The investigation of emulsifiers of petroleum emulsions has for a long time attracted the attention of investigators of various countries with the development of petroleum-extraction and petroleum-refining industries. This is understandable, since more than 70% of petroleum produced in the world is an emulsion of water in petroleum of various concentration. The amount of water which can be emulsified in petroleum changes in a dependence on characteristics of the petroleum containing in it natural emulsifiers, the composition of stratal water extracted with the petroleum, and the degree of mixing. Certain petroleums give stable emulsions with a maximum water content of 10-15% and more. The nature and composition of material-emulsifiers of stable petroleum emulsions has been studied little to date.

It was reported in the earliest works [1-5] that asphalt, tarry materials, oil-soluble organic acids, and materials predominately moistened with an oily phase (petroleum) are adsorbed on the boundary of separation of petroleum-water and act as emulsifiers.

Attempts have been made repeatedly to isolate film-forming materials from crude petroleums and to establish their chemical nature. Metal-porphyrin complexes [6, 7], free naphthenic acids and their salts [8], and oxidized asphalt-tarry materials [9] present in petroleum have been referred to as surface-active materials.

At this time many investigators lean to the conclusion that the main stabilizers of petroleum emulsions are materials colloidal dispersed in the petroleum. In the opinion of authors of [10] namely metal-porphyrin complexes are found in a colloidal state in petroleum. These compounds possess the greatest surface activity and, being adsorbed on the interphase surface of separation of petroleum-water, stabilize petroleum emulsions [11].

In the study of emulsifiers of petroleum emulsions they are most frequently isolated from petroleum using some low-molecular hydrocarbons or ethers as solvents. Sometimes the dispersed medium of the petroleum emulsion is washed with low-boiling solvents, separating only the layer which stabilizes water droplets [12]. But despite the simplicity and accessibility of these methods, with their help it is possible to obtain a complete characterization of stabilizers of petroleum emulsions in their natural form, particularly those colloidal dispersed in petroleum. Many of the used solvents possess a flocculating effect [13].

The most convenient method of separating colloidal particles is ultracentrifugation. During separation of emulsifiers by ultracentrifugation the petroleum is not subjected to thermal treatment or to the effect of any reagent or solvents. Emulsifiers separated in this way are reversible. They can again be easily introduced into that petroleum from which they were isolated [14]; in this case all of the physicochemical characteristics of the restored petroleum do not differ from characteristics of the initial petroleum.

We used a Spinco ultracentrifuge to isolate colloidal dispersed compounds. The majority of experiments on the separation of emulsifiers were carried out at a separating ability of the ultracentrifuge of 80,000 g; separate experiments were carried out at a separating ability of 250,000 g. Time of centrifugation was varied in broad intervals (from 3 to 125 h).

A precipitate of colloidal dispersed materials is separated during ultracentrifugation. The weight of the residue increases upon increasing the time of centrifugation, but the main portion of colloidal dispersed materials is separated during the first hours of the experiment which is seen from the graph (Fig. 1). The experiment was carried out at 80,000 g and 20°C.
We carried out separation of colloidally dispersed compounds from petroleum not with the purpose of demonstrating the colloidal nature of petroleum, which had already been done by other investigators [5], but to determine the role played by colloidally dispersed compounds in stabilization of emulsions of water in petroleum. We found a large difference in stability of emulsions obtained from crude petroleum and from the same petroleum after separation of colloidally dispersed particles on the ultracentrifuge.

We carried out the evaluation of the role of colloidally dispersed materials in stabilization of water-petroleum emulsions on a vibrator mixer constructed by us. Water emulsions were prepared with a cyclohexane solution of the initial petroleum and with the petroleum after ultracentrifugation simultaneously and under extremely identical conditions.

The average results of stabilization of such emulsions with time are presented in Table 1. All emulsions contained 43% water and the petroleum concentration in cyclohexane was 1.31%.

From Table 1 it is seen that the main stabilizers of petroleum emulsions are separated from petroleum upon ultracentrifugation in the first 3 h. After ultracentrifugation the petroleum is not able to be stabilized by the emulsion, which confirms the hypothesis that the main stabilizers of petroleum emulsions are colloidal compounds of petroleum. We isolated colloidally dispersed compounds by ultracentrifugation from Romashkino, Ust-Balyks, and Arlansk crudes.

In the investigation of colloidally dispersed compounds isolated by ultracentrifugation from American petroleum [15], metal-porphyrin complexes were not observed in them. Using a slightly modified method [16] we extracted the precipitates obtained on the ultracentrifuge with ethanol and obtained peaks on the spectrophotometer characteristic for porphyrin complexes of vanadium (Fig. 2). Consequently, the presence of porphyrin complexes of vanadium was demonstrated spectrometrically in the residue separated from petroleum.

An interesting fact which gives a certain concept about the effect of deemulsifiers on colloidally dispersed stabilizer of petroleum emulsions should also be noted. It is seen from experiments on ultracentrifugation of petroleum containing a deemulsifier that a slightly smaller amount of colloidally dispersed compounds is isolated in this case than upon centrifugation of the same petroleum without a deemulsifier. From Ramashkino crudes containing 70 g of D-157 deemulsifier per 1 ton of petroleum 17-20% less precipitate was isolated than from petroleum without emulsifier.

The petroleum was ultracentrifuged at 80,000 g for 24 h at room temperature. Simultaneously by treating petroleum in one rotor with Dissolvan 4411, D-147, and OZhK deemulsifiers and petroleum without a deemulsifier we established that colloidally dispersed compounds are separated from petroleum in an amount inversely proportional to the deemulsifying effectiveness of the added deemulsifier. This effect can only be explained by the...