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CURRENT PROBLEMS

IMPROVING THE ENVIRONMENTAL AND PERFORMANCE PROPERTIES OF AUTOMOTIVE GASOLINES. Detergent Additives

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The environmental characteristics of the automobile and their conservation during use are directly dependent on the quality of the motor fuels used. For this reason, auto and fuel manufacturers use joint programs to solve environmental problems. Stiffening of the environmental requirements for automobile engines is forcing auto manufacturers world-wide to search for new technical solutions which ensure that the approved standards are satisfied. The composition of the exhaust gases is more rigorously regulated with the complicated design of vehicles and the increase in their power. Conserving fuel has become an important goal.

The development of neutralization systems became the most effective measure for reducing the toxicity of exhaust gases. The catalytic converter allows “detoxifying” up to 90% of the toxic substances [1]. However, for efficient operation of the system, the automobile must have a fuel injection system, since an ordinary carburetor does not ensure the stable, optimum composition of the mixture. The use of a fuel injection and distribution system in gasoline engines was an unconditional advance by auto manufacturers: improving fuel combustion increased the power of the vehicle while simultaneously reducing fuel consumption and the exhaust gas toxicity [2].

Autos with fuel injection began to be manufactured in 1980. Since 1990, more than 70% of auto engines abroad have been equipped with fuel injectors.

Approval of the emissions toxicity standards – Euro-3 and Euro-4 – required manufacturers to further improve the designs of automobile engines. The technical innovations included the preheating neutralizer, exhaust gas recirculation systems, etc. Beginning in 2000, use of on-board systems for diagnosis of gasoline engines became mandatory. Such systems can control emissions from a motor vehicle during its entire lifetime.

The progress in building auto engines constantly dictates new fuel quality requirements. In the entire world, the laws on environmental protection are providing for conversion to use of environmentally clean motor vehicles requiring the corresponding fuels.

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Under the plan for developing domestic auto manufacture approved by the RF government, auto plants began manufacturing automobiles that satisfy the requirements of Euro-2 and Euro-3 in 2004. However, even after the new environmental requirements took force, the constant "exceptions from the rules" allow them to continue manufacturing obsolete products (Euro-0).

The Russian passenger auto fleet consists of 24 million units, and the annual increase is 0.9-1 million units. Despite such high growth rates, 50% of the vehicles are more than 10 years "old", 31% are 5-10 years, and 19% are less than 5 years old. The proportion of passenger autos that satisfy the environmental characteristics is thus 90% for Euro-0, 5% for Euro-1, 4% for Euro-2, and only 1% for Euro-3.

The new requirements for fuel quality defined by the European Directive were introduced in two stages: in 2000 and in 2005. The basic indexes for the toxic properties of gasolines are: lead, sulfur, aromatics (including benzene), and olefin content and evaporability. The main gasoline quality requirement is the absence of alkyl lead antiknocks, since catalytic converters are incompatible with leaded gasolines, and without the converters, it is impossible to satisfy the environmental requirements [3].

In EU countries, leaded gasolines have not been used since 2000. In Russia, after GOST R 51105–97 came into effect in 1997, almost all oil refineries have manufactured gasolines that satisfy Euro-2 standards.

On July 1, 2002, GOST R 51866–2002, which is an authentic translation of EN 228:1999 and the corresponding Euro-3 standards, took force in the territory of Russia. Production of gasolines according to this standard has been implemented at Novo-Ufa and Moscow Oil Refineries, Surgutsk FBC, and Slavneft'–Yaroslavnefteorgsintez Co. Production of these gasolines at Ryazan', Novokuibyshev, and other oil refineries is planned.

The Federal law "On Prohibition of Production and Recycling of Leaded Automotive Gasoline in the Russian Federation" took force on July 1, 2003. Grounds for reliable performance of autos equipped with catalytic converters were created with the manufacture of unleaded gasolines.

The necessary standards and technical and manufacturing base for manufacture of commercial gasolines that satisfy current European requirements have thus been created in Russia. However, production of gasolines that satisfy the Euro-3 and Euro-4 standards implies an important change in the technology and high costs, while the use of such gasolines is only justified in modern autos of the corresponding class.

At the same time, harmful atmospheric emissions can be reduced significantly and consequently the environmental situation can be improved if detergent additives are incorporated in automotive gasolines. This is due to the correlation of the cleanness of the carburetor, starting system, and combustion chamber with engine operating efficiency and exhaust gas composition.

Many changes in engine design to boost power and reduce fuel consumption and toxicity (closed crankcase ventilation system, recirculation of exhaust gases, use of fuel injection) have strengthened the tendency toward formation of deposits on engine parts [4]. This process is most intensive in the jets, in the carburetor strangler, and in the injectors and intake valves. Formation of deposits on these parts perturbs initial engine control, increases fuel consumption, reduces power, and increases exhaust gas toxicity.

According to European Directive 98/70/EC, the automobile should remain "clean" during its entire "lifetime," and its environmental characteristics should be stable for 100,000 km. This can only be attained during use by using special additives, in particular, detergents and multifunctional additives, since the existing technologies for production of automotive gasolines do not allow obtaining the required level of properties that would ensure a clean fuel system.

Modern engines are increasingly more sensitive to formation of deposits. Even a small amount of deposits in the fuel supply system or combustion chamber can perturb operation of the engine and make it inefficient [5].

Operation of the latest models equipped with on-board computer diagnostic systems becomes impossible without using effective additives that prevent formation of deposits in the entire fuel system.

Detergents not only improve the performance properties of automotive fuel but also expand its use. New brands were created at Gelios Service Stations (Kazakhstan) and YAK (Ukraine) as a result of adding the BASF (Germany) multifunctional additive to gasolines: Eco Force and A-95+, and the demand for these brands is increasing significantly.

There are relatively good domestic analogs of this additive. New fuels can be created at service stations with these analogs, and the amount pumped each day can be increased in this way. Addition of a detergent to the fuel in service stations is a good positioning method in a competitive market that attracts the most solvent client groups.

Table 1

Indexes	Gasoline quality category			Testing method
	1	2	3	
Octane number, min				
research	91; 95; 98	91; 95; 98	91; 95; 98	ASTM D 2699–86
motor	82; 85; 88	82.5; 85; 88	82.5; 85; 88	ASTM D 2700–86
Oxidation induction period, min, minimum	360	480	480	ASTM D 525–95
Mass fraction of sulfur, %, max	0.1	0.02	0.003	ASTM D 2622–94
Concentration of, g/dm^3				
metals				
lead	0.013	Absent		ASTM D 3237–97
phosphorus	–	«		ASTM D 3231–94
manganese	–	«		ASTM D 3831–94
oxygen, %, max	2.7	2.7	2.7	ASTM D 4815–94
existent gums, mg/100 cm^3, max	5	5	5	ASTM D 381–94
Volume fraction of hydrocarbons, max				
olefins	–	20	10	ASTM D 1319–95a
aromatics	50	40	35	ASTM D 1319–95a
benzene	5	2.5	1	ASTM D 4420–94
Density at 15°C, kg/m^3	715–780	715–770	715–770	ASTM D 4052–96
Copper strip test	Passed, class 1			ASTM D 130–94
External appearance	Clean, transparent			Visually
Cleanness				
carburetor, points, min	8	–	–	CEC F-03-T–81
fuel injector, % decrease throughput, max	10	5	5	ASTM D 5598–95a
intake valve				
points, min	9	–	–	CEC F-04-A–87
mg, max	–	50	30	CEC F-05-A–93
Intake valve sticking	–	Passed		CEC F-16-T–96
Deposits in combustion chamber, %, max	–	140	140	ASTM D 6201–97

The recommendations of automotive engineering manufacturers for the quality of automotive fuels are stated in the World Fuel Charter. In addition to standardizing the indexes for the properties of automotive gasolines, it sets out the requirements for fuel system cleanness (Table 1). These requirements can only be ensured if additives that prevent formation of deposits in the engine are used. Three categories of the quality of unleaded gasolines were established as a function of the environmental requirements of the markets:

1 – with no or minimal requirements for exhaust gas composition;

2 – with severe requirements for exhaust gas composition or other restrictions;

3 – with high requirements for exhaust gas composition or other restrictions.

Research on creating detergents for automotive gasolines has been conducted for almost 50 years [6]. Progress in automobile engine design has dictated new requirements for fuel additives. The changes in engine design are reflected in the functional properties of the additives designed to clean the fuel system and keep it clean.

Fuel additives are divided into generations abroad as a function of the functions performed. In addition to the detergent function, the same compounds can execute the function of carburetor deicer and corrosion inhibitor. For this reason, this division is arbitrary to a great degree.

Detergent additives can be divided (again, arbitrarily) into carburetor cleaners; injector cleaners; additives that prevent formation of deposits in intake valves; combustion chamber cleaners. Each successive generation of additives executes the functions of the preceding generation and has new properties that logically reflect the changes in engine design, operating conditions, and fuel quality requirements.

The effect of detergents on engine performance efficiency and exhaust gas toxicity has been demonstrated by many studies and tests both abroad and in Russia [1, 3].

The use of detergents in automotive gasolines ensures:

- reduced deposits: by 60% in the carburetor and by 70% in the intake valves on average;
- reduced fuel consumption – by 3%;
- decreased content in exhaust gases: carbon monoxide and hydrocarbons by 50-60%; nitrogen oxides by 20%.

In turn, this allows:

- increasing the reliability of operation of the fuel system;
- prolonging the lifetime;
- reducing servicing costs, etc.;
- reducing soot formation in the combustion chamber and thus decreasing the engine requirements for the octane number of the gasoline.

The importance of using gasoline additives is increasing markedly. In the USA, addition of detergents to gasolines has been mandatory since 1996. In Western Europe, ~80% of gasolines contain detergent additives [1].

Russia also has experience in use of detergent additives. Decisions have been made in some regions to manufacture gasolines with these additives.

Environmental problems are especially crucial for Moscow, as for any megalopolis with a high concentration of motor vehicles. For this reason, motor fuel quality standards corresponding to Euro-2 were introduced in the city in 1997, and gradual conversion of motor vehicles to quality standards corresponding to the requirements of Euro-3 is planned in 2005-2006. According to this plan, a model standard “Unleaded Automotive Gasolines (for vehicles used in Moscow)” is being developed.

Table 2

Euro-92 Regular Gasoline	Weight, mg	
	deposits in intake valves	soot in combustion chamber
With no additive	75.9	727
With AlcorAUTO additive	23.7	719
With foreign analog	21	857

Beginning on January 1, 2006, high-octane automotive gasolines used in the capital must contain detergents. The new Russian standards – GOST R 51105–97 and GOST R 51866–2002 (EN 228:1999) – permit incorporation of additives that improve performance properties, including detergents, in automotive gasolines. However, oil refineries are producing a limited volume of gasolines with detergent and multifunctional additives. One reason is the lack of large-tonnage domestic production of detergent additives.

In 2004, third-generation AlcorAUTO detergent, which keeps the engine starting system clean (TU 02 57-003-11475232–2003), was tested at VNII NP with positive results [1]. This additive makes up for the shortage of domestic additives to some extent. Euro-92 Regular automotive gasoline with this additive manufactured at Novo-Ufa Oil Refinery is recommended by the working group of scientific experts for use in automotive engineering.

The results of tests of AlcorAUTO in Euro-92 Regular automotive gasoline in comparison to the foreign analog are reported in Table 2. They confirm its high effectiveness. In operating an engine on gasoline with this additive, the amount of deposits in the intake valve was 3.2 times less than in operation on a base gasoline. In contrast to the foreign analog, when it was used, carbon formation in the combustion chamber did not increase.

Additives must have not only high functional effectiveness but also properties that make it possible to incorporate them in gasoline and use the gasoline in the operating conditions. Solubility of the additive in gasoline and stability of the solutions at low temperatures and in contact with water are primarily such properties. In addition, the additive should not worsen the physicochemical and performance properties of gasolines.

The studies showed that the domestic additive AlcorAUTO readily dissolves in automotive gasolines, does not precipitate from solutions into sediment during storage, and does not worsen the physicochemical properties of gasolines. Solutions of the additive in gasoline are stable at temperatures below –60°C and emulsions do not form on contact with water.

Improving the environmental properties of gasolines, primarily with detergent or multifunctional additives, is also necessary to ensure optimum and efficient operation of catalytic converters. In the course of the experimental studies, it was found that multifunctional detergent packages of additives have the following properties:

- they reduce fuel consumption;
- they boost power by 3-4% and improve the dynamic characteristics of the engine;
- they reduce exhaust smoke and exhaust gas toxicity;
- they remove carbon from fuel injectors, pistons, sparkplugs, valves, and combustion chamber walls;
- they restore assigned fuel injection parameters;
- they eliminate hotbulb ignition;
- they reduce the probability of engine knock in operation on low-grade gasolines;
- they bind and remove moisture from the fuel system.

Gasolines with detergent additive packages ensure environmental cleanness, higher dynamic characteristics, and a long engine lifetime.

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STANDARDIZATION OF THE QUALITY OF VISCOUS PAVING ASPHALTS

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The status of standards for viscous paving asphalts is discussed. The drawbacks of the existing standards and standards under development are noted. Necessary changes in them were proposed.

According to GOST 22245–90, paving asphalts are subdivided into five grades based on penetration (needle penetration depth) at 25°C. Some intermediate temperature sensitivity is standardized for each brand. To prevent use of asphalts with higher temperature sensitivity, requirements were introduced for their softening point and brittleness temperature, penetration at 0°C, and minimally required penetration index.

The use of asphalts with lower temperature sensitivity is restricted by ductility (extensibility) requirements and the maximum acceptable penetration index. Production of two classes of asphalts is provided for: BND, which have lower temperature sensitivity, and BN.

In our country, the lifetime of pavment is usually much lower than the value in the standards due to the low crack resistance of asphalt concretes. The crack resistance is a function of the low-temperature properties of asphalts. Class BN asphalts (as well as BNN according to TU 0256-097-00151807–97) have much worse properties than class BND asphalts, so that their use is prohibited by decision of the Federal Highway Agency of the RF Ministry of Transportation [1].

A new draft standard for paving asphalts which will replace TU 0256-096-000151807–97 and TU 0256-097-00151807–97 is being developed at the Institute of Problems of Petrochemical Processing. However, this standard has no chance of being approved by users due to the insufficiently high requirements for the low-temperature properties of asphalts in it.

The draft standard for paving asphalts (GOST R) was developed by the Federal Road Research and Study Institute. The temperature sensitivity requirements (and correspondingly also the low-temperature properties) of asphalts remained almost the same as in the active GOST 22245–90 for class BND. This standard provides for a

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Table 1

Asphalt sample	Penetration, 0.1 mm		Softening point,°C	Brittleness, °C	Ductility, cm		Penetration index	Plasticity range, °C
	at 0°C	at 25°C			at 25°C	at 0°C		
1	2	3	4	5	6	7	8	9
1	52	17	55.5	–12	55	2.5	0.18	67.5
2	50	21	57	–16	40.2	2.4	0.41	73
3	48	23	63.5	–18	8.6	2.8	1.6	82.5
4	49	20	57	–15.5	33.1	3.8	0.36	72.5
5	55	20	55.5	–15	33.9	3.3	0.32	70.5
6	50	20	61.5	–16	8.5	2.5	1.32	77.5
7	48	18	56	–14	41.4	2.8	0.1	70
8	48	22	60	–17	12.6	3	0.93	77
9	48	25	64.5	–19	7.1	2.8	1.92	83.5
10	54	22	52	–17	59.5	3.5	–0.53	69
11	72	19	51.5	–14	97.5	3.8	0.09	65.5
12	80	26	51.5	–19	87.5	4	0.39	70.5
13	78	29	54.5	–21	38.4	3.7	1.05	75.5
14	82	24	50.5	–18	76.4	4.2	0.2	68.5
15	72	22	51	–16.5	62.1	4.6	–0.04	67.5
16	67	25	56.5	–18.5	19.9	3.2	1.07	75
17	70	25	51.5	–19	65.5	3.5	0.01	70.5
18	64	28	56.5	–20	18.8	3.2	0.94	76.5
19	64	31	59.5	–22	10.1	3	1.58	81.5
20	65	24	53	–17	70	3.7	0.18	70
21	106	24	46.5	–18	114.8	6	–0.14	64.5
22	109	30	48	–21	93	6.9	0.41	69
23	110	33	49	–22	67	5	0.73	71
24	110	26	48.5	–19	82	4.8	0.59	67.5
25	98	25	49	–18.5	66	5.8	0.34	67.5
26	114	34	49	–22	63.1	5.3	0.86	71
27	110	33	47	–22	83	4.4	0.14	69
28	109	43	49.5	–26	34	4.4	0.84	75.5
29	106	44	51.5	–27	17	3.7	1.29	78.5
30	105	30	46.5	–20.5	106	5.5	–0.17	67
31	187	33	41.5	–19	77.8	14.5	0.3	60.5
32	154	37	45	–21	88.2	9.5	0.75	66
33	140	38	46.5	–22	61	5.8	0.87	68.5
34	142	28	46	–19	80.4	6.7	0.76	65
35	140	29	47	–19	65.9	7.9	1.03	66
36	153	37	45	–22	66.4	7.2	0.73	67
37	180	48	43	–23	46.6	6.5	0.72	66
38	150	53	45	–26.5	40	5.5	0.65	71.5
39	175	65	44.5	–30	24	4.6	1.14	74.5
40	172	39	42.5	–22	76	9.5	0.32	64.5
41	260	32	40	–17	73.5	21.7	1.42	57
42	215	43	41.5	–21	98.1	14.7	0.99	62.5
43	273	52	41	–22	55.8	17.5	2.2	63

Table 1 (continued)

1	2	3	4	5	6	7	8	9
44	270	37	41	–19	69.1	50	2.12	60
45	246	39	43.5	–19	64.4	18	2.58	62.5
46	272	50	41	–22	60.6	15.3	2.18	63
47	290	66	42	–25.5	41.6	11.6	3.07	67.5
48	240	73	42	–27.5	42.2	6.5	1.82	69.5
49	250	82	42	–30	28.5	5	2.07	72
50	258	46	40.5	–21	50	27	1.6	61.5

more fractional division of asphalts by brands, but it is unfortunately not well substantiated [2]. Introduction of requirements for adhesion of asphalts with stone materials of very different origins is noteworthy.

These requirements can only be satisfied if special adhesive additives are incorporated in the asphalts. However, these additives are not thermostable, so that their incorporation at the oil refinery is not expedient: they will lose activity both in the stage of preparation and testing and in shipping of the asphalts to the user. As a result, this draft standard has no chances of being accepted by oil refiners.

GOST 22245–90, class BND, will thus remain the basic standard for paving asphalts for the foreseeable future, although it has a number of shortcomings.

In particular, not all of the asphalts manufactured according to this GOST can ensure crack resistance for pavements due to their deficient low-temperature properties [2]. In addition, redundant and even more important, unbalanced requirements are characteristic of the standard. As a result, manufacture of several grades of asphalts is difficult or even impossible [3].

To objectively evaluate this standard, it is necessary to compare the properties of a sufficiently large number of asphalts of significantly different origins with its requirements. Such asphalts were made at Saratov Oil Refinery (OR) [3]. In addition, asphalts obtained by compounding different oxidized and unoxidized petroleum residues were used for the analysis. The properties of the asphalts are reported in Table 1.

Ten samples of asphalts corresponded to each of the five grades considered by the standard. The first three samples were obtained by oxidation of high-, medium-, and low-viscosity vacuum resids, the next three were made by oxidation of similar vacuum resids from lighter crudes, and the last four were made by compounding of the deeply oxidized vacuum resids indicated above with diluents. The penetration at 25°C for all of the analyzed asphalts was the average region of values for each grade.

The plasticity range (range between the softening point and brittleness temperature) was used as the temperature sensitivity index. Both the balance of the standardized indexes with each other and the necessity of changing the requirements in the standard can be judged from a comparison of the properties attained by asphalts in the plasticity range with the requirements in the standard.

Based on the logic of the existing standards requirements, we could predict that the plasticity range of asphalts is correlated with the penetration index by a single dependence for all asphalts. However, this was not observed. A common dependence is only seen for three grades of the most viscous paving asphalts (lower line in Fig. 1a). In going to grade 130/200 and especially 200/300, the penetration indexes increased significantly (upper line in Fig. 1a). As a result, their values can go outside the limits required by the standard for class BND (from –1 to 1), although all of the other properties corresponded to the standard's requirements.

The results obtained indicate the unsuitability of the penetration index for characterizing the temperature sensitivity of domestic asphalts. This is due [2] to the high content of solid waxes that affect the softening point

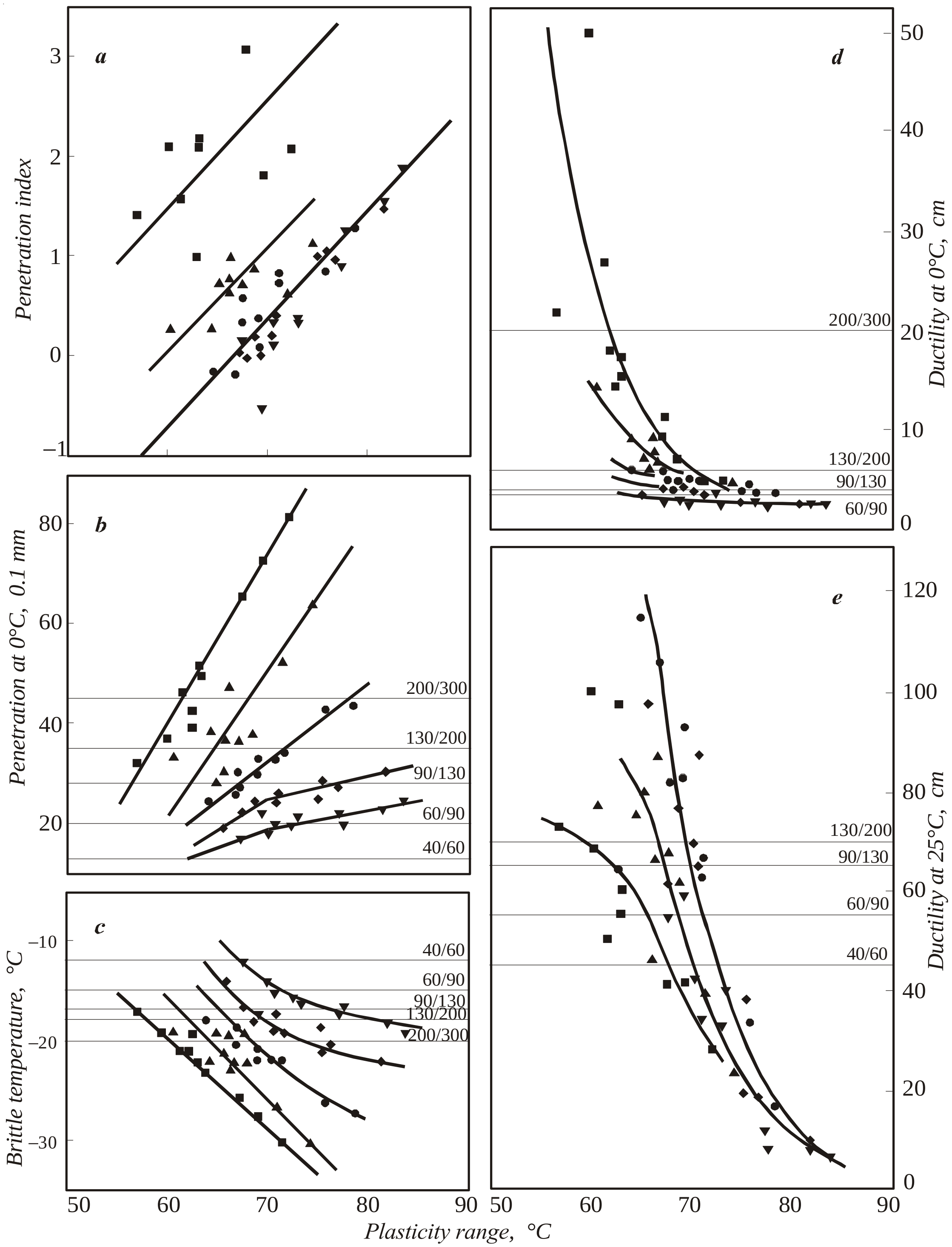

Fig. 1 Indexes of the properties of different grades of paving asphalts as a function of their plasticity range: ▼– 40/60; ◆ – 60/90; ● – 130/200; ■– 200/300; thin horizontal lines – GOST 22245 – 90 requirements for properties of class BND asphalts of the correspondent grades.

of the asphalts. This particularly significantly affects low-viscosity asphalts. However, for the least viscous asphalts as well, the softening point is usually much higher than the value in the standard (see Table 1). As a result, the requirements for this temperature are essentially formal in character.

The requirements for penetration at 0°C and the brittleness temperature limit the use of asphalts with a small plasticity range. For a large number of grades, these requirements balance each other. Use of grade 200/300 asphalts with a plasticity range of less than 61-62°C, grade 130/200 asphalts with a plasticity range of 62-64°, and grades 90/130 and 60/90 asphalts with a plasticity range of 66-67°C is restricted based on both indexes (see Fig. 1b and c).

For grade 40/60, these requirements are not balanced. To ensure the standard's penetration at 0°C, a minimum plasticity range of 61° is required, and to ensure the standard's brittleness temperature, a minimum plasticity range of 68° is required (see Fig. 1b and c). To ensure that these indexes are balanced, it is necessary to stiffen the requirements for the minimally required penetration at 0°C for grade 40/60 asphalts to 17 units.

The ductility at 0°C is sometimes considered as an index of the low-temperature behavior of asphalts. However, the dependences of this index in comparison to other previously examined indexes of the low-temperature properties (see Fig. 1b and c) on the plasticity range for different grades of asphalts (see Fig. 1d) have the opposite character. However, the directions of the changes in ductility at 0 and 25°C totally coincide (see Fig. 1d and e). For this reason, the existing requirements in GOST 22245–90 for the ductility at 0 and 25°C have the same purpose: to prohibit use of asphalts with extremely low temperature sensitivity.

It follows from Fig. 1d and e that the requirements for ductility at 25°C are more severe for grades 130/200-60/90 asphalts than for the ductility at 0°C. As a consequence, in satisfying the requirements for ductility at 25°C, these grades of asphalts are guaranteed to also satisfy the requirements for ductility at 0°C. The latter requirements are thus superfluous.

