

Increasing the Effectiveness of Detergent-Dispersant Additives in Motor Oils

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Abstract:

This article examines the increase in the effectiveness of detergent-dispersant additives in motor oils. It was revealed that the possibility of electrophysical indicators for assessing the detergent-dispersant properties of additive compositions. A significant influence of the composition of the oil-solvent on the effectiveness of subsidence has been shown. The presence of quinazoline and acrylamide derivatives in the solvent oil reduces the detergent-dispersant properties of composite additives by 25.0-45.0%.

Keywords: detergent-dispersant additives, internal combustion engines, thermal-oxidative processes, quinazalondione-2,4, acrylamide, alkyl salicylates.

Introduction. It is known that during the operation of motor oils in internal combustion engines (ICE), additives designed to give the oil the required level of performance properties gradually lose their effectiveness. As a result, the process of additive activation and changes in the composition of oils lead to a decrease in their quality, which negatively affects the reliability of equipment.

A decrease in the quality of oils makes it necessary to determine their performance and establish a replacement period. Changes in the state of oils and a decrease in the effectiveness of additives are largely determined by the formation of a constantly changing colloidal system, in which additives, components of the original base, and aging products formed during the operation of motor oils play an equally important role [1,2].

The purpose of this work is to identify the possibility of increasing the service life of motor oils prepared using local raw materials by studying the interaction of additives with motor oil components and assessing the kinetics of these interactions.

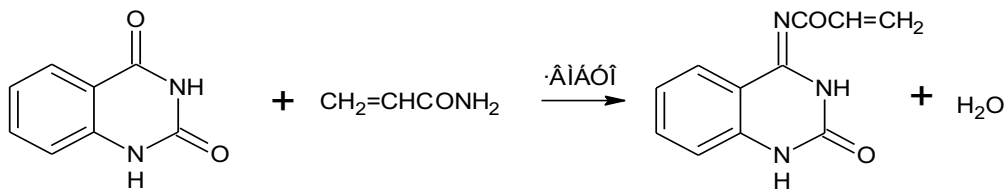
Theoretical part. Due to increased alkalinity, detergent-dispersant additives must actively counteract the development of thermal-oxidative processes by neutralizing and solubilizing their products, maintaining their effectiveness in an acidic environment for as long as possible. This should ultimately ensure the required reliability of the equipment for a given oil performance.

The main characteristic of motor oil, indicating the amount of detergent-dispersant additives it contains, in this case is its neutralizing ability, determined by the value of the alkaline number (or alkaline reserve) of the oils. Detergent-dispersant additives, depending on their chemical composition and degree of carbonitability, have different alkalinity and, therefore, based on their alkalinity, are divided into neutral, medium-, high- and super -alkaline groups.

Based on their chemical composition, the main detergent-dispersant additives are divided into the following groups: - a mid quinazalondionyl-2,4-acrylamides; alkyl salicylates; metal sulfonates. In these additives, the metals Ba , Ca , Mg and metal carbonates are carriers of alkalinity.

Experimental part. Detergent-dispersant additives based on quinazalondione-2,4 and acrylamide were obtained in the following way:

Place 47.5 g (0.3 mol) into a four-neck flask equipped with a stirrer, thermometer, dropper and reflux condenser. quinazolindione-2,4 and with continuous stirring, add dropwise a benzene solution of 23 g (0.3 mol) of acrylamide. At this temperature, the reaction mixture was maintained at 30 ° C using an ice bath. After the addition of the acrylamide solution was completed, the reaction mixture was stirred for another 15 minutes, and then the temperature of the reaction mass was increased to 150 ° C and maintained at this level for 60 minutes until water was released in the amount of 6 ml (0.3 mol). Then filtered using a vacuum pump and dried to obtain 58.2 g (81.5%) of the amide.



The IR spectrum of the amide obtained on the basis of quinazalondione-2,4 and acrylamide is shown in Fig. 1. It can be seen that the absorption band at 752.24 cm⁻¹ refers to plane bending vibrations

NH groups, and the absorption region 1037.10 cm⁻¹ , 1138.00 cm⁻¹ stretching vibrations of alkylamide groups, as well as the average intense absorption band 1238.30 cm⁻¹ and 1404 cm⁻¹ belong to amide groups, 1614.42 cm⁻¹ , 1660.71 cm⁻¹ absorption band is deformation vibrations of NH groups, 1693.50 cm⁻¹ C=O carbonyl groups, 3250.05 cm⁻¹ absorption band refers to secondary amide groups.

