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Detergent-dispersant additives are the most important of the additives used in motor oils. Theories as to the mechanism through which these additives act are of great practical importance in developing new additives and in selecting effective additive packages. This importance is reflected in the large number of studies that have been reported in this area over a number of years [1-4].

It is generally agreed [2] that the action of detergent-dispersant additives can be explained largely in terms of solubilization of the oil-insoluble products from oil and fuel decomposition, or by stabilization of colloidal dispersions of these products in the oil, so as to prevent the precipitation of decomposition products on metal surfaces in the form of sludge, varnish, and carbon deposits. Also helping to prevent such deposition is the formation of protective films of these additives on metal surfaces [5].

The stability of colloidal dispersions is determined by their resistance to aggregation, i.e., resistance to coagulation. In evaluating the factors affecting the stability of contaminant/oil dispersions against aggregation, we have used carbon black (Grade PM-75) as a model compound. By the use of this carbon black to evaluate high-temperature dispersancy in accordance with the procedure given in [6], data have been obtained that correlate satisfactorily with engine test results in the Petter A-1 diesel engine [7].

The stability of colloidal particles against aggregation will depend on the existence of forces opposing approach of the particles under the influence of van der Waals attractive forces [8]. For particles with a diameter of  $0.1 \mu\text{m}$ , the energy of van der Waals attraction is 100-200 times greater than  $kT$  [9]. Stable particles of contaminants in engines may be up to  $1.5 \mu\text{m}$  in size [3]. Thus, in the absence of any forces opposing the van der Waals attraction, the particles must coagulate rapidly; when detergent-dispersant additives present, this does not take place.

In order to ensure that colloidal systems are stable against aggregation, there must be an energy barrier preventing approach of the colloidal particles, with a magnitude  $V_n > 10 kT$  [8] with  $V_n = V_r + (-V_a)$ , where  $V_n$  is the net energy of particle interaction,  $J$ ;  $kT$  is the energy of thermal motion of the particles,  $J$ ;  $k$  is Boltzmann's constant,  $J/\text{deg}$ ;  $T$  is the absolute temperature,  $^{\circ}\text{K}$ ;  $V_r$  is the energy of repulsion,  $J$ ;  $V_a$  is the energy of attraction of the particles (with a minus sign),  $J$ . In addition, the depth of the secondary minimum (van der Waals attractive forces), arising at a distance between particles corresponding to contact of their adsorption-solvate shells, must not be greater than  $kT$  [10].

According to currently held views, repulsion between colloidal particles may be electrostatic (with adsorption of low-molecular-weight ions or ionized surfactants on the particles) or steric (with adsorption of nonionic or undissociated surfactants or polymers) [8]. In nonpolar media (for example, in hydrocarbons), it is more probable that stability against aggregation may be provided through the steric mechanism. The smaller influence of electrostatic repulsion on the effectiveness of detergent-dispersant additives (at least in the original oils) is demonstrated by the fact that both ashless dispersant additives (nonionic surfactants) and ash-containing detergents (anionic surfactants) lower the electrokinetic potential of carbon black dispersions [11].

The stability of nonaqueous and primarily hydrocarbon colloidal systems, when it is a consequence of the adsorption of polymers or nonionic surfactants, is explained by the theory of steric (entropy) repulsion of Mackor and van der Waals [12] which was subsequently extended and refined [13]. It has been shown that the improved theory of steric repulsion is applicable only with a low density of surfactant adsorption on the colloidal particles [14]. The formation, on the particle surface, of adsorbed layers (for surfactants) and solvate shells (for the dispersion medium) will give a considerable reduction in the energy of van der Waals interaction. Thus, with a favorable ratio of the van der Waals interaction constants (the Hamaker constant), for colloidal particles with a diameter of  $0.1 \mu\text{m}$  and a thickness of the adsorbed or solvated layer greater than  $20 \text{ \AA}$  ( $V_a \ll kT$ ), such particles may be stabilized as a result of "thermal peptization" (Brownian motion of the particles) [9].

For calculation of the van der Waals attractive energy for particles containing adsorption/solvate shells, the following equation has been derived [9]:

$$\frac{V_a}{kT} = \frac{1}{12kT} (A_m^{1/2} - A_s^{1/2})^2 H_s + (A_s^{1/2} - A_p^{1/2}) H_p + 2 [(A_m^{1/2} - A_s^{1/2}) (A_s^{1/2} - A_p^{1/2}) H_{ps}]$$

where  $V_a$  is the energy of interaction, J;  $A_m$  is the Hamaker constant for the disperse phase, J;  $A_p$  is the Hamaker constant for the dispersion medium, J;  $A_s$  is the Hamaker constant for the surfactant, J;  $H_p$ ,  $H_s$ , and  $H_{ps}$  are dimensionless Hamaker functions.