The ductility at 25°C is not standardized for grade 200/300 asphalts. The ductility at 0°C is standardized at a minimum level of 20 cm. With such severe requirements, almost all asphalts of this grade do not correspond to the standard (see Fig. d). It is necessary to decrease the requirements for minimum ductility at 0°C to ~10 cm for grade 200/300 asphalts.

Grades 60/90 and 90/130 asphalts (upper line in Fig. 1e) have the highest ductility at 25°C, and grade 200/300 asphalts have the lowest (lower line in Fig. 1e). In consideration of this, the standard's requirements for ductility at 25°C are insufficiently substantiated and balanced for grades 40/60-130/200 asphalts.

As a result of the imperfection of these requirements, the plasticity range at which the standards in GOST 22245–90 both for the low-temperature properties of asphalts and for the ductility at 25°C are satisfied is very small and is not the same for the different grades. It is 4-5° for brand 60/90, 3-4° for grades 90/130 and 130/200, and 2° for grade 40/60 (see Fig. 1b, c, and e).

The very small acceptable range of the temperature sensitivity of asphalts is the primary cause of difficulties in their production. However, the fact that the too severe 25°C ductility requirements limit production of asphalts with the best low-temperature properties which could increase the crack resistance of pavements is no less important.

It is necessary to set the acceptable plasticity range for each grade at a minimum level of 5° to guarantee production of asphalts of the quality in the standards. Leaving the existing requirements for the low-temperature properties of asphalts unchanged, the requirements for the minimum required ductility at 25°C can then be defined based on the data in Fig. 1. For grades 40/60, 60/90, 90/130, and 130/200, it should be equal to 30, 55, 55, and 60 cm.

The requirements for the minimum required ductility of grade 200/300 asphalts at 25°C were determined similarly and was equal to 55 cm. This value can be incorporated in the standard instead of the requirements for the ductility of this grade of asphalts at 0°C.

The necessity of changing the requirements in the standard basically concerns simplifying them and making them correspond to each other. An important question remains open: the degree to which satisfying the requirements in the standard can ensure the longevity of pavements. The low-temperature properties of asphalts should primarily be discussed here.

These properties can be improved by reducing the temperature sensitivity regulated by the standard. However, the users have selected another method. They propose incorporating polymeric additives in class BND asphalts according to GOST 22245–90. In their opinion, the low-temperature properties can only be improved significantly with this method and only asphalts with polymeric additives are suitable for high-category pavements [4].

The necessity of significantly improving the low-temperature properties is because the brittleness temperature of the asphalts used in paving must be lower than the maximum possible negative temperatures for the given vicinity. It is believed that only in this way can formation of temperature cracks in pavement be prevented. On this basis, the standard for polymer-asphalt binders – OST 218.010–98 – provides for much more severe requirements for their temperature properties than the active standard for asphalts, GOST 22245–90.

These notions are erroneous. First, the properties of asphalts cannot be absolutized. Their indexes are somewhat arbitrary and are only intended for comparing asphalts with each other.

The conditions of defining the standard properties of asphalts differ sharply from the conditions of their performance in asphalt concretes, where they are in the thin-film state. For example, the Fraas brittleness temperature decreases sharply with a decrease in the thickness of the asphalt films [5]. As a result, even grade BN asphalts acquire a brittleness temperature below the maximum possible negative temperatures for most regions of our country.

Second, the notion that the basic cause of crack formation in pavements is cooling in winter is not true. Special studies [6] and domestic and foreign experience indicate that asphalts with relatively poor low-temperature properties, for example, similar to those used abroad or class BN according to GOST 22245–90, can ensure performance of pavements in wet weather with no formation of temperature cracks.

Repeated sagging caused by traffic during thawing of the soil in the road bed is the primary cause of crack formation in pavements in our country [2, 6]. Pavements are designed for these traffic effects, but idealized asphalt concrete is used in the calculations. Its real properties cannot correspond to the calculated properties as a function of the quality of the asphalts.

It was found [6] that only asphalts with a maximum brittleness temperature of –15°C can ensure the deformability of asphalt concretes used in calculations of pavements. This requirement concerns all regions of our country where the ground freezes in winter. It was suggested in [2, 6] that the following requirements be set for the brittleness temperature of grades 40/60, 60/90, 90/130, 130/200, and 200/300 paving asphalts in consideration of the allowance for aging of asphalts: maximum of –16, –17, –18, –19, and –20°C, respectively. Then penetration at 0°C of these grades of asphalts should be a minimum of 21, 24, 28, 35, and 45 (see Fig. 1b and c).

It is thus necessary to stiffen the requirements for the low-temperature properties of asphalts to ensure the crack resistance of pavements in our country: very insignificantly for grades 130/200 and 90/130, slightly more for grade 60/90. The low-temperature properties should be significantly stiffened for grade 40/60 alone. Polymeric additives do not have to be incorporated in asphalts.

It is clear that the proposed norms can only be incorporated in the standard combined with the previously mentioned less severe requirements for the ductility of asphalts at 25°C. For grade 40/60, the requirements for the minimum required ductility at 25°C must be reduced even more – to 20 cm. Only in this case will the acceptable temperature sensitivity range be large enough and asphalts with such a range can actually be manufactured.

In conclusion, we note that the approach to asphalts, like the approach to the feedstock for fabricating polymer–asphalt binders, is not productive. Petroleum asphalts can also provide the brittleness temperature and penetration at 0°C required for polymer–asphalt binders without addition of any additives. It is only necessary to regulate even lower temperature sensitivity for this purpose, in particular, to decrease the requirements for the ductility of asphalts at 25°C to the level in OST 218.010–98 for polymer–asphalt binders: minimum of 15, 25, and 30 cm for grades 40/60, 60/90, and 90/130-200/300.

Unfortunately, the question of defining the possible limit of the decrease in the temperature sensitivity of paving asphalts has still not been answered. The properties of asphalt concretes which can worsen with a decrease in the ductility at 25°C are also not clear, and this impedes establishing substantiated requirements for the ductility of binders.

We can draw the following conclusions from the above:

1. The penetration index is not suitable for characterizing the temperature sensitivity of domestic asphalts, especially low-viscosity asphalts. The requirements for this index should be excluded from the standard on paving asphalts.

2. The ductility at 0°C is not correlated with the low-temperature properties of asphalts but with the ductility at 25°C. The restrictions on the ductility at 0 and 25°C in GOST 22245–90 serve one purpose – to exclude use of asphalts with extremely low temperature sensitivity. To simplify evaluation of the quality of binders, the requirements for the ductility at 0°C can be eliminated.

3. The minimum necessary ductility at 0°C for grade 200/300 asphalts required by GOST 22245–90 is overstated. It should be decreased to 10 cm.

4. The brittleness temperature of grades 40/60, 60/90, 90/130, 130/200, and 200/300 asphalts should be standardized at a maximum of –16, –17, –18, –19, and –20°C, and the penetration at 0°C should be a minimum of 21, 24, 28, 35, and 45. When these requirements are incorporated, the crack resistance of pavements will be ensured without incorporating polymeric additives in the asphalts.

5. The active GOST 22245–90 sets extremely narrow limits for the temperature sensitivity of binders. As a result, they are difficult to manufacture. In addition, asphalts with the best low-temperature properties cannot be used. To correct the situation, requirements for the minimum necessary ductility of binders at 25°C must be set at the level of 20, 55, 55, 60, and 55 cm for grades 40/60, 60/90, 90/130, 130/200, 200/300 combined with the low-temperature properties indicated above.

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TECHNOLOGY

PRINCIPLES FOR SELECTION OF EXTRACTION SYSTEMS AND COMBINED PROCESSES FOR SEPARATION AND TREATMENT OF PETROLEUM PRODUCTS

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The parameters and results of extraction and combined processes for separation of aromatic hydrocarbons from reformates, production of environmentally clean motor fuels, and increasing the quality of vacuum gasoils and atmospheric resid as feedstock for hydrocatalytic processes are reported. Principles are formulated for selecting extraction systems and combined methods that will increase the selectivity and efficiency of separation of petroleum products and expand the assortment of feedstock used.

The requirements for the admissible content of sulfur in motor fuels, benzene in automotive gasolines, and total aromatic hydrocarbons, especially polycyclic hydrocarbons in diesel fuels [1] have increased sharply and will continue to be stiffened.

The sulfur content, particularly in diesel fuels, can be reduced to 10 ppm with hydrogenation methods. However, in this case important revamping of the hydrotreating units is necessary: installation of additional reactors, replacement of existing catalysts by more efficient catalysts, decreasing the feedstock space velocity and end point, chemisorption treatment of circulating gas to remove hydrogen sulfide, increasing the partial hydrogen pressure, incorporating treatment of hydrogen-containing gas to remove contaminants by short-cycle adsorption, increasing the hydrogen:feedstock ratio, etc. [2].

Hydrogen consumption is almost doubled – from 34 to 59 m^3/m^3 of feedstock, and the length of the catalyst utilization cycle is decreased from 5 to 1.5-2 years. Revamping requires important outlays – \$6300 for processing 1 m^3/day of feedstock in output of the units of 4.8-8000 m^3/day.

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The degree of hydrogenation of aromatic hydrocarbons in the hydrotreating conditions is insufficient, and new units designed to operate at higher pressure are necessary, which results in a significant increase in investments and operating expenses [3].

Extraction processes for reducing the content of aromatic hydrocarbons and heteroatomic compounds in motor fuels can be used as an alternative to hydrogenation methods. This is demonstrated by the successful use of the first industrial extraction units in the USA for production of environmentally clean diesel fuels [4].

Extraction and combined technologies aimed at perfecting separation of aromatic hydrocarbons from reformates, producing environmentally clean motor fuels, and increasing the quality of vacuum gasoils and atmospheric resid as feedstock for hydrocatalytic processes are being developed at St. Petersburg State Institute of Technology together with KINEF Ltd. [5-11]. A brief characterization of the proposed processes for separation and treatment of crude oil cuts is reported in Table 1.

The principles for selecting extraction systems and combined methods in developing these processes that allow increasing the selectivity and efficiency of separation of petroleum products are formulated below.

1. *Use of extractants that include an associated selective solvent and a highly selective extractant with a close boiling point* which form azeotropic mixtures with a minimum boiling point and endothermic mixing effect. Addition of sulfolane to triethylene glycol (process I) or N-formylmorpholine to diethylene glycol satisfies the requirements noted above. This increases both the selectivity and the dissolving power with respect to arenes and also reduces power consumption in regenerating the mixed extractants.

2. *Use of extractants that form azeotropes with the saturated hydrocarbons in the feedstock and do not form azeotropic mixtures with the extracted components.* The following satisfy this condition: acetonitrile – in selective treatment of the kerosene cut (process V), DMF, and DMA – in treatment of diesel and dewaxed 200-320°C cuts (processes VI, VII), N-methylpyrrolidone – in treatment of atmospheric gasoil (process VIII), ethylene glycol – in treatment of vacuum gasoils (process X). The selectivity of separation, arene content in the aromatic concentrate, and yield of raffinate increase as a result of additional removal of saturated hydrocarbons in regeneration of the extractant from the extract phase in the form of azeotropes with the extractant.

3. *Use of extraction systems that include a polar extractant and polar solvent* (pentane) *limitedly soluble in each other.* Pentane concentrated in the raffinate phase selective for the saturated hydrocarbons in the feedstock as a solvent reduces their content in the extract phase and increases the hydrocarbon separation factor. In addition, the difference in the densities of the equilibrium phases increases and their separation is accelerated in the presence of pentane (processes V-VII).

4. *Use of extraction systems that include a polar extractant and a nonpolar solvent which form an azeotropic mixture with the minimum boiling point*, for example, N-methylpyrrolidone–undecane (or undecane fraction). The boiling point of this mixture is 25° lower than for N-methylpyrrolidone. Return of some of the undecane after separation of the cooled azeotropic mixture in a separator to the next fractionation tower for regeneration of N-methylpyrrolidone from the extract phase decreases the maximum temperature of the process, reduces the danger of thermal and hydrolytic decomposition of the extractant and products of its oxidation, and causes less corrosion of the equipment (processes VIII, IX, XI).

5. *Use of saturated hydrocarbons from the extract phase* (process IV) for separation of arenes, for example, total xylenes (process III) *or from* C_6-C_8 *aromatic extracts from azeotropic rectification with high-octane components as azeotrope-forming agents.* The advantage of using this principle is that the distilled azeotropic mixtures can be used as components of reformulated gasoline and because no power is required for regeneration of the azeotrope-forming agents.

Table 1

Process	Basic parameters	Results
I. Extraction of benzene, toluene, xylenes in the KINEF LG-35-8/300B unit from 62-105°C cut reformate, combined with the doxylene fraction, mixtures of triethylene glycol (TEG) with sulfolane	Composition of extractant, wt. %: 60-65% TEG, 30-35% sulfolane, 5% water; ratio of extractant and recirculate to feedstock: 6:1 and 0.8:1 (wt.), respectively	47,400 tons of doxylene fraction from total xylene unit with separation of more than 14,200 tons benzene and toluene additionally processed. Savings in steam were 9 million rubles, total economic effect, 66.6 million rubles
II. Combined process of separation of C_6-C_8 arenes from 62-105°C cut reformate by extractive fractionation followed by extraction of the benzene that partially enters the distillate	Composition of extractant in extraction rectification stage, wt. %: 30% sulfolane, 70% N-methylpyrrolidone (mixture has a synergistic effect), in the extraction stage ? mixture of the same components in the amount of 90 and 10 wt. %	High degree of extraction of arenes, 99.8%, for lower total ratio of selective solvents to feedstock (1.7:1 vol.) than in the most efficient extraction or extractive rectification processes with sulfolane or N-formylmorpholine
III. Separation of total xylenes from xylene fraction of reformate by azeotropic rectification with high-octane alcohols, 2-butanol, for example	Ratio of 2-butanol to saturated hydrocarbons in feedstock of approximately 4:1 (wt.)	Losses of C_8 arenes with distillate 14 times lower than in simple rectification. Distilled azeotropic mixtures can be used as a component in reformulated gasoline without regeneration of 2-butanol
IV. Combined separation of C_6-C_{9+} arenes from naphtha cut reformate by extraction with sulfolane followed by extractive-azeotropic rectification of the extract phase with sulfolane and ethanol	Ratio of sulfolane to feedstock in extraction stage, 1.6: 1 (wt.), in second stage, 0.2:1 (wt.), ethanol to feedstock, 3.2% (wt.)	At a low total ratio of sulfolane to feedstock (approximately 1:1 vol.), the following are obtained: benzene, toluene, C_8 and C_{9+} arenes with degree of extraction of 89, 77, 69, and 24%, as well as ethanol-containing component of naphtha that satisfies Euro-5 requirements with yield of 65 wt. % in feedstock
V. Extraction treatment of hydrotreated kerosene cut with acetonitrile in the presence of pentane combined with azeotropic rectification of C_9-C_{10} saturated hydrocarbons from the extract phase forming heteroazeotropes with acetonitrile	Ratio of acetonitrile with 3 wt. % water to feedstock of 3:1 (wt.), pentane to feedstock of 1:1 (wt.); number of theoretical extraction stages, 5	Yield of treated jet fuel containing 8.5 wt. % arenes of approximately 94%. Increase in arene content from 83.6 wt. % in extract to 99.5 wt. % in aromatic concentrate due to removal of saturated hydrocarbons from the extract phase
VI.Combined treatment of diesel cut by extraction with dimethylformamide (DMF) or dimethylacetamide (DMA) in the presence of pentane followed by azeotropic rectification in regeneration of polar solvents, forming azeotropes with C_{10}-C_{14} saturated hydrocarbons of the extract phase and hydrotreating of raffinate to remove saturated organosulfur compounds	Ratio of DMF with 3 wt. % water to feedstock of 5:1 (wt.), pentane to feedstock of 0.7:1 (wt); number of theoretical extraction stages, 5	Yield of raffinate of 83 wt. %. Raffinate contains 2.5 times less arenes and 3 times less sulfur than in feedstock, aromatic concentrate ? 98 wt. % aromatic compounds (arenes, homologs of thiophene, benzothiophene, dibenzothiophene)

Table 1 (continued)

1	2	3
VII. Extraction of arenes from dewaxed 200-320°C cut with dimethylformamide with pentane followed by azeotropic rectification in regeneration of DMF from extract phase	Ratio of DMF with 2 wt. % water to feedstock, 5:1 (wt.), pentane to feedstock, 0.7:1 (wt.); number of theoretical stages, 5	Yield of raffinate with 5 wt. % arene content from feedstock with 28.1% arenes: 72 wt. %. Fractions separated from raffinate by rectification satisfy the requirements for RZh-3 and RZh-8 working fluids
VIII. Extraction treatment of atmospheric gasoil with N-methylpyrrolidone (N-MP) in the presence of undecane (or undecane fraction) followed by hydrotreating of raffinate to remove saturated organosulfur compounds	Ratio of N-MP with 0.5 wt. % water to feedstock of (2-2.5):1 (wt.), undecane to feedstock, (0.3-0.4):1 (wt.); number of theoretical extraction stages, 4	Decrease in arene content from 28-29 wt. % in feedstock to 10 wt. % in raffinate, sulfur from 1.15-1.17 wt. % to 0.45-0.47 wt. %; 17° decrease in 90% endpoint in standard distillation of raffinate; 9-point increase in cetane index
IX. Extraction treatment of light and heavy vacuum gasoils with N-MP in the presence of undecane (or undecane fraction)	Ratio of N-MP with 5 wt. % water and undecane to feedstock in extraction treatment of heavy vacuum gasoil – respectively 3:1 and 0.7:1 (wt.); number of theoretical extracton stages, 4	Decrease in sulfur content from 2 wt. % in feedstock to 1 wt. % in raffinate, carbon residue from 0.37 wt. % to 0.21 wt. %. Yield of raffinate: 80.5 wt. %
X. Extraction treatment of heavy vacuum gasoil with N-MP in the presence of a nonpolar solvent followed by elimination of saturated hydrocarbon contaminants from the extract phase by azeotropic rectification with ethylene glycol	Ratio of N-MP with 8 wt. % water and nonpolar solvent to eedstock – respectively 3:1 and 0.4:1 (wt.), ethylene glycol to feedstock, 0.05:1 (wt.); number of theoretical extraction stages, 3	Decrease in sulfur and polycycloarene content from 1.18 and 27.1 wt. % in feedstock to 0.51 and 17.4 wt. % in raffinate, carbon residue (Conradson) from 0.9 wt. % to 0.41 wt. %. Degree of extraction of nickel and vanadium of 60.3 and 62.7%
XI. Extraction treatment of atmospheric resid with N-MP in the presence of undecane (or undecane fraction)	Ratio of N-MP with 0.5 wt. % water and undecane to feedstock, respectively 2:1 and 0.5:1 (wt.); number of theoretical extraction stages, 5	Decrease in sulfur content from 1.95 wt. % in feedstock to 1.08 wt. % in raffinate, carbon residue (Conradson) and ash content from 9 and 0.21 wt. % to 6.5 and 0.12 wt. %. Yield of raffinate of 74 wt. %

6. *Use of mixtures of a highly selective extractant* (sulfolane, for example) *limitedly miscible with the feedstock and a comparatively low-boiling, selective solvent with high dissolving power with respect to the components to be separated* (for example, N-methylpyrrolidone). Homogenization of the mixed solvent–separated components system in the tower trays and the decrease in the process temperature increases the selectivity of separation and has a synergistic effect (process II).

7. *Combination of extractive rectification and extraction processes which mutually supplement each other using in both stages mixed selective solvents of the same qualitative* (sulfolane–N-methylpyrrolidone, for example) *but different quantitative composition with predominance of the highly selective solvent* (sulfolane) *in extraction and the solvent with high dissolving power* (N-methylpyrrolidone) *in the extractive rectification stage*. This principle ensures conducting regeneration of the selective solvents in a single common block and increasing the degree of extraction of the target components at a low total ratio of selective solvents and feedstock (process II).

8. *Combination of processes that mutually supplement each other for production of motor fuels – extraction, where polycycloarenes and homologs of thiophene, benzothiophene, dibenzothiophene, and aromatic*

nitrogen-containing compounds are most easily removed, and hydrotreating, where comparatively poorly extracted saturated organosulfur compounds are easily removed. As a result, environmentally clean automotive gasolines and jet and diesel fuels are obtained in mild conditions. The assortment of feedstock for production of diesel fuel can be expanded by using atmospheric gasoil. The raffinate obtained from this feedstock by extractive treatment after hydrotreating can be used as a diesel fuel component.

9. *Use of extractive treatment instead of vacuum distillation of atmospheric resid.* In this case, the yield of raffinate is greater than takeoff of vacuum gasoils, which allows increasing the production scales of feedstock for hydrocatalytic processes.

The proposed extraction and combined processes are a promising direction for production of motor fuels that satisfy the stiff environmental requirements.

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THE PLACE OF DELAYED COKING IN MODERN OIL REFINERIES

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International and domestic experience in use of delayed coking units (DCU) is generalized. Methods and prospects for developing this process at Russian oil refineries (OR) are examined.

Delayed coking of petroleum residues is one of the most dynamically developing processes in world oil refining. The dynamics of development of coking capacities in recent years in different countries and regions of the world is shown in Table 1 [1]. As these data show, these capacities increased by 47.3 million tons from 1999 to 2005.

The North American region, the United States in particular, has the highest production potential for coking processes: 53.9% of world coking capacities. They grew from 117.7 to 136.3 million tons for the period examined, and 54 million tons/year of coke was produced [1].

World consumption of coke in the aluminum industry and electrometallurgy is at the level of 14 million tons/year, so that production of gasoils for motor fuels and exhaustive refining of crude as the final product are the basic application of the delayed coking process.

In addition to the USA, China, with 15.4 million tons (or 7.4% of world capacities), Venezuela with 8.8 million tons (3.5%), Germany with 5.7 million tons (2.3%), and Japan and Russia with 5.3 million tons each (2.1%) occupied the leading positions in 2005.

The proportion of coking of petroleum residues with respect to primary refining of crude in the world is 6.1%, and it increased by 0.9% over the 6 years examined (see Table 1). From 1999 to 2005, world coking capacities increased by 23%, and the growth rates significantly outstripped the growth rates (3.4%) of primary oil refining capacities. This naturally led to savings of crude oil for production of motor fuels.

The popularity of delayed coking is because in addition to production of petroleum coke, many technologies that provide for its wide use in production of motor fuels are realized:

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Table 1

Region, country*	Coking capacity, millions of tons/% of refined crude						
	1999	2000	2001	2002	2003	2004	2005
North America	122.4/12.2	122.6/12.2	127.2/12.7	130.3/12.9	135.5/13.3	137.6/13.4	142.1/13.8
USA	117.7/14.2	117.9/14.2	122.4/14.7	125.6/15.1	130.8/15.6	132.9/15.8	136.3/16.2
Canada	2.3/2.4	2.3/2.4	2.3/2.4	2.3/2.4	2.3/2.3	2.3/2.3	2.7/2.7
APR countris	27.9/3	28.4/2.9	29.2/3	30.1/3.1	30.2/3.1	30.4/3.1	37.4/3.7
China	16.4/7.6	15.8/7.3	16.8/7.7	17.7/7.8	17.7/7.8	17.7/7.8	15.4/6.6
Japan	3.7/1.5	5.1/2.1	5.1/2.1	5.1/2.1	5.2/2.2	5.3/2.3	5.3/2.3
Western Europe	16/2.1	19.3/2.6	19.5/2.6	18.4/2.5	18.4/2.5	17.6/2.4	18.7/2.5
Italy	2.8/2.1	2.8/2.2	2.8/2.2	2.8/2.3	2.8/2.3	2.8/2.3	2.8/2.3
Germany	7.1/6.3	7.2/6.3	7.4/6.5	6.2/5.5	6.2/5.5	4.7/4	5.7/4.9
Great Britain	3.9/4.2	3.9/4.4	3.9/4.4	3.8/4.2	3.8/4.2	3.8/4.1	3.8/4.1
Spain	1.8/2.6	1.8/2.6	1.8/2.6	1.8/2.6	1.8/2.6	2.7/3.9	2.7/3.9
Netherlands	2.3/3.6	2.3/3.6	2.3/3.5	2.4/3.8	2.4/3.7	2.4/3.7	2.4/3.7
SIC	12.7/2.9	12.7/2.9	12.7/2.9	12.7/3	12.7/3	12.7/3	12.8/3.1
Russia	5.2/1.9	5.2/1.9	5.2/1.9	5.2/1.9	5.2/1.9	5.2/1.9	5.3/2
Others	7.5/4.6	7.5/4.6	7.5/4.7	7.5/4.7	7.5/5	7.5/4.9	7.5/5.5
Latin America	15.8/4.9	21.9/6.6	23.7/6.9	23.7/7.1	27.6/8.1	27.6/8	28.2/8.4
Brazil	4.6/5.2	4.6/5.1	4.6/4.8	4.6/5.1	5/5.4	5/5.2	5/5.2
Venezuela	3.2/5.1	8.8/13.5	8.8/13.1	8.8/13.1	8.8/13.1	8.8/13.1	8.8/13.1
Middle East	4.6/1.7	5.1/1.7	5.1/1.7	5.1/1.7	5.1/1.6	5.3/1.7	5.3/1.7
Africa	1.3/0.9	1.3/0.9	1.3/0.8	1.3/0.8	1.3/0.8	2.6/1.6	2.6/1.6
Egypt	1/3.3	1/3.3	1/2.6	1/2.6	1/2.6	2.3/6.3	2.3/6.3
Eastern Europe	4.9/4.8	4.9/4.9	4.7/4.6	4.7/4.7	5.6/5.7	5.7/5.8	5.8/5.9
Romania	3.9/15.5	3.9/15.9	3.8/15.3	3.8/15.3	3.8/15.3	3.8/15.3	3.8/15.3
Total in the world	205.6/5.2	216.1/5.4	223.3/5.5	226.2/5.6	236.4/5.8	239.5/5.8	252.9/6.1

Note. *Ranking by decreasing primary oil refining capacity.