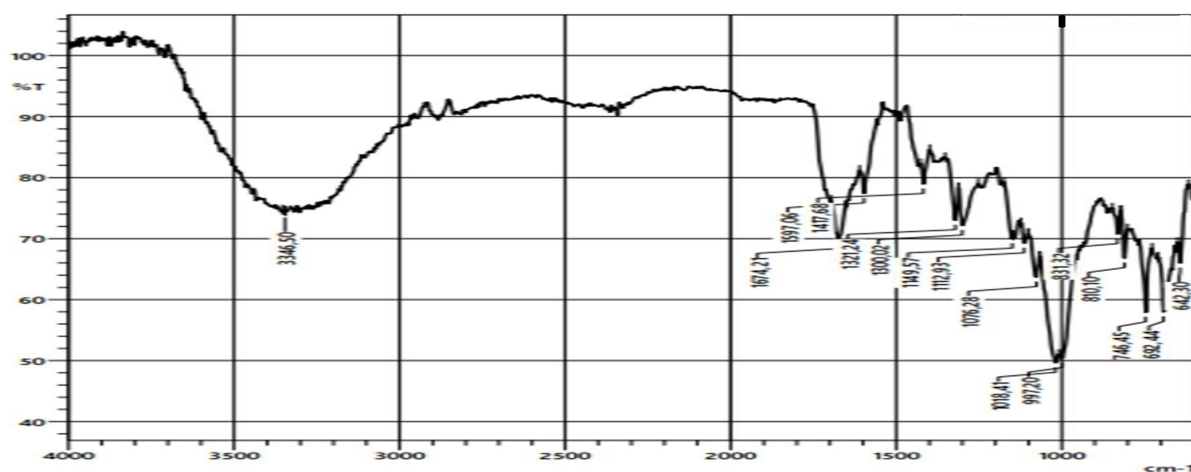


Fig.1. IR spectrum of an amide obtained from quinazalondione-2,4 and acrylamide

Discussed results. The influence of the structural group composition of the oil on the formation of high-temperature deposits was studied , and the interaction of detergent-dispersant additives of various types with base oil components was also assessed .

To evaluate the high-temperature properties of base oils, six samples (three petroleum fractions, as well as a mixture of them and two synthetic base oils) were subjected to high-temperature catalytic oxidation for 180 minutes at 230 °C and assessment of varnish-forming properties for 45 minutes (Table 1).

Table 1. Propensity of base oils to form high temperature deposits

No.	Basic basis	EKO (180 min. 230 °C)		Amount of deposits % mass
		Aspen.	Env .	
1	PAO-4	0.2 5	0.11 4	0.4 1
2	PAO-8	0.44	0.24 5	0.8 3
3	fr. 350-420	0.9 0	0.37 1	4.3 5
4	fr. 420-500	1.4 1	0.52 2	12, 2
5	0st>500	1.6 2	0.63 5	29.5
6	M-14 mixture	1.1 3	0.42 3	20, 7

Synthetic base oils (PASM and PAO-8) had the least tendency to deposits and destruction of the base. As the boiling point of oil fractions increased, the amount of deposits increased with a parallel increase in optical density. The small amount of sediment in synthetic oils is due to the presence of free double bonds in the PBO.

