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SYNTHETIC ADDITIVES OF THE DISPERSANT TYPE

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At present, synthetic additives to lubricating oils are widely used which, in addition to other properties, possess a "detergent" action. In some additives this property is expressed so strongly that they are usually called "detergents." In the presence of such additives, the amount of carbonaceous deposits formed in the engine from the products of oxidation and incomplete combustion of the hydrocarbons of the oil and fuel is significantly reduced. The term "detergent" additives has become widespread above all because the action of such additives is in some respects similar to that of well-known detergents used in aqueous solutions (salts of organic acids, sulfonates, etc.). In one of our papers (1) it was pointed out that this term, as applied to the type of additives under consideration, should not be regarded as apt. A rational name for this type of additive should have a scientific basis and, above all, reflect the actual mechanism of their action. The mechanism of action of additives has been discussed to one degree or another in a number of papers (1-7) on the stabilization of suspensions.

In the present work it is shown that the "detergent" action of additives is due to their adsorption on insoluble particles of oil suspensions, which leads to an increase in the dispersion of the suspension and to stabilization of the suspension.

Most of the investigations were carried out with polyfunctional additives of the nickel dialkyldithiophosphate type. As was shown in the preceding paper (8), nickel di-*n*-octadecyldithiophosphate $[(C_{18}H_{37}O)_2PSS]_2Ni$ possesses a strong "detergent" action.

As a model suspension, a suspension of carbon black in toluene was used. A suspension was prepared from a definite amount of a solution of dialkyldithiophosphate in toluene and carbon black. After adsorption equilibrium had been established and the carbon black subsequently separated, the amount of dialkyldithiophosphate remaining in solution was determined; then, from the difference relative to the amount of dialkyldithiophosphate taken, the amount of dialkyldithiophosphate adsorbed on the amount of carbon black taken was established. Usually, in measurements of this kind, the greatest difficulties arise in determining very small amounts of additive contained in dilute hydrocarbon

Fig. 1. Adsorption isotherms of nickel dialkyldithiophosphates on carbon black. Carbon black—toluene suspension. Carbon black concentration 0.00061%. 1 —nickel di-*n*-octadecyldithiophosphate $[(C_{18}H_{37}O)_2PSS]_2Ni$; 2 —nickel di-*n*-decyldithiophosphate $[(C_{10}H_{21}O)_2PSS]_2Ni$; 3 —nickel di-*n*-butyldithiophosphate $[(C_4H_9O)_2PSS]_2Ni$.

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solutions. We carried out this determination in the following way. After removal of the toluene, the nickel dialkyldithiophosphate was decomposed with a mixture of concentrated nitric and sulfuric acids, and the nickel salt obtained was converted into an intensely colored complex compound of nickel with dimethylglyoxime, in which the nickel content was determined colorimetrically.

Figure 1 gives the results of experiments on the adsorption of various nickel dialkyldithiophosphates on carbon black. The equilibrium concentration of dialkyldithiophosphates in individual experiments varied within the range from 37 to 700 mg, or from 0.03 to 0.5 mmole per 1 liter of the solvent—toluene.

It follows from Fig. 1 that the dependences obtained for the amount of adsorbed dialkyldithiophosphate on its equilibrium concentration are

typical adsorption isotherms. Thus it was shown that additives of the nickel dialkyldithiophosphate type are indeed adsorbed from a hydrocarbon solution on carbon-black particles.

The values of the maximum—limiting—adsorption, corresponding to complete saturation of the adsorption layer at the toluene—carbon black interface (A_∞), determined from the adsorption isotherms, for nickel *n*-butyl-, *n*-decyl-, and *n*-octadecyldithiophosphates were, respectively, 5.70; 4.08 and 3.17 mmoles per 1 g of carbon black (channel black). In other words, 1 g of carbon black adsorbed 3.1 g of di-*n*-butyldithiophosphate, 3.6 g of di-*n*-decyldithiophosphate, and 4.2 g of di-*n*-octadecyldithiophosphate.