- high-efficiency thermal deasphalting of petroleum residues: the coke number of the initial feedstock is 25-30% and higher and the coke number of the coking products is a maximum of 0.3-0.5%;
- demetallization of petroleum feedstock: the metal content in the initial feedstock is up to 300 ppm and more, 3-5 ppm in the coking products, and 95-98% of the metals pass into the coke;
- refining of oil sludges and other wastes, producing fuel coke and gaseous and liquid products suitable for production of motor fuels, which allows considering delayed coking as a powerful OR “nurse.”

In addition, the presence of high-output DCU in the refinery allows adapting to a change in the composition of the crude refined more quickly, since the coke number of the coking products and metal content in these products are almost independent of the quality of the feedstock, i.e., these indexes are the same in refining both atmospheric resids and asphalts, both low-sulfur and high-sulfur crudes.

When petroleum coke is used as energy fuel, environmental pollution decreases sharply. For example, in burning 6 million tons of furnace residual fuel oil with a 3 wt. % sulfur content, 360,000 tons/year of sulfur compounds is emitted into the environment.

In coking of the same amount of atmospheric resid, approximately 700,000 tons/year of petroleum coke with a ~3.5 wt. % sulfur content is formed, and burning it emits 49,000 tons/year of sulfur compounds, i.e., much less than in burning atmospheric resid. In view of this, many refineries are building their own energy units using coke as fuel.

In the USA, approximately 30 thermal electric generating stations have converted to burning petroleum coke mixed with coal. This totally solves the problem of marketing petroleum coke and guarantees year-round, failure-free operation of refineries: the coke can be stored for a long time and the problem of exporting it is not as pressing as the problem of exporting atmospheric resid (in filling tank farm tanks with atmospheric resid, the refinery output goes down). A warehouse that provides for a one-year storage volume can be organized for shipping it.

Feedstock with a wide range of properties can be processed in the DCU: from distillates to vacuum resids, cracking residues, asphalts, bituminous sands, petrochemical products, products of coal chemistry and burning of coals.

All of these advantages make delayed coking the promising, least expensive, and economically attractive method of producing motor fuels from heavy petroleum residues in comparison to many other processes that allow refining petroleum residues into motor fuels.

Visbreaking of vacuum resids. This process is relatively common in OR, especially in Europe. However, the rates of construction of visbreaking units are constantly decreasing. This process is almost not used in the USA. In Russia, there are visbreaking units at Omsk, Ufa, Ryazan’, Nizhnekamsk, and Saratov OR. Their total capacity is approximately 6 million tons/year.

The unpopularity of the visbreaking process in world oil refining is due to the low efficiency of using it for more exhaustive oil refining. Out of 100 kg of vacuum resid refined, 92-94 kg of the same vacuum resid is formed, only with lower viscosity. Exhaustive refining is attained by extracting a small amount of vacuum gasoil from atmospheric resid, which then undergoes catalytic refining.

Technology has been developed for separate distillation of visbreaking resid which allows reducing the yield of boiler fuel from 92-94 to 55-70% [2]. The balances of ordinary visbreaking and visbreaking with separate

Table 2

Feedstock, product	Visbreaking with technology	
	traditional	with separate distillation of reaction products
	Taken, % (thousand tons/year)	
Vacuum resid	100.0 (1100)	100.0 (1100)
	Obtained, % (thousand tons/year)	
Gas (with respect to C_4)	3.3 (36)	3.3 (36)
Naphtha (IBP-180°C)	5.3 (59)	5.3 (59)
Gasoil cut	–	35.7 (392)
Grade M100 boiler fuel	90.7 (997)	55.0* (605)
Total	100.0 (1100)	100.0 (1100)

Note. *Dependent on the quality of the refined crude and varying within the limits of 55-70%.

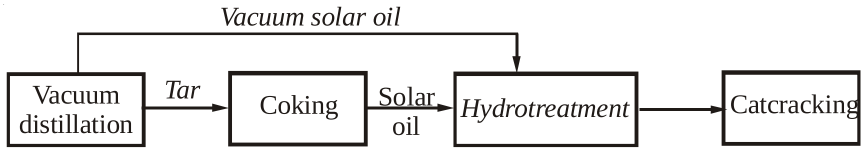

Fig. 1. Combination of delayed coking with catalytic processes.

Fig. 2. Use of hydrodesulfurizing of vacuum resid for preparation of feedstock for delayed coking units.

distillation of the reaction products are compared in Table 2. However, even with the new technology, the yield of residue is high.

Direct catalytic cracking of atmospheric resid. The process allows obtaining 40-50% (in atmospheric resid) high-octane gasoline in one stage, and the yield of coke on the catalyst attains 8-10% in feedstock. The coke is burned in a regenerator and pollutes the environment. The high yield of coke increases catalyst consumption. In addition, heavy metals that decrease catalyst activity are concentrated in atmospheric resids, and this also increases catalyst consumption. In refining atmospheric resid, catalyst consumption can attain tens of kilograms per ton of feedstock.

Technology for catalytic cracking of vacuum gasoil with addition of 10-15% atmospheric resid per unit charge has become relatively widespread. For example, in the type MSCC cat cracker in Turkmenbashi (Turkmenistan), consumption of catalyst in refining vacuum gasoil is 400 g per ton of feedstock; in addition of 10% straight-run atmospheric resid with a 5-7 ppm vanadium content, it increases to 600 g per ton of feedstock, i.e., by almost 1.5 times. For this reason, the potentials of this technology, although it is somewhat widespread, are limited.

Hydrocracking and hydrodesulfurizing of residues. The processes are implemented on the industrial scale, but are not widespread since the high metal content in the feedstock also deactivates the catalyst. In hydrocracking of 1 million tons/year of vacuum resid, 1000 tons/year of used catalyst is formed which is not regenerated and subject to reuse. Although processing of used catalysts with separation of metals also exists, its capacities are limited. In addition, the process is very expensive, since high pressure is required to implement it.

Coking in a fluidized bed (fluid), flexicoking, gasification of residues. These processes are also not widely used, since they have a poor material balance. The high temperature of the processes causes high gas formation and a low yield of liquid products. In delayed coking, the total yield of coke and gas is 30%, while the yield of liquid products used in production of motor fuels is the remainder.

In summarizing the above, we find that there is no process in world oil refining that would allow refining residues into motor fuels in one stage and would thus be economical and suitable for mass circulation.

The combination of delayed coking (at the head of the circuit) with catalytic cracking, hydrotreating, or hydrocracking is the most widespread. The scheme shown in Fig. 1 is the most common.

There is experience in hydrodesulfurizing of residues followed by coking of the desulfurized resid (Fig. 2). The process was implemented by Chevron in Pascagoula (USA). However, it is not widely used due to high catalyst consumption because of rapid coking of the furnaces.

An interesting combination of processes (Fig. 3) was realized in refining Venezuelan crude at the Shell refinery in Houston. A mixture of gasoils from a large-tonnage DCU undergoes hydrocracking. The coke obtained is sold as waste based on the price, which is much lower than the price of crude. The economic effectiveness is ensured by selling the products of hydrocracking and catalytic cracking.

Despite the obvious attractiveness of delayed coking in solving the problem of more exhaustive refining of crude, not even one unit has been built in Russia and CIS countries since the 1980s. Naturally, this situation is to some degree due to the drawbacks of the process, especially if we consider that the units were built 20-25 years ago.

The slow introduction of the process in domestic OR is due to both subjective and objective reasons. The most important ones are listed below.

1. *Lower level of automation and mechanization of labor-intensive operations.* Modern units are equipped with the system for opening and closing the upper and lower manholes developed by Delta Valve. The system allows opening the manholes in 3-4 min in the automatic mode, without human intervention. Its introduction ensures total automation of operation of the unit, including starting up and stopping.

2. *Environmental: environmental pollution with dust and gases released in steaming and cooling the coke and aqueous wastes containing phenols, coke fines, and petroleum products.* The current units are equipped with units for steaming and cooling the coke chambers. Gases are emitted through relief valves to tower K-1. The units operate in a closed water supply cycle, and water losses are less than 1%.

3. *Short runs between repairs, frequent labor-intensive repairs.* The run of modern units between repairs is extended to two years by equipping them with modern furnaces, introduction of technology for removing coke from the coils without shutting down the entire unit, and fractional water feed for cooling the coke, equipping the reaction coils with surface thermocouples, ensuring feed of water and antifoam additives at the top of the coke chambers, use of linear dilatometers for measuring the deformation rate of the coke chambers.

4. *Lack of a market for coke with a high sulfur content.* In the current stage of the problem, there is no market for medium- and high-sulfur coke.

5. *Lack of finished products.* Combining delayed coking and catalytic processes ensues a 90% degree of crude refining with production of motor fuels that satisfy all current requirements.

6. *Unjustifiably severe requirements for the basic users of petroleum coke – aluminum manufacturers – for sulfur content (maximum of 1.5%) and vanadium content (maximum of 150 ppm).* Coke with a less than 3% sulfur content is used abroad for melting aluminum.

7. *Lack of a clear state policy that would stimulate refining of atmospheric resid into motor fuels.* In our opinion, it is necessary to limit atmospheric resid production at all domestic OR to accelerate finding a solution to

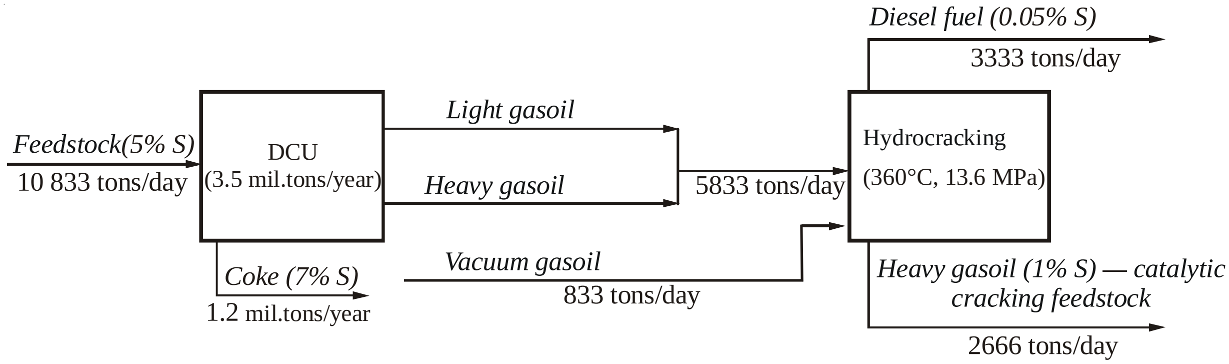

Fig. 3. Combination of hydrocracking and delayed coking (shell, developer - Foster Wheeler).

the problem of more exhaustive refining of crude. Atmospheric resid should only be manufactured for Russia's needs.

Based on the above, delayed coking should in our opinion occupy a well-deserved position in domestic OR in the next 10-15 years. DCU are being constructed in Komsomol'sk-na-Amure, a unit with output in feedstock of 1.2 million tons/year is planned in Ufa (at Ufaneftekhim Co.) and in Tatarstan. Bids are out for construction of DCU in Ufa at Ufa OR Co. and in Salavat.

Attention should especially be turned to the operation of existing units. All of them, built 23-50 years ago, are naturally obsolete. The lifetime of the coke chambers is exhausted in all units, and the furnaces need to be replaced as their efficiency is at the 65-70% level. Calculations show that it is much more economical to build a new unit with two coke chambers 7 m in diameter than to replace the furnaces and four coke chambers 5.5 m in diameter and also to bring the existing units up to the existing State Committee on Supervision of Industrial Work Safety and Mines standards. However, building new DCU takes time.

Moreover, the existing units can be revamped in a short time with low investments, increasing their output by 1.6-2 times. Revamping will allow totally covering the shortage of coke for aluminum plants and stop coke imports, which are ~600,000 tons/year. The proposals on revamping existing DCU will be reported in the next article.

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ETHERS AS SOLVENTS FOR DEWAXING RAFFINATES.
Communication 2

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UDC 665.637.73:66.061

In 1984, a method for dewaxing oil raffinates using methyl *tert*-butyl ether (MTBE) together with polar solvents, including C_3-C_6 ketones, was patented in the USA [1].

In our country, the possibility of using MTBE instead of toluene in dewaxing raffinates and deoiling slack waxes was communicated in 1988 [2]. It was noted that when MTBE replaced toluene, the feedstock suspension filtration rate increased by 1.2-2 times. Today MTBE is a large-tonnage product processed in many oil refineries

Table 1

Indexes			
	300 – 400°C (II)	350 – 420°C (III)	350 – 420°C (III)
Density at 20°C, kg/m^2	852	867	876
Viscosity, mm^2/sec			
at 50°C	7.6	16.7	30
at 100°C	3.2	4.65	7.8
Flash point (open cup), °C	152	186	201
Solid point, °C	20	32	41
Distillation, °C			
IBP	272	318	340
98 %	418	468	495
Group hydrocarbon content, wt. %			
paraffin-naphthene	78	66	60
aromatic	21.5	33.3	39.2
resins	0.5	0.7	0.8

Grozny State Petroleum Institute. Ufa State Petroleum Engineering University. Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 3, pp. 19 – 21, May – June, 2007.

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and petrochemical plants according to TU 38.103704–90. It is a member of the group of oxygenates [3] and is widely used as a high-octane component of automotive gasolines both in Russia [4] and abroad [5].

MTBE satisfies the requirements for dewaxing and deoiling solvents on many parameters. It is characterized by thermal stability, low viscosity, and boiling and solid points.

In 2001, the possibility of replacing MEK:toluene solvent by acetone:MTBE solvent was investigated at Ufa State Petroleum Engineering University. It was found that the dissolving power of MTBE is slightly lower

Table 2

Indexes	Dewaxing of distillate raffinates with solvent					
	MEK:toluene with regime			acetone:MTBE with regime		
	1	2	3	1	2	3
Solvent:feedstock (wt.) in stage						
I	4:1	3.2:1	3.5:1	4:1	3.2:1	3.5:1
II	5:1	3.5:1	4:1	5:1	3.5:1	4:1
Filtration temperature in stage I, °C	–52	–23	–23	–52	–23	–23
Filtration rate, $m^3/(m^2 \cdot h$	0.62	0.54	0.65	1.09	0.68	0.78
Dewaxing temperature gradient, deg	7	8	8	7	8	8
Yield of dewaxed oil, %	72	80	78.4	71.5	79.6	76.8
Solid point of dewaxed oil, °C	–45	–15	–15	–45	–15	–15
Oil content in slack wax, %	30	25.6	28.8	31.5	26.4	30.4

Note. * In all regimes, solvent consumption for washing in stage I was 100% in feedstock.

Table 3

Indexes	Acetone	MEK	ETAC	Toluene	MTBE	DIIPE
Density at 20°C, kg/m^3	791	805	901	867	740.5	725
Boiling point,°C	56.2	79.6	77.2	110.6	55.2	67.5
Solid point, °C	–95.5	–85.9	–83.6	–94.9	–108.6	–85.9
Viscosity at 20°C, kPa·sec	0.325	0.417	0.442	0.59	0.36	0.37
Saturated vapor pressure at 20°C, kPa	24.64	9.93	9.82	2.91	44.63*	21.06
Dipole moment, *D*	2.72	2.76	1.81	0.37	1.36	1.64
Solubility at 20°C, wt. %						
solvent in water	∞	22.6	7.8	0.037	4.8	0.94
water in solvent	∞	9.9	2.6	0.034	1.5	0.87
Composition of azeotropic mixture,** wt. %						
solvent	–	89	91.8	80.4	–	95.53
water	–	11	8.2	19.6	–	4.47
Maximum acceptable concentration, mg/m^3	200	200	200	50	100	1050
Toxicity class	IV	IV	IV	III	IV	IV

Notes. * at 30°C

**Acetone and MTBE do not from an azeotropic mixture.

than toluene's. The acetone:MTBE solvent (30:70 vol.) is very close to the traditional MEK:toluene solvent (60:40 vol.) in dissolving power [6].

The raffinates (Table 1) were dewaxed with MEK:toluene (60:40) and acetone:MTBE solvents (30:70) in laboratory conditions.

As Table 2 shows, the acetone:MTBE solvent is as good as the traditional MEK:toluene solvent in providing for a high filtration rate and the required dewaxing temperature gradient. However, it has an important drawback: higher dissolving power with respect to water.

The solubility of water at 50°C (60:40 vol.) is 2 wt. % [7] in MEK:toluene solvent and 5 wt. % in acetone:MTBE solvent (30:70 vol.). This to some degree complicates dehydration of the circulating solvent in the dewaxing unit system.

For this reason, diisopropyl ether (DIIPE) and ethyl acetate (ETAC) were investigated as components of the binary solvent [8]. The first will be widely used as an oxygenate in the very near future [9], and the second is a large-tonnage product processed according to GOST 8981–78 and widely used as a solvent in different sectors [10].

The basic physicochemical properties of these solvents are reported in Table 3. In comparison to the components of MEK:toluene solvent, the investigated ethers are characterized by a lower boiling point and viscosity and lower water content in the azeotropic mixture. In our opinion, this will all improve the technical and economic indexes of the process.

The possibility of using diisopropyl ether instead of toluene and ethyl acetate instead of methyl ethyl ketone was investigated in dewaxing oil cut raffinate III (see Table 1). Solvent consumption for dilution was 300 vol. % in raffinate and consumption for washing was 100 vol. % in raffinate, and the residual pressure in filtration was 50 kPa.

The data obtained (Table 4) show that in comparison to toluene, DIIPE has slightly lower dissolving power with respect to solid hydrocarbons, and this ensures a smaller dewaxing temperature gradient and a good filtration rate.

In using ethyl acetate (ETAC) instead of methyl ethyl ketone (MEK), loose sediments form, as indicated by the greater thickness of the slack wax cake and lower yield of dewaxed oil.

Table 4

Indexes	Dewaxing with solvent		
	MEK:toluene	MEK:DIIPE	ETAC:toluene
Filtration regime			
temperature, °C	-18	-18	-18
rate, $m^3/(m^2 \cdot h)$	1.38	1.32	1.05
Temperature gradient, deg	5	3	3.5
Yield of dewaxed oil, wt. %	75.8	74.7	73.8
Solid point of dewaxed oil, °C	-13	-15	-14.5
Viscosity of dewaxed oil, mm^2/sec			
at 50°C	19.3	19.2	18.9
at 100°C	5.14	5.18	5.24
Slack wax cake thickness, mm	7.5	7.5	9

Note. * Composition of all solvent mixtures: 60:40 (vol.).

Table 5

Indexes	Dewaxing with ETAC:DIIPE (vol.) solvent							
	100:0	90:10	70:30	65:35	60:40	50:50	40:60	20:80
Filtration rate, $m^3/(m^2 \cdot h)$	4.92	2.74	1.3	1.14	1	0.93	0.82	0.45
Dewaxing temperature gradient, deg	-3	-1	3	3	3.5	4	6	8
Yield of dewaxed oil, wt. %	31	51.8	71.2	70.8	73.8	64.2	61.4	51.8
Solid point of dewaxed oil, °C	–21	–19	–15	–15	–14.5	–14	–12	–8
Viscosity of dewaxed oil, mm^2/sec								
at 50°C	17.05	18.06	18.15	18.35	18	18.26	18.26	17.7
at 100°C	4.69	5	5.11	4.99	5	5.07	4.98	4.89
Slack wax cake thickness, mm	9	10	11	11	10	12	14	16

Note. * Filtration temperature of –18°C in all cases.

A solvent consisting of two ethers: ethyl acetate and isopropyl ether (ETAC:DIIPE) was investigated. To determine its optimum composition, dewaxing was conducted at an ETAC content in the solvent from 100 to 20 vol. %.

As Table 5 shows, the best results were obtained with the solvent consisting of 60% ETAC and 40% DIIPE. However, these results (yield of dewaxed oil, filtration rate) were slightly worse than with MEK:toluene solvent.

The optimum cooling rate and portion dilution scheme must definitely be determined for ETAC:DIIPE solvent. This will allow increasing the filtration rate and yield of dewaxed oil.

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EQUIPMENT

REVAMPING THE REACTOR BLOCK OF THE KT-1 UNIT CAT CRACKER

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UDC 665.644.2

Revamping of cat cracker reactor block equipment which would allow significantly increasing the technical and economic indexes of the combined KT-1 unit is described.

The combined KT-1 unit has been operating at Pavlodarsk Petrochemical Plant (PNKhZ Co.) since 1984. It includes sections for vacuum distillation of atmospheric resid, hydrotreating of vacuum gasoil, and catalytic cracking (CC) of the hydrotreated vacuum gasoil.

During operation for more than twelve years, the process technology and equipment in the CC reactor block have not changed significantly, primarily due to a reduction in the volume of crude refined at PNKhAZ Co. in the mid-90s.

Beginning in 2004, there was a trend toward increasing the feedstock load at the company, making it necessary to revamp the old and obsolete CC reactor block equipment. In the first stage, it was decided to replace the unit for introducing the feedstock in the flow-through reactor and reactor cyclones.

The feedstock initially entered through a low-pressure nozzle installed coaxially with the flow-through reactor at its lower connecting pipe end. The feedstock was mixed with regenerated catalyst at the site of connection of the catalyst conduits with the flow-through reactor. The disadvantages of this unit include intensive back mixing in the zone of initial contact of the catalyst, and coarsely disperse spraying of the feedstock and worsening of the selectivity of formation of the target products.

VNIINP OJSC; Avtotekhproekt Ltd. PNKhZ JSC. Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 3, pp. 22 – 24, May – June, 2007.

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In the new unit, the feedstock is fed in by eight radial feedstock nozzles installed several meters above the connection of the catalyst conduit with the flow-through reactor and a steam nozzle replaces the old feedstock nozzle located in the lower end of the connection (Fig. 1).

In the lower part of the flow-through reactor, the regenerated catalyst is accelerated by the steam and transported in an ascending stream for mixing with the feedstock. The concentration of catalyst in this stream is regulated by the steam flow rate.

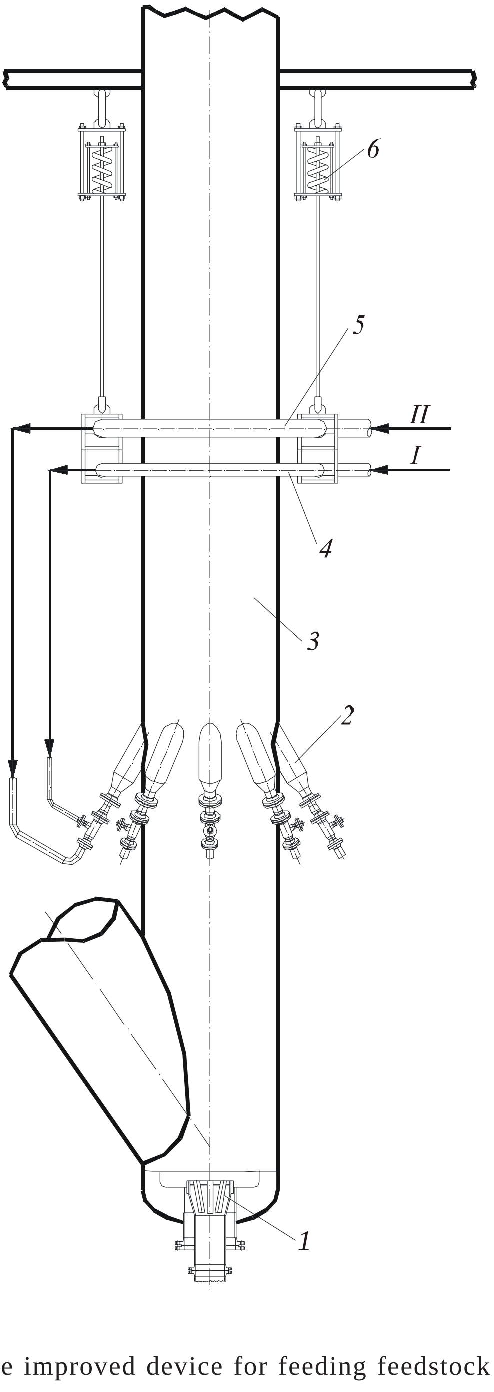

Fig. 1. Diagram of the improved device for feeding feedstock into the flow-through catalytic reactor: 1) steam nozzle; 2) feedstock nozzle; 3) flow-through reactor; 4, 5) ring collector for steam and feedstock feed; 6) spring suspension; I) steam; II) feedstock.

On one hand, it must provide a sufficient amount of solid particles for intensive contact with the feedstock drops and fast evaporation of the drops, and on the other, it must not prevent uniform distribution of the feedstock over the cross section of the flow-through reactor. In the new design of the lower part of the flow-through reactor, uniform distribution and minimum back mixing of the catalyst in the zone of its initial contact with the feedstock are attained.

The radial nozzles are uniformly positioned over the perimeter of the flow-through reactor at an angle of 30° to its vertical axis. the preliminary feedstock dispersion chamber (disperser) and modified Venturi nozzle with a slit distribution tip* are the basic design elements of the nozzles.

The feedstock is dispersed in the chamber by fractionating the liquid jet with a high-velocity steam jet and homogeneous mixing of the liquid and vapor phases. The feedstock is additionally dispersed in the modified Venturi nozzle. The feedstock is finally sprayed into the catalyst stream through the slit tip, forming a flat fan-shaped jet.

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*Russian Patent No. 2078115.

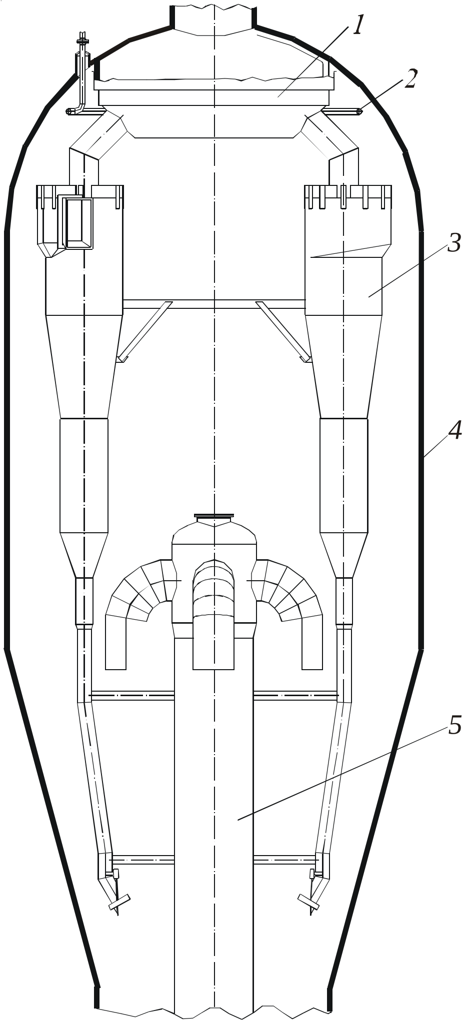

Fig. 2. Diagram of high-efficiency single-stage cyclones for the catalytic reactor: 1) gas collector; 2) ring steam distributor; 3) cyclone; 4) reactor; 5) flow-through reactor.

