Study of the Interaction of S- and Se-containing Derivatives of Spatial-obstructed Phenols in Reactions with Peroxides

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Abstract

Based on a study of the geometric and electronic structure using high-level quantum-chemical calculations, the reactivity of the compounds under study used as antioxidant additives was evaluated. It is shown that large deformations of the valence angle ($\angle C_{14}N_{15}C_{18}$=128.78°, $\angle C_{16}C_{14}N_{15}$=121.93°, $\angle N_{15}C_{18}C_{19}$=123.11°), an increase in the bond length ($r(C_{14}–C_{16})$=1.402 Å, $r(C_{17}–C_{14})$=1.401 Å, $r(C_{14}-N_{15})$=1.409 Å) in the compounds lead to the occurrence of strong tension and, as a consequence, to an increase in their reactivity. The mechanism of action of oxidation inhibitors is that they interact with the ROO• and R• radicals through electrophilic attack centers — through oxygen and nitrogen, as a result of which the concentration of radicals decreases with the termination of the chain reaction.

The ability of antioxidant additives to effectively inhibit the oxidation of fuel fractions (195–315°C) (as well as deeply purified oils) is explained by the fact that the compounds in them almost completely deactivate the radicals formed at a low rate, leading to an active break of the oxidative chains at the beginning of their nucleation, which prolongs the induction oxidation period of the fraction. According to the research results, the greatest inhibitor efficacy established in the study is due to:

- high inhibitor activity in reaction with peroxide radicals,
- the absence for the resulting radical of reactions of continuation of the oxidation chains.

The addition of additives to the fuel during oxidation reduces the oxygen consumption per reaction. The formation of hydroperoxides in this case is sharply inhibited, and the resulting hydroperoxides are destroyed. Additives are not able to inhibit the oxidation process when introduced into the fuel in the developed autocatalytic stage. They are relatively effective only when added to the original fuel before the start of oxidation. At temperatures above 160–180°C, the effect of the additives decreases rapidly and at higher temperatures it becomes ineffective.

It has also been established that S- and Se-containing derivatives of spatially obstructed phenols, exhibiting an effect of auto-synergism, have more effective antioxidant, anti-corrosion and antimicrobial properties.