The Effect of Ultrasonic Exfoliation and the Introduction of a Surfactant on Particle Size and Aggregative Stability Water Dispersions of Carbon Black

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Abstract. The effect of Neonol AF9-10 surfactant on the process of ultrasound treatment and stabilization of N375 carbon black dispersions in water has been studied. According to laser diffraction data, it was found that in the process of ultrasonic carbon black exfoliation in an aqueous Neonol AF9-10 solution with concentrations of 0.0015 and 0.0030 mol/l, carbon black is dispersed to particles with sizes from 0.3 to 1.0 μm. For N375 particles in aqueous dispersions, the values of the ξ-potential were determined by the method of electrophoretic light scattering.

INTRODUCTION

Carbon black (CB) is a solid, characterized by a defective graphite-like structure consisting predominantly of carbon atoms in the state of sp2-hybridization [1]. CB can be attributed to the so-called transition forms of carbon, which in its structure have crystalline and amorphous sections [2]. Due to its physico-chemical properties, CB is widely used in various fields: from rubbers, filled polymers and electrochemistry to coloring printer and printing compositions, as well as sorbents, catalysts, filters and electrodes [3-9]. CB is a biocompatible material and chemically stable under non-oxidizing conditions [10,11]. CB has a developed porous texture, high thermal conductivity, good electrical conductivity, mechanical stability [12,13].

The use of technical specifications in several of technologies requires a thin and homogeneous dispersion of the powder in a liquid, which water is usually used for, which is due to its ecological purity and low price. However, in the preparation of soot aqueous dispersions, thin primary particles of CB with sizes of 0.01-0.1 μm consisting of 90-99% of elemental carbon, which is a hydrophobic material, tend to form agglomerates with sizes of more than 100-300 μm. This is a serious problem, since insufficient dispersion of the powder can become a serious obstacle to its effective use in applied processes and lead to a decrease in the quality of the final products. The process of dispersing CB in water can be represented in three consecutive stages, namely: wetting the powder with a liquid phase, mechanically destroying the agglomerates of CB in suspension, and re-agglomeration of the carbon particles. One of the most important issues in the preparation and storage of carbon dispersions is the prevention of re-agglomeration and deposition of carbon particles, i.e. the question of stabilizing the water dispersion of CB.

Stabilization of technical specifications in water can be achieved by increasing the hydrophilicity of the carbon surface. Several methods for increasing the hydrophilicity of a carbon surface are known, one of which is chemical modification or oxidation [14,15]. In the liquid-phase oxidation, nitric acid, mixtures of nitric and sulfuric acids, mixtures of sulfuric acid with hydrogen peroxide, potassium permanganate, etc. are used as oxidants. In gas-phase oxidation, the most widely used oxidants are carbon dioxide, water vapor, oxygen of air, ozone [16]. Carbonyl, hydroxyl, phenolic, lactone and carbonyl groups are formed in the process of carbon oxidation on the graphene

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surface [16], which causes an increase in the dispersibility of carbon powder materials in polar solvents. The main disadvantages of this method are the complexity of organizing a safe ecological process when working with acids, the need to increase the temperature during the organization of the gas-phase oxidation process, as well as the destruction of the π-electron structure of carbon under the influence of strong oxidants [2].

Another method of stabilizing aqueous dispersions of CB - the introduction of surfactants - is by far the most widespread. The introduction of a surfactant, as a rule, facilitates the humidification of carbon particles, the subsequent destruction of the agglomerates of the CB to small aggregates and prevents their repeated agglomeration, which is caused by an increase in the electrostatic repulsion between the carbon particles.

The adsorption of a surfactant on CB particles in water depends on various factors, among which one can distinguish: the type of functional groups present on the solid carbon surface, the molecular structure of the surfactant and the conditions of the aqueous phase, such as pH, temperature and the presence of the electrolyte. A large number of publications are known in which disaggregation of carbon agglomerates is carried out when anionic, cationic and nonionic surfactants are introduced into the composition of the dispersion medium [17, 18].

It should be noted that ultrasound treatment is the most common method that promotes disaggregation during or after the modification of carbon nanostructures [19]. The ultrasonic effect contributes to the cleavage of the CB aggregates from each other. In this case, surfactant molecules penetrate into the gaps between the aggregates and prevent their re-aggregation. Depending on the ability of the surfactant to dissociate in the solvent, the stability of the resulting carbon dispersions is determined by the electrostatic or steric factor.