The distribution of the feedstock and steam stream velocities over the design elements of the nozzles is calculated so that with a moderate pressure drop in the nozzles, the maximum velocity was ensured in the elements in which the kinetic energy of the vapor phase is consumed with the highest efficiency in dispersion of the feedstock.

Each nozzle is protected by a jacket that protects the tip, which extends inside the flow-through reactor, from erosive wear by the ascending catalyst stream. Feedstock and steam are fed into the nozzles through ring collector pipes installed concentrically to the flow-through reactor on spring suspenders.

According to the initial design of the KT-1 unit, four groups of two-stage cyclones were installed in the catalytic reactor. Stage I cyclones were suspended on two vertical rods attached in the upper end plate of the reactor, the stage II cyclones were installed on their own discharge pipe welded to the spherical bottom plate of the collector.

The design of the vertical suspension rods for the stage I cyclones did not allow them to freely rotate in the direction of horizontal movement of the devices attaching the rods to the cover of the cyclone during heating. Due to this, excess stresses arose during thermal expansion of the design elements.

These cyclones were distinguished by low height-to-diameter ratios of the cylindrical part of the body (~3.7) and area of the cross section of the body to the area of the cyclone intake pipe (~4.3), which limited the dedusting efficiency.

To increase the efficiency and reliability of the dedusting system, new single-stage cyclones were developed and the design of their suspension was improved (Fig. 2). Four cyclones were installed in the catalytic reactor, welded by the discharge pipes to the new gas collector and additionally attached to it with two vertical rods and one tilted rod.

The design of the suspender for the single-stage was simplified significantly and the problem related to additional stresses in thermal expansion of equipment parts was eliminated.

The new cyclones are characterized by a high (~5) length-to-diameter ratio of the cylindrical part of the body and the optimum ratio of the area of the cross section of the body to the area of the intake pipe. These geometric parameters are responsible for the high dedusting efficiency and the erosion resistance of the cyclones. The inner surfaces of the cyclones and the upper part of the dust-return stacks are lined with erosion-resistant concrete applied on an armored screen 25 mm thick.

The dust return stacks in the cyclones are equipped with cutoff valves of a more reliable and improved design. The cutoff plate suspender keeps it close to the edges of the catalyst discharge pipe. The more durable design of the restricting frame can withstand important cyclic loads at high temperatures.

To prevent coke deposits on the inside of the upper floor of the reactor and the outside of the gas collector in the cyclones, a ring steam distributor equipped with nipples with a through channel of variable section was installed in the reactor dome.

The new devices for introducing the feedstock and the reactor cyclones were installed during the overhaul of the unit in 2006. In determining the process indexes before and after overhaul of the unit, hydrotreated vacuum gasoil of almost the same quality was refined. Its average physicochemical properties are: density at 20°C of 895 kg/m^3; end point of 520°C; 5 vol. % content of cuts under 350°C; carbon residue (Conradson) of 0.17 wt. %; sulfur content of 0.28 wt. %.

The process was conducted with finely disperse SPECTRA-945 catalyst from Grace Davison. The activity of the equilibrium catalyst was 68 wt. % with the MAT Davison method.

After introducing the new feedstock input device, the yield of naphtha cut under 205°C increased by 2.9 wt. % (to 53.8 wt. %) with a 10 rel. % increase in the output of the unit. The octane number of the gasoline almost did not change and was 93.8 by the research method and 82.9 by the motor method.

As a result of introducing the new single-stage cyclones in the reactor, the particulate contaminant content in sludge deceased from 0.15 to 0.06 wt. % and the calculated dedusting efficiency reached 99.995%.

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CHEMMOTOLOGY

A MULTIFUNCTIONAL ADDITIVE FOR DIESEL FUELS

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UDC 665.7.038:665.753.4

A composition for a multifunctional additive was developed; in the concentration of 0.02-0.05 wt. %, it improves the quality of diesel fuel on six indexes simultaneously: it decreases the solid point and limiting filterability temperature with production of winter fuel on a summer fuel base for regions with a temperate climate; it ensures sedimentation stability at negative ambient temperatures; it improves antiwear properties; it increases the cetane number; it decreases exhaust smoke. A zero-waste, environmentally safe process for manufacturing the additive is proposed.

With more exhaustive refining of crude oil, the quality of diesel fuels (DF) is constantly worsening. It must satisfy the requirements of GOST 305–82 in Russia. According to this GOST, domestic DF are classified in four grades: "S" – summer, "W-35" and "W-45" – winter, and "A" – Arctic. These grades of fuels differ significantly in distillation, density, kinematic viscosity at 20°C, and other quality indexes.

In Europe and the USA, the DF quality requirements have increased sharply, including due to abrupt worsening of the environmental situation. In Europe, it is evaluated on correspondence to European standard EN 590, which distinguishes six grades of DF (A, B, C, D, E, F) with the same distillation but with different low-temperature characteristics.

In the Russian standard, the low-temperature properties are assessed with two indexes – the solid point t_s and the cloud point t_c , while they are evaluated in EN 590 with one index – the cold filter plugging point t_p, designated as CFPP.

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The new GOST R 52368–2005 (EN 590:2004) was developed in Russia in 2005 and allows bringing the quality of domestic DF close to the quality of European DF. The new GOST is intended for production of Euro Class DF. It is essentially the analog of EN 590 and also provides for manufacture of six grades of DF: with t_p from +5 to –20°C through every 5°. Each grade is subdivided into three types with a different sulfur content. It must be no greater than 350 mg/kg for type 1, 50 mg/kg for type 2, and 10 mg/kg for type 3.

Decreasing the sulfur content in DF unconditionally decreases emissions of harmful sulfur oxides, which improves the air quality but inevitably worsens the lubricity of the fuel, i.e., its antiwear properties. For this reason, the index "lubricity: corrected wear scar diameter at 60°C," which should be a maximum of 460 mm, was included in the new GOST, as in EN 590.

In Euro DF for regions with a temperature climate, the polycyclic aromatic hydrocarbon content must not exceed 11 wt. % and the cetane number of such fuels must not be less than 51 units, which also favorably affects the environment in our country. In addition, freely exporting Euro DF manufactured in Russia to any country in Europe is possible.

Of the many methods of improving the environmental indexes of operating diesels, the most common ones are: use of low-sulfur DF; incorporation of afterburners in the design of diesels; use of additives with different functional applications to improve the quality of DF, including the environmental characteristics [1-3].

In our opinion, the last method is the most expedient. However, there is no wide-scale production of DF additives in Russia today. For this reason, development and introduction of additives capable of improving the quality of DF with respect to several indexes simultaneously, including the environmental indexes, are critical.

We investigated the characteristics of production of a multifunctional additive that improves the low-temperature and environmental properties of DF and the environmental characteristics of diesel engines.

It was necessary to solve the following problems to do this:

- study the effect of the conditions of manufacturing the additive on its performance properties;
- determine the optimum conditions;
- study the mechanism of action of the additive in the DF;
- develop a zero-waste, environmentally safe manufacturing process for production of the multifunctional DF additive.

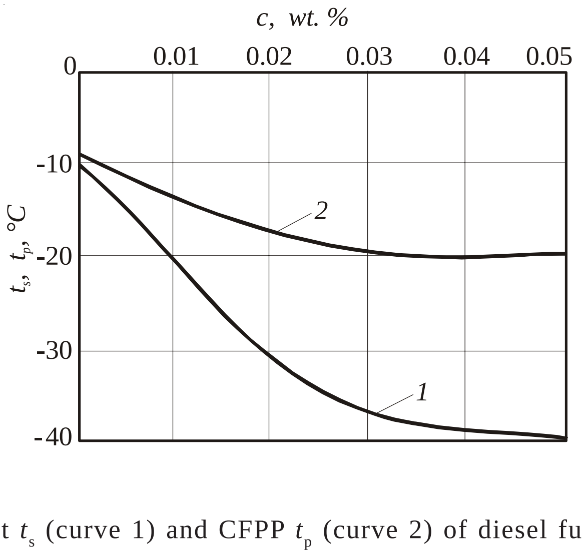

Fig. 1. Solid point t_s (curve 1) and CFPP t_p (curve 2) of diesel fuel as a function of concentration c of composite additive in it.

“Multifunctional additive” means an additive which simultaneously improves the following quality indexes after it is added to DF:

- sedimentation stability, i.e., it has a dispersing effect, preventing separation of the fuel at negative temperatures;
- lubricity (antiwear properties), i.e., it reduces the wear scar diameter to the values provided by the standard, a maximum of 460 mm;
- solid point t_s and cold filter plugging point t_p, i.e., it has the properties of a depressant, improving the low-temperature characteristics of the fuel;
- cetane number, i.e., it has the property of ignition promoter;
- exhaust smoke, i.e., it has antismoke properties.

Such an additive must obviously be a composite. Domestic, readily available products which could improve the DF indexes listed above were selected as its components based on the published data:

low-molecular-weight (number-average molecular weight of ~5000) copolymer of ethylene and propylene (NEP) – pour depressant;

succinimide S-5F – dispersion component;

calcium alkylsulfonate S-150 – antismoke component;

2-ethylhexyl nitrate (EHN) – ignition promotor;

synthetic fatty acid alkylamides (SFA AA) – a component that improves the antiwear properties.

The conditions for manufacturing an additive that ensured maximum effectiveness in the fuel in the minimum concentration were considered optimum. In studying the characteristics of production of the composite additive, the following optimum conditions were found: temperature of 40-42°C; time of 1-1.5 h; reaction mixture diluent – a mixture of DF with gasoline; content of components in the additive: up to 10% NEP; up to 5% S-5A; up to 15% S-150; up to 10% EHN; up to 10% SFA A; up to 50% diluent.

The additive obtained in these conditions does not separate, i.e., it has thermodynamic stability for a minimum of one year of storage and retains its performance properties.

The dependences of t_p and t_s of the fuel on the concentration of composite of the optimum composition are shown in Fig. 1. The additive, in the concentration of a total of only 0.025 wt. %, decreases the t_s of the fuel from –10 to –35°C and the t_p from –9 to –19°C.

DF with the optimum additive composition i.e., with the optimum content of S-5A dispersing component, passes the sedimentation stability test with the BASF method [4]. After holding DF with the additive in a cold chamber, the t_c does not change and t_p increases by 1°. We should note that DF without the additive does not have sedimentation stability: its low-temperature properties after holding in the cold vary by 5-9°, i.e., more than 2° greater than the change provided by the method for DF with sedimentation stability.

Table 1

DF with composite additive in concentration of, %	Wear scar diameter, mm	Cetane number
0	663	42
0.01	460	42
0.015	451	–
0.02	417	–
0.025	–	47
0.05	–	51

The additive thus allows obtaining winter grade DW_p based on summer DF with a maximum t_s of –30C and maximum t_p of –15°C and according to EN 590, based on grade C DF with a maximum t_p of –5°C and grade E DF with a maximum t_p of –15°C. Moreover, the composite additive ensures obtaining winter grades of DF with sedimentation stability.

It should be noted that the depressant component (NEP) alone added to DF in the same concentration as the composite does not result in winter grades of fuel with sedimentation stability. As a consequence, only the combined use of a pour depressant and dispersing component (NEP and S-5A) in the composite results in synergism and improvement of the quality of the base summer DF.

Data on the dependence of the antiwear properties of DF (wear scar diameter at 60°C) on the content of composite additive of the optimum composition are reported in Table 1. As should have been expected, these properties of low-sulfur (0.03 wt. % sulfur) DF do not satisfy the standard: for DF with no additive, the wear scar diameter is 663 mm, while it is a maximum of 460 mm in the standard [3].

Addition of a total of only 0.01 wt. % composite additive to DF produces a positive result. With a further increase in the additive content, the antiwear properties of DF continue to improve. The optimum concentration of the composite additive can be considered 0.01 wt. %. In this concentration, the wear scar diameter is 460 mm, which satisfies current requirements.

Data on the dependence of the cetane number (CN) of DF on the composite additive content are also reported in Table 1. As we see, the initial summer DF does not satisfy the requirements in GOST 305–82 for CN, and especially in EN 590: its CN is less than 45 units. When the composite additive is incorporated in a concentration of 0.025 to 0.05 wt. %, CN increases to 51 units, i.e., to the value required by the European standard and the new Russian standard GOST R 52368–2005 (EN 590:2004).

With respect to CN, a 0.025-0.05 wt. % concentration of composite in DF can be considered optimum.

The dependence of the decrease in exhaust smoke D*S* on the concentration and composition of the additive was investigated to assess the effect of the additive on the environmental indexes of operation of diesel engines. This parameter is characterized by the rate of the rate of formation of the soot particles contained in “black smoke” to their burn-out rate [1]. A D65N engine bench manufactured by Rybinsk Motor Works equipped with a BOSh smoke gauge was used for testing the additive.

The results obtained (Fig. 2) indicate that when the concentration of composite additive increased from 0.05 to 0.2 wt. %, the exhaust smoke decreased by 25-55%. The maximum decrease was attained with a

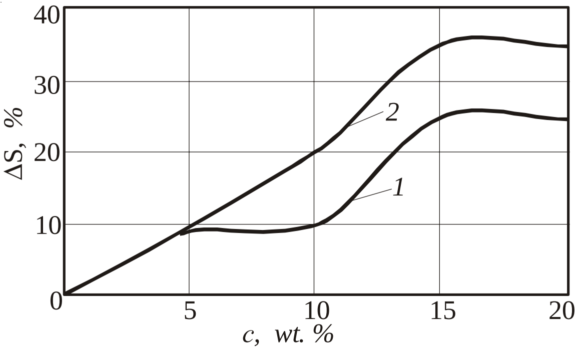

Fig. 2. Decrease in exhaust smoke ΔS as a function of component S-150 content *c* in the composite additive in different concentrations in diesel fuel: 1, 2) 0.05 and 0.1 wt. %, respectively.

composite containing 15-20 wt. % S-150 – the component responsible for antismoke properties. In the absence of this component, the additive had no antismoke properties.

The optimum ratio of the components in the additive thus allows considering it as a multifunctional additive that improves the quality of summer DF on six indexes simultaneously. This additive ensures obtaining fuel based on summer DF which is suitable for use in winter in regions with a temperature climate (corresponding to Euro grade C).

Moreover, due to the multifunctional additive, the fuel retains sedimentation stability at negative ambient temperatures and improves the environmental indexes of operation of a diesel by reducing exhaust smoke.

The mechanism of action of the multifunctional additive in DF, as the studies showed, is similar to the mechanism of action of SF in disperse systems [5, 6]. Due to the chemical nature of the component, the additive has the properties of a SF and the DF is a disperse system (DS) [7].

The additive, which is a SF, is adsorbed on the phase boundary, with the polar part oriented toward the polar phase and the nonpolar part is oriented toward the nonpolar phase. The surface tension on the phase boundary decreases and the performance properties of the fuel are stabilized and improved.

The experimental data obtained in measuring the surface tension of fuel DS with and without the additive and in determining the average disperse phase particle size by light scattering confirmed that the additive increases the dispersion (average disperse particle diameter decreased by almost two times in the presence of the additive) and stability of the fuel.

As a result of the studies, a scheme for a unit for periodic production of the additive was developed. Calculation of the material balance showed that the process is zero-waste, since it is conducted in a closed cycle, and is environmentally safe – there are no harmful emissions or wastewaters.

The additive is manufactured in the form of a 37-40% concentrate in DF. Since it improves the quality of DF on six indexes simultaneously and the environmental indexes of diesel operation, it can be considered a multifunctional additive with no analogs.

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CHEMMOTOLOGY. Theoretical Principles

STRUCTURAL CRITERION FOR THE ANTIWEAR PROPERTIES OF LUBE OILS

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UDC 621.833

A new concept was developed for evaluating the antiwear properties of lubricants – based on the value and distribution of the micromechanical characteristics in the near-surface layer deformed by friction. A diagnostic parameter for wear-fatigue processes is proposed: the micromechanical strength characteristic gradient, expressed in terms of the structural state criterion, formed in the near-surface layer of steel parts as a result of friction. This criterion can be used for assessing the antiwear and antiscuff properties of lube oils. Oils with high antiwear characteristics form minimal positive micromechanical property gradients in the near-surface layer of the metal.

Approximately 90% of the most dangerous damage to heavy-duty tribosystems in conditions of contact interaction with transmission of a working cyclic load (in sliding, rolling, slipping, etc.) is due to bearing fatigue. In [1], for example, in studying products of wear in lube oils for heavy-duty gears operating in the transmissions of traveling machines with the method in [2], the fatigue nature of their formation was established.

Wear particles with a maximum cross section of 3 mm subsequently pass through the stage of oxidation of metallic iron to oxide (Fe_2O_3-hematite), ferrous oxide (FeO–wüstite), and mixed oxide (Fe_3O_4–magnetite). Such particles can only be formed as a result of the appearance and coalescence of supercritical microcracks under the effect of repeated deformation of discrete microvolumes of the near-surface layer of the metal under roughness protrusions.

Dislocation processes of formation of supercritical microcracks and separation of metal particles are in turn regulated by the state of the structure of the metal in the friction-deformed microvolume. Classic tribological

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methods for studying the fine degradation processes characteristic of well-lubricated substances are not suitable. Such processes are localized in thin near-surface layers at the level of substructural changes in the crystal lattice, and this means that micro- and nanotechnologies must be developed and used for studying them.

The drawbacks of the existing methods of assessing the wear resistance of lubricated surfaces to cracking are due to the lack of investigation of the micromechanical properties and kinetics of degradation of the thin (under 8 mm) near-surface layer. Mechanical parameters characterizing the bulk properties of the material are used for tribotechnical engineering calculations. The properties of the thin near-surface layers differ significantly from the bulk properties, including because of the effect of lubricants.

Investigating such degradation is a complex problem in micromechanics and tribology on the micro and nano levels. Solving this problem will open up promising new ways of increasing the lifetime of machines while simultaneously reducing costs, tools, and materials in production and use.

Correctly selecting the materials for friction pairs and the lubricant is especially important in increasing the wear resistance of heavy-duty lubricated friction units. The principles for selecting lubricants for such units are laid out in the most detail by I. A. Buyanovskii et al. [3].

They propose determining the friction regime in the first stage with the criterion

$$\lambda = h_{min} / \left(R_{a1}^2 + R_{a2}^2\right)^{0.5}$$

where $h_{\min}$ is the minimum thickness of the lubricating layer in the gap between rubbing parts; R_{a1} and R_{a2} are the heights of microroughnesses on the working surfaces of these parts, and it is necessary to verify if necessary the work capacity of the lubricant based on its critical temperature Θ_{cr} in friction in the second stage.

Work capacity is ensured if the total temperature Θ_{S} in a heavy-duty bearing is no higher than the critical temperature Θ_{cr} of the lubricant in friction. This approach makes it possible to purposefully correct the chemical composition of the lubricant.

In consideration of the large number of lubricants of the same type where these criteria can coincide or be very close in value in use, we propose assessing the service properties of a lubricant by evaluating the substructural criterion that characterizes its antiwear properties.

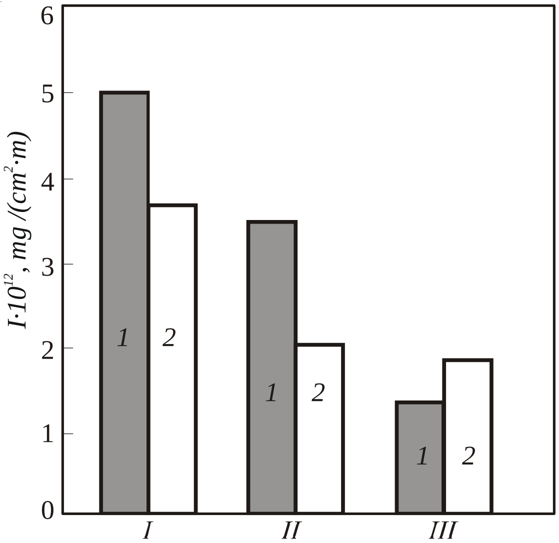

Fig. 1. Intensity I of wear of samples of steels in transmission oils: 1) according to TU 32TsT-551–84; II) TSp-14gip; III) TAP-15V; 1, 2) 25XGT and 18X2H4MA steel.

We hypothesize that the intensity of wear is not a function of the thickness of the oil layer that separates the friction surfaces and its temperature parameters alone, but also of the physicochemical effect of the lubricant on the strength characteristics of steel in the thin near-surface layer of a contacting friction pair.

This criterion is thus a binary service characteristic of a lubricant. One of its constituents is conditional upon the friction parameters in the gear and the other is conditional upon the wear parameters of the contacting friction surfaces.

According to the findings of a comprehensive study of lube oils of the same type that include tribotechnical and x-ray studies by layers, lube oils of different chemical composition affect the strength properties of the metal in the near-surface layer in friction differently, which also causes a different degree of wear in the samples as well.

An x-ray structural study of the state of the structure of the metal in the thin near-surface layer was performed before and after the tribotechnical tests on samples of steels 25XGT and 18X2H4MA with the following mechanical characteristics: flow stress σ_f, respectively 1100 and 850 MPa, fatigue limit σ_f of 1500 and 1150 MPa. The hardness of the friction surfaces of the samples after nitrocementation, quenching, and low-temperature tempering was *HRC* 58-60 for roughness of $R_a = 1.25$ μm.

The microstructure of the near-surface layer of samples of both steels was almost the same: fine-needled martensite, sometimes with traces of residual austenite, whose amount decreased over the depth, which corresponded to the parameters of real gears.

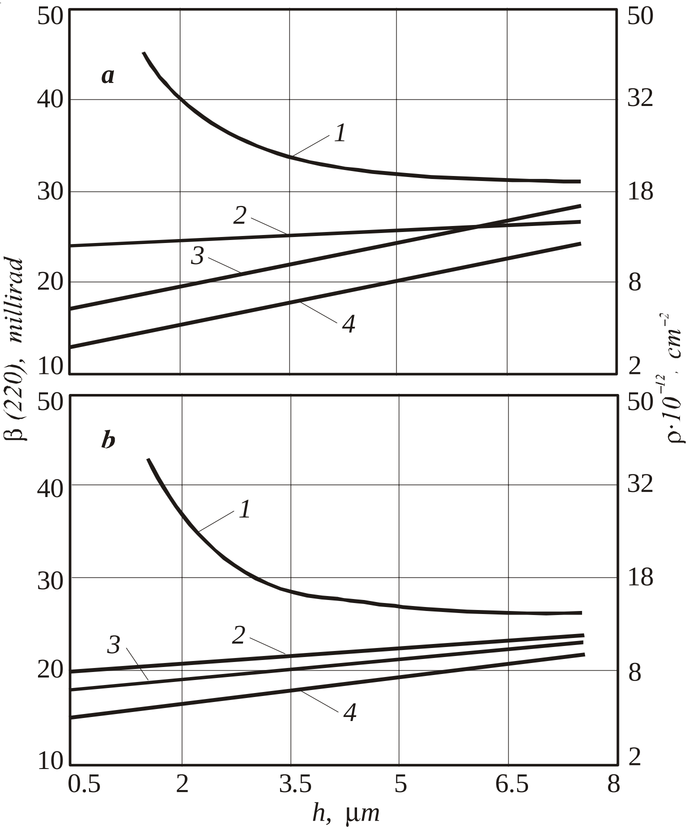

Fig. 2. Change in α-phase x-ray line width β (220) and dislocation density ρ over depth of the near-surface layer of steels 25XGT (a) and 18X2H4MA (b): 1) before friction; 2, 3, 4) after friction in TAP-15V, TSp-14gip oils and according to TU 32TsT-551–84.

The antiwear properties of lubricants were investigated on a SMTs-2 friction machine with the roller–roller scheme at contact pressure of 740 MPa, overall rolling velocity ν_S = 3.5 m/sec, and relative slipping velocity ν_{sl} = 0.7 m/sec. Such load–velocity friction regimes are similar to the most characteristic friction regimes in the real gears in the axial reduction gears of ADM traveling machines at a speed of 40 km/h with the load on the platform.

The results of the tribotechnical tests of samples of steels in TAP-15B, TSp-14gip transmission oils and in lube oil according to TU 32TsT-551–84 are shown in Fig. 1.

The diffractometric studies of newly prepared samples of steels 25 XGT and 18X2H4MA showed that in the initial state, their surface layers have a very high density of dislocation agglomerates that decreases exponentially to 8 mm over the depth of the investigated layer (Fig. 2a and b, curves 1).

Such a dislocation picture of the near-surface layers of these steels in the initial state reflects the proportional change in the micromechanical characteristics of the steel in the layer. Figure 2a and b shows that in the initial state, the near-surface layers of both steels have an important negative mechanical property gradient over the depth of the layer. This indicates the existence of work hardness in the near-surface layer after shotblast treatment of the surfaces of the gears and adequate roller samples.

The studies [1] of the kinetics of the structural state of the near-surface layers of metal in friction make it possible to determine the real local flow stresses in friction-deformed near-surface layers with data from x-ray analysis:

$$\sigma_{f(h)} = \alpha G b \rho^{0.5}$$

where $\sigma_{f(h)}$ is the real value of the yield point in the microvolume investigated; α is a coefficient; G is the shear modulus; b is the Burgers vector; ρ is the density of dislocations in the investigated microvolume.

The method of determining the density of dislocations r is based on its quadratic dependence on x-ray line width β:

$$\rho = A\beta^2$$

where A is a coefficient dependent on the elastic properties of the metal, dislocation characteristics (Burgers vector), etc.

