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## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

### NEW ASPECTS IN THE MECHANISM OF INHIBITORY ACTION OF SULPHUR CONTAINING METAL COMPLEX COMPOUNDS IN THE OXIDATION OF HYDROCARBONS

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**To cite this Article** Ivanov, Slavi K.(1979) 'NEW ASPECTS IN THE MECHANISM OF INHIBITORY ACTION OF SULPHUR CONTAINING METAL COMPLEX COMPOUNDS IN THE OXIDATION OF HYDROCARBONS', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 6: 1, 141 — 142

**To link to this Article:** DOI: 10.1080/03086647908080344

**URL:** <http://dx.doi.org/10.1080/03086647908080344>

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NEW ASPECTS IN THE MECHANISM OF INHIBITORY  
ACTION OF SULPHUR CONTAINING METAL COMPLEX  
COMPOUNDS IN THE OXIDATION OF HYDROCARBONS

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The first studies dealing with the antioxidizing action of sulphur containing organic compounds in the stabilization of petroleum products, polymers, rubber etc., suppose an interaction of these inhibitors with hydroperoxides and the decomposition of the latter to molecular inactive products. The absence of reaction of the peroxide radicals, leading the chain of the autoxidation, with the inhibitor is presumed. The initiating properties of the inhibitors-peroxide decomposers were unknown/1,2,3/. As a result of our and other authors' investigations was shown, that the sulphur containing antioxidants react with the peroxide radicals and they are able to initiate the autoxidation processes, because in the oxidation of hydrocarbons in the simultaneous presence of hydroperoxides and sulphur containing compound, a prooxidizing effect is observed i.e. acceleration of the oxidation in a certain period of the process/4,5,6/. It was observed, that a period of rapid oxidation, followed by autoretardation of the oxygen absorption, appears in the oxidation of tetraline and cumene, respectively in the presence of tetraline and cumene hydroperoxides and metal dialkyldithiophosphates, dithiocarbamates and dithiolates. The oxidation of cumene and tetraline, initiated by AIBN at 60°C in the presence of zinc dithiophosphate, zinc dithiocarbamate and nickel dithiolate, proceeds with the appearance of induction periods. In this way, the existence of interaction between  $RO_2^\bullet$  and sulphur containing metal complex compounds is verified

The stoichiometric coefficient of inhibition depends on the concentration of the used inhibitor, which is a proof that in the induction period, the inhibitor is consumed not only by an interaction with the peroxide radicals, but by means of another reaction. This fact explains the existence of different values of the stoichiometric coefficients, measured by different groups of authors, using different initial concentrations of the studied inhibitors. At a definite correlation between AIBN and sulfur containing complexes in the oxidation of cumene, an effect of oscillation is observed i.e. the induction period is followed by a periodical change of the oxygen absorption rate /7,8/. The frequency of oscillation increases with time and the differences between the inflexion become greater. A similar effect was observed in the initiated by AIBN oxidation of cumene in presence of Zn-bis(diisopropyl)dithiophosphate-(I), Zn-bis(diethyl)dithiocarbamate-(II), Ni-bis(diphenylethylene)-dithiolate-(III). The existence of oscillating effect obviously is due to the competition of two parallel processes - the absorption and the liberation of gas. With the help of mass spectral analysis, it was shown that as a result of the reaction of (I), (II), (III) inhibitors and hydroperoxides, oxygen is liberated. The use of acceptors of singlet oxygen (9,10-diphenylanthracene) shows that the liberated gas is singlet oxygen/9/.

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