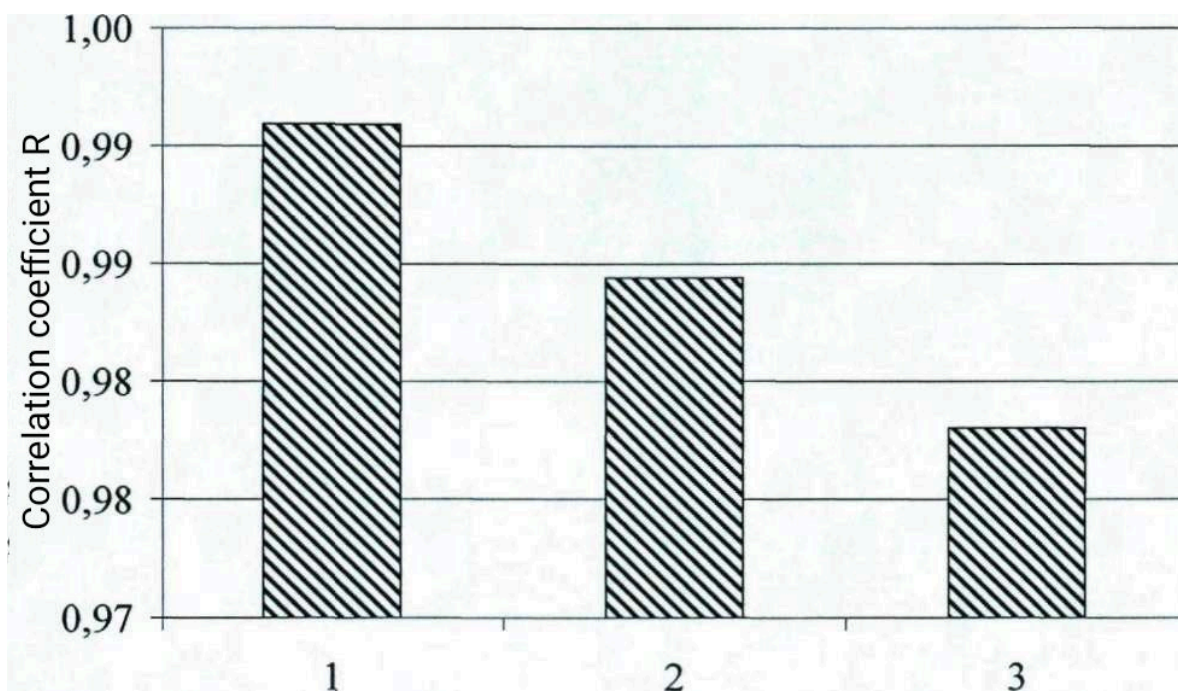
During operation, engine oil ages, accompanied by changes in the structural and group composition. We assessed the change in the composition of the base base after three hours of oxidation of the residual base oil (Table 2.)

Table 2. Structural and group composition of OST >500

Structural and group composition	Content, wt.%		
	original fraction	oxidized fraction	d
naphtha+paraffins	60.18	48.22	-11.96
unicycle _ and rum.	23.59	19.69	-3.90
bike , aroma	6.56	7.33	+0.77
polycycle _ aroma	6.71	9.35	+2.65

resins	2.96	6.76	+3.79
asphaltenes + copper naphthenates	0.00	8.65	+8.65
Total:	100.00	100.00	-

Thus, the assessment of the oxidability of oils by the VKO method showed that as the oil oxidizes, an increase in bi- and polycyclic hydrocarbons and resins occurs, which increase the tendency of the oil to form high-temperature deposits, coefficient (R) was determined for various groups of hydrocarbons in oil fractions and the amount of deposits determined by the “Folder” method (Table 1). Correlation coefficient (R) characterizes the static relationship between two random variables. If it is assumed that the values of the variables have a strict order relation, then *a negative correlation* is correlation, in which an increase in one variable is associated with a decrease in another variable, and the correlation coefficient may be negative; *a positive correlation* in such conditions is a correlation in which an increase in one variable is associated with an increase in another variable, and the correlation coefficient can be positive [3,4].



Rice. 2 . The influence of the structural group composition of oil on the formation high temperature deposits: 1 - bicyclic aromatic hydrocarbons; 2 - polycyclic aromatic hydrocarbons; 3- resins

In the case of naphthene - o - paraffin hydrocarbons, the correlation coefficient is negative, which indicates that with an increase in the content of these hydrocarbons, the amount of deposits in the oil decreases; in the case of other groups of hydrocarbons, the correlation coefficient is positive. The closer the value of the correlation coefficient is to 1, the greater the influence of the hydrocarbon group on the formation of high-temperature deposits (Fig. 2) .

The influence of colloidal chemical interactions of additives with resins on their high-temperature properties was assessed. To do this, heat treatment was carried out for 10 minutes at a temperature of 240 °C (Table 3).