According to L. I. Mirkin and Ya. S. Umanskii, $A = 2\times10^{16}$ cm^{-2} for aluminum, tungsten, molybdenum, iron, and their alloys. For steels, the real value of the yield point in the investigated microvolume of near-surface layer using the measured x-ray line width can be represented as:

$$\sigma_{f(h)} = 1.4\cdot10^{8}\alpha G b \beta$$

The difference in the structures of steels 18X2H4MA and 25XGT in the initial state is due to the approximately 6 mm difference in the dislocation density in the depth of relative stabilization of the structural parameters: it is higher for steel 25XGT (see Fig. 2a, curve 1) than for steel 18X2H4MA (see Fig. 2b, curve 1). These differences are probably due to the difference in the chemical composition of the steels and consequently the strength characteristics of the near-surface layers after mechanical and chemical and thermal treatment of the samples in the same conditions.

After testing for 8 h in TAP-15V and TSp-14gip transmission oils and lube oil according to TU 32TsT-551–84, the near-surface layers of the samples again underwent an x-ray structural study.

As Fig. 2a and b shows. the picture of the change in a phase x-ray line width b (Miller index: 220) and corresponding dislocation densities r was similar for both steels.

The dislocation picture in the thin near-surface layers of steels 18X2H4MA and 25XGT changed for all of these oils after testing: the dislocation density and correspondingly the mechanical strength decreased. In all cases, the near-surface layers acquired positive mechanical property gradients so that the probability of cohesive bulk tears in the oil film and coalescence of friction surfaces was minimal.

The analysis of the change in the characteristics of the structure over the depth of the near-surface layer of steels 18X2H4MA and 25XGT showed the mechanism of the change in the gradients of dislocation densities r and type II microstresses (D*a/a*) with a change in the size of regions of coherent scattering: more intensive surface wear corresponds to larger near-surface layer softening gradients.

This finding shows that for the same kind of wear (mechanochemical) of surfaces in conditions of a boundary friction regime, the rate of accumulation and advance of fatigue microcracks, regulated by external factors (in the given case, different oils), differs. It is necessary to note the important difference between the negative and positive gradients of the change in the state of the structure in the near-surface layers of both steels.

The negative gradients at a depth of up to 8 mm have the form of a diminishing exponential function and the positive gradients in all cases have the shape of a linear function of the type:

$$\boldsymbol{\rho = a + bh}$$

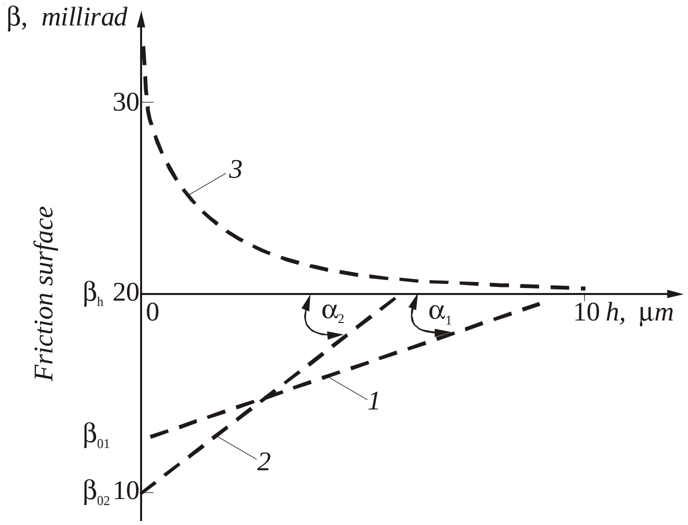

Fig. 3. Generalized characteristic changes in x-ray line width b over depth a of the near-surface layer of steel samples: 1, 2) after friction in lube oils of different chemical activity; 3) in initial state before friction; b_h – x-ray line width corresponding to the maximum depth *h* of the physicochemical effect of triboprocesses in a gear (triboprocesses in a gear below this layer do not affect the state of the structure of the steel); b_{01}, b_{02} – x-ray line width corresponding to the minimum identifiable distance from the surface after friction of the same steel samples in lube oils of different chemical activity for the same load-velocity friction parameters.

where *a*, *b* are coefficients; *h* is the distance from the surface.

For 25XGT steel after working in lube oil according to TU 32TsT-551–84, the dislocation density was $6 \cdot 10^{12}$ cm^{-2} at a depth of 0.5 mm from the surface and 2.310^{12} cm^{-2} at a depth of 7 mm (see Fig. 2a, line 4). The intensity of wear in this oil was equal to $5.2 \cdot 10^{-12}$ mg/($cm^2 \cdot m$) – see Fig. 1.

The lowest wear intensity of steel 25XGT of $1.3 \cdot 10^{-12}$ mg/($cm^2 \cdot m$) was observed in work in TAP-15V oil. In this oil, the dislocation density and micromechanical characteristics in the near-surface layer of steel 25XGT was highest at the depth of 0.5 mm in comparison to the other oils.

The smallest slope of line 2 in Fig. 2a reflects the specific capacity of TAP-15V oil to soften the structure of steel 25XGT with a lower intensity but a greater depth. The dislocations were more uniformly distributed in the friction-deformed near-surface layer and did not accumulate in a small volume, which accelerated formation of submicrocracks over the sliding surfaces.

Due to its chemical composition, TSp-14gip transmission oil provides for an important gradient of the change in the state of the structure over the depth of the thin near-surface layer for triboconjugation from steel 25XGT (see Fig. 2a, line 3). However, in comparison to the oil according to TU 32TsT-551–84, it provides a dislocation density gradient in higher regions and consequently higher micromechanical characteristics of the near-surface layer of the steel, and decreases the intensity of wear-fatigue degradation (wear) of the steel from $5.2 \cdot 10^{-12}$ to $3.8 \cdot 10^{-12}$ mg/($cm^2 \cdot m$), see Fig. 1.

Similar distribution of dislocation densities as a function of the type of lube oil is observed in the structure of steel 18X2H4MA. However, for this steel, in comparison to steel 25XGT, the scattering of the wear intensity values as a function of the chemical composition of the oil is smaller, which is probably due to the higher content of alloying elements: 1.5% chromium, 4.2% nickel, 0.4% molybdenum.

It follows from these results that the more the oil medium affects the decrease in the micromechanical characteristics in the thin near-surface layer of steel, the greater the surface wear will be.

The change in the state of the structure in friction also affects the depth of the near-surface layer, i.e., a characteristic gradient of the change in the state of the structure of local micromechanical characteristics over depth *h* of the active near-surface layer of the steel corresponds to each lube oil in the same loading-velocity friction regimes for steel samples.

As a consequence, this gradient, expressed in terms of x-ray line width b, is a stable characteristic for evaluating the effect of the environment on the distribution of the micromechanical characteristics of the material in a near-surface layer deformed by friction.

Table 1

Lube oil	β_0, millirad	β_h, millirad	K_s	$I \cdot 10^{12}$, mg/($cm^2 \cdot m$)
Steel 25XGT				
According to TU 32TsT-551–84	13	30	2.347	5.2
TSp-14gip	17		1.791	3.6
TAP-15V	24		1.251	1.5
Steel 18X2H4MA				
According to TU 32TsT-551–84	15	25	1.676	3.8
TSp-14gip	18		1.395	2.2
TAP-15V	20		1.262	1.9

The generalized dependences of the characteristic changes in the x-ray line width over the depth of the active near-surface layer of steel after friction in lube oils of different chemical activity and in the initial state are shown in Fig. 3. Lines 1 and 2 obviously correspond to gradients of the change in the state of the structure of the near-surface layer of the steel as a function of the properties of the oil used.

Angle a between the normal to the surface and the direction of the change in x-ray line width b quantitatively characterizes the magnitude of these changes. X-ray line width β, depth h of the effect of the environment, and angle α thus completely reflect the physicochemical effect of the lube oil on the micromechanical characteristics of the near-surface layer deformed by friction.

Based on these data, criterion K_s of the structural state which reflects the effect of physicochemical processes in a lubricated tribocontact on accumulation and distribution of imperfections in the crystal lattice (wear fatigue processes) of the friction-deformed near-surface layer:

$$\boldsymbol{K_s = \beta_h / \beta_0 \cos\alpha}$$

The results of the tribotechnical and x-ray studies shown in Figs. 1 and 2 are summarized in Table 1. The numerical values of substructural criterion K_s are also reported there.

The dependences between the parameters were plotted to analyze the correlation between the intensity of wear of the steel samples in the different oils and the state of the structure in the thin near-surface layers, expressed in terms of the criterion of the structural state of these samples (Fig. 4).

These dependences are straight lines and are individual for each steel, which also follows from the results of the tribotechnical tests (see Fig. 1) and x-ray studies (Fig. 2). It is perfectly evident that in comparison to steel 18X2H4MA, the fine crystal structure of the near-surface layer of steel 25XGT is more sensitive to the kind of lubricant. This is objectively reflected in the intensity of its wear.

One of the basic advantages of the substructural state criterion is the unambiguous reflection of the magnitude and sign of the mechanical property gradient (stress state of the structure) in the near-surface layer of the steel. When $\beta_h > \beta_0$, $K_s > 1$, when $\beta_h = \beta_0$, $K_s = 1$, and when $\beta_h < \beta_0$, $K_s < 1$. As a consequence, when $K_s > 1$, the

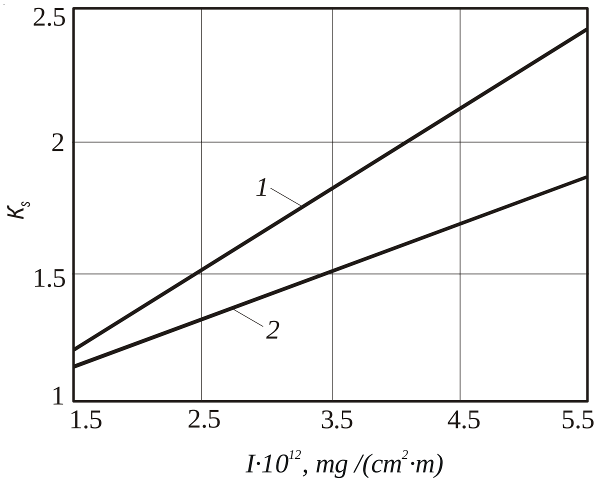

Fig. 4. Correlation between criterion K_s of the structural state and intensity I of wear of samples of steels 25XGT (1) and 18X2H4MA (2) in transmission oils.

near-surface layer of the steel has a positive mechanical property gradient, and when $K_s < 1$, it is negative over the depth.

Our proposed criterion K_s of the structural state is especially important in calculations of the intensity of wear for boundary lubrication conditions and more severe conditions. It objectively characterizes the strength distribution in the friction-deformed bulk of a metal. In boundary friction, the load is not only perceived by the lubricant film but also by juvenile sections of the metal at sites where the film has ruptured, where a metallic bond can form.

If in the condition of $K_s < 1$, i.e., there is a negative mechanical property gradient over the depth of the near-surface layer, coalescence and cohesive separation of some volume of metal from the surface, i.e., scuffing, will be the results of the metallic bond.

If $K_s > 1$, i.e., there is a positive mechanical property gradient, mechanical destruction of bridge bonds of juvenile surfaces directly on the surface – a mechanically weaker region than the underlying layers – will be the result of the metallic bond of juvenile surfaces. The weaker the upper layers are, i.e., the more K_s is greater than one, the higher the intensity of friction surface wear.

Mechanical separation of a discrete volume of metal (wear particles) at the site of formation and coalescence of supercritical microcracks in the friction-deformed near-surface layer will take place with a positive micromechanical property gradient.

As a consequence, the preferred value of K_s is unity. At this value of the criterion, the gradient of the change in the mechanical properties over the depth of the near-surface layer will be equal to zero, which will exclude cohesive tears of surface fragments in the metallic bond if the oil film ruptures. In addition, in the region of positive mechanical property gradients, the maximally high mechanical characteristics of the friction surface which prevent elevated mechanochemical wear are ensured.

Such qualitative characteristics of the near-surface layer can be attained as a result of optimum selection of active additives to base oils for the concrete steels and friction regimes. Our lube oil provides for the lowest wear of friction surfaces for samples of steel 25XGT and is characterized by a significant angle α, which indicates reserves in improvement of the lubricant composite.

The role of lube oil in the triboprocess thus also consists of preventing accumulation of elastic energy in the thin near-surface layer in the physicochemical reaction of the oil with the surface of the metal by facilitating emergence of dislocations on the surface. Microcracks can then be annihilated (collapsed).

Cyclic stress relaxation takes place in the near-surface layer of a friction-deformed metal. The energy of the friction generated in a gear circulates from without into the surface layer and back to the oil layer, organizing it.

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RESEARCH

MATHEMATICAL MODELING OF PLATFORMING

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UDC 665.664.4

Catalytic reforming of low-octane naphtha cuts into a high-octane component of commercial gasoline is conducted in a three- or four-reactor block with a stationary bed of solid (pelleted) Pt,Re/γ-Al_2O_3 catalyst. This catalyst is sensitive to moisture and sulfur and nitrogen compounds. For this reason, the naphtha cut that distills within 85-180°C undergoes hydrotreating at high temperature and a cut containing hydrocarbons from the three basic classes is obtained: paraffins, naphthenes, and aromatics without contaminants of sulfur and nitrogen compounds. The naphthene hydrocarbons consist of cyclohexane and cyclopentane fractions.

Aluminum oxides can exist in the form of eight modifications: λ-Al_2O_3, ä-Al_2O_3, ÷- Al_2O_3, è- Al_2O_3, η-Al_2O_3, β-Al_2O_3, γ-Al_2O_3, α- Al_2O_3. In industry, only γ–Al_2O_3 is used as a support for platforming catalysts. This oxide is most stable at temperatures of 500-600°C and it turns into a- Al_2O_3 at 700°C and higher.

Ensembles of polyhedrons in $\{AlO_4{\cdot}AlO_6\}$ containing $[AlO_4]$-tetrahedrons and $[AlO_6]$-octahedrons bound at the apices in its crystal lattice are an important property of g- Al_2O_3. According to the theory of catalysis by polyhedrons, the $[AlO_4]$-tetrahedron exhibits high catalytic activity in cracking and isomerization of hydrocarbons due to the elevated acceptor capacity, acidity, and chemisorption capacity.

The α-Al_2O_3 modification is a closely packed lattice of combinations of ensembles of $\{AlO_6{\cdot}AlO_6\}$-octahedrons bound at the apices, edges, or faces. These ensembles exhibit insignificant catalytic activity in the reactions indicated above. For this reason, α- Al_2O_3 is not used as a reforming catalyst support.

The acid or acceptor properties of γ- Al_2O_3 improve when it is combined with zeolites in the H form. The lattice of the zeolites is constructed of ensembles of $\{AlO_4{\cdot}SiO_4\}$-tetrahedrons. In these ensembles, the silicon oxygen tetrahedron plays the role of a promoter, increasing the acceptor strength of the aluminum oxygen tetrahedron.

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Reforming catalysts must exhibit activity not only in reactions of the "acid" type (cracking, isomerization, dismutation, etc.), but also in dehydrogenation, hydrogenating, and dehydrocyclization reactions. The metal phase on the surface of the support – aluminum oxide, zeolite, or a mixture of both – give the catalyst these properties.

The metal phase is applied on the surface of the support from aqueous solutions of the corresponding salts. After drying, heat treatment, and reduction, it consists of discrete particles 1-10 nm in size. It also contains metal particles such as $[PtPt_4]^0$, $[PtPt_4]^{2+}$, or $[MeMe_4]^0$, $[MeMe_4]^{2+}$, where Me is rhenium, palladium, tin, etc.

As a consequence, the atoms and ions in the metal phase are packed in tetrahedrons bearing a different charge. These tetrahedrons have elevated donor properties and catalyze dehydrogenation of naphthenes and dehydrocyclization of *n*- and isoparaffins, as well as hydrogenation of coke deposits on the surface of the catalyst.

Catalysts prepared by the impregnation method exhibit multifunctional properties after sulfuring. They induce so-called fast reactions – dehydrogenation and hydrocracking – as well as slow reactions – dehydrocyclization and dehydroisomerization of alkylpentanes.

After halogenation, the catalysts undergo sulfiding in a stream of hydrogen sulfide or sulfur-containing compounds to regulate the rate of hydrocracking and dehydrocyclization of paraffins, i.e., to decrease the rate of the first reaction and increase the rate of the second reaction.

It follows from the above that platforming of low-octane naphtha cuts in the presence of multifunctional catalysts is a multiparametric process, and the degree of freedom of variation of the parameters is significant with respect to their number and the limits of variation. Creating a mathematical model for such a complex process is more an art than a rigorously defined problem. In operation of reforming units, the laws of random interactions of the parameters, which have been determined in the simplest case, play an important role.

Statistical and determined sets of parameters thus interact in conditions of reforming of naphtha cuts on multifunctional catalysts. The number and degree of variation of the parameters are a function of the design and operating conditions of the unit – ideal displacement, ideal mixing, or intermediate regime of flow of the reagents through the reactor.

An important number of mathematical models of the platforming process is described in the literature; they usually reflect the level of knowledge of the investigator concerning the given problem and his predilection for a particular method of creating such models – empirical or theoretical. For this reason, there are no mathematical models that are invariant with respect to the content and set of equations.

Creation of a mathematical model of the platforming process in our case included the following stages:

- accumulating a significant mass of experimental data from an industrial unit concerning the effect of different parameters on the quality and yield of reformate and hydrocarbon gas;
- processing these data to reveal certain patterns by a statistical-mathematical method (method of least squares);
- constructing tables and graphs to determine the correspond correlations between the parameters and then analyzing them;
- creating a kinetic scheme of the process;
- deriving kinetic equations for stationary and nonstationary process conditions and for a heterogeneous system with consideration of the hydrodynamic regime;
- establishing the adequacy of the kinetic equations with experimental dependences using kinetic constants determined with the experimental data.

KINETIC SCHEME OF REFORMING

In creating the kinetic scheme, it was assumed that the following reactions of transformation of hydrocarbons of the paraffin, naphthene, and aromatic classes take place on Pt,Re/γ- Al_2O_3 catalyst: dehydrogenation of naphthenes, dehydroisomerization of alkylpentanes into naphthenes followed by dehydrogenation, dehydrocyclization of paraffins and destructive isomerization of *n*-paraffins. These reactions can take place parallelly, parallelly-sequentially, or in one stage.

The kinetic scheme of catalytic reforming of the naphtha cut was represented as:

$$\mathrm{ACP} \xrightarrow{\mathrm{k}_1} \mathrm{Np} \xrightarrow{\mathrm{k}_3} \mathrm{Ar} + \mathrm{v}_1\mathrm{H}_2 \xrightarrow{\mathrm{k}_4} \upsilon_3\mathrm{G} + \upsilon_4\mathrm{C} \tag{1}$$

$$n-\mathrm{PR} \rightarrow \left| \begin{array}{l} \xrightarrow{\mathrm{k}_2} \mathrm{Np} \\ \\ \xrightarrow{\mathrm{k}_5} i-\mathrm{PR} + \upsilon_2\mathrm{H}_2 \xrightarrow{\mathrm{k}_6} \upsilon_3'\mathrm{G} + \upsilon_4'\mathrm{C} \end{array} \right. \tag{2}$$

where ACP are alkylcyclopentanes; Np are naphthenes; Ar are aromatics; G is hydrocarbon gas; C is coke; *n*-Pr, *i*-Pr are *n*- and isoparaffins; k_1-k_6 are the rate constants of the corresponding stage of the process; ν_1–ν_4, ν_3', ν_4' are stoichiometric coefficients.

KINETIC EQUATIONS IN GENERAL FORM

Catalytic reforming of the naphtha cut in the presence of hydrogen-containing hydrocarbon gas is conducted: in the gas phase of the reaction mixture; in a stream; in conditions of ideal displacement of the reaction mixture over a stationary catalyst bed. In industrial conditions, it takes place in stationary conditions after a fixed time.

Based on these assumptions, the equations for the rate of conversion of hydrocarbons of the corresponding classes with consideration of the basic postulate of chemical kinetics for schemes (1) and (2) are:

for *n*-paraffins

$$\frac{dn_{n\text{-}\mathrm{Pr}}}{Sdl} = (k_2 + k_5)\delta_{n\text{-}Pr} \tag{3}$$

for isoparaffins

$$\frac{dn_{i\text{-}\mathrm{Pr}}}{Sdl} = k_5\delta_{n\text{-}\mathrm{Pr}} - k_6\delta_{i\text{-}\mathrm{Pr}} \tag{4}$$

for naphthenes

$$\frac{dn_{Np}}{Sdl} = (k_1 + k_2)\delta_{n\text{-}Pr}k_3\delta_{Np} \tag{5}$$

for aromatic hydrocarbons

$$\frac{dn_{Ar}}{Sdl} = k_3 \delta_{Np} - k_4 \delta_{Ar} \tag{6}$$

for hydrocarbon gas

$$\frac{dn_{G}}{Sdl} = k_6 \delta_{i\text{-}\mathrm{Pr}} \delta_{H_2} + k_4 \delta_{Ar} \delta_{H_2} \tag{7}$$

where *n* is the molar feed rate for the corresponding hydrocarbons; *S, l* are the surface area and length of the catalyst bed; ä is the fraction of the surface of the catalyst occupied by the corresponding hydrocarbons and hydrogen.

After transformations, Eqs. (3)-(6) become:

for *n*-paraffins

$$n_A^0 \frac{d(x-y)}{Sdl} = k_1^* (1 - x - z) \tag{8}$$

for isoparaffins

$$n_A^0 \frac{d(z-u)}{Sdl} = k_1^* (1 - x - z) - k_6^* (\gamma_{n-Pr} + z - u) \tag{9}$$

for naphthenes

$$n_A^0 \frac{d(x-u)}{Sdl} = k_1^* (1 - x - z) - k_3^* (\gamma_{Np} + x - y) \tag{10}$$

for aromatic hydrocarbons

$$n_A^0 \frac{d(y-u)}{Sdl} = k_3^* (\gamma_{Np} + x - y) - k_4^* (\gamma_{Ar} + y - u) \tag{11}$$

where n^0_A is the molar feed rate of the initial naphtha cut; *x, y, z, u* are the fractions of substances converted and obtained; k_1^* are the rate constants of the corresponding stages of the process, including the real rate constants and adsorption coefficients; γ is the ratio of the number of moles of the corresponding classes of hydrocarbons to the number of moles of the initial naphtha.

The following simplified kinetic equations for transformation of hydrocarbons of each class are obtained by integration of Eqs. (8)-(11):

for paraffins

$$\boldsymbol{n}_{\boldsymbol{A}}^{0}(1-\boldsymbol{x}-\boldsymbol{y})=\boldsymbol{k}_{1}^{*} \tag{12}$$

for isoparaffins

$$\boldsymbol{n}_{\boldsymbol{A}}^{0}(\gamma_{\mathbf{i-Pr}}+\boldsymbol{z}-\boldsymbol{u})=\frac{\boldsymbol{k}_{1}^{*}}{\boldsymbol{k}_{1}^{*}-\boldsymbol{k}_{6}^{*}}\left(\boldsymbol{n}_{\boldsymbol{A}}^{0}\mathbf{e}^{-\boldsymbol{k}_{1}^{*}/\boldsymbol{n}_{\boldsymbol{A}}^{0}}-\boldsymbol{k}_{6}^{*}\right) \tag{13}$$

for naphthenes

$$\boldsymbol{n}_{\boldsymbol{A}}^{0}(\gamma_{\mathbf{Np}}+\boldsymbol{x}-\boldsymbol{u})=\frac{\boldsymbol{k}_{1}^{*}}{\boldsymbol{k}_{1}^{*}-\boldsymbol{k}_{6}^{*}}\left(\boldsymbol{n}_{\boldsymbol{A}}^{0}\mathbf{e}^{-\boldsymbol{k}_{1}^{*}/\boldsymbol{n}_{\boldsymbol{A}}^{0}}-\boldsymbol{k}_{3}^{*}\right) \tag{14}$$

for aromatic hydrocarbons

$$\boldsymbol{n}_{\boldsymbol{A}}^{0}(\gamma_{\mathbf{Ar}}+\boldsymbol{x}-\boldsymbol{u})=\boldsymbol{k}_{4}^{*} \tag{15}$$

The rate constants k_1^*, preexponential factors in the Arrhenius equation, and activation energies were calculated with the experimental kinetic dependences using the Arrhenius equation.

The dependences of the rate constants on the temperature in Arrhenius form have the following concrete form:

$$\boldsymbol{k}_{1}^{*}=17700\,\mathbf{e}^{-26000/RT}$$
$$\boldsymbol{k}_{3}^{*}=2.34\cdot 10^{7}\,\mathbf{e}^{-62300/RT}$$
$$\boldsymbol{k}_{4}^{*}=21000\,\mathbf{e}^{-28000/RT}$$
$$\boldsymbol{k}_{6}^{*}=56\,\mathbf{e}^{-2500/RT}$$

where R is the universal gas constant; T is the temperature.

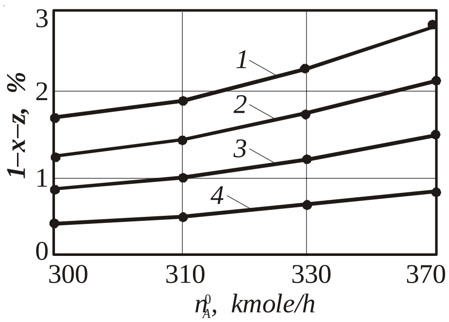

Fig. 1. Residual content 1–*x*–*z* of *n*-paraffins in reformate as a function of the molar feed rate n^0_A of naphtha cut into the reactor at the temperature of: 1) 480°C; 2) 490°C; 3) 500°C; 4) 510°C.

The fit of these equations to the experimental data can be judged on the example of the graphic dependence of the residual content of *n*-paraffins in the reformate on the molar feedstock feed rate n^0_A into the reactor (see Fig. 1). As we see, the experimental data – points – coincide with the curves calculated with Eq. (12).

According to this mathematical-kinetic model, hydrocarbons of different classes are transformed at different rates in the reforming conditions.