For calculation of the energy of repulsion for colloidal particles with dense adsorbed layers of surfactant on the surface, solvated with the dispersion medium, the following equation has been proposed [15]:

$$V_r = -\frac{4\pi}{3} B' C_g \left( d - \frac{a}{2} \right) \left( 3r + 2d + \frac{a}{2} \right)$$

where  $B'$  is the second virial coefficient (from the equation for the osmotic pressure of polymer solutions),  $J \cdot m^3/kg^2$ ;  $C_g$  is the concentration of surfactant in the adsorption/solvate shell,  $kg/m^3$ ;  $d$  is the thickness of the adsorption/solvate shell,  $m$ ;  $a$  is the distance between surfaces of the uncoated particles,  $m$ ;  $r$  is the particle radius,  $m$ .

According to these views, the energy of repulsion arises as a result of local osmotic pressure in the zone of mutual penetration of the adsorption/solvate shells. The magnitude of this energy is proportional to the second virial coefficient, which characterizes the interaction of polymer or surfactant molecules with the solvent. Colloidal systems that are stabilized by this mechanism are lyophilized lyophobic colloids. In other words, colloidal particles coated with adsorbed shells of surfactant behave like polymers containing the alkyl radicals of these surfactants. The validity of this theory has been supported by experimental studies [14-16].

Colloidal dispersions of carbon black (and also dispersions of other contaminants in used oils), stabilized by adsorbed surfactant shells, can be classed with such systems. They should be reversibly precipitated (flocculated) by the addition of a solvent that is a precipitant for hydrocarbons (for the alkyl radicals of the surfactant). This hypothesis has been confirmed; colloidal dispersions of carbon black stabilized by succinimides or by metal sulfonates or salicylates are precipitated from hydrocarbon solutions by lower ketones and lower alcohols.

From the formula of Fischer [15] that was cited above, it follows that the effectiveness of particle stabilization under the influence of a structural-mechanical barrier is influenced by the quantity of surfactant adsorbed on the particle surface, the thickness of the adsorption/solvate shell, and interaction of the alkyl radicals of the surfactant with the solvent (as characterized by the second virial coefficient in the equation for the osmotic pressure of polymer solutions). In calculating the energy of repulsion of carbon black particles, data are needed on the quantity of additive adsorbed on the carbon black and the thickness of the adsorption/solvate shells, i.e., the adsorbed layers of surfactant, swollen in oil.

The quantity of additive adsorbed on carbon black was determined gravimetrically after adsorption, with a dispersion of carbon black in a solution of the additive in white mineral oil (carbon black content 2%, additive content 1.5% active ingredient). We obtained data for various ratios of carbon black and additive (concentration curves); however, since the indicated ratio of additive and carbon black gave the maximal dispersancy, all calculations were carried out for particular concentrations. In order to separate out the carbon black with adsorbed additive, the dispersion, diluted with hexane (1 : 5), was centrifuged at 7000 rpm; the resulting precipitate was dispersed ultrasonically (22 kHz, 5 min) in hexane, and then again precipitated by centrifuging. Thus, we determined only the quantity of irreversibly adsorbed (chemisorbed) additive. The dimensions of the carbon core of the dispersed particles were determined by electron microscopy and by measurement of the specific surface of the dispersions, both of these techniques being applied after heating in a stream of inert gas at 400°C to decompose and remove the adsorbed additive. The two techniques gave virtually identical results.

Data on the adsorption of additives at different temperatures, with different dimensions of the particles and of the adsorption/solvate shells, are presented in Table 1. The size of the particles with the adsorption/solvate shells was determined viscometrically. The thickness of the swollen shells was determined on the basis of the effective volume of the particles, which was calculated in accordance with the equation [17]

$$\eta_{sp} = 2.5f + k(2.5f)\varphi$$

\* As in Russian original; it appears that  $A_m$  should refer to the dispersion medium, and  $A_p$  to the disperse phase (particles) - Translator.