Nonionic surfactants used as dispersing and stabilizing agents of carbon material dispersions are compounds containing a hydrophobic hydrocarbon radical (fatty acids or acylphenols), on the one hand, and a hydrophilic part of the molecule, which is usually a polyethoxylated chain. It is known that for the stabilization of suspensions of CB, Neonols with an average degree of oxyethylation n = 6, 8, 9, 10, 12 are often used. It was shown in [20] that such nonionic surfactants with a massive hydrophilic group are the most efficient dispersing agents of carbon suspensions due to the steric stabilization by long oxyethylene chains.

The stability of carbon black suspensions with a specific surface of 80 m^2/g (Alfa Aesar GmbH & Co KG, Germany) in an aqueous medium in the presence of a nonionic surfactant of oxyethylated isononylphenol, with varying degrees of hydroxyethylation (n = 4, 6, 10; 30). The authors note that oxyethylated isononylphenols exhibit a high affinity for CB particles, as evidenced by an increase in the ξ-potential of particles in the aqueous suspension upon the addition of Neonol. It was shown that the nonionic surfactant oxyethylated isononylphenol stabilizes the CB particles, which is due to the molecular structure and bulk properties of this surfactant. The authors showed that the average particle size of the CB in an aqueous medium is reduced when a nonionic surfactant is introduced from 24.00 to 5.35 μm.

It is known that the aggregation of particles in the dispersion is predetermined by the sign and charge [18,21], which appears on the surface of particles due to the ionization of surface functional groups and the adsorption of electrolytes. In connection with this, it is important to obtain data on the charge, magnitude and variation of the electrokinetic potential (ξ-potential) of the surface of carbon particles when the composition of the dispersion medium varies, its pH, the presence of electrolytes, or the modification of the carbon surface.

The purpose of this study is to study carbon black in an aqueous medium with the addition of a nonionic surfactant, Neonol-AF9-10 using laser diffraction and electrophoretic light scattering.

EXPERIMENTAL PART

The initial carbon material was represented by furnace carbon black N375 produced at the Omsk Carbon group. Physicochemical characteristics of CB used in the study are listed in Table 1.

TABLE 1. Physicochemical characteristics of CB N375.

CB grade	**N375**
Specific surface area, S_{BET}, m^2/g	96
The total pore volume, $V_Σ$, cm^3/g	0.894
The microporous volume, V_{mi}, cm^3/g	0.002
The volume of mesopores, V_{me} , cm^3/g	0.892
Average pore diameter, Å	41.1
DBP absorption, ml/100 g	87
pH of the aqueous suspension	6

Adsorption–desorption isotherms of nitrogen at 77.4 K were measured using a static volume vacuum system ASAP2020M (Micromeritics) in the range of equilibrium relative pressures P/P_0 from 10–3 to 0.996. Specific surface area was determined by the low-temperature adsorption of nitrogen at 77.4 K on a Sorbtometr instrument (Katakon, Russia).

DBP absorption of CB samples was measured according to ASTM D 2414. Nonionic surfactant Neonol AF 9-10 (oxyethylated nonylphenol) was used in this work. This surfactant has a constant hydrophobic group composition and ethylene oxide (EO) group with an average degree of oxyethylation 10. The chemical structure of the surfactant is given in Fig. 1.

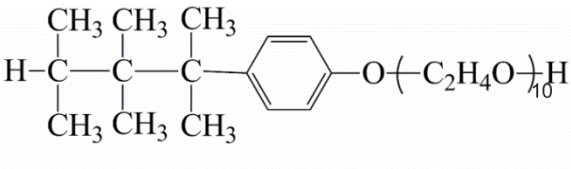

FIGURE 1. Structure of Neonol AF 9-10

Ultrasound treatment of carbon black was performed both in the presence of surfactant, and without it using a laboratory ultrasound unit (Ultrasonic Technique - INLAB, Russia) with a when using an extended waveguide-concentrate with a diameter of 30 mm with an acoustic power of 400 W and a frequency of 22 KHz. The ultrasonic particle dispersion time of the CB particles ranged from 30 to 120 min.

The size of CB aggregates was estimated by laser diffraction on a SALD-2101 (Shimadzu, Japan) laser analyzer with the measurement range of 0.03–1000 μm. To assess the aggregative stability of carbon dispersions, particle size measurement of CB in aqueous dispersions was carried out after keeping the dispersion in a quiescent state at room temperature for 1, 7 and 21 days.