Table 3. The influence of resins on the detergent-dispersant properties of additives

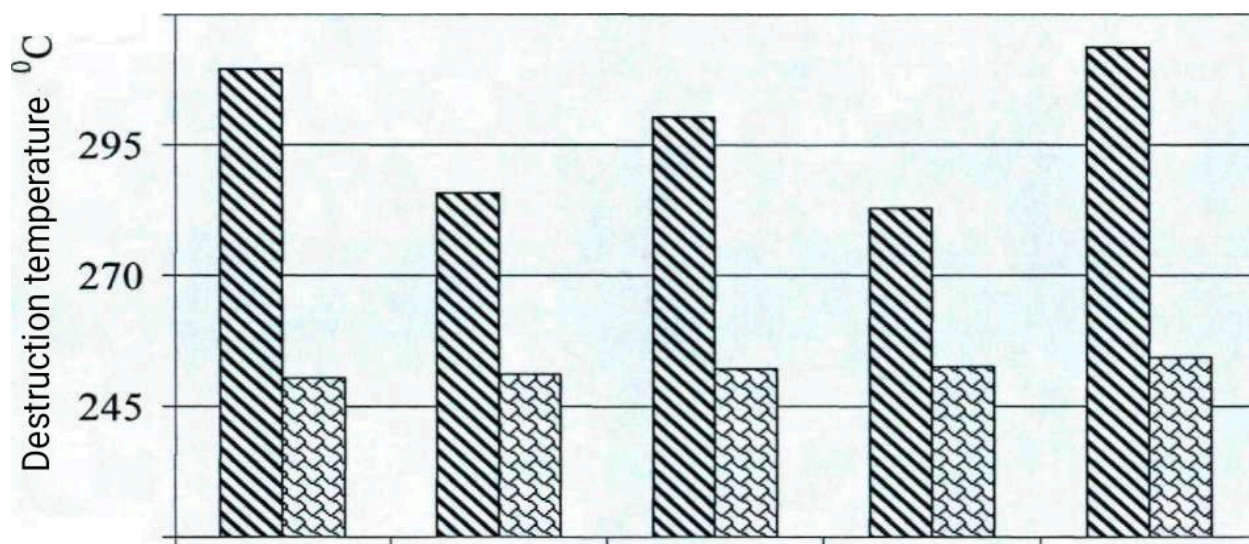
No.	Additive name	Optical density, O_{si}			Change in contact potential difference L11, mV		
		ref.	0.5% resins (10% additive)	4.5% resins (50% for additive)	ref.	0.5% resins (10% additive)	4.5% resins (50% for additive)
1	PAOM-4	0.004 8	0.12 4	0.23 3	160	165	225
2	S-150	0.125 0	0.04 2	0.04 6	195	215	275
3	B-7120	0.104 1	0.10 3	0.16 2	150	225	150
4	K-51	0.501 5	0.44 2	0.52 5	122	90	125
5	A-22	0.720 2	1.28 7	1.54 8	130	115	100

When resins are added to calcium sulfonate, its solubility increases, but the additive does not interfere with the process of polycondensation of aromatic hydrocarbons, as indicated by a decrease in the optical density of the solution.

However, at a concentration of 3.5%, a sharp increase in the contact potential difference occurs, which is probably due to the fact that the additive can no longer hold such an amount of resins in the oil volume and the resins are deposited on the metal surface. Data obtained on the interaction of calcium phenolate with resins obtained using conductometric titration were confirmed when assessing thermal stability and detergent properties. As can be seen, the interaction of calcium phenolate with resins not only inhibits the polycondensation process, but also increases the thermal stability of the phenolate. It is likely that the resins have opposite charges and when the additive interacts with them, the charge of the resins decreases. At a high concentration of the pollutant, the phenolate cannot interact with it and excess resins are adsorbed on the metal surface, resulting in a decrease in the change in the EDC.

