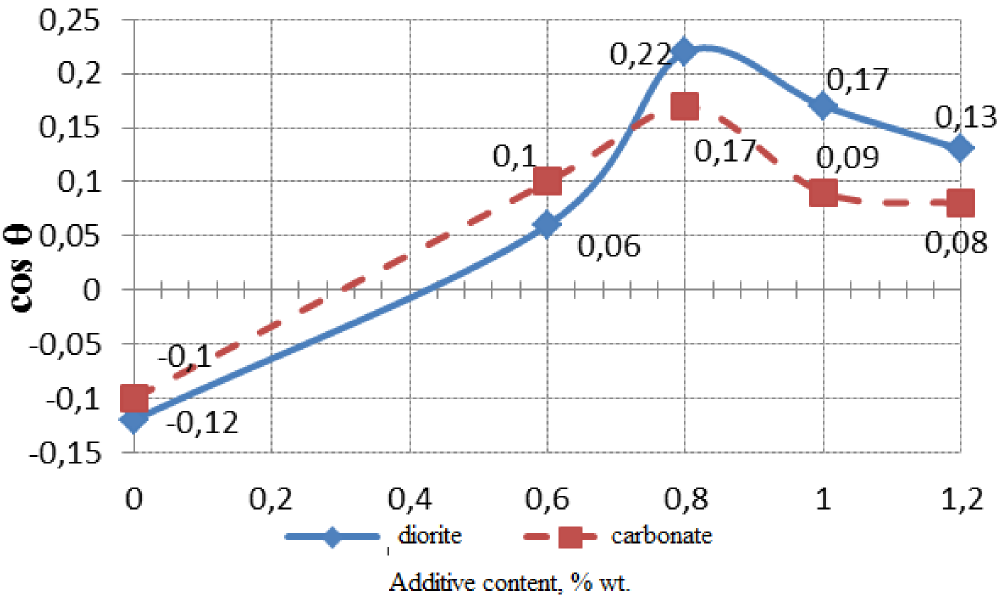

Fig. (3). - Dependence of the contact angle of wetting the mineral materials surface on the content of the 'Adhesoline' additive

Bitumen adhesion to mineral materials represents the work spent on separating a bitumen layer from these materials [21]. For the purpose of estimation of work of bitumen adhesion to substrates under investigation we measured the bitumen surface tension in presence of the 'Adhesoline' additive. Surface tension at the interface binder – air (σ_{BB}) is the essential factor determining intensity of wetting of the mineral substrate by the binder [22].

Today there are no sufficiently strict methods of estimation of surface tension of real fluids. This is due to a number of causes: firstly, the intermolecular forces theory is underdeveloped; secondly, surface tension is a property depending on a number of factors. At the same time each of the factors features its functional dependence. Surface tension is the function of intermolecular forces, molecule geometry and the number of atoms in it. Since surface tension is free energy of the surface layer its determining factors will be: free energy of intermolecular forces; molecule orientation in the surface layer determining force fields direction; presence of molecules of one phase in another one; chemical interaction of molecules of both contacting phases [23].

It is known that surface tension at the interface bitumen – air regardless of the nature of raw material makes 25-28 dyne/cm (25-28 mN/m) at 150 ^{0}C and 32,1-34,4 dyne/cm (32,1-34,4 mN/m) at 25 ^{0}C [24].

For all samples measurement of the surface tension was performed with the use of the tensiometer EasyDyne S K20S by KRUSS using the ring method. The bitumen samples were previously dissolved in toluene at the mass ratio toluene: bitumen equaling 1:1,5. The attempt to find approach to determination of the surface tension having established correlation of between the surface tension of a pure substance with surface tension of its solutions was undertaken in the work [25]. It consists in analysis of the concentration-based dependence of surface tension of such solutions in which in which the dissolved substance demonstrates its surface-active properties. In this case, as is known, adsorption of the dissolved matter at the interface surface (formation of the 'Gibbs' monolayer') takes place and it may happen that upon further increase in the solution concentration this monolayer will be as much compacted that it will reach the degree of substance casing in the solid state and then the surface tension of solution will become comparable to the surface tension of the dissolved substance [25]. Measurements were performed at the temperature 25 ^{0}C.

Calculations were performed according to the formula:

$$\sigma = \frac{F_{max} - F_v}{L \cdot \cos\theta}, \quad (2)$$

Where σ – surface or interfacial tension; F_{max} – maximum load on the ring; F_v – weight of fluid under the ring; L – length of the surface being wetted (total of the inner and external ring outline); θ – contact angle between the ring and fluid (θ = 0^0; cos θ = 1). The contact angle θ is reduced with increase in the fluid tension and equals to 0^0 at the maximum tension, at this moment cos θ = 1 [26].