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It is interesting to note that, in the adsorption of nickel dialkyldithiophosphates on carbon black (from toluene), a regularity was obtained, with respect to the effect of the length of the hydrocarbon radicals, opposite to that obtained for the adsorption of the same additives at the hydrocarbon—water interface. Apparently, the hydrocarbon radicals of the molecules of nickel dialkyldithiophosphates adsorbed on carbon black are arranged in space differently than in the case of adsorption at the hydrocarbon—water interface; molecules with longer radicals have a less compact structure and occupy a larger area on the surface of the carbon black.

Electron-microscopic photographs were taken of carbon-black preparations obtained from samples of carbon-black suspension in toluene, with and without the addition of nickel dialkyldithiophosphate. From these photographs the average size of the carbon-black particle was then determined ([9]), and from the quantitative adsorption results—the average number of additive molecules adsorbed on one carbon-black particle. About $6 \cdot 10^4$ molecules of nickel di-*n*-octadecyldithiophosphate were adsorbed on one (averaged) carbon-black particle.

As a result of adsorption, the carbon-black particles are covered with a layer of molecules of nickel dialkyldithiophosphate, with the hydrocarbon groups directed into the hydrocarbon medium. In accordance with this, the oleophilicity of the particles increases sharply and the suspension as a whole becomes more stable.

It should be noted that the surface of particles of various types of carbon black is heterogeneous and, to one degree or another, oxidized. This applies to the greatest extent to channel black, whose suspensions in a hydrocarbon medium may be regarded as model systems in relation to real oil suspensions. The nature of the surface of carbon-black particles, at the same time, also determines the adsorption of dialkyldithiophosphate molecules by their polar part, while the nonpolar part of the molecules (hydrocarbon groups) is directed into the hydrocarbon medium.

The stabilization of a carbon black—toluene suspension was studied by two methods. In the first method, the time required for complete settling of the carbon black from the suspension in special cylinders was determined, or under centrifugation in a centrifuge equipped with a device for temperature regulation. In the second method, the relative change in the concentration of carbon black in the suspension over time was determined by measuring the optical density of the suspension. Using additives of different structures as examples, it was shown that the stabilizing action of the additives is in complete agreement with their activity as "detergent" additives.

In the series of dialkyldithiophosphates, the stabilizing effect increases with increasing length of the hydrocarbon radicals contained in their molecule.

This ratio would seem not to agree with the results of studies of the adsorption of the same compounds.

Thus, for example, the number of molecules of nickel di-*n*-butyldithiophosphate adsorbed on one particle of channel black was approximately 2 times greater than the number of molecules of di-*n*-octadecyldithiophosphate. However, the hydrocarbon radicals of di-*n*-octadecyldithiophosphate are almost 5 times longer than the hydrocarbon radicals of di-*n*-butyldithiophosphate, which is of decisive importance. Apparently, only sufficiently long hydrocarbon radicals create the oleophilicity of the soot particle covered with an adsorption layer that is necessary for stabilization.

Thus, additives of the type under consideration—which, in addition to dialkyldithiophosphates, should include salts of organic acids (alkylphenolates, sulfonates)—are surface-active substances that are adsorbed from a hydrocarbon medium (oil) on the surface of insoluble particles, thereby preventing their coalescence (agglomeration) into larger particles and their settling out of the oil suspension. Large agglomerates that have already formed, in which fine particles are bound by relatively weak molecular cohesive forces, may, in the presence of additives, be destroyed and dispersed.

The overall action of the additives therefore consists in increasing the dispersity of the oil suspension formed during engine operation and in stabilizing this suspension. In other words, a process of adsorption dispersion of insoluble products in oil takes place. Since, when particles coalesce (flocculation), relatively loose aggregates are formed in the oil, their dispersion is essentially a process of peptization (^10).

The "detergent" action of the additives may be regarded as the dispersing (or peptizing) action of the additives, and, accordingly, "detergent" additives should be called dispersants (or peptizers).

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