TABLE 1. Adsorption of Additives on PM-75 Carbon Black from 2% Solution (Active Ingredient) in White Mineral Oil

Type of additive and method of carbon black pretreatment	Quality of adsorbed additive, mass % relative to original carbon black	Carbon black particle size (according to specific surface, BET method) $\mu\text{m}^*$
Succinimide additive S-5A; adsorption at 20°C (mechanical stirring for 5 min at 2500 rpm, ultrasonic dispersion at 22 kHz for 5 min); dilution with hexane (1 : 5), separation of insoluble material by centrifuging; redispersion in hexane by ultrasonic treatment (22 kHz for 5 min), followed by centrifuging and drying	18.7	0.052
Same, but thermostated at 250°C after adsorption (3 h)	8.0	0.051
High-basicity calcium alkylsalicylate (MASK); procedures as described in first entry (above)	18.7	0.054
Same, after thermostating (250°C, 3 h)	9.3	0.051
Neutral calcium sulfonate; sample preparation same as in first item, above	30.0	0.048
Same, after thermostating (250°C, 3 h)	18.0	0.050
High-basicity sulfonate (S-300); sample preparation same as in first item, above	44.0	0.052
Same, after thermostating (250°C, 3 h)	36.0	0.054

\* Carbon black particle size, as determined by electron microscopy, was 0.04-0.07  $\mu\text{m}$  in all cases.

where  $\eta_{sp} = (\eta/\eta_0) - 1$ ;  $\eta$  is the viscosity of the dispersion;  $\eta_0$  is the viscosity of the dispersion medium;  $\varphi$  is the volume fraction of disperse phase;  $k$  is a coefficient accounting for interaction of the particles;  $f$  is the number of times  $\varphi$  is increased due to the adsorption/solvate shell.

The average particle size of the PM-75 carbon black (at 250°C) is 517 Å. For the succinimide additive S-5A, which is based on polybutene with a molecular mass of 850 and diethylenetriamine, the relative viscosity  $\eta/\eta_0$  is 1.2 (at 100°C) with an adsorbate content of 2 g/100 ml and an adsorbed additive quantity of 0.18 g/g of carbon black. For the alkylsalicylate additive MASK, the value of  $\eta/\eta_0$  at 100°C is 1.41 with an adsorbate content of 1.8 g/100 ml and an adsorbed substance quantity of 0.33 g/g of carbon black. For the S-5A additive,  $\varphi = (1.2 - 1)/2.5 = 0.08 \text{ cm}^3/\text{cm}^3$ .

The original volume fraction of the oil-unswollen adsorbate in the case of the succinimide S-5A is  $0.0115 \text{ cm}^3/\text{cm}^3$ . We also found the concentration of adsorbed additive in the swollen adsorption shell ( $44.5 \text{ kg}/\text{m}^3$ ). The viscosity was determined in accordance with GOST 33-66; the electroviscous effect was not taken into account. The initial volume of the carbon black particles after adsorption of the S-5A additive increases by a factor of 1.33, and the diameter by a factor of 1.075; i.e., the diameter is  $517 \cdot 1.075 = 557 \text{ Å}$ . After swelling of the adsorbed layers in oil, their volume increases by a factor of 6.9, and the diameter by a factor of 1.9; i.e., the diameter is now 1057 Å. As a result, the thickness of the adsorption/solvate shell in the experiments with the carbon black and the succinimide additive S-5A proves to be 270 Å. By an analogous calculation it was found that the concentration of the alkylsalicylate additive MASK in the adsorption/solvate shell is  $19.8 \text{ kg}/\text{m}^3$ , and the thickness of this shell is 490 Å.

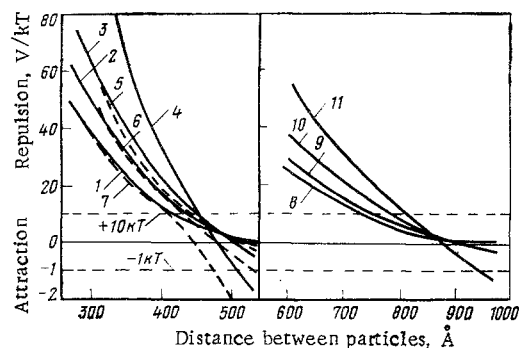


Fig. 1. Energy of interaction of PM-75 carbon black particles (1-4) and graphitized carbon black particles (5-7) stabilized with succinimide additive S-5A and PM-75 carbon black stabilized with alkylsalicylate additive MASK (8-11), as functions of the distance between particles with the following diameters: 1, 8) 400 Å; 2, 9) 600 Å; 3, 10) 1000 Å; 4, 11) 2000 Å; 5) 200 Å; 6) 300 Å; 7) 500 Å.