For aqueous dispersions of CB by the method of electrophoretic light scattering on the Zetasizer Nano ZS, Malvern, the electrokinetic potential (ξ-potential) particles CB in water and aqueous solutions surfactant (Neonol AF 9-10). The determination was made at room temperature in the range of the gradient of the external electric field of 6-15 V/cm, with at least three parallel measurements for each sample, the relative error of the measurements not exceeding 5%.

RESULTS AND DISCUSSION

The presence of agglomerates in sizes of up to 100-300 μm and the hydrophobicity of the carbon surface make it difficult to obtain aggregate-stable water-carbon dispersions with carbon particle sizes of not more than 0.1-0.5 μm and a narrow particle size distribution.

The influence of the treatment time of water-carbon dispersions, as well as the concentration of surfactants in the composition of the dispersion medium on the particle size, the particle size distribution, and the ξ-potential of the CB dispersions was verified. The results are shown in Fig. 2 - 4 and in Tables 2, 3.

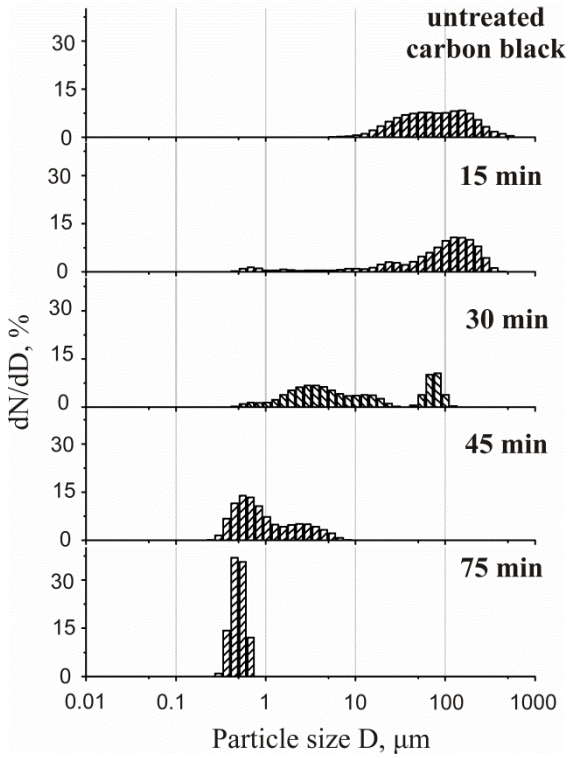

FIGURE 2. Effect of ultrasonic treatment time on particle size and particle size distribution for CB N375. The content of surfactants in the dispersion medium is 0.003 M

Figure 2 shows histograms of the particle size distribution for water dispersions of CB after ultrasonic treatment for 15 - 75 min. As the illustrative material shows, that the ultrasonic treatment after 75 min of the water-carbon dispersion, the minimum particle size of the CB in water-carbon dispersions and the narrow particle size distribution of the CB are achieved.

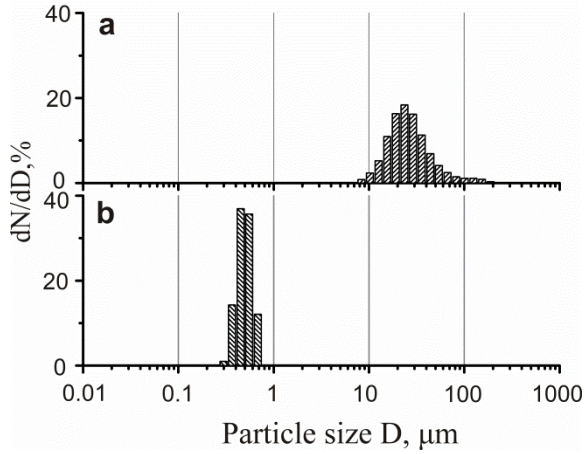

FIGURE 3. Effect of the presence of surfactants in the dispersion medium on the particle size and particle size distribution for technical carbon of grade N375 in water-carbon dispersions with a CB concentration of 1%. Dispersions were prepared by ultrasonic exfoliation for 75 min

Figure 3a, b shows histograms of particle size distribution for technical carbon varieties of N375 grades prepared by ultrasonic exfoliation. Water was used as dispersion media (Fig. 3a) and aqueous surfactant solution (Fig. 3b). The content of surfactant (Neonol AF9-10) in the dispersion medium was 0.003M. As can be seen from Fig. 3a, the

particle sizes of CB N375 in the aqueous suspension prepared by the ultrasonic exfoliation method vary from 9 to 100 μm. The introduction of a surfactant dispersion medium and the use of ultrasonic exfoliation lead to the production of an aqueous-carbon suspension with carbon particle sizes from 0.3 to 0.8 μm.

