Colloidal silica as a finely dispersed material is finding uses as a thickening agent for lubricating greases. In order to impart hydrophobicity to inorganic thickening agents, they are subjected to chemical treatment to modify the surface. In particular, the hydrophobization of colloidal silica is accomplished by treatment with higher fatty alcohols, chlorosilanes, chlorine derivatives of alkylpolysiloxanes, polyamines, etc. [1]. Modified silica gel is used in the production of a number of commercial greases: VNII NP-262, VNII NP-264, VNII NP-279, SIOL, and others [2].

Additives are used to improve the antwear and extreme-pressure properties of greases. In the overwhelming majority of cases, the additives are the shortest in supply and the most costly components of the grease [2].

As reported previously [3], we had accomplished the chemical grafting of alkylpolysiloxane radicals to the surface of silica, thus making it feasible to produce a thermally stable, hydrophobic thickening agent that is suitable for thickening petroleum and siloxane oils. Further, by varying the nature of the radicals grafted to the thickener surface, the grease properties can be adjusted in any desired direction; this applies not only to the water resistance, but also to the strength of the lubricating film that is formed, the antwear and extreme-pressure properties of the finished lubricant formulation, etc. Chemical modification opens up a route to the development of thickening agents of such a nature that additives will not be needed. To this end, it has been of interest to carry out the chemical modification of a silica gel thickening agent with organic and organosilicon radicals including atoms of boron, phosphorus, and sulfur, and to investigate their influence on the antwear properties of the finished lubricant formulations.

The silica used as the starting material in this work was Aerosil 175; the modifying agents were polydimethylsiloxanes of various molecular weights, polydimethylsiloxane rubbers containing boron and phosphorus, a polydimethylsiloxane rubber combined with sulfur or phosphorus, and an EFR epoxy resin.

The modification of the Aerosil was accomplished by the use of mechanochemical methods used previously in grafting organic and heteroorganic radicals to the surface of natural silicates [3-6]. A mixture of the original silica and the modifying agent (or a 10% solution in toluene) was exposed to a 19-20 kHz acoustic field, or to grinding in a vibratory mill operating at 1410 oscillations per minute. Control samples were prepared by holding the Aerosil in a medium of the modifying agent for 24 h.

The mixtures after modification, as well as the control samples, were centrifuged; the solid precipitates were solvent-washed in an extraction apparatus for a period of 20 to 40 h, depending on the modifying agent used. For the silicon-containing modifying agents, the completeness of washing was judged by the absence of silica in the filtrate, as determined spectroscopically. The washed samples were dried to constant weight at 105-130°C.

The carbon contents of the modified and control samples of the Aerosil were determined by combustion in the presence of CO_2. The contents of phosphorus and sulfur were determined on solutions obtained by fusing the samples with soda and borax and dissolving the melt in hydrochloric acid. Phosphorus was determined by precipitation of a phosphorus-molybdenum complex with quinoline, sulfur by precipitation in the form of barium sulfate, and boron by potentiometric titration of the mannitol* of boric acid.†

*Chemical terminology as in Russian original - Translator.
†The chemical analyses were performed in the analytical laboratory of the I. V. Grebenshchikov Institute of Silicate Chemistry, Academy of Sciences of the USSR.

The specific surface of the thickening agents was determined by a method based on the thermal desorption of argon [7] and was calculated by the Temkin formula [8].

The hydrophobicity of the samples was determined by a method of VNII NP [All-Union Scientific-Research Institute for Petroleum Processing] [9], defining the hydrophobicity as the percentage of test sample unwetted by boiling water.

Samples of silica gel greases were prepared by adding 15% of the Aerosil (calculated as SiO₂) to a pharmaceutical white oil, with subsequent homogenization of the mixture in a colloid mill. These samples of silica gel greases were tested by standard methods to determine the yield stress at 20°C, the apparent viscosity at 20°C and 100 sec⁻¹, and the colloidal stability [oil bleeding]. The mechanical stability of the test formulations was determined by a procedure given in [10]. The resistance of the greases to washout was determined from the loss of grease in flowing hot water [11]. The antiwear and extreme-pressure properties of the lubricant formulations were evaluated in a four-ball friction tester with stepwise increase of axial load.

The mechanisms of the processes taking place in the mechanochemical modification of solids have been examined in [3-5, 12, 13]. The reaction products were new organic and heteroorganic derivatives of silica, with rather high thermal stability. On the basis of data obtained by differential thermal analysis in an MOM derivatograph, burnoff of the radicals grafted to the Aerosil surface takes place at temperatures from 400° to 550°C.

Water—alcohol extracts from the samples of Aerosil modified with borosiloxane and borophosphorosiloxane polymers had practically the same pH as extracts from a sample of the original Aerosil. The pH was