Succinimide (2nd group), when interacting with a pollutant under the influence of temperature, is destroyed and promotes the process of polycondensation (Table 3). The compounds formed as a result of destruction are retained in volume, as indicated by a slight change in the CRP. The decrease in optical density with the introduction of resins (0.5% mass) is associated with their solubilization; the size of these particles does not exceed 3 nm. Based on the results obtained, it can be assumed that the destruction of succinimide results in the formation of radicals rather than polar compounds. In the case of zinc dithiophosphate A-22, the additive is destroyed, as indicated by a sharp increase in optical density and precipitation on the metal surface. As has been shown that it is possible to increase the thermal stability of zinc dithiophosphate by selecting a synergistic composition with group I additives (sulfonate, phenolate, calcium salicylate).

As a rule, additives are added to commercial oils not individually, but in half-packages or packages. Therefore, it was of practical interest to study the influence of resins not only on individual additives, but also on their combinations. The influence of resins on the combination of neutral, highly alkaline sulfonates, as well as their mixtures with zinc dithiophosphate. Using thermogravimetry, we assessed the influence various combinations of additives on carbon formation, and using differential scanning calorimetry, the change in the destruction temperatures of additives was assessed. The differential thermal analysis (DTA) curve records thermal effects associated with physicochemical transformations of the additive;

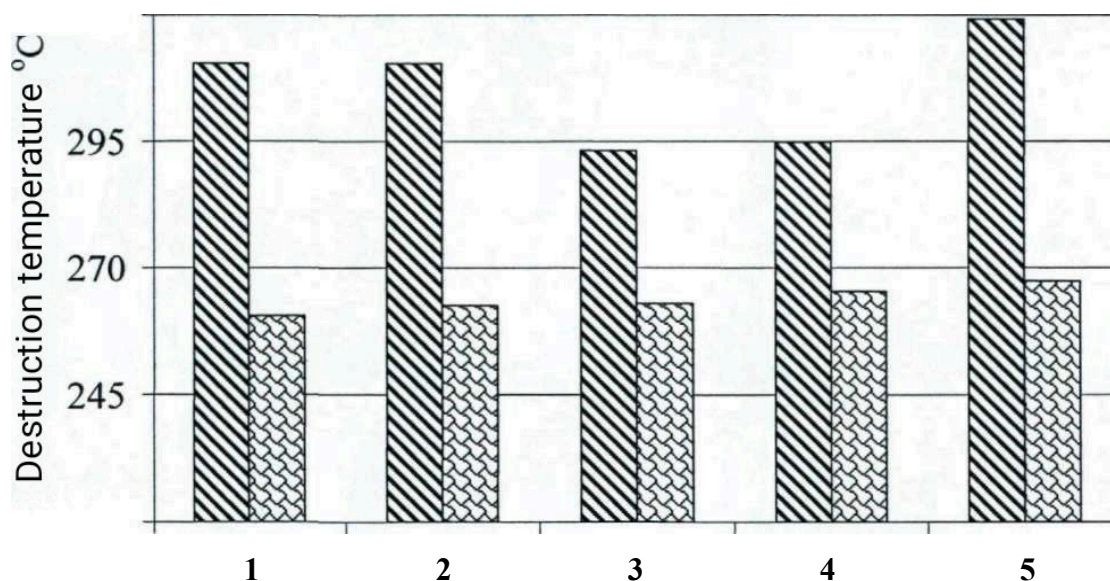


1 2 3 4 5

IK-31 0 mixture of K-31 and A-22

Rice. 3 . Effect of resins on the thermal stability of neutral sulfonate calcium and its combination with zinc dithiophosphate : 1 - without resins; 2 - 5% resins; 3 - 15% resins; 4 - 30% resins; 5 - 50% resins

the thermogravimetric curve (TGA) characterizes the decrease in its weight when heated, and the differential thermogravimetric curve (DTG) determines the rate of decrease in the weight of the additive. The criterion for assessing the thermal stability of the additives under study is the temperature of the onset of decomposition, identified with the temperature of the onset of formation of volatile products (TTM).