The experimental values of the rate constants and activation energies are in the order:

$$\boldsymbol{k}^{*}_{\mathbf{Np}} > \boldsymbol{k}^{*}_{\mathbf{n-Pr}} > \boldsymbol{k}^{*}_{\mathbf{Ar}} > \boldsymbol{k}^{*}_{\mathbf{i-Pr}}$$

$$\boldsymbol{E}_{\mathbf{Np}} > \boldsymbol{E}_{\mathbf{Ar}} > \boldsymbol{E}_{\mathbf{n-Pr}} > \boldsymbol{E}_{\mathbf{i-Pr}}$$

According to these data, dehydrogenation of naphthenes and transformation of aromatic hydrocarbons are fast processes and dehydrocyclization and destructive isomerization of *n*-paraffins are slow processes.

As a consequence, the kinetic model can be used to not only refine the kinetic scheme of a very complex process but also to determine the distribution of the reagents by kinetic rates with identification of fast and slow reactions.

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THE STRUCTURE OF ADDITIVES WITH A SUPERSTOICHIOMETRIC CATION CONTENT

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UDC 665.733.035

The previously* advanced hypothesis that additives with superstoichiometric cation content are solutions of macromolecular substances in hydrocarbon medium needs more detailed theoretical substantiation.

The generally accepted technology for production of highly and ultrabasic alkaline-earth cation sulfonates requires respecting the following conditions:

- presence of a duosol (a mixture of methanol and toluene is most common) of defined composition in the amount of ~50% in reaction mass;
- conducting carbonation with intensive mechanical stirring to disperse the carbon dioxide;
- adding small amounts of inorganic salts or organic compounds containing hydroxyl or carboxyl groups in many cases to correct the viscosity.

Products even with a base number of 500-600 mg KOH/g can be synthesized in these conditions. Elementary calculations show that the metal carbonate content in them is over 50%.

The homogeneity (transparency) and stability of 10% solutions of these additives in "poor" solvents (heptane, hexane, light Nefras) cannot be explained by the heterogeneity of these colloidal structures – systems which are between elastic bodies and Newtonian fluids based on their properties.

Let us consider the conditions listed above from the point of view of the possible formation of polymer-like molecules consisting of an organic part and a polymer chain of counterions. Use of a duosol (methanol and

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toluene) is evidently the most important condition. Mixed media are the most “useful” solvents, since they allow flexibly combining the ability to stabilize the hydrophilic and hydrophobic compounds present in the reaction mass.

We will use the following information to explain the effectiveness of this mixed medium.

Based on the change in the relaxation time of molecules of monohydric alcohols, it was found that polymer associates of linear structure (up to seven molecules) are present in alcohols together with free molecules. These associates do not form the three-dimensional networks of hydrogen bonds characteristic of water and glycols – dihydric and polyhydric alcohols.

Dissolution of nonpolar organic compounds in methanol, toluene for example, has no structuring or destructuring effect on the alcohol molecules. An important difference between monohydric alcohols and glycols is manifested here. In dissolution of nonpolar compounds in polyhydric alcohols, relaxation of the alcohol molecules increases, which indicates their ability to form three-dimensional networks of hydrogen bonds and exhibit structuring and destructuring effects.

Actually, in plotting the dependence of the refractive index n_D^{20} of a mixture of methanol and toluene (prepared by dissolving methanol in toluene) on its composition, we obtained a straight line. The value of n_D^{20} in the segment of the change in the concentration of toluene in the mixture from 85 wt. % to zero (pure methanol) changes additively to the composition of the mixture and in the segment from 100% (pure toluene) to ~95 wt. %, it changes nonadditively. In the range of concentrations of toluene from ~85 to ~95 wt. %, the absolutely transparent solution becomes optically nontransparent, so that it is not possible to determine the value of n_D^{20}.

The existence of a region in which the methanol–toluene mixture does not form an isotropic liquid medium is due to the large difference in the densities of the cohesive energy of the components of the mixture (it is more than twice as high in methanol). The cohesive energy density is a measure of the energy required for formation of a “cell” in the solvent medium large enough to place a molecule of the dissolved substance in it.

In dissolving methanol in toluene, molecules of methanol are easily introduced in the “cells” between the molecules of toluene. As the concentration of methanol increases, its molecules begin to associate according to a dipole-dipole mechanism and the deviation from additivity observed on the initial segment is probably due to this.

With a further increase in the concentration of methanol from ~5 to 15 wt. %, the solutions become optically nontransparent. This is also most probably due to formation of a new structure – placing of toluene molecules in “cells” between associates of methanol molecules, which results in anisotropy of the solutions.

In view of separation of water during carbonation, let us consider the properties of the water–methanol system. Extrema are observed on the curves of a number of physical properties (heat of mixing, partial molar volume, water activity coefficient, enthalpy and entropy of solvolysis, chemical shifts of OH^{-}group protons in the NMR spectra, noise absorption, viscosity, etc.) as a function of the composition of the mixtures of water and alcohols.

Our dependence of the refractive index n_D^{20} on the composition of the solution of methanol in water is also extremal: for a 45% solution of methanol in water, n_D^{20} is equal to 1.3405; it is 1.3290 for methanol, and 1.3330 for water. This indicates formation of a structure in water that is destroyed when the concentration of methanol is increased.

The concept concerning the similarity of these structures to crystalline clathrate hydrates is the most developed. According to this concept, at a low concentration of methanol, each molecule is surrounded by a polyhedron of a large number of water molecules. Construction of these shells is completed at the extremal point.

On further addition of methanol, these structures coalesce with formation of complex polyhedrons with common faces which are then destroyed.

In the carbonation process examined here, the water content in the reaction mass increases from 3-4 to 20-30% (in methanol) as a function of the base number level attained. The entire process is thus conducted in the unstable region of formation of clathrate hydrate structures.

A water–methanol–toluene system is actually formed during carbonation. In studying the behavior of methanol–toluene solutions, it was found that a 20-30% solution of methanol in toluene begins to separate when 10-13% water (in methanol) is added.

Finally, in real conditions in the presence of a SF dissolved in toluene, separation of the system should occur at a higher water content. Actually, direct experiments showed that the effect of separation of the reaction mass (appearance of an upper, transparent water–methanol layer) begins to occur at a preliminary water content of ~30% (in methanol).

It is easy to see that formation of the system of interest to us takes place in polar water–methanol medium in which high concentrations of Ca^{2+} cation and hydroxyl OH^- are ensured by dissociation of calcium hydroxide and high concentrations of H^+ and CO_3^{2-} ions are ensured as a result of dissolution of carbon dioxide.

It is also understandable that all ions not only react with each other (associate) but also undergo solvation (hydration) to some degree. At a low water content, the ions are solvated by molecules of methanol. In addition to the absorption band of free and polymeric molecules of methanol, the IR spectra of nonaqueous methanol–anion systems contain the bands of complexes of methanol with anions.

As the water content increases, hydration begins to predominate. It was qualitatively found that the reaction of anions with water takes place by formation of hydrogen bonds. The anions are in the following order with respect to diminishing reaction energy:

$$CO_3^{2-} \geq SO_4^{2-} \geq OH^- \geq RCOO^- \geq Cl^- \geq NO_3^- \geq ClO_4^-$$

The hydration number of alkaline-earth metal cations is a function of the value of the charge. For Mg^{2+} and Ca^{2+}, they are from 4 to 10 on average according to the data from different methods. It was found that the intensity of libration vibrations of water molecules in solutions of salts is not a function of the temperature (they are attenuated in pure water), i.e., the thermal stability of the hydrate structure of the ions is confirmed.

While not going into the theories of counterion association in detail, we note that in sufficiently concentrated solutions, counterions are bound by chains of water molecules (from 4 to 8). The stability of the hydrogen bond bridges increases with an increase in the concentration of the solutions.

Due to the high dipole moments of ion pairs, dipoles associate into quadrupoles and aggregates of higher order in solvent with a dielectric constant of $D < 10$. If we assume that the chain structures of these ion pairs behave similar to polyions, a decrease in the D of the medium will cause them to twist into coils.

To confirm the possibility of stabilizing polymer chains from associates of counterions, we mention the results of spectroscopic studies of polyelectrolytes. In layers of polyelectrolytes, each ion is surrounded by “ordered” water with respect to the direction to the counterion and “disordered” water with respect to the direction of ions of the same kind. In addition, higher ordering of the water molecules between ions arises in the presence of nonpolar molecules (in our case, toluene molecules or lube oil hydrocarbons).

We report the arguments above to show that the currently available experimental data do not contradict our notions concerning the possibility of formation of polymer-like stable chains of counterions in the carbonation conditions described.

Now let us examine what happens with the system formed in water–methanol–toluene medium in the stage of elimination of volatile components (water, methanol, toluene) followed by fabricating a solution of the additive in mineral oil.

The thermally stable hydration shell, which consists of an inner shell rigorously oriented toward the ions, and an outer, distant coordination sphere of water molecules around the ions in the chain, prevents reaction of the counterions of neighboring aggregates and binds and stabilizes the ion pairs in the chain.

As the volatile components are eliminated and the polarity of the medium decreases, the tendency toward association of the organic ion ($RArSO_3^-$ or $RArSO_3Me^+$) dissolved in toluene with the counterions increases. We note that for a "weak" anion such as $RArSO_3^-$, its binding with cations is weakened in the following order due to charge delocalization with respect to three atoms:

$$K^+ > Na^+ > Ba^{2+} > Ca^{2+} > Mg^{2+}$$

In addition, since "weak" anions form less stable solvate-separated ion pairs than so-called "strong" OH^- and RCO_2^- anions, the possibility of calculating the cation content in magnesium sulfate (in contrast to calcium sulfonate) and in additives of another type – phenolates, salicylates, etc., becomes understandable.

In view of the above, in synthesis of magnesium sulfonate in toluene, the $RArSO_3^-$ anion will probably be dissolved, and in synthesis of calcium sulfonate, the $RArSO_3Ca^+$ cation will be dissolved. In the first case, the organic ion will associate with the cation chain and in the second, it will associate with the anion of the polymer chain of counterions.

When the organic ion is joined with the chain structure of ion pairs, i.e., in formation of an amphiphilic molecule, the ion groups and hydrocarbon groups separate as the value of *D* decreases, with formation of aggregates of molecules (aggregation number within the limits of 5-10, rarely 30 at very low values of *D* and molecular weight of the hydrocarbon part of the amphiphilic molecule). These same conditions require the polymeric ion chains of the molecules to roll up into coils and assume a shape that is more thermodynamically stable in nonpolar medium.

The chains twisted into coils surrounded by hydrocarbon groups form spherical aggregates. The stability of the aggregates is ensured by the presence of water, which causes formation of interionic hydrogen bonds and increases the volume of the ion nucleus of aggregates.

As a function of the concentration of the solutions of such aggregates in nonpolar hydrocarbon medium, their properties can vary from optically isotropic, characteristic of low-viscosity liquids, to optically anisotropic, characteristic of gel-like, wax-like substances with pronounced birefringent characteristics similar to liquid crystals (mesomorphic phase).

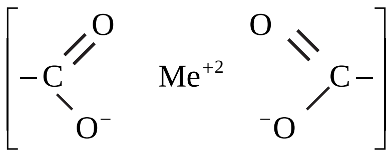
As a function of the distillation conditions, the appearance of aggregates of different shape and size and obtaining solutions of different viscosity, up to solutions almost immobile at room temperature, are probable.

This detailed exposition of our notions concerning the mechanism of formation of amphiphilic molecules with polymer chains of counterions on the example of sulfonates is due to the fact that the concepts concerning their heterogeneity are substantiated in the structure of these highly basic additives.

In synthesis of highly basic phenates using the low-temperature version of carbonation in conditions similar to the conditions of synthesis of sulfonates, it was not possible to obtain an additive with a base number greater than 200 mg KOH/g. Methanol was replaced by glycol and the process temperature was increased to 170-180°C as a result, and this ensured dissociation of protons from both ethylene glycol hydroxides and created the conditions for building the solvation shells of the ions from molecules of ethylene glycol, and thus the conditions for synthesis of phenate additives with a higher base number.

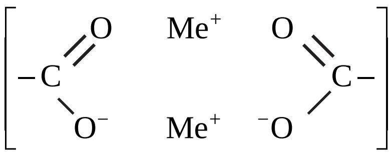
A positive effect was also obtained in synthesis of additives based on mixtures of alkylphenols and carboxylic acids of different structure.

In nonaqueous media, carboxyl anions (RCO_2^-) behave in association so that their effective radius slightly differs from the radius of OH^- hydroxyl. This behavior is caused by the structure of the anion, which allows the cation to simultaneously be in contact with both oxygen atoms, utilizing the entire negative charge. Associates of linear structure are formed with alkaline-earth metal cations:



The maximum base number with an acceptable viscosity–temperature characteristic corresponds to the optimum ratio of components in synthesis of additives of this type.

The existence of associations of carboxyl anions with alkali metal cations of stratified polymeric structure in nonaqueous media



and especially the ability of alkali metal carbonates to form polymer chain or laminar structures should also be noted. The CO_3^{2-} anions in such associates are separated and joined through cations and additional anions (OH^-, Cl^-, etc.).

The capacity of these counterions for coordination reactions stabilize these structures. The stability should evidently increase when compounds capable of creating a strong solvation shell of ions with hydrogen bonds or ion-dipole interactions (for example, high-molecular-weight alcohols, including phenols) are added to the reaction medium.

Using these theoretical assumptions, we were able to synthesize a new type of additives based on high-molecular –weight organic compounds of the acid type and alkali metals.

We hope that the arguments presented here will be sufficient for substantiating our notions concerning the structure of additives with a superstoichiometric cation content.

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HEAVY BAKU CRUDES AS FEEDSTOCK FOR PRODUCTION OF T-1500 TRANSFORMER OIL

R. Sh. Kuliev, F. A. Kuliev, and S. R. Kulieva

UDC 66.062.032.32

The possibility of manufacturing T–1500 transformer oil for equipment operating on electric power transmission lines with voltage of 1500 kV from Balakhany heavy and Binagady paraffin–base crudes and from mixed Baku paraffin–base crudes from off–shore fields was investigated with a new method.

Establishing the suitability of petroleum feedstock for production of oils is a lengthy and laborious process that requires important investments. The method in [1] allows significantly reducing both the time and the costs. The essence of the method consists of separating the feedstock into separate groups of hydrocarbons by adsorption chromatography and obtaining composites corresponding to oils with different degrees of treatment.

Table 1

Indexes	Distillate		
	A	B	C
Cut points, °C	261 – 422	252 – 415	236 – 419
Density at 20°C, kg/m^3	890.2	889.2	874.6
Refractive index	1.4945	1.4911	1.4835
Viscosity at 50°C, mm^2/sec	9.9	7.65	7.56
Molecular weight	268	281.7	263
Acid number, mg KOH/g	0.081	0.083	0.02
Flash point (closed cup), °C	147	142	145
Solid point, °C	-55	-47	-45
Color, CST units	3.5	3	3.5

Note. * The distillates were neutralized with a base before determination of the physicochemical properties.

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Distillates of Balakhany heavy and Binagady low–wax crudes and mixed paraffin–base crudes from Neft Dashlary and 28 Maya offshore fields were used for the study. We will designate them for convenience as A, B, and C, respectively.

Distillates A and B had a low solid point so that they were not dewaxed. Distillate C was dewaxed with carbamide. These distillates differed in physicochemical properties (Table 1) and in the content and physicochemical properties of the individual groups of hydrocarbons and resins (Table 2).

The distillates were separated into hydrocarbon groups according to GOST 1211244–85 by the refractive index n_D^{20}: paraffins and naphthenes, under 1.49; light, 1.49–1.53; medium 1.53–1.59; over 1.59, heavy aromatic hydrocarbons. The cuts with low n_D^{20} remaining after separation of heavy aromatic hydrocarbons were resins.

The compositions were composed of these groups of hydrocarbons in accordance with their yields in the distillate. The composition and physicochemical characteristics of these compositions and the requirements of GOST 982–80 for T–1500 transformer oil quality are reported in Table 3 [2]. The paraffins and naphthenes

Table 2

Group of compounds	Yield, % in distillate	Density at 20°C, kg/m^3	Refraction index	Viscosity at 50°C, Mm^2/sec	Molecular weight	Solid point, °C
Distillate A						
Hydrocarbons						
paraffins and naphthenes	72.5	861.1	1.4726	7.8	276	–45
aromatics						
light	9.3	925.3	1.5146	11.8	270	–48
medium	9	974.2	1.5524	12.1	240	–44
heavy	6.7	1037.1	1.6064	19.4	225	–34
Resins	2.5	1028.3	–	–	285	–
Distillate B						
Hydrocarbons						
paraffins and naphthenes	77.6	867.2	1.4758	6.07	285.7	–46
aromatics						
light	7.2	912.2	1.5106	8.7	274	–54
medium	6.5	980.2	1.5584	10.35	269	–33
heavy	4.7	1035.8	1.6086	17	247.5	–22
Resins	4	1038.9	–	–	279	–
Distillate C						
Hydrocarbons						
paraffins and naphthenes	71.1	848.5	1.4688	6.82	272	–43
aromatics						
light	13.1	903.2	1.5019	7.18	259	–47
medium	8	951.4	1.5580	9.1	227	–51
heavy	6.2	1025.1	1.6018	11.2	209	–35
Resins	1.6	1032.7	–	–	284	–

Table 3

Composition of hydrocarbon groups separated from distillate	Density at 20°C, kg/m^3	Viscosity, mm^2/sec		Acid number, mg KOH/g	Sodium test, optical density units	Solid point, °C	tg δ	Oxidation stability* (according to GOST 981–75)		
		at 50°C	at 100°C					sediment content, %	acid number, mg KOH/g	low–molecular–weight volatile acid content, mg KOH/g
1	2	3	4	5	6	7	8	9	10	11
				Distillate A						
PN	861.1	7.8	839	Neutral	0.12	–45	0.13	3.08	16.06	8.01
PN + A_l	867.8	7.9	963	0.005	0.28	–51	0.3	Отс.	0.051	0.04
PN + A_l + A_C	977.7	8	1045	0.007	0.38	–57	0.45	«	0.059	0.04
PN + A_l + A_C + 50% A_h	881.8	8.1	1260	0.01	0.71	–56	0.67	0.04	0.26	0.41
PN + A_l + A_C + 100% A_h	886	8.3	1600	0.023	0.91	–55	1.71	0.07	0.28	0.52
PN + A_l + A_C + Ah + 25% R	887.9	8.3	1565	0.027	0.97	–55	6.55	0.19	0.58	0.97
PN + A_l + A_C + Ah + 50% R	888.8	8.4	1605	0.031	0.97	–55	11.21	0.39	0.71	1.43
				Distillate B						
PN	867.2	6.07	841.4	Neutral	0.13	46	0.11	3.9	9	7.9
PN + A_l	870.1	7.17	975	0.004	0.27	53	0.29	Отс.	0.056	0.04
PN + A_l +A_C	875.7	7.26	1050	0.006	0.36	51	0.48	"	0.06	0.04
PN + A_l +A_C + 50% A_h	882.9	7.32	1245	0.01	0.75	51	0.79	0.65	0.58	0.36
PN + A_l +A_C + 100% A_h	886.5	7.45	1530	0.021	0.85	51	1.68	0.87	0.58	0.5
PN + A_l +A_C + A_h + 25% R	887.8	7.49	1570	0.024	0.9	49	6.27	0.91	0.63	0.95
PN + A_l +A_C + A_h +50% R	888.6	7.6	1591	0.029	0.95	49	10.51	1.08	0.67	1.36

Table 3 (continued)

1	2	3	4	5	6	7	8	9	10	11
Distillate C										
PN	848.5	6.82	813.4	Neutral	0.11	43	0.09	3.2	7.1	6.8
PN + A_l	853	6.88	942	0.005	0.2	45	0.16	Abs..	0.049	0.04
PN + A_l + A_C	859.2	7.07	1080.1	0.007	0.28	47	0.31	"	0.057	0.04
PN + A_l + A_C + 50% A_h	862.5	7.19	1124.1	0.009	0.39	47	0.57	0.29	0.26	0.17
PN + A_l + A_C + 100% A_h	864.2	7.33	1359.2	0.019	0.47	45	1.06	0.46	0.28	0.3
PN + A_l + A_C + A_h + 25% R	866.8	7.38	1392.7	0.021	0.56	45	4.17	0.61	0.43	0.55
PN + A_l + A_C + A_h + 50% R	869.5	7.41	1415.6	0.024	0.58	45	8.05	0.79	0.56	0.81
Standard GOST 982–80 for T–1500 oil	max 885	max 8	max 1100	max 0.01	max 0.4	max -45	max 0.5	Abs.	max 0.2	max 0.04

Notes. PN – paraffins and naphthenes; A_l, A_C, A_h – light, medium, and heavy aromatics; R – resins.

* With 0.3% Ionol additive

separated from distillates A and B totally satisfy these requirements; the same hydrocarbons from distillate C do not satisfy them with respect to the solid point alone.

The compositions from paraffins and naphthenes and light aromatic hydrocarbons and compositions from paraffins and naphthenes, light, and medium aromatic hydrocarbons satisfy the GOST requirements on all indexes. After addition of 50 and 100% heavy aromatic hydrocarbons and 25 and 50% resins from their content in the distillates, the compositions stopped satisfying the requirements with respect to many quality indexes. Increasing the amount of heavy aromatic hydrocarbons to 100% and resins to 50% further worsened these indexes.

Addition of aromatics to paraffins and naphthenes decreased their solid point due to the depressant properties of aromatics. However, all compositions satisfied the requirements on this index. The decrease in the solid point was more pronounced for compositions from hydrocarbons separated from distillates A and B. A synergistic effect could arise when the groups of hydrocarbons was mixed.

Table 4

Indexes	Standard GOST 982–80 for T–1500 oil	Oil fabricated by selective treatment and hydrotreating of distillate		
		A	B	C
Density at 20°C, kg/m^3	max 885	851.5	855	848.9
Viscosity, mm^2/sec				
at 50°C	max 8	7.52	7.35	7.2
at –30°C	max 1100	1100	1098.6	1050
Acid number, mg KOH/g	max 0.01	0.002	0.004	0.005
Sodium test, optical density units	max 0.4	0.32	0.09	0.36
Solid point, °C	max –45	–55	–53	–47
tg δ at 90°C, %	max 0.5	0.5	0.47	0.44
Group chemical composition, wt. %				
hydrocarbons				
paraffins and naphthenes	–	84.1	83.5	77
aromatics				
light	–	8.2	8.4	14.2
medium	–	7.3	7.4	8.6
heavy	–	0.1	0.2	–
resins	–	0.3	0.5	0.2
Oxidation stability (according to GOST 981–75)				
sediment content, %	Abs.		Abs.	
acid number, mg KOH/g	max 0.2	0.2	0.14	0.18
low–molecular–weight volatile acid content, mg KOH/g	max 0.04	0.04	0.04	0.04

For testing for oxidation stability according to GOST 981–75, 0.3% Ionol antioxidant was added to the composition. Oxidation was conducted in the presence of a catalyst – copper – at 135C for 30 h with oxygen feed of 50 ml/min [3]. Paraffins and naphthenes were tested without addition of Ionol.

Of the investigated compositions, the compositions consisting of paraffins and naphthenes and light aromatic hydrocarbons and the compositions made of paraffins and naphthenes and light and medium aromatic hydrocarbons satisfy the requirements of GOST 981–75. Addition of heavy aromatic hydrocarbons and resins to the compositions worsens their antioxidant properties.

The investigated distillates underwent selective treatment with 200, 250, and 300 wt. % furfural followed by hydrotreating on aluminum–nickel–molybdenum catalyst at 335°C, pressure of 5 MPa, hydrogen flow rate of 1000 $m^3/(m^3 \cdot h)$, and feedstock space velocity of 1 h^{-1} to obtain T–1500 oil that satisfied the requirements of GOST 982–80.

Selective treatment of the distillates and hydrotreating of raffinates were conducted in a continuous experimental unit. The studies showed (Table 4) that only the oil obtained by treatment with 300% furfural followed by hydrotreating totally satisfied the requirements.

The selective–treatment transformer oils were identical to the recommended compositions with respect to the hydrocarbon composition. They contained 0.1 and 0.2% heavy aromatic hydrocarbons and 0.2–0.5% resins. Oil C contained no heavy aromatic hydrocarbons.

Using the new method, the possibility of obtaining T–1500 transformer oil for high–voltage transmission lines from Balakhany heavy and Binagady low–wax crudes and from mixed Baku paraffin–base crudes from offshore fields was thus established. Heavy aromatic hydrocarbons and resins must be totally removed from distillates of these crudes to do this.

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From the editorial board

Rasul Shirinovich Kuliev left us in March. This remarkable man and talented scientist, long–standing author and friend of our journal was 93.

Rasul Shirinovich worked at the Acad. Mamedaliev Azerbaidzhan Scientific–Research Institute of Petrochemical Processes for more than 55 years – initially as director of the largest laboratory (until 1986) and then professor and chief scientific staff member. He patented tens of inventions, conducted a multitude of scientific studies, published more than 500 works, and prepared more than 30 students for candidate degrees and doctorates.

Until the end of his life, despite serious illness, R. Sh. Kuliev was devoted to fundamental science and was a real scientist – he wrote articles and managed data.

We will hold the shining memory of Rasul Shirinovich in our hearts.

Chemistry and Technology of Fuels and Oils, Vol. 43, No. 3, 2007

ION EXCHANGERS AND ADSORBENTS FROM PETROLEUM RESIDUES

Yu. V. Pokonova

UDC 661.183.123

A cation exchanger with an exchange capacity of 4.85 meq/g and mechanical strength of 96% was obtained by sulfonation of a styrene copolymer grafted to petroleum asphaltite. It can be used for sorption of ions at temperatures up to 100°C and radiation doses of up to 6.710^6 Gy. The adsorbents made from this type of raw material are characterized by a developed micropore structure.

I have studied the reactivity of petroleum residues for many years [1-3]. A new type of concealed reactivity was found for the first time in 1977 [4], revealed by irradiation. Petroleum residues acquire properties of macromolecular initiators under the effect of radiation. When unsaturated monomers are present in the system, radical graft copolymerization takes place. The graft copolymers obtained are new reactive feedstock from petroleum residues. The mechanism of these reactions was described previously in [2-4].

It is not possible to conduct such a reaction for petroleum resids with a temperature effect. Petroleum asphaltites containing 60-79% asphaltenes obtained by naphtha deasphalting or in a redox reaction of acid tars with straight-run vacuum resids are most appropriate for these purposes.