The particles of CB N375 were separated from the dispersion medium by centrifugation and dried in a vacuum at a temperature of 80 °C, after which some physico-chemical indices were analyzed and the results are shown in Table 2.

TABLE 2. Physical and chemical parameters of CB after ultrasonic treatment in the presence of surfactants

CB grade	**CB N375**
Specific surface area, S_{BET}, m^2/g	98
The total pore volume, V_{Σ}, cm^3/g	0.896
The microporous volume, V_{mi}, cm^3/g	0.002
The volume of mesopores, V_{me} , cm^3/g	0.894
Average pore diameter, Å	42.0
DBP absorption, ml/100 g	96
pH of the aqueous suspension	6

The obtained results indicate the preservation of texture indexes, the pH of the aqueous suspension and the adsorption of DBP to 96 cm^3/100 g after ultrasonic treatment at the level of values for the starting material.

Thus, the results shown in Fig. 2, 3 and in Table 2 show that ultrasonic exfoliation leads to the splitting of agglomerates to the level of aggregates and, accordingly, to the reduction of particle sizes in aqueous dispersions without affecting the texture characteristics of the CB.

The influence of the surfactant concentration in the composition of the dispersion medium and the time of ultrasonic treatment on the particle size of the CB in the aqueous dispersion was verified, the results are shown in Fig. 4.

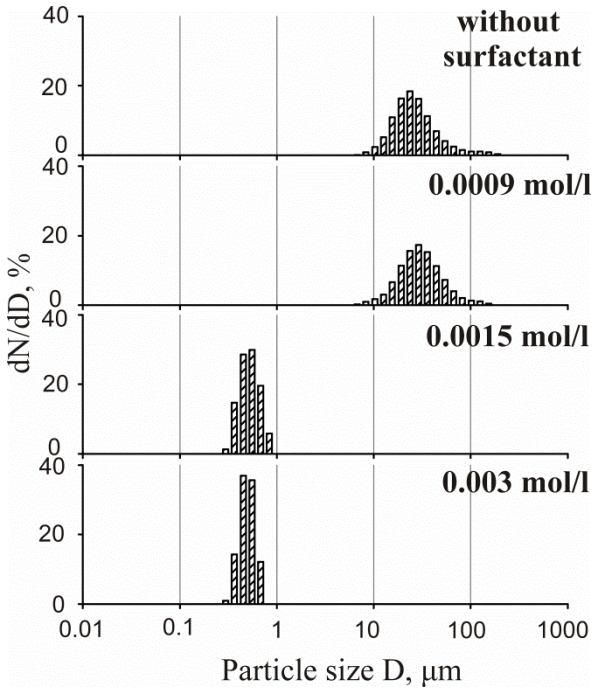

FIGURE 4. Influence of surfactant concentration in dispersion medium on particle sizes and particle size distribution in aqueous dispersions with a CB concentration of 1%. Dispersions were prepared by ultrasonic exfoliation for 75 min. The number in the figures correspond to the content of surfactants in the dispersion medium (mol/l)

As can be seen from Fig. 4, when 0.0015 - 0.003 mol/l Neonol AF9-10 is added to the dispersion medium, the particle size of the CB is 0.5-0.9 μm and this sample is characterized by a narrow particle size distribution.

Thus, the obtained results indicate that the introduction of surfactants (Neonol AF9-10) into the dispersion medium in an amount of 0.0015-0.0030 mol/l and the ultrasonic exfoliation of the CB dispersion for 75 min. ensure the production of aqueous dispersions of CB with particle sizes 0.3-0.9 μm and a narrow particle size distribution.

It is known that the aggregative stability of dispersions is largely determined by the sign and the magnitude of the charge that appears on the surface of the particles due to the ionization of surface functional groupings and the adsorption of electrolytes. In connection with this, it is important to obtain data on the charge, the magnitude and the change in the ξ-potential of carbon particles when the composition of the dispersion medium changes, its pH, the presence of electrolytes or the modification of the carbon surface.