Table 3 – Surface tension of bitumen samples

Bitumen samples	Reference	Adhesoline content, % wt.			
		0,6	0,8	1,0	1,2
Mean average value, $\sigma_ж$, mN/m	33,04	31,38	31,34	31,46	31,42

As can be seen from the data provided in the Table 3, surface tension is reduced by introduction of additive. This is consistent with the information [24] that the surface tension at the interface bitumen – solid body is reduced with increase in the SAS content. Surface tension together with adhesive properties provides the idea of the strength of bitumen adhesion to the mineral material.

On the basis of obtained values of θ and σ the wetting energy or adhesive tension was calculated [27, 28].

$$W_э = \sigma_ж \times \cos\theta \quad (3)$$

The adhesion work was calculated according to the Young-Dupre equation [4]:

$$W_a = \sigma_ж \times (1 + \cos\theta) \quad (4)$$

For assessment of the force of interaction of components in the bitumen samples the cohesion work was calculated. The work of cohesion is determined by energy consumption for reversible tearing of the body by the cross section that equals to an area unit. As by tearing the surface of two area units arises then the cohesion work makes:

$$W_k = 2 \times \sigma_ж \quad (5)$$

For characterizing the wetting process the spreading coefficient S is used – the difference between the work of adhesion W_a and work of cohesion $W_к$ [29]. Upon the complete wetting S →0.

$$S = W_a - W_k = \sigma_ж \times (\cos\theta - 1) \quad (6)$$

The relationship between the work of adhesion and cohesion may be expressed through the relative value [29, 30]:

$$Z_a = \frac{W_a}{W_k}, (7)$$

Where Z_a – relative work of the fluid adhesion.

If we express W_a and $W_к$ through the values determined in the equations (4) and (5) then:

$$Z_a = (1 + \cos\theta)/2 \quad (8)$$

All estimated values of the above-specified characteristics of surface properties of the system 'mineral material – organic binder' are presented in the Table 4.

Table 4 – Physico-chemical characteristics of surface properties of the system 'mineral material – organic binder'

Bitumen samples	Diorite					Carbonate				
	Wetting energy, $W_э$, mN/m	Adhesion work, $W_а$, mN/m	Cohesion work, $W_к$, mN/m	Spreading coefficient S	Relative work of adhesion, Z_a	Wetting energy, $W_э$, mN/m	Adhesion work, $W_а$, mN/m	Cohesion work, $W_к$, mN/m	Spreading coefficient S	Relative work of adhesion, Z_a
1*	-3,97	29,08	66,08	-37,01	0,44	-3,30	29,74	66,08	-36,34	0,45
2	1,88	33,26	62,76	-29,50	0,53	3,14	34,52	62,76	-28,24	0,55
3	6,89	38,23	62,68	-24,45	0,61	5,33	36,67	62,68	-26,01	0,59
4	5,35	36,81	62,92	-26,11	0,59	2,83	34,29	62,92	-28,63	0,55
5	4,09	35,50	62,84	-27,34	0,57	2,51	33,93	62,84	-28,91	0,54

*1 – reference bitumen; 2, 3, 4, 5 – bitumen samples containing the additive at the amount 0,6, 0,8, 1,0, 1,2 % wt., respectively.

4. CONCLUSION

The analysis of data obtained shows the adhesive additive 'Adhesoline' being adsorbed at the phase interface promotes to better wetting of the mineral material surface with bitumen.

At that reduction of the contact angle θ takes place, the spreading coefficient with the maximum by dosing 0,8 % wt. is increased, cohesion work is reduced. Also, by introduction of additive growth of the relative work of adhesion with peak of the additive dosage 0,8 % wt.: 0,44→0,53→0,61←0,59←0,57 to diorite and 0,45→0,55→0,59←0,55←0,54 to carbonate is observed.

The Za value approximates to one. Therefore, cohesive forces between bitumen and mineral materials approximate in their magnitude to the cohesive forces of bitumen itself which promotes to formation of material with homogenous defectless structure.

5. SUMMARY

Therefore, experimental data obtained indicate the high ability of the 'Adhesoline' additive to increase wetting of the mineral materials surface, increasing bitumen adhesion to mineral materials, reduce surface tension between the fluid and solid phases. It was established that the designed reagent may be used as an adhesive additive, in particular, to asphalts.

CONFLICT OF INTERESTS

The author confirms that the data provided does not contain the conflict of interests.

ACKNOWLEGEMENT

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

REFERENCES

[1] Kolbanovskaya, A.S., Mikhaylov, V.V. Asphalt cements. Publishing House 'Transport'. - 1973. - 264 p.

[2] Bogdanova, Y.G. Adhesion and its role in assuring strength of polymer composites // Text book, Moscow. – 2010. - 68 p.

[3] Levkina, N.L., Bychkova, E.V. Adhesion in polymer composite materials // Methodological guidance, Saratov. - 2011. - 28 p.

[4] Frolov, Y.G. Course in colloid chemistry. Surface phenomena and disperse systems. Text book for colleges. – 2d revised and enlarged edition. - M.: Chemistry. - 1988. - 464 p.: illustrated.