These highly concentrated residues contain alkyl-substituted condensed arene, cycloalkylarene, and heterocyclic molecules which are dealkylated by irradiation. The "captured" free radicals formed initiate radical graft copolymerization.

The primary stable radicals in the petroleum residue can also be activated by radiation. In addition, separation of several fragments of resin and asphaltene molecules is possible. The low content of oil phase does not cause significant evolution of gas during irradiation.

The synthesis of sulfonic cation exchangers based on a new kind of feedstock – products of the reaction of asphaltite and styrene, i.e., a copolymer of styrene basically grafted to asphaltite, and the properties of the sulfo derivatives obtained are described. The reactions take place according to the scheme:

St. Petersburg State Institute of Technology – Engineering University. Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 3, pp. 43 – 45, May – June, 2007.

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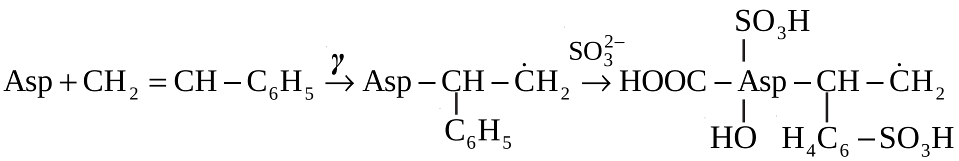
Table 1

Dose of radiation, 10^4 Gy	Number of paramagnetic centers, 10^{-19} PMC/g	Relative concentration of free radicals, %	Yield of hydrocarbons, vol. %
0	2.15	100	—
6	6.13	120	11.7
8	9.77	157	10.8
9	12.02	239	6.9
20	9.09	312	7.8

Table 2

Indexes	Styrene	Mixture (1:1) of styrene and asphaltite
Dose of radiation, 10^5 Gy	3	10
Rate constant, 10^{-5} sec^{-1}	0.242	0.0547
Activation energy, kJ/mole	38.33	73.07



$$\mathrm{Asp} + \mathrm{CH_2} = \mathrm{CH} - \mathrm{C_6H_5} \xrightarrow{\gamma} \mathrm{Asp} - \underset{\mathrm{C_6H_5}}{\mathrm{CH}} - \dot{\mathrm{C}}\mathrm{H_2} \xrightarrow{\mathrm{SO_3^{2-}}} \mathrm{HOOC} - \underset{\mathrm{HO}}{\overset{\mathrm{SO_3H}}{\mathrm{Asp}}} - \underset{\mathrm{H_4C_6 - SO_3H}}{\mathrm{CH}} - \dot{\mathrm{C}}\mathrm{H_2}$$

$$\mathrm{CH_2 = CH{-\!\!-}C_6H_5} \xrightarrow{\gamma} \dot{\mathrm{C}}\mathrm{H_2{-\!\!-}CH{-\!\!-}C_6H_5^{\bullet}} \xrightarrow{\mathrm{SO_3^{2-}}} \mathrm{CH_2{-\!\!-}HC{-\!\!-}C_6H_4{-\!\!-}SO_3H}$$

where Asp are resin and asphaltene molecules.

We used asphaltite separated from Arlan crude vacuum resid having a molecular weight of 1520, density of 1113 kg/m^3, and the following elemental composition, wt. %: 83.35% C, 8.26% H, 0.77% N, 6.1% S, 1.61% O.

Irradiation was conducted on a MRKh-g-20 with a ^{60}Co source with activity of 20,000 geq radium. The dose rate according to a ferrosulfate dosimeter was 0.8 Mrad/h. The spectra were recorded on a standard RE-1301 radiospectrometer. Mn^{2+} (S* = 5.2) was used as the intensity standard and the magnetic field scale standard in the measurements.

The spectra were recorded on a UR-20 spectrometer. The samples were prepared by molding KBr pellets or in the form of solutions. The analyses of hydrocarbon gases were performed by GLC on a Tsvet-104 gas chromatograph, a katharometer was the detector, argon was the carrier gas, and its flow rate was 20 ml/min.

To establish an increase in the number of free radicals under the effect of g-radiation, the intensity of the signal of the initial and irradiated samples in the EPR spectrum was related to the intensity of the standard line of Mn^{2+} with consideration of the weight of the sample. Setting the number of free radicals in the initial sample of asphaltite at 100%, the relative increase in the irradiated samples was determined (Table 1). The gaseous products consisted of C_1-C_4 hydrocarbons, as established previously in [2, 3].

A mixture (1:1 wt.) of asphaltite and styrene was irradiated to obtain the graft copolymer. Pure styrene with a boiling point of 144-146°C was polymerized in the same conditions. The kinetic constants of the polymerization and graft copolymerization reactions are reported in Table 2. To obtain a strong block, after

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*S – energy of magnetic interaction with the nucleus of the unpaired electron in the s orbital.

irradiation for 6 h at 160°C, it was additionally treated with heat. The yield of graft copolymer with styrene was 50%.

The monolith obtained was crushed and sieved into fractions. The 0.5-2 mm fraction was used for subsequent sulfonation. Sulfonation was conducted with 3% oleum for 3 h with copolymer:oleum = 1:3 pts. by wt. After neutralization and washing off the unreacted styrene and asphaltite with benzene, the product was analyzed as an ion exchanger. It was a sulfonated mixture of styrene polymer with the copolymer of styrene and asphaltite. The ion exchange was converted to the H form before the analysis.

The physicochemical properties of the sulfonic cation exchanger obtained are reported below:

Moisture content, %	11
Relative swellability	1.8
Specific volume, ml/g	
in swollen state	2.96
in air-dried state	1.69
Bulk density, g/ml	0.592
Mechanical strength, %	96
Static exchange capacity, meq/g	
total	4.85
by groups	
$-SO_3H$	2.12
–COOH	0.53
–OH	2.2

The thermohydrolytic stability of the sulfonic cation exchanger was determined in sealed ampuls in the 90-170°C temperature range. The matrix did not decompose in these conditions [5]. After heat treatment, the samples were washed to neutral reaction. Thermohydrolytic decomposition of ionogenic groups can be described by a first-order equation:

$$\log E_{\tau} = \log E_{\mathrm{in}} - K$$

Table 3

Indexes	Sulfonic cation exchanger after thermohydrolytic treatment (24-h exposure)		
	90°C	120°C	170°C
Total static exchange capacity (TSEC) meq/g	5.85	4.94	4.54
Increase (%) in exchange capacity by groups			
$—SO_3H$	2.38	2.26	1.6
—COOH	1.27	0.4	0.15
—OH	2.2	2.28	2.79
Swellability, %	70	68	66
Weight loss, %	8.5	13.1	16.4
Thermohydrolysis rate constant, 10^{-3} sec^{-1}	1.3	5.76	12.2
Activation energy, kJ/mole	22.38	22.38	22.38

where E_{in}, E_τ are the capacity of the initial ion exchanger and the ion exchanger at time τ; K is the decomposition rate constant.

The activation energy of thermohydrolytic decomposition was found from the Arrhenius equation (Table 3). The sulfonic cation exchanger was thermohydrolytically more stable than the industrial cation exchanger. For example, heating of SBS-3 [6] for 24 h at 175°C caused a 47.6% loss in TSEC, while heating of KU-2´5 and KU-2´12PS for the same time at 170°C caused a 19.4 and 22.0% loss.

For the synthesized sulfonic cation exchanger at 90 and 120°C, the exchange capacity for sulfo groups increased, which can be attributed to an increase in the number of sulfo groups available for ion exchange due to possible breaking of some of the crosslinks in the matrix.

To study the radiochemical transformations, the samples of the cation exchanger were irradiated in sealed ampuls in distilled water in the same MRKh-g-20 unit as the graft copolymer. After irradiation, the ampuls were opened and the contents were transferred to a filter and washed to neutral reaction. The results of the study (Table 4) showed that the composition of the ionogenic groups changed and the amount of the most radiation-stable phenol groups increased significantly (to 5.67 meq/g) in irradiation.

In the $(1\text{-}6.7)10^6$ Gy dose range, coefficient b and the rate constant of radiochemical transformations were small. Under the effect of g-radiation, transformations took place in several directions in the cation exchanger [4]: decomposition of initial ionogenic groups, emergence of new groups, reaction with the products of radiolysis of water, reaction of the groups with each other, crosslinking, and decomposition of the matrix.

The inconstancy of the values of b indicates the variety of the reactions that continuously and simultaneously take place in radiolysis.

The rate constant of the radiochemical transformations is not constant for the same reason. It follows from the comparison with industrial sulfonic cation exchangers based on the copolymer of styrene and divinylbenzene [6]: KU-2-8 at the dose of $1.3 \cdot 10^6$ Gy loses 10% of SEC, Dowex-50 at the dose of $6 \cdot 10^6$ Gy loses 24% of the initial capacity.

Adsorbents were fabricated with the industrial scheme in [7] using a mixture consisting of 52% products of the reaction of styrene and asphaltite, 17.5% coal dust (coal from the Kuznetsk basin, Central

Table 4

Indexes	Cation exchanger after absorption of integral dose, 10^6 Gy			
	1	3	5.1	6.7
Static exchange capacity (SEC), meq/g				
total	4.68	4.45/4.81	3.93	6
for new groups				
—COOH	1.53	1.13/1.97	0.15	0.24
—OH	3.15	3.32/2.84	3.78	5.76
Coefficient b of radiochemical transformations of ionogenic groups, meq/(g·Gy^{-1})	2.19	0.81/0.69	0.58	0.13
Rate constant of radiochemical transformations, Gy^{-1}	0.38	0.14/0.12	0.11	0.02
Radiochemical yield of decomposed ionogenic groups per 100 eV absorbed energy	0.26	9.62/8.2	7.56	1.37

Note. In the numerator – after irradiation in distilled water; in the denominator – in air.

Table 5

Indexes	Adsorbent with degree of activation (combustion loss), %			
	0	3	7	20
Density, g/cm^3				
bulk	0.549	0.52	0.515	0.5
apparent	0.87	0.85	0.83	0.8
Total pore volume, cm^3/cm^3				
for methanol	0.58	0.62	0.62	0.67
for benzene	0.51	0.58	0.63	0.69
for CCl_4	0.45	0.49	0.58	0.67
Heteroatom content, %	—	7.05	8.9	13.4
Strength, %	92	90	90	90
Volume, cm^3/cm^3				
micropores	—	0.16	0.18	0.24
mesopores	—	0.01	0.03	0.04
macropores	—	0.21	0.25	0.27
Specific volume,* cm^3/cm^3				
for methane	5.7	10.7	14.9	13.6
for carbon dioxide	101	87	82	76
for xenon	11.7	137.6	169.8	268.7

Note. * For AG-2, the specific retained volume for methane, carbon dioxide, and xenon is equal to 16.2, 33, and 158.2 cm^3/cm^3.

Mine, 13.2% volatiles content) and 10% total shale phenols – mixtures of alkylresorcins. Wood tar was used in the amount of 34%.

Carbonization was conducted in a rotary furnace in carbon dioxide atmosphere at a final temperature of 800°C and activation was conducted in water vapor atmosphere at 800-820°C. The pore structure of the adsorbents was characterized by adsorption of benzene vapors at 20°C on a vacuum microbalance. For calculating the specific volumes of micro- and mesopores, the isotherms were processed with the Kiselev method. The parameters of the micropore structure were calculated in accordance with the Dubinin theory of volume filling.

Judging by the data in Table 5, low-combustion-loss adsorbents have an important micropore volume and a higher level of sorption properties than AG-2 industrial adsorbent. However, liberation of sulfur oxides in production of these adsorbents requires additional environmental protection, which to some degree levels out their high sorption indexes. Because of this, they cannot be recommended for wide use in practice.

Polyfunctional cation exchangers with a total exchange capacity of 4.85 meq/g, containing sulfate, carboxyl, and phenol–hydroxyl groups, were thus synthesized from a new type of feedstock – the copolymer of asphaltite and styrene. The thermohydrolytic and radiation stability of these sulfonate cation exchangers is higher than for industrial samples. The low-combustion-loss adsorbents have higher sorption capacity for gases than the AG-2 commercial adsorbent.

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Chemistry and Technology of Fuels and Oils, Vol. 43, No. 3, 2007

METHODS OF ANALYSIS

FAST ANALYSIS FO THE QUALITY AND ENVIRONMENTAL SAFETY OF MOTOR FUELS

E. V. Shatokhina

UDC 681.2:681.518.52:665.7

The relationships of the density, dielectric constant, and octane number were investigated. The possibility of creating instruments based on fast methods of analysis of these characteristics was examined. A portable petroleum product quality analyzer – the octanometer – based on measurement of the dielectric constant is described.

The requirements for petroleum motor fuels – automotive gasolines and diesel fuels – are becoming increasingly severe. Developing fast methods for analyzing their quality and environmental safety is becoming more urgent for this reason.

In monitoring the quality of gasolines, the antiknock value (octane number) is considered the fundamental index. It has been noted that many high-octane gasolines have high density, but there are aerated gasolines which correspond to A-76 gasoline in octane number with very low density.

The results of many measurements of the density and octane number (research) of gasolines at many Russian refineries revealed the approximate correlations between these indexes.

For AI-80 gasoline (Fig. 1a), the scattering of the average density values was 715-740 kg/m^3, but most of these values were grouped, and the average was equal to 724 kg/m^3. Within this interval, the density decreased with an increase in the octane number. These data can be represented in the form of a linear regression with the method of least squares.

For AI-93 gasoline (Fig. 1b), the average density was 750 kg/m^3 with scattering from 730 to 770 kg/m^3. Within this interval, the density increased with an increase in the octane number.

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For AI-95 gasoline (Fig. 1c), the scattering of the density values was 740-770 kg/m^3 with an average value of 756 kg/m^3. The regression was a straight line that increased with an increase in the octane number.

For SUPER AI-98 gasolines (Fig. 1d), scattering of the few density values was 750-765 kg/m^3. With such a small number of measurements, the linear regression is not reliable.

After averaging the density values for the different types of gasolines, we will plot the dependence of the density on the research octane number with a linear regression equation (Fig. 2). This dependence, which reflects the increase in the density with an increase in the octane number, is very approximate: the accuracy of determining the octane number is 3-4 units.

Methods of monitoring the quality of petroleum products with their dielectric constant were found from an analysis of the patent literature. There are methods of determining the water content in crude oil and petroleum products and the methanol content in gasolines in selecting fuel for race cars with this index.

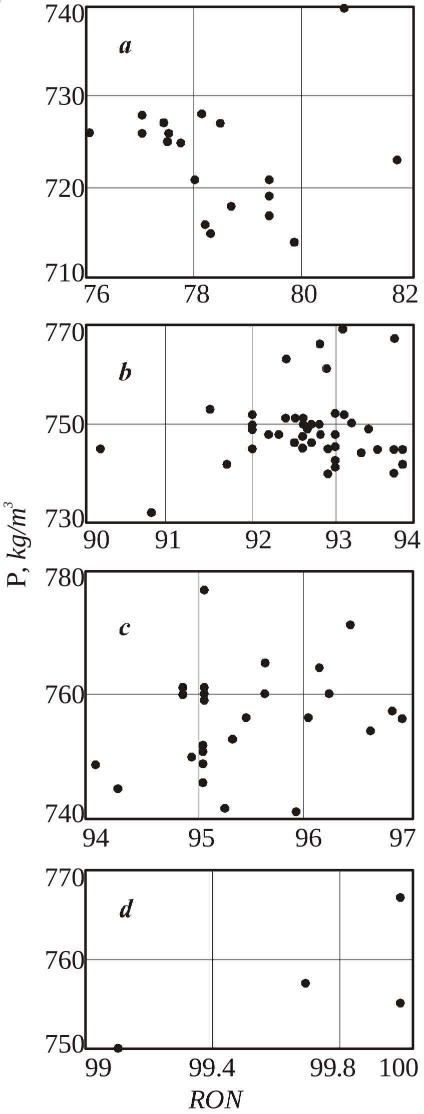

Fig. 1. Average values of the density for gasolines: a) AI-80; b) AI-93; c) AI-95; d) SUPER AI-98.

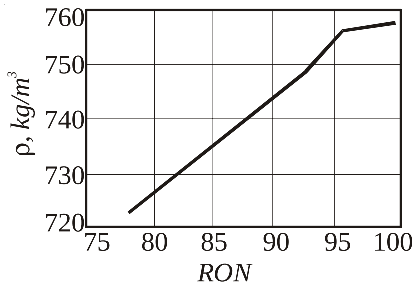

Fig. 2. Average density ρ of gasolines as a function of their octane number (RON).

Fuels consist of compounds whose molecules are weakly polar. For this reason, the values of the dielectric constant are close for fuels of different grades. Nevertheless, in highly accurate measurement of this parameter, the quality of a petroleum product can be evaluated accurately enough [1].

The dielectric constant of automotive gasolines changes by a total of 10% when the octane number goes from 60 to 90. The dielectric constant must be measured with accuracy of 0.1% to ensure 0.5 unit accuracy of measurement of the octane number.

The dielectric constant increases with an increase in the content of aromatic hydrocarbons and high-boiling cuts in the fuel. It also increases in exhaustive oxidation of the fuel, accompanied by an increase in the content of gums, organic acids, and other oxygen-containing compounds [2].

The values of the dielectric constant e of gasolines, diesel fuels, isooctane, and aviation fuel are reported in Table 1 [3].

Theoretically, there is not always a regular correlation between the chemical structure of the compounds and their dielectric constant. When a correlation is found experimentally, it is complex. The independent use of the dielectric (based on the dielectric constant) method of analysis of the composition of petroleum products is limited, since they are a very complex mixture of different hydrocarbons and other compounds.

However, the value of this method is exceptionally high, since the dielectric constant, combined with such characteristics as density, conduction, and optical transparency, as well as with the data from spectral analysis, makes it possible to accurately evaluate the quality of petroleum products.

Based on the GOST and ASTM, the quality of gasoline is determined on type UIT-65 engine units. There are no measuring instruments for this. As a consequence, the method of determining the dielectric constant and conduction and subsequently comparing these values with standard gasoline quality indexes is a highly effective method of fast analysis. The dielectric constant and conduction of gasoline correlate well with its stability indexes, and this allows determining the induction period and consequently the possibility of prolonged storage of gasoline, which indicates its low tendency to form deposits.

The urgency of creating portable instruments based on fast methods is because the traditional methods of assessing the quality of fuels have become obsolete, since they do not satisfy current scientific requirements, in particular, the use of computers and microprocessors, and minimization of the size and power consumption of the instruments used.

Petroleum product quality analyzers based on fast methods should thus replace the basic standard instruments which cannot be used in field conditions.

The developers of the instruments focused attention on the possibility of converting nonelectrical values in the sensor into electrical signals with both direct and indirect methods, which would allow operatively assessing

Table 1

Fuel	ε
Isooctane	1.971
AI-80	2.047
TS-1	2.116
AI-92	2.162
Winter DF	2.188
Summer DF	2.208
AI-95	2.211
AI-98	2.3

the quality of petroleum products. A number of instruments for petroleum product quality control was found as a result of a patent and literature analysis.

Quality analyzers of the “acceptable–unacceptable” type (AUQA) present the result of the analysis on the display in graphic form, since the operator servicing aircraft does not require digital data and only requires authorization for filling. These instruments are obsolete and are rarely used.

In the USA, a device for determining the octane number by a spectral method has been patented [4]. The octane or cetane number of a complex mixture containing hydrocarbons and/or substituted hydrocarbons is monitored in the near infrared region.

The absorption value is measured at one wavelength in one or more ranges selected from the group of ranges: 1572-1698, 1700-1726, 824-884, 2058-2130 nm. This signal is then mathematically transformed into an output signal that determines the octane or cetane number of the mixture. The instruments are made in tabletop and portable versions.

The lack of sensitivity for additives (in particular, metal-containing additives) that increase the octane number of gasolines is an important drawback of the spectral method: the lines of the additives are outside the limits of the measurable spectrum of gasolines, which significantly restricts the area of application of these instruments and results in low accuracy of measurement.

The instrument based on measurement of the dielectric constant in [5] is highly sensitive to additives containing lead, manganese, or other metals. This was established in tests at oil refineries using technology for bringing the octane number of the base gasoline up to the standard with additives.

The dielcometric octanometer consists of a sensor (Fig. 3a) and computation unit (Fig. 3b). The sensor, connected to the circuit of a frequency-dependent generator, is a capacitor with 30 pF capacitance, which consists of communicating coaxial cylinders with a temperature sensor $Rt°$ inside. The electric field of the capacitor is enclosed inside plates and is determined by the design of the outer cylinder.

The dielcometric octanometer operates as follows (see Fig. 3b). After switching on the power supply from the frequency-dependent generator output (timer), voltage with frequency f_0, corresponding to the electrical capacitance of the unfilled capacitance sensor, enters the processor (computer) input.

When the beaker of this sensor is filled with a sample of the investigated petroleum product, the electrical capacitance of the sensor changes and voltage with frequency f_1 characteristic of the given sample and dependent on the dielectric constant of the petroleum product, enters the computer input from the timer output.

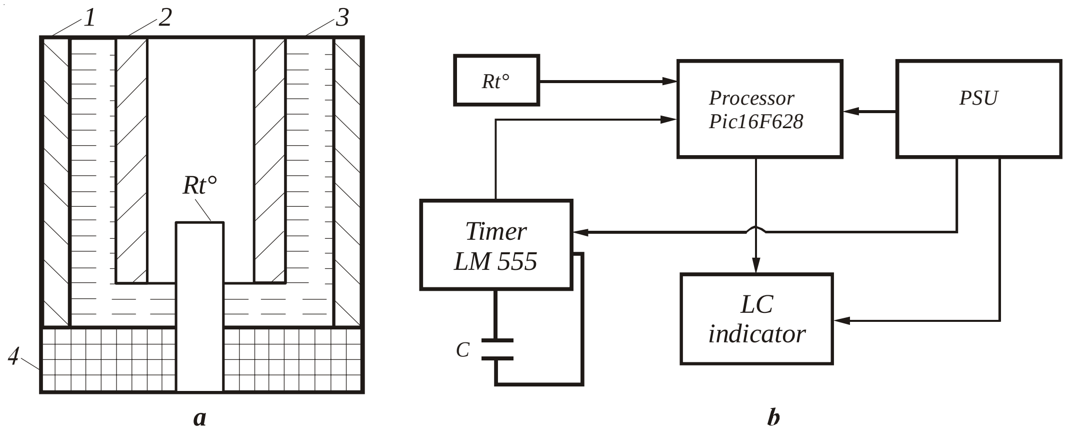

Fig. 3. Sensor (a) and block-diagram (b) of the octanometer: 1, 2) outer and inner capacitor cylinders; 3) gasoline; 4) sensor; *Rt*° – temperature sensor; *C* – sensor capacitor capacitance.

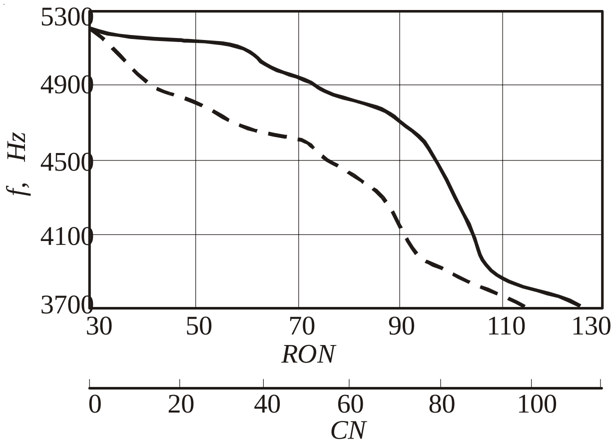

Fig. 4. Generator frequency *f* as a function of octane number *RON* of gasoline (solid curve) and cetane number *CN* of diesel fuel (dashed line).

The values of the dielectric constant of gasolines, diesel fuels, and other petroleum products manufactured in Russia and abroad were systematized based on the data from the computation block. This makes it possible to monitor gasolines in octane number units and diesel fuels in cetane number units, and also to screen motor oils.

The integral dependence of the generator frequency on the temperature is formulated with the results of studies of the temperature curves of the petroleum products and capacitance of the sensor and measuring circuits. The data from the computation block microprocessors result in data at the temperature of 20°C.

The curves of the generator frequency reflecting the dielectric constant as a function of the octane number of gasoline and the cetane number of diesel fuel are shown in Fig. 4. A decrease in the frequency (increase in the dielectric constant) is correlated with an increase in the values of these characteristics.

The overall dependences of the properties of petroleum products on the indexes of their physical properties which can be measured by electrical methods, namely, the dependences of the octane and cetane numbers on the dielectric constant, were found in this way.

Development of fast methods based on measurement of the indexes of the physical properties of petroleum products by electrical methods will make it possible to use portable instruments for petroleum product quality analysis. However, the efficiency of these instruments will be a function of the comprehensive use of traditional and fast methods for solving the concrete problem.

Small instruments for fast analysis of the quality of petroleum products will be used at tank farms, in oil refinery laboratories, at service stations, custom houses, in environmental and monitoring organizations, and for monitoring manufacturing processes in production of gasolines, diesel fuels, and regenerated motor oils.

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IR SPECTROSCOPIC DETERMINATION OF THE VAPORIZABILITY OF BASE OIL COMPONENTS

V. G. Spirkin, E. O. Panina, and N. V. Vizhgorodskii

UDC 665.637.6:621.9.079

A method is proposed for efficient determination of the vaporizability of motor oils in production conditions by IR spectroscopy. Its advantages over the traditional Noack method and the expediency of replacing the latter method are demonstrated.

In the oil refining industry, feedstock and semifinished product quality control is conducted in all stages of production. Fast and accurate quality control ensures high quality commercial petroleum products.

Most methods of analyzing motor oils are laborious and require important amounts of time, which makes it difficult to control the quality of the oils in conditions of continuous production. The method of IR spectroscopy using new computer algorithms based on factorial analysis can significantly facilitate the task of rapid quantitative determination of the parameters of petroleum products, including lubricants [1].

We examined the possibility of using this method for determining the vaporizability of motor oils. It differs from the currently used laborious Noack method of determining vaporizability (DIN 5158) by the efficiency and simplicity of executing the analysis and the accuracy of the results obtained.