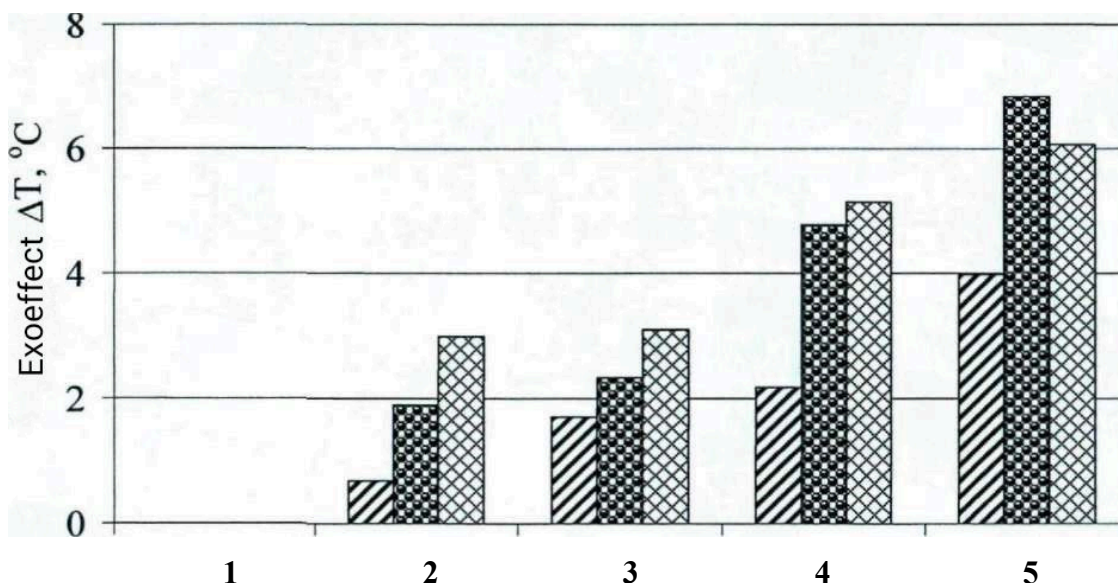


0 K-312 N mixture of K-312 and A-22

Fig.4. The influence of resins on the thermal stability of highly alkaline sulfonate calcium and its combination with zinc dithiophosphate : 1- without resins; 2 - 5% resins; 3 - 15% resins; 4 - 30% resins; 5 - 50% resins.

The results of processing thermograms are presented in Fig. 3 , 4 and 5. When zinc dithiophosphate is added to calcium sulfonates , the thermal stability of these combinations decreases (Fig. 4). In

the presence of dithiophosphate together with a neutral sulfonate, the “pollutant becomes heavier” slightly (Fig. 3.) Pure The sulfonate is capable of retaining up to 30-40% of the pollutant. Above this value, the exoeffect peak shifts toward higher temperatures. In the case of highly alkaline Calcium sulfonate (K-312) obtained an identical trend (Fig. 5), however, the combination of neutral sulfonate and dithiophosphate more effectively prevents the process of compaction of the “pollutant” hydrocarbons, as indicated by the lower temperature values of the exo-effects . The temperature increase was also calculated when adding a “pollutant” in various concentrations for a mixture of calcium sulfonate with dithiophosphate (Fig. 5). The smallest increase in temperature with increasing concentration of the “pollutant” is for the neutral sulfonate with dithiophosphate . The data obtained can be explained by the fact that this sulfonate has a greater solubilizing ability compared to the highly alkaline one and is capable of interacting with the “pollutant” and preventing the process of its compaction. The mixture of sulfonates occupies an intermediate position in its ability to interact with the “pollutant” up to its concentration of 30-40% .



And K-31 and A-22 EZ K-312 and A-22 And mixture (K-31 and K-312) and A-22

Rice. 5 . The influence of resins on the magnitude of the exoeffect shift calcium sulfonates different alkalinity and its combination with zinc dithiophosphate : 1 - without resins; 2 - 5% resins; 3 - 15% resins; 4 - 30% resins; 5 - 50% resins

Conclusions: It was revealed that the possibility of electrophysical indicators for assessing the detergent-dispersant properties of additive compositions. A significant influence of the composition of the oil-solvent on the effectiveness of subsidence has been shown. The presence of quinazoline and acrylamide derivatives in the solvent oil reduces the detergent-dispersant properties of composite additives by 25.0-45.0%.

A principle for selecting components when developing motor oils is proposed. This principle is a set of methods, including the assessment of colloid-chemical interactions between the components of motor oil and subsequent high-temperature tests. This principle makes it possible to reduce time and economic costs when developing all-season universal motor oils.

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