Table 3 shows the values of the ξ-potential for CB in aqueous dispersions obtained by ultrasonic exfoliation without the introduction of a surfactant and in the presence of a surfactant for 75 min.

Table 3. ξ-potential CB N375 in aqueous dispersions.

CB grade	Surfactant content in the dispersion medium, mol/l	ξ- potential, mV
N375	-	6.4
N375	0.0015	– 29.0
N375	0.003	– 32.0

As can be seen from Table 3, the largest values of the ξ-potential (in absolute value) for CB N375 were obtained for the CB dispersions, when a surfactant with a concentration of 0.0015 and 0.0030 M was introduced into the dispersion medium and ultrasonic exfoliation of the CB in an aqueous solution of Neonol AF9-10 for 75 min. Taking into account the well-known fact that high values of the ξ-potential (in absolute value) are the criterion of aggregate stability of dispersions, it can be assumed that it is precisely these dispersion data that will distinguish high stability.

The experimental verification confirmed the above. Holding the samples for 21 days and analyzing the particle sizes showed that the particle size distribution curves remained practically unchanged.

Thus, as a result of the conducted studies, the method of ultrasonic exfoliation of the CB has been developed, which ensures the production of water dispersions of CB with a narrow particle distribution from 0.3 to 0.9 μm, which preserve aggregative stability for a long time.

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REFERENCES

1. E. Furimsky, *Carbon and Carbon Supported Catalysts in Hydroprocessing: IMAF Group* (Ontario, Ottava, 2005), pp. 159.
2. A. Krueger, *Carbon materials and nanotechnology* (WILEY-VCH Verglag GmbH & Co. KgaA, Weinheim, 2010), 474 p.
3. F. El-Tantawy, K. Kamada and H. Ohnabe, Mater. Letters **57**, 242–251 (2002).
4. Kang Min-Joo, Heo Young-Jung, Jin Fan-Long and Park Soo-Jin, Carbon Letters ***18****, 1-10 (2016).*
5. G. Schwartz, S. Cerveny and A.J. Marzocca, Polym. **41**, 6589–6595 (2000).
6. H. Münstedt and Z. Starý, Polym. **98**, 51-60 (2016).
7. A.A. Al-Ghamdi, O.A. Al-Hartomy, F.R. Al-Solamy, N. Dishovskyc, P. Malinova, G. Atanasova and N. Atanasov, Composites Part B **96**, 231-241 (2016).
8. J.C. Calderon, M.J. Nieto-Monge, S. Perez-Rodrı´guez, J.I. Pardo, R. Moliner and M.J. Lazaro, Int. J. Hydrogen Energy **41**, 19556 -19569 (2016).
9. Y. Kameya, T. Hayashi and M. Motosuke, Appl. Catalysis B: Environю **189**, 219–225 (2016).
10. H. Kim, K. Park and M. Lee, Toxicol Res **28**, 209–216 (2012).
11. J.-B. Donnet, *Carbon Black: Science and Technology,* Second Edition (CRC Press., 1993), 461 p.
12. J. Wang, Q. Li, Ch. Wu and H. Xu, Polym. Polym. Compos. **22**, 393-399 (2014).
13. D. Pantea, H. Darmstadt, S. Kaliaguine and Ch. Roy, Appl. Surf. Sci. **217**, 181-193 (2003).

14. M. Carmo, M. Linardi, J. Guilherme and R. Poco, Appl. Catal. A Gen. **355**, 132-138 (2009).
15. H. Bryan, R. Suryanto and Ch. Zhao, Chem. Comm. **38**, 6439-6442 (2016).
16. J.L. Diaz de Tuesta, A.Quintanilla, J.A.Casas and J.J.Rodriguez, Appl. Catal. B Environ. **209**, 701-710 (2017).
17. C. Eisermann, C. Damm, B. Winzer and W. Peukert, Powder Technol. **253**, 338-346 (2014).
18. H. Sis and M. Birinci, Colloids Surf. A Physicochem. Eng. Asp. **341**, 60-67 (2009).
19. S.J. Chen, B. Zou, F. Collins, X.L. Zhao, M. Majumber and W.H. Duan, Carbon **77**, 1-10 (2014).
20. A.R. Gataollin, M.S. Salina., S.A. Bogdanova and Y.G. Galyametdinov, Rus. J. Appl. Chem. **86**, 1656-1662 (2013).
21. R. Xu, C. Wu and H. Xu, Carbon **45**, 2806-2809 (2007).