The duration of spectral analysis of a sample of oil (with parallel measurements) is no longer than 5 min. With the Noack method, it takes 1 h to evaporate only one sample. Additional time is spent on such preparative operations as heating the bath to 250°C, weighing the empty crucible, and cooling the crucible after evaporation for reweighing.

For obtaining a reliable result, it is necessary to perform parallel measurements with a maximum acceptable error of 5%. As a result, the total duration of determining the vaporizability of oil is over 2 h. In addition, one analysis with the Noack method requires 60 g of oil, while 10-15 ml is sufficient for taking the IR spectrum.

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Table 1

Sample number	Vaporizability, wt. %		Error of determination with IR spectroscopy, %
	with IR spectroscopy	with Noack method	
1	19.82	20.08	0.65
2	19.26	19.85	1.50
3	19.62	20.70	2.67
4	19.64	20.60	2.39
5	19.56	20.58	2.53
6	19.04	19.84	2.06
7	20.72	20.24	1.18
8	20.15	20.74	1.44
9	19.45	19.77	0.82
10	19.51	19.89	0.95
11	20.17	20.05	0.30
12	20.33	19.91	1.04
13	19.05	18.63	1.11
14	19.24	18.93	0.83
		Average error, %	1.39

Table 2

Sample number	Content of volatile cuts, wt. %	Absorption peak height, nm	
		before distillation of light cuts	after distillation of light cuts
1	15	0.04334	0.03977
2	5	0.04565	0.03981
3	5	0.04437	0.0398

The accuracy of the measurement with the Noack method is not high enough: the convergence between parallel measurements is no greater than 5% (deviation from the arithmetic mean value).

The accuracy of the vaporizability measurements with IR spectroscopy was evaluated using statistical data (Table 1) obtained at Ryazan’ Oil Refining Co. (ORC). Since the vaporizability of oil is to a significant degree a function of its distillation and is established in primary refining of crude oil, samples of the hydrotreated medium-viscosity component of the oil (MCO) were used for the analysis.

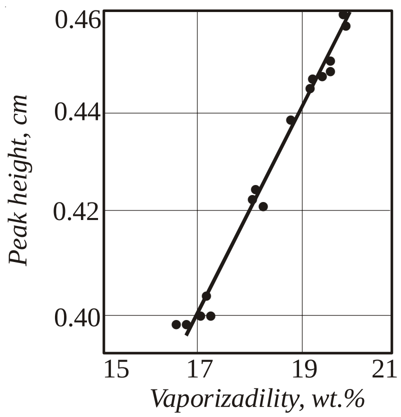

Fig. 1. Absorption peak height for oil samples as a function of their vaporizability.

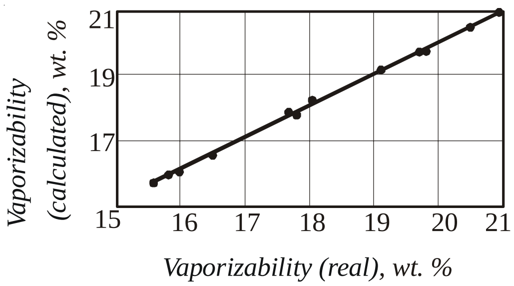

Fig. 2. Correlation between vaporizability values calculated with the IR-spectroscopic method and experimentally determined with the Noack method (correlation coefficient of 0.9973).

As Table 1 shows, the average error of determination of the vaporizability by IR spectroscopy is less than 2%.

The method of determining the vaporizability of oil by IR spectroscopy was experimentally perfected on a Perkin Elmer Spectrum One instrument. Zinc selenide was used as the optical material, since it is not as hygroscopic as sodium chloride or potassium bromide, and the transmission area is greater than for calcium fluoride. The entire transmission area of the IR spectrum characteristic of zinc selenide was primordially processed.

In studying the group composition of MCO with the IR-spectroscopic method, the effect of hydrocarbons of different classes on the vaporizability was determined. The signal corresponding to vibrations of carbon atoms in the aromatic ring is not intensive and the shift in it is a function of the character of the substituent. The intensity of the signal of long-chain paraffins corresponding to deformation vibrations of $(CH_2)_n$ groups, where $n > 4$, is relatively high.

The method of determining the group composition of an oil is based on recording the intensity of the signal at a constant thickness of the layer of the investigated sample, and the calculation is based on the peak height.

The peak corresponding to $(CH_2)_n$ group vibrations is located in the region of 760-700 cm^{-1} [2]. Since the initial boiling point or presence of relatively light cuts distilling under 400°C affects the vaporizability of the oil cut, the MCO samples – initial and after distillation of volatile cuts– were compared with respect to the absorption peak height (Table 2).

It is more convenient to use a frustrated total internal reflection attachment (FTIR) for laboratory control of the vaporizability of the oil component. This attachment greatly simplifies the technician's work – the sample is easily washed off by rinsing with a solvent. The same zinc selenide is used as the optical material.

Since the FTIR is less sensitive than the cuvette, not one, but all peaks in the 1300-650 cm^{-1} region are examined in the analysis [2, 3]. Different deformation and skeleton vibrations of the molecules appear in this region, so that even an insignificant change in the composition or structure of the molecule will markedly change the structure of the spectrum in this section.

The overall dependence of the peak height on the vaporizability is shown in Fig. 1. A working calibration curve was plotted with it (Fig. 2). The spectra were made on a Perkin Elmer Spectrum One instrument with the Spectrum v2.00 program and processed with the Spectrum Quant+ program.

It follows from the data obtained that the IR-spectroscopic method allows significantly reducing the time for determining the vaporizability of oils and increases the accuracy of the analysis. The error of determination is two times less than the acceptable error with the Noack method.

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ECOLOGY

BIOFOULING OF EQUIPMENT IN WASTEWATER TREATMENT SYSTEMS.
Methods of Protection

V. I. Goncharov and V. N. Smolin

UDC 628.543.8

Microbes, bacteria, microalgae, and higher microorganisms: aquatic fungi, infusoria, rotifers, etc., live and multiply on the surfaces of pipelines immersed in water, refrigerators and heat exchangers, inside flameless heating equipment in the presence of aqueous media, and in systems for biochemical treatment of wastewaters. Heat and mass exchange worsen sharply, thermal power consumption increases, output and passability decrease, accidents occur in manufacturing units, and corrosion of metal surfaces intensifies as a result of biological fouling of this equipment [1].

The following are methods of protection against biofouling:

Ï% mechanically removing deposits, i.e., manually, with scrapers and blades;

Ï% physically acting on microorganisms: with ultrasound, ultraviolet radiation, electrical current;

Ï% chemically acting on microorganisms: with toxic reagents added to the medium of their habitat.

Chlorine, calcium hypochlorite, and copper sulfate are widely used as chemical reagents in domestic oil refineries. However, this experiment has not been very successful. Attempts to use potassium permanganate, phenol chlorine derivatives, quaternary ammonium bases, and carbon dioxide were also not promising [2].

For this reason, we investigated hexachlorobutadiene, beta-nitrostyrene – a mixture of bistrichloromethylsulfone and beta-bromine (60:40), ethyl mercury phosphate, etc., as new reagents. The thermal conductivity of the steel wall of the treated equipment was measured during the experiments. The effect of traditional compounds: chlorine – for protecting against bacteria, and copper sulfate for protecting against algae, was parallelly investigated.

Hypochlorous acid is the active substance when chlorine is used. With strong oxidizing properties, a small molecule, and electrical neutrality, it rapidly passes through the cell membrane of a microorganism and

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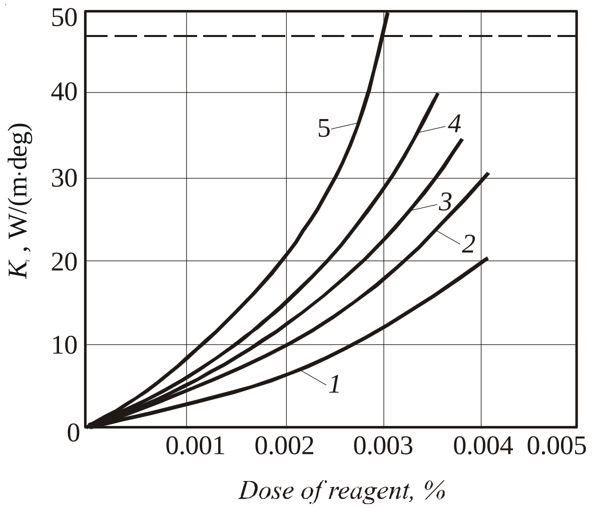

Fig. 1. Thermal conductivity K_t of steel as a function of dose (% of output of unit) of reagent: 1) copper sulfate; 2) chlorine; 3) hexachlorobutadiene; 4) beta-nitrostyrene; 5) ethyl mercury phosphate; — — —: K_t = 45.4 W/(m·deg), thermal conductivity of pure steel.

perturbs its vital processes. However, due to the chemical reaction of chlorine with impurities in the water, the effectiveness of this reagent is reduced significantly.

In treating a medium with copper sulfate, the Cu^{2+} copper ion penetrates the cell membrane of algae and destructively acts on the intracellular substance. In dying, the algae separate from the treated surface [3]. The minuses of this reagent are: insufficient degree of heat exchange, insignificant decrease in demand in cooling water, reduction of copper with precipitation on the metal surface and as a result, active galvanic corrosion of the surface.

Subsequent laboratory studies and industrial tests on cooling towers, in immersed coolers and other equipment in wastewater treatment systems revealed a highly effective and comparatively harmless reagent – ethyl mercury phosphate (see Fig. 1).

Used in a small dose, 0.5 mg/liter every 10 days of operation of the treatment unit, it has an elevated biocidal effect. It actively inhibits development of microorganisms, including microbes, bacteria, fungi, infusoria, rotifers, and microalgae. It significantly improves heat and mass exchange during the manufacturing process, which causes stable and fault-free operation of all equipment. The time between repairs is increased by 19%.

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REVIEWS

PHYSICOCHEMICAL ASPECTS OF PRODUCTION OF FUEL SUSPENSIONS

S. L. Khil'ko and E. V. Titov

UDC 541.183:622.33

The basic physicochemical principles of preparation of fuel suspensions are analyzed. The effect of the nature and content of solid and liquid phases and the type of chemical additives – regulators of the properties of these two-phase systems – is examined.

Coal suspensions are systems based on finely ground coal, a liquid carrier, and special chemical additives. In this form, coal can be used as a liquid energy carrier without chemical treatment, an alternative to crude oil and petroleum products [1, 2].

The use of coal suspensions as liquid fuel includes three basic stages: preparation of the coal and preparation of the suspension; transport and storage; burning. To optimize each of the stages, it is necessary to solve a number of problems: fundamental scientific, industrial-manufacturing, design, and economic [1-4].

Developing methods of obtaining fuel suspensions with physicochemical properties that meet all of the requirements of colloidal fuel technology is the most important stage. These requirements are primarily related to obtaining highly concentrated systems which are sedimentation- and aggregate-resistant for a long time (15-30 days) and have acceptable rheological properties – a low level of viscosity (high fluidity) and initial shear stress – and no thixotropic and dilatant properties.

As indicated in [5, 6], dilute disperse systems of the solid–liquid type have properties similar to solutions if the differences in the disperse phase particle size and molecular dimensions of the structures in the dispersion medium are not considered. As the concentration of disperse phase in the systems increases, the physicochemical properties gradually change due to formation of a three-dimensional network of disperse (solid) phase particles, i.e., a coagulation structure.

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The strength of the system increases sharply. The three-dimensional structures formed are characterized by the structural and mechanical (rheological) properties: viscosity, fluidity, plasticity, elasticity, etc.

Under the effect of external force, the structural network of the disperse system is destroyed. This is accompanied by accumulation of stresses and the appearance of strains (elastic and residual) in the system. The correlation between stress σ (Pa), strain ε or strain rate $\dot{\varepsilon}$ (sec^{-1}) and the changes in these parameters in time characterizes the rheological behavior of crosslinked disperse systems.

Many arbitrary strength characteristics have been calculated with the flow curve $\sigma = f()$, and the following are the most important ones for suspension fuels [7]:

- the dynamic (Bingham) yield point σ_0 (Pa), or initial shear stress, characterizes the strength of the structural network in the suspension; its value should be within the limits of 5-15 Pa;
- static yield point σ_1 (Pa), or boundary shear stress, at which the structural network begins to decompose; the acceptable value is 1-5 Pa;
- effective viscosity η_{ef} (Pa·sec) at a strain (shear) rate of ≈ 10 sec^{-1} allows defining the operating conditions of fuel pumps designed for such a shear rate; the values of η_{ef} should be within 1-2.5 Pa·sec.

Disperse systems can exhibit the property of *thixotropy*, expressed by the dependence of the rheological parameters on time. It is defined as the ability of disperse systems to reversibly liquefy with intensive mechanical effects (stirring, shaking) and lose fluidity at rest [5, 6].

This property must be taken into consideration in storing or transporting suspension fuel by rail or water and in pumping it in pipes, since systems with pronounced thixotropy can "harden" at rest, for example, if the pumps shut down [4, 8].

Disperse systems with a high solid-phase content can exhibit *dilatant* properties, manifested by an increase in the viscosity in some middle strain range [5, 9]. Such effects frequently complicate production and transport of fuel suspensions.

To eliminate possible thixotropic and dilatant effects, surfactants (SF) capable of a high degree of lyophilization of the surface of the solid phase are added to the fuel compositions.

The type of flow, i.e., the overall shape of the curve of $\sigma = f(\dot{\varepsilon})$, is an important index of the quality of fuel suspensions with respect to suitability for transport and storage. According to [7], viscoplastic (close to Newtonian) flow of a homogeneous fuel suspension maximally lyophilized with SF is the most reliable and safest type of flow.

Such flow is characterized by linearity of the curve of $\sigma = f(\dot{\varepsilon})$. It can only be realized when the rheological properties of the suspensions are stable during transport and storage, including when the flow rate and pressure change.

The type of flow can vary, since it is not possible to eliminate possible changes in the properties of the suspension between production and burning of the fuel as a result of exposure to different external factors: fluctuations in the temperature, pressure, alternate starting and stopping feed of the suspension, etc. For this reason, monitoring the physicochemical properties of the suspension fuel in all stages of use is important.

The physicochemical properties of fuel suspensions are primarily a function of the following factors: the nature of the solid and liquid phases and the type of chemical additives used to regulate these properties. Let us examine these factors.

EFFECT OF THE NATURE OF THE SOLID PHASE

The physicochemical properties of disperse systems are primarily a function of the properties of the surface of the disperse (solid) phase. For coal suspensions, these properties are primarily correlated with the degree of coalification (metamorphism) of the coal particles, their degree of oxidation and petrographic composition, and the type and amount of mineral impurities in the coal. In addition, the particle size and shape and the structure of the surface of the solid phase – porosity, cracks, etc., have a great effect on the rheological properties of coal suspensions.

So-called "energy" coals are usually used for production of fuel suspensions. They include coals of low (grades D and G) and high (grades T and A) stages of metamorphism, usually used in thermoenergetics. However, in some cases, coals from the middle stage of metamorphism (coking coals grades G, J, and OS), for example, in utilizing coal-concentration sludges or hydraulic mining of coal.

The surface of coal is essentially a function of the stage of metamorphism. The amount of oxygen-containing groups (–COOH, –OH, –CO, etc.) gradually decreases and as a consequence, the surface hydrophoby increases with an increase in the degree of coalification in the structure of the coals [10].

The largest amount of oxygen-containing groups is characteristic of coals of low stages of metamorphism, so that the surface of such coals has some hydrophilicity. The higher the stage of metamorphism of the coal, the more it is carbonized and consequently the more hydrophobic its surface will be [10].

The rheological behavior and stability of suspension fuels are essentially a function of the stage of metamorphism of the coal constituting the solid phase [11-14].

The properties of the surface of coals of different stages of metamorphism and the physicochemical properties of the suspensions made from them are a function of the petrographic composition of the coals [15, 16]. At a high (32-37%) content of fusinite in the coals, the degree of surface hydrophoby increases significantly. Fusinite is a soot lithotype of humic coals with a high carbon content, so that it is almost not wettable by water [17].

During mining and subsequent storage and in grinding, the surface of coal can undergo important changes due to oxidation by atmospheric oxygen. Even for coals of the same stage of metamorphism, it can differ due to a change in the hydrophobic-hydrophilic balance. As a consequence, the properties of the suspensions prepared from such coals will also differ [18].

The surface properties of fuel suspensions are essentially also a function of the composition and amount of inorganic (mineral) constituents in the coal. Coals from different mines can differ significantly in the amount and composition of the accompanying rocks. The most varied minerals in all possible combinations can be contained in the mineral constituent of coal. After concentration, a small amount (3-10%) of mineral impurities, the residual ash content of the coals, can persist in coals.

The basic components of the mineral constituent of coal are clay minerals and sand (quartz). Mineral impurities in the solid phase of suspension fuels can significantly affect the rheological properties and stability of these systems. Some clay minerals (montomorillonite, hydromica) exhibit a pronounced ability to form strong coagulation structures, even in small concentrations in the solid phase [19-22].

In manufacturing suspension fuels, some carbon-containing solid components, including petrochemical and coal-chemistry industry wastes, are frequently added to the disperse phase. Petroleum coke, petroleum asphalt, solid residues from burning coal, and coal tar are most frequently used as additives [23-26]. Coal pitch [27-29] or similar products of concentration of coals [30] can also be used in important amounts.

These hydrocarbon-containing components can to some degree change the overall hydrophilic-hydrophobic balance of the surface of the solid phase and consequently the physicochemical properties of the fuel suspensions.

Blends of coals that differ in the degree of coalification and blends of coals and peat or wood are sometimes used as the solid phase in fuel suspensions [31-33]. The physicochemical properties of such suspensions are determined by the overall hydrophilic-hydrophobic balance of the surface of the solid phase. This is due to a combination of hydrophobic fragments of highly metamorphized coals and the hydrophilic constituents of coals or lower stages of metamorphism, brown coal, peat, or wood.

The physicochemical properties of two-phase systems are essentially a function of the distribution of solid phase particles by size – the granulometric composition. Three groups of systems are distinguished based on the effect of the granulometric composition of the solid phase on the rheological properties and stability of the suspensions [7, 8, 34].

Systems containing solid material with weighted-average particle size (d_0) whose precipitation rate obeys Stokes' law belong to the first group. Such systems are sedimentation-unstable, but are resistant to formation of strong three-dimensional structures, i.e., they are aggregate-stable.

Blends of the second group contain particles whose average size is one order of magnitude smaller than d_0. Such systems are sedimentation-stable for a long time but are not resistant to formation of aggregates with strong coagulation contacts.

The third group consists of systems containing particles whose size is in the range of $0.1d_0$–d_0. Such suspensions are of interest, since they can have either the properties of unstratified suspensions or systems from the first group or a combination of these properties as a function of the disperse composition and number of very small particles.

In determining the optimum disperse particle size at which stable systems with the necessary rheological parameters can be obtained, it is necessary to consider the type of suspension. The sizes can differ significantly as a function of the nature of the solid and liquid phases of the suspension. The nature of the liquid phase is their determining parameter for coal suspensions.

For the water–coal suspensions most widely used as colloidal fuel, the question of the effect of the particle size on the rheological properties and stability have been relatively well investigated and is discussed in many publications, for example, [35-40]. According to established opinion, the closest packing per unit of volume is created at a certain ratio of large (100-200 mm) and small (0-50 mm) particles. This allows increasing the concentration of solid phase in the suspension while keeping the rheological parameters of the system within acceptable limits [4, 7].

The complexity of ensuring the optimum granulometric composition of suspension fuels should be noted. This problem is frequently solved empirically for each type of suspension, since the grindability of coal is a function of many factors: the grade, moisture content, mineral impurity content, degree of oxidation, hardness index, etc.

EFFECT OF THE NATURE OF THE LIQUID PHASE

Different liquids can be the dispersion medium for suspension fuels: water, alcohols, petroleum refining products.

It follows from an analysis of the patent and scientific and technical literature that coal suspensions with water as the dispersion medium – water–coal fuels – are of greatest interest for industrial use. However, there are many studies that propose using alcohol–coal or oil–coal suspensions as liquid fuel.

The nature (polarity) of the dispersion medium significantly affects the rheological properties and stability of coal suspensions. The results of the studies in [41, 42] show that the decrease in the polarity of the dispersion medium in going from water (dielectric constant of 78.8) to decane (2) increases the strength of the structure of the suspensions and causes an important shift in the concentration curves of the shear stress s in the region of lower concentrations C_s of the coal.

The existence of a critical crosslinking concentration (CCC), corresponding to the transition from an almost unstructured suspension to a solid-phase structure, and the sharp increase in the strength of the structure in a relatively narrow range of concentrations of the solid phase are characteristic of different liquid media – water, methanol (dielectric constant of 32.63), ethanol (25.2), acetone (21.5), isopropanol (18.3), *sec*-butanol (17.7), etc.

The limiting concentration of coal in the suspension is attained at maximum close packing of the particles in the solid phase. A decrease in the polarity of the dispersion medium decreases the CCC and limiting concentration of coal in the suspensions. This is due to an increase in the strength of the contacts (interaction energy) between particles [6].

The polarity of the medium has a large effect on the aggregate and sedimentation stability of coal suspensions. The aggregate stability of suspensions of coal in aqueous medium is due to manifestation of the ionic-electrostatic factor in stability.

This is indicated by the relatively high values of the electro kinetic potential: $\xi = -30\ldots-40$ mV [42, 43]. The formation of a developed double layer near the, on the whole nonpolar, surface of coal is correlated with the presence of oxygen-containing groups capable of ionization on this surface: –COOH and –OH.

In the less polar media of *sec*-butanol and decane, the x-potential of the coal particles is much lower than in aqueous medium: –16.4 and –9.7 mV, respectively [42], which is insufficient to prevent aggregation of the particles.

Based on an analysis of the published data, we can conclude: a strong enough decrease in the polarity of the dispersion medium will weaken the reciprocal electrostatic repulsion of carbon particles. This in turn will cause aggregation of the particles and an important increase in the strength of the structure and viscosity of the suspension.

CHEMICAL ADDITIVES

The problem of producing suspension fuels is closely correlated with the necessity of stabilizing and plasticizing disperse systems. Suspensions can be given aggregate and sedimentation stability and the necessary rheological properties (viscosity, fluidity, etc.) by adding chemical additives to the dispersion medium – stabilizers, plasticizers (dispersers, diluents), etc., to the dispersion medium. Chemical additives are adsorbed on the surface of particles of the solid phase, altering the conditions of their interaction with each other and with the medium.

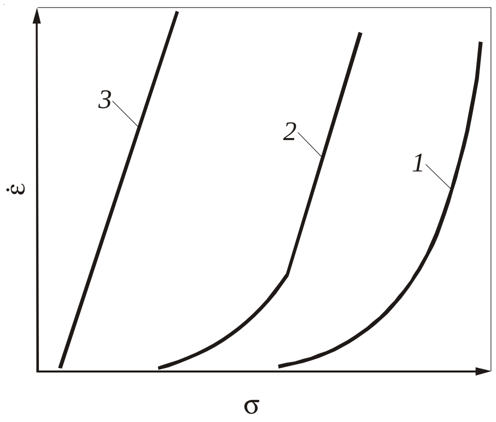

Fig. 1. Rheological curves of flow of a suspension: 1) with no plasticizer (pseudoplastic type of flow); 2) with plasticizer A; 3) with plasticizer B (viscoplastic type of flow).

Organic SF of different kinds (ionogenic and nonionogenic) and polymers are usually used as stabilizers and plasticizers for fuel suspensions. In reacting with ionogenic SF, like electric charges arise on the particles of the solid phase, and this favors reciprocal repulsion of the particles.

According to the general theory of stability of disperse systems (DLVO), the electrostatic constituent of the disjoining pressure (repulsion) is characteristic of systems with aqueous media in which conditions for dissociation exist [41, 44].

The mechanism of formation of an electric double layer around particles of disperse phase is related to surface dissociation of the substance of the particle, adsorption of chemical additives (ionogenic SF) on the surface of the solid phase, and orientation of the dipoles of the molecules of the solvent or dissolved substances. Organic ionogenic SF and sometimes also inorganic electrolytes are used in fuel suspensions to ensure the aggregate stability of the system and as plasticizers [45, 46].

Adsorption layers of organic SF and polymers decrease the surface tension on the boundary of the solid and liquid phases, bind part of the dispersion medium, and form a protective solvation (hydration in the case of water) shell around the particle. The disperse systems are stabilized as a result of lyophilization of the surface of the particles of solid phase.

Strong stabilization, which can only be attained with SF whose adsorption layers are crosslinked and have high strength and viscosity for this reason ("colloidal protection"), is necessary for the stability of concentrated fuel suspensions [47, 48].

The quality of the plasticizers and stabilizers is evaluated from the point of view of satisfaction of their manufacturing requirements.

Plasticization of suspension fuels consists of obtaining systems with low viscosity and strength characteristics after addition of the additives: effective viscosity at shear rate $\dot{\varepsilon}$ = 10 sec^{-1} is 1-2.5 Pa·sec; the dynamic yield point σ_0 is 5-15 Pa.

For stabilizing suspension fuels, it is necessary to select additives that result in sedimentation- and aggregation-resistant systems.

The minimum concentration in the system at which the effect of chemical additives becomes pronounced is usually considered a criterion of the effectiveness of these additives [49]. For suspension fuels, the effectiveness of the plasticizer is determined by the minimum concentration C_{pl} at which given values of the effective viscosity and initial shear stress are attained. In other words, the lower C_{pl} is, the more effective the plasticizer is.

A general type of complete rheological flow curve s = $f(\dot{\varepsilon})$ is proposed in [50] as a criterion of the effectiveness of plasticizers in suspension fuels. A plasticizer which ensures linearity of the curve in standard conditions (temperature, type of coal, granulometric composition, ash content, type of liquid phase, etc.), should be considered optimum for suspension fuels.

In other words, an effective plasticizer should ensure a viscoplastic (or close to Newtonian) type of flow of a limitedly lyophilized suspension (see Fig. 1, curve 3).

According to [7], this type of flow is preferred, since the coagulation structures formed in the system are reversibly destroyed in a narrow range of variation of the shear rate. This makes them easy to transport in fuel manufacturing systems. In addition, such systems do not have thixotropic and dilatant properties.

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