On the basis of these data, using the Fischer formula [15], we calculated the energy of osmotic repulsion of carbon black particles with diameters of 400, 600, 1000, and 2000 Å. The value of the second virial coefficient was taken as  $B' = 1 \text{ J} \cdot \text{m}^3/\text{kg}^2$  for both additives (i.e., the same as for the "medium-quality" solvent). Then, using the equation of Vold [9], we calculated the energy of van der Waals attraction between carbon black particles with diameters of 40, 600, 1000, and 2000 Å, with a shell thickness corresponding to the experimentally determined values (with allowance for the greatest possible interpenetration of the shells). For the S-5A, the following values of the Hamaker constant were assumed: for the carbon black,  $A_p = 2.17 \cdot 10^{-19} \text{ J}$  [18]; for the oil,  $A_m = 7 \cdot 10^{-20} \text{ J}$ ; for the surfactant (additive),  $A_s = 7.1 \cdot 10^{-20}$  [19]. For the carbon black stabilized with the MASK additive, the following values were assumed:  $A_p$  the same as above;  $A_m = 6 \cdot 10^{-20} \text{ J}$ ;  $A_s = 6.1 \cdot 10^{-20} \text{ J}$  [19].

On the basis of these data, values were obtained for the net interaction of carbon black particles  $V_n = V_r - V_a$  (see Fig. 1). These data indicate that the additives S-5A and MASK should be effective stabilizers for particles with diameter  $\leq 0.1 \mu\text{m}$ , since for such particles we find observance of both criteria of stability:  $V_r > 10 \text{ kT}$  and  $V_a < 1 \text{ kT}$  (in the secondary minimum). For particles with a diameter of  $0.2 \mu\text{m}$ , the first criterion of stability is fulfilled, but when the particles approach to a distance corresponding to contact of their adsorption/solvate shells, a secondary potential minimum appears; for S-5A this is equal to 2.04 kT, and for the MASK it is 1.52 kT. Consequently, such particles may coagulate as a result of adhesion of the adsorption/solvate shells.

Thus, we see that both additives sterically stabilize carbonaceous contaminants with particle diameters from 0.02 to  $0.06 \mu\text{m}$ ; this conclusion is in accord with the experimental data. Hence, the proposed theoretical approach is applicable in analyzing the mechanism of detergent-dispersant additive action (in the case of the MASK additive, the stability of the carbon black against aggregation may also be increased as a result of electrostatic repulsion). An analysis of the equations of Vold [9] and Fischer [15] shows that the depth of the second minimum which in the stabilization of particles under the influence of adsorption/solvate shells will limit primarily the maximum size of stable particles, depends principally on the overall Hamaker constants:  $A^1 = (A_m^{1/2} - A_p^{1/2})^2$ . Hence the maximal diameter of stable particles will be greater with lower Hamaker constants for the disperse phase and high Hamaker constants for the stabilizing surfactant and the dispersion medium (lubricating oil). Hence, greater dispersancy should be shown by high-molecular-weight oils and surfactants; this view is supported by practical data.

Heating carbon black to temperatures above  $1400^\circ\text{C}$  leads to graphitization, and as a result, the Hamaker constant increases severalfold [18, 20]. Consequently, in high-performance engines, the carbon that is formed (in the same particle size range of  $0.04\text{--}0.07 \mu\text{m}$ ) should be more difficult to hold in suspension than the carbon formed in engines operating in less severe thermal regimes. In order to establish the magnitude of this factor, we calculated the energy of van der Waals attraction for particles of completely graphitized carbon black, stabilized with S-5A succinimide (the Hamaker constant was taken from [18]). The energy of osmotic repulsion was assumed to be the same as for normal carbon black. On the basis of values calculated for the

net energy of particle interaction (see Fig. 1) it is evident that particle coagulation is possible for diameters  $\geq 0.03 \mu\text{m}$ ; i.e., the particle size limit for stability against aggregation has been reduced almost threefold.

Theoretical concepts explaining dispersancy by the formation of a steric (adsorption/solvate) barrier are based on irreversibility of adsorption of surfactant molecules on particles of carbonaceous contaminants. A considerable part of the total amount of additive is adsorbed irreversibly, i.e., is not desorbed when heated to  $250^\circ\text{C}$  (see Table 1). Thus, we find still another condition for effectiveness of dispersant additives at elevated temperatures, namely, the strength of their adsorption bonding to the surface of the contaminant particles. For succinimide additives, the heat of adsorption is 34-50 kJ/mole, and for metal-containing additives such as sulfonates and phenolates it is 130-170 kJ/mole [21].

