NITROGEN COMPOUNDS OF PETROLEUM OILS (REVIEW)

V. S. Aksenov, V. I. Titov, and V. F. Kam'yanov

The literature data on the quantitative percentages, group and individual compositions, and structures of nitrogen compounds of all types that have been identified in petroleum oils and directly distilled petroleum fractions are systematized. The general regularities in the structures of the molecules of petroleum nitrogen compounds and their structural relationship with other aromatic components of petroleum oils are noted. The modern concepts regarding the genesis of the most important classes of nitrogen-containing components of petroleum are discussed.

Nitrogen in the form of diverse organic compounds is included in the composition of virtually all petroleum oils. The nitrogen components of petroleum oils and petroleum products have a negative effect on petroleum refining processes [1, 2] and reduce the performance qualities of fuels and oils. A knowledge of the nature of the nitrogen compounds is necessary for the solution of fundamental problems that are associated both with the formation and transformations of petroleum oils under the conditions in the depths of the earth and with the search for ways to utilize these compounds. The unflagging interest of researchers in nitrogen-containing petroleum substances is reflected in the previously published reviews (e.g., see [3-8]).

The overall fraction of nitrogen in the elementary composition of most petroleum oils ranges from 0.1 to 0.3%, although in some cases it may reach 0.8-1.5% [9, 10]. It has been shown that the nitrogen concentration in petroleum oils from various regions (Uralo-Povolzhe and Western Siberia [11, 12], the Fergansk Basin [13], Dagestan [14], etc.) is related in a regular way to the tar content and density of petroleum oils and to the percentage of sulfur and metals in them. The bulk of the nitrogen is concentrated in the tar-asphalt components of petroleum oils. Thus, according to the data in [11], 52-63% of the total nitrogen content is associated with the neutral tars extracted from petroleum oils from Povolzhe and Siberia, and another 37-42% is associated with the asphaltenes. It is proposed that during the isolation of the tar-asphalt substances the nitrogen compounds may coprecipitate with them in the form of associates that are formed by means of donor-acceptor interactions [15]. A correlation of the percentage of nitrogen with the above-noted properties of petroleum oils is natural, since most of the heteroelements are concentrated in the tar-asphalt compounds, and the density of an oil is also determined to a great extent by its tar content.

Statistical analysis of the voluminous literature data (more than 1200 samples of petroleum oils of all of the petroliferous provinces of the USSR [4, 9, 16-25]) shows that the average nitrogen concentration in the oils of almost all of the regions and the stratigraphic complexes decreases as the degree of stratification and catagenic transformational character of the system increases, in conformity with the concepts of Dobryanskii [26]. The youngest (Pliocene) petroleum oils, for which a reverse dependence is observed, constitute an exception to this. Thus the overall percentage of nitrogen compounds in petroleum oils is intimately associated with the conditions under which the petroleum components were formed, accumulated, and found throughout the entire history of the existence of the deposit.

A great deal of data on the distribution of nitrogen compounds in petroleum oils, directly distilled fractions, and the products of thermal and thermal-catalytic refinement of crude petroleum oil has been accumulated thus far. Unfortunately, in many cases it is difficult or even impossible to establish whether the detected components are present in the crude oil or were formed in one or another step of refining and concentration. Measures designed to preserve the original nature of the compounds have been established only in a few studies, as,
for example, in the proceedings of the American Petroleum Institute [27-35]. In these studies all of the procedures were carried out in a pure nitrogen atmosphere (containing no more than 0.0002% O₂). The temperature during the operations involving heating did not exceed 225°C, and the duration of the action of temperatures above 100°C was no longer than 1 min; the action of light was excluded.

A promising possibility for the preservation of the original structures of the nitrogen compounds is their isolation from the deasphalted oil by means of chromatographic methods [36-41] or complexing methods [42] that make it possible to exclude thermal action on the substances to be analyzed.

**Group Composition of Petroleum Nitrogen Compounds**

The nitrogen compounds of petroleum oils are traditionally divided into two large groups in conformity with their chemical behavior: basic groups, which are extracted by mineral acids, and neutral groups [43]. The fraction of basic nitrogen in petroleum oils may vary over wide ranges: 25-34% in oils from the United States and the Near East [44], 30-48% in oils from Sakhalin [9], 10-40% in the oils from Belorussia [25, 45, 46], and 21-58% in the oils from Tadzhikistan [13].

Bezinger and Gal'pern [47] have suggested that the group analysis of nitrogen component of oil be detailed by using potentiometric titration before and after reduction of the neutral and weakly basic substances with lithium aluminum hydride. This formed the basis of the development of a classification scheme, according to which the petroleum nitrogen bases are divided into A (strong bases), B (weak bases), and C (untitrable or neutral compounds) groups. The weak bases were divided, according to their behavior during reduction [48], into B₁ (reduced to strongly basic substances), B₂ (reduced to neutral substances), and B₃ (unreducible substances) types [48].

Researchers who made analyses by means of these schemes [25, 27, 47, 48] assumed that group A includes pyridines and their benzologs, group B₁ includes amides, group B₂ includes pyrrole and indole derivatives, and group C includes carbazole derivatives. Okuno and co-workers [49] isolated components of the B₂ group and found that they are absent in crude oil, develop during its storage in air, and correspond in composition to saturated cyclic sulfoxides — products of the oxidation of petroleum thiacyclanes. It was therefore proposed that the B₂ type be excluded and that petroleum nitrogen compounds be divided into four groups instead of five. It was shown that group C includes not only carbazoles but also large poly-cyclic molecules of many types [5, 50]. Kiričenkova and co-workers [51] demonstrated experimentally that group analysis by titration before and after reduction with lithium aluminum hydride does not give accurate results for amides and compounds of the pyrrole type. Thus the possibility of a clear assignment of each of groups A-C to a definite structural type of compound is not realized in practice.

**Nitrogen Bases**

Because of the relative ease of isolation, bases have been the subject of the greatest amount of study of the entire group of nitrogen compounds of oil. It has been reliably established that the overwhelming mass of the nitrogen compounds with basic character in crude oils and directly distilled fractions is represented by derivatives of pyridine and its benzologs. The presence of small amounts of primary and secondary amines (primarily aromatic) has also been noted in individual studies. Thus amines have been detected in the oils of the Tadzhik depression [25] in 4-9% amounts of the total base content. Much higher concentrations of amines are found in the products of thermal refining: in shale gasoline [52], in clear hydrocracking products [53-58], and in commercial reactive fuels [59]. There is some basis for the assumption that primary and secondary amines are not characteristic for crude oils and may be regarded as products of degradation of high-molecular-weight compounds in the oil. In any case, there are no reliable indications of their presence in oils that have not been subjected to heat treatment.

Ion-exchange chromatography on various cation-exchange resins [25, 41, 60, 61] and adsorption chromatography on silica gel and aluminum oxide [25, 40, 41, 62] or in activated charcoal, which makes it possible to effect separation with respect to the number of aromatic rings in the molecule, are frequently used for fractionation of the bases. Molecular distillation and thermal diffusion are used less frequently [63]. Potentiometric titration in conjunction with acylation or hydroformylation [25, 60, 61], spectral methods, and, particularly