[5] Kinlock, E. Adhesion and adhesives: Science and technology: Translated from English. - M.: Mir. - 1991. - 484 p.: illustrated.

[6] Anderson, W. G., "Wettability Literature Survey- Part 1: Rock/ Oil/ Brine Interactions and the Effects of Core

Handling on Wettability", Journal of Petroleum Technology. – 1986. - 38(11). - 1125-1144.
[7] Anderson, W. G., "Wettability Literature Survey- Part 2: Wettability Measurement", Journal of Petroleum Technology. – 1986. - 38(12). - 1246-1262.
[8] Maryam Rajayi, Apostolos Kantzas Effect of temperature and pressure on contact angle of quartz-water-bitumen system / International Symposium of the Society of Core Analysts held in Abu Dhabi, UAE, 29 October-2 November, 2008
[9] Kulik, E.P. Impact of adhesive additives on the basis of crypto-anionic SAS on adhesion of asphalt cement to mineral materials // Journal of HNADU, Vol. 30. - 2005. – PP. 9-12
[10] Kudryashov, P.A. et al. Impact of adhesive additives on bitumen thermal stability and ageing / P.A. Kudryashov, V.G. Germashev, V.V. Yadykina, K.A. Polezhayev. - URL: http://nanosintez.kz/sites/default/files/Vliyanie%20na%20termostabilnost%20bituma.pdf
[11] Kemalov, A.F. Intensification of production of oxidized bitumens and modified bituminous materials on the basis thereof. Abstract of Thesis of Doctor of Engineering Sciences, Kazan State Technical University, Kazan. - 2005. - 42 p.
[12] Summ, B.D., Goryunov, Y.V. Physico-chemical fundamentals of wetting and spreading, M.: Chemistry. – 1976. - 232 p.
[13] Emelyanycheva, E.A. Modification of asphalt cements with the use of polymer and organo-mineral additives: Abstract of Thesis of Candidate of Engineering Sciences, Kazan National Research University, Kazan. - 2011. - 20 p.
[14] Fakhretdinov, P.S. Functionally-substituted N-[poly(alkilenoxy)-carbonylmethyl] ammonides. Synthesis, properties and application in the oil industry: Thesis of Candidate of Chemical Sciences. Kazan State Technical University, Kazan. - 1997. - 290 p.
[15] Fakhretdinov, P.S. The concept of non-classic cationic surface-active substances // Abstracts of the 18th Mendeleev conference in general and applied chemistry. Moscow, Vol.1. – 2007. - P. 483.
[16] Kuramshina, O.I. The study of the micelle formation process on the basis of results of physico-chemical studies and molecular dynamics methods // Journal of the Udmurtia University, Issue 2. - 2010. – PP. 28-42
[17] Mukhamatdinov, I.I. et al. New adhesive additive for asphalt cements // Oil refining and petroleum chemistry. - № 12. – 2013. - PP. 33-36
[18] Mukhamatdinov, I.I. et al. Impact of the adhesive additive on the physico-mechanical characeristics of asphalt cement // Science and technology in the road industry, Vol. 4. – 2014. - PP. 30-31
[19] Bogdanova, S.A., Tretyakova, A.Y., Sashkina, O.R. et al. Colloid chemistry of SAS and high-molecular compounds / Methodological guidance, KSTU, Kazan. - 2005. - 53 p.
[20] URL: http://stroyfirm.ru/articles/bitum36.html
[21] Workshop on petroleum engineering. Edited by E.V. Smidovich and I.P. Lukashevich. 3d revised and enlarged edition, M.: Chemistry. - 1978.
[22] Zolotarev, V.A., Kudryavtseva, S.V., Efremov, S.V. Impact of joint introduction of polymers and adhesive additives on bitumen properties // Journal of HNADU, № 40. - 2008
[23] Abramson, A.A. Surface-active substances: Properties and application. – 2d revised and enlarged edition. - L.: Chemistry. - 1981. - 304 p., illustrated.
[24] Gun, R.B. Oil asphalts. M.: Chemistry. - 1973
[25] Finerman, A.E., Lipatov, Y.S., Kulik, V.I. Concerning correlation of the surface tension of polyester with the surface tension of its solutions // Colloid j. - 1969. - Vol. 31. - № 1. - PP. 140-146.
[26] Tensiometer EasyDyne S. Application manual.
[27] Berlin, A.A., Basin, V.E. Fundamentals of polymer adhesion. M. - 1969. - 319 c.
[28] Zimon, A.D. Fluid adhesion and wetting. M. - 1974. - 413 p.
[29] Yakovlev, A.D. Chemistry and technology of paint-and-lacquer coatings. L. - 1989. - 384 p.
[30] Kiselev, V.P., Efremov, A.A., Tolstikhin, K.B. Modification of surface tension of asphalt cements with herbal substance tar distillate // Chemistry of herbal substances, 2002. - №3 - PP. 39-42