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Structural alteration of native solid hydrocarbons by thermolysis (by the IR-spectroscopy and AFM data)

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A vast experimental material on the chemical structure of natural solid bitumens has been accumulated to date using IR spectroscopy. However, there are no data in the literature on the chemical structure and supermolecular organization (by atomic force microscopy (AFM) of solid bitumens subjected to high-temperature pyrolysis. The purpose of this work was to study the effect of temperature on the structural changes in natural solid bitumens of the carbonization series: asphalt – asphaltite – kerite – anthraxolite and solid products of their thermal treatment. Studies were carried out using IR spectroscopy, pyrolysis gas chromatography and AFM.

The solid bitumen samples were thoroughly powdered, and their spectra were recorded on an Avatar 360 FT-IT spectrometer (Nikolet Instruments, USA) using a Nicolet Smart MIRacle frustrated multiple internal reflection attachment (Pike Technologies, USA) in the wave number interval from 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1}. The absorbance of bands in IR spectra was determined by the baseline method from peak heights. The spectral factors characterizing the chemical structures of solid bitumens were determined as the ratio between absorbances at maximums of the corresponding absorption bands: aliphatic (720, 1380, 1465 cm^{-1}) and aromatic moieties (1600 cm^{-1}) and sulfoxide groups (1030 cm^{-1}). The following factors were used: C_1=D_{1600}/D_{720} (aromaticity), C_2=D_{1710}/D_{1465} (oxidation), C_3= D_{720} + D_{1380})/D_{1600} (aliphaticity), and C_4= D_{1030}/D_{1465} (sulfurization).

It was established, that the IR spectroscopy and pyrolysis-gas chromatography study of the temperature effect on the structural transformations of solid bitumens in the carbonization series asphalt–asphaltite–kerite–anthraxolite has shown that the heat treatment of solid bitumens at high temperatures (500^{o}C) leads to a considerable change in their molecular structure. It has been found that low-molecular-mass saturated are primarily produced upon the thermal degradation of solid bitumens. In addition, insignificant amounts of unsaturated, aromatic, and cyclic hydrocarbons are formed, which evidently indicates the occurrence of the hydrogen redistribution process under the pyrolysis conditions. The main starting material for hydrogen redistribution is high-molecular-mass naphthenic hydrocarbons producing lower hydrocarbons, predominantly paraffinic and aromatic hydrocarbons. Light hydrocarbons, which volatilize upon pyrolysis, contain a lower relative amount of carbon and more volatile foreign compounds, which is indicated by a decrease in the aliphaticity factor and degrees of oxidation and sulfurization. The residual substance is gradually enriched in carbon and is the most associated product of thermal decomposition. This process proceeds through the formation of aromatic rings, which are grown together to form polycyclic structures, which is accompanied by an increase in the intensity of absorption bands of polynuclear aromatic structures at 900-700 and 600-400 cm^{-1} and the appearance of new bands in these IR spectral regions of the pyrolysis products of solid bitumens. A single mechanism can be established for the transformation of solid bitumens both in the initial state and after pyrolysis, which manifests a tendency to form a thermodynamically stable structure. This mechanism suggests changes that resulting in structure ordering, wherein thermal treatment enhances this process.

So, the general character of thermally induced changes in the composition and structure of solid bitumens can be presented as follows: – loss of volatile products formed as a result of hydrogen redistribution, as well as destruction of N,S,O hetero bonds; – molecular association and formation of the homeopolar framework of molecules as fused polycyclic aromatic structures; – molecular-structure condensation due to the formation of giant planar molecules resembling the structure of atomic layers in a graphite crystal.

In the structural relation natural solid bitumens are characterized by the supermolecular organization with the sizes of elements from tens nanometers up to micron. Basic elements supermolecular structurizations in bitumens are globules, fibrous and packs. The most informative method of research nanometrical structurizations is AFM method.

The obtained AFM snapshots of the surface of the chip of the asphalts are uniformly structured mass with a smooth relief where no any features of nanostructurization are observed.

Porous fiber supermolecular structure is observed in the AFM-snapshots of the asphaltites. It reminds “chain armor” made of the rings of various diameters. The fiber diameter of this “chain armor” is about 100nm. Structural-morphologic features of a chip often correspond to fiber supermolecular structure. Vermiform fibrils with the constant diameter ranging from 200-300nm locate in a chaotic way, and quite often they are curved and curled.

AFM-snapshots of the kerites show occurrence of various supermolecular elements (globular, fibrillar, striped, dendritic, banded elements). It was determined that structure-formation inside the kerites go by two directions. One of the direction is characterized by occurrence of complex fibrillar and dendritic structures, commonly composed of globules, the other is characterized by formation of coarseglobular areas where compact packing of the deformed and linked globules their sporadic linking into the firbiles are observed.

Spheroidal shapes of the supermolecular elements are characteristic of the anthraxolites being commonly composed as packed aggregates. It was established that globular, "striped". Fibrillar, dendritic, sperolitic supermolecular structures are the characteristics of both the anthraxolites and the kerites. It can be assumed supermolecular structure-formation for the bitumens of the specific class arisen from the globules (glomes (balls) of the bonded macromolecules and their little packs), the globules could link into chains-fibrils either into larger globules that could link into the coarse chains-fibrils and therefore unite into the spheroliths representing as coarser packs of the fibrils.

Therefore, main regulations of supermolecular ordering of the solid bitumens are established. Asphaltites have a branchy composition and they locate randomly so that it is hard to determine a direction of the movement. Less mutually oriented arrangement of the fibers are observed in the low-class kerites, the fibers become longer. The oriented arrangement of the fibers are preserved in the high-class kerites, however, the fibers become shorter, and globule-like formations are observed in the general fiber mass. When referring to the high-class anthraxolites globules represent the supermolecular structure.

The results obtained confirm the idea that the thermal treatment is an important factor in the maturation of organic matter.