In order to evaluate the possibility of desorption with the above-indicated values for the heat of adsorption, let us compare these values with the energies of thermal motion of the molecules ( $kT$ ). At 20, 100, 200, and  $300^\circ\text{C}$ , the respective values of  $kT$  are  $4.04 \cdot 10^{-21}$ ,  $5.14 \cdot 10^{-21}$ ,  $6.52 \cdot 10^{-21}$ , and  $7.91 \cdot 10^{-21}$  J/molecule. The values given above for the heat of adsorption, when converted to J/molecule, are: 34 kJ/mole =  $34 \cdot 10^3 / 6.023 \cdot 10^{23} = 5.64 \cdot 10^{-20}$  J/molecule; 50 kJ/mole =  $8.3 \cdot 10^{-20}$  J/molecule; and 170 kJ/mole =  $2.82 \cdot 10^{-19}$  J/molecule. Thus, any value for the heat of adsorption is greater than the energy of thermal motion of the molecules, even at  $300^\circ\text{C}$ . Nonetheless, additive desorption does take place at  $250^\circ\text{C}$ . This may be explained on the basis that, according to Maxwell's law, an increase in temperature is accompanied by a rapid increase in the fraction of the molecules with velocities many times greater than the average [22].

Evidently, as a criterion for adequate heat of adsorption we should adopt  $q > 10 kT$  (by analogy with the analogy with the energy of repulsion required to ensure stability against aggregation). In this case, the heat of adsorption of the additives must be no less than  $7.91 \cdot 10^{-20} \cdot 6.023 \cdot 10^{23} / 10^3 = 47.64$  kJ/mole. Since additive-dispersed contaminant particles in the zone of the piston rings are heated to  $\sim 300^\circ\text{C}$ , not only desorption is possible, but also thermal or thermal-oxidative breakdown of these additives.

#### LITERATURE CITED

1. E. G. McLaughlin and F. A. Stuart, Proc. Seventh World Pet. Congr. (Mexico City), Vol. 8, Elsevier, New York (1967), p. 57.
2. P. I. Sanin, I. V. Blagovidov, et al., Proc. Eighth World Pet. Congr. (Moscow), Vol. 5, Applied Sciences Publ., London (1971), p. 91.
3. G. P. Wood, J. Inst. Pet., 55, No. 544, 194-204 (1969).
4. M. Wilderotter, VDI-Berichte, No. 177, 41-50 (1972).
5. K. K. Papok, in: Additives for Lubricating Oils and Fuels (S. É. Krein et al., editors) [in Russian], Gostoptekhizdat, Moscow (1961), p. 185.
6. E. V. Glavati, I. L. Rabinovich, et al., Khim. Tekhnol. Topl. Masel, No. 3, 60-62 (1976).
7. E. V. Glavati, I. L. Rabinovich, et al., Papers from Second International Symposium on "Research on the Mechanism of Additive Action," Halle (East Germany) (1976), pp. 143-149.
8. G. Lyklema, Adv. Colloid Interface Sci., No. 2, 65-114 (1968).
9. M. G. Vold, J. Colloid Sci., 16, No. 1, 1-12 (1961).
10. G. D. Parfitt and N. H. Picton, Trans. Faraday Soc., 64, No. 6, 1955 (1968).
11. B. Valigura, M. Palyukh, et al., Neftekhimiya, 15, No. 6, 928-931 (1975).
12. L. L. Mackor and J. H. van der Waals, J. Colloid Sci., 7, No. 6, 535-549 (1952).
13. P. Bagcni and R. D. Vold, J. Colloid Interface Sci., 33, No. 3, 405-419 (1970).
14. D. H. Napper, Trans. Faraday Soc., 64, No. 8, 1701-1711 (1968).
15. E. W. Fischer, Kolloid-Z., 160, No. 2, 120-141 (1958).
16. E. E. Bibik and L. V. Bodrova, Kolloidn. Zh., 36, No. 6, 1194-1195 (1974).
17. G. I. Fleer, L. K. Koopal, et al., Kolloid Z. Z. Polym., 250, No. 7, 689-702 (1972).
18. G. Visser, Adv. Colloid Interface Sci., 3, No. 4, 331-363 (1972).
19. B. Vincent, J. Colloid Interface Sci., 42, No. 2, 270-285 (1973).
20. R. E. Day, F. G. Greenwood, et al., Proc. Int. Congr. Surface-Active Substances, Vol. II, Section B, Brussels (1964), pp. 1005-1013.
21. A. J. Groszek, Proc. Int. Congr. Surface-Active Substances, Vol. II, Section B, Brussels (1964), pp. 1015-1027.
22. V. A. Kireev, Short Course in Physical Chemistry [in Russian], Khimiya, Moscow (1978), p. 624.