

reaction with AA. It is reasonable to assume that the factor responsible for the much lower molecular weight of the polymers prepared in presence of ammonia and of small caustic soda additions could well be an increase in the rate of NPA formation.

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ON THE STABILIZATION OF POLYMERS BY PHOSPHOROUS ACID ESTERS*

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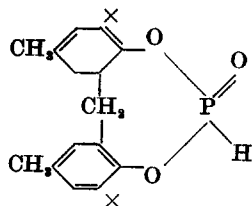
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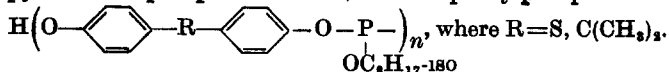
Accelerated ageing was the method used for investigation of the antioxidative properties (the existence of critical concentrations and the displacement of the latter in the presence of a decomposer of hydroperoxides) of phosphites of the cyclic

* Vysokomol. soyed. **A16**: No 2, 370-375, 1974.

acid


 $(X = C(CH_3)_3)$

and its α -naphthyl and octyl esters; likewise the 2,3,6-tritert.butylphenyl ester of pyrocatecholphosphorous acid, tri- α -naphthylphosphite and the polyphosphites:

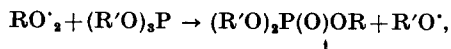


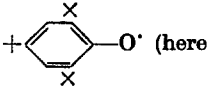
The capacity of phosphorous acid esters for terminating kinetic chains or for suppressing branching during the oxidation of polymers was estimated on the basis of an analysis of the results obtained by investigating model reactions of the phosphites with stable nitroxyl radicals or with isopropylbenzene hydroperoxide to determine their stabilizing properties. Possible mechanisms for the stabilizing action of mixtures based on aromatic phosphites are proposed.

MIXTURES of some phosphites with phenolic inhibitors of thermooxidative degradation of polymer exhibit a marked synergetic effect [1-3]. On analysing the effect in question the cited authors [3] reached the conclusion that the scheme of oxidation of the high molecular hydrocarbon in the presence of the inhibitor of free radical action must include termination of kinetic chains on inhibitor and the breakdown, practically without radicals, of hydroperoxides of the polymer (i. e. the suppression of degenerate branching). From a kinetic standpoint a scheme of this type is borne out by the displacement of the critical concentration of inhibitor towards lower values in the presence of a phosphite (diphenylisooctylphosphite) under conditions of inhibited oxidation of polypropylene (200°, $p_{O_2} = 300$ torr). A further example illustrating the ability of phosphites to suppress degenerate branching came to light through the results obtained by authors [4] measuring the free radical yield in the reaction of diphenylisooctylphosphite with a model substance, tert.butyl hydroperoxide (20°, benzene, absence of O_2), who found that the yield was of the order of 10^{-4} . Finally, there is the fact that under conditions that generally result in a considerable rate of depolymerization, the molecular weight remains practically constant in the presence of diphenylisooctylphosphite (up to the moment of complete consumption of the phosphite), and this too may be explained in terms of a mechanism of suppression of degenerate branching [5].

In view of this one may assume that generally speaking the use of phosphites decomposers of hydroperoxides will give rise to the appearance of a synergetic effect.

Moreover, it is known that complete aromatic phosphites may themselves terminate kinetic chains in the high temperature oxidation of polymers (180-200°) by a radical exchange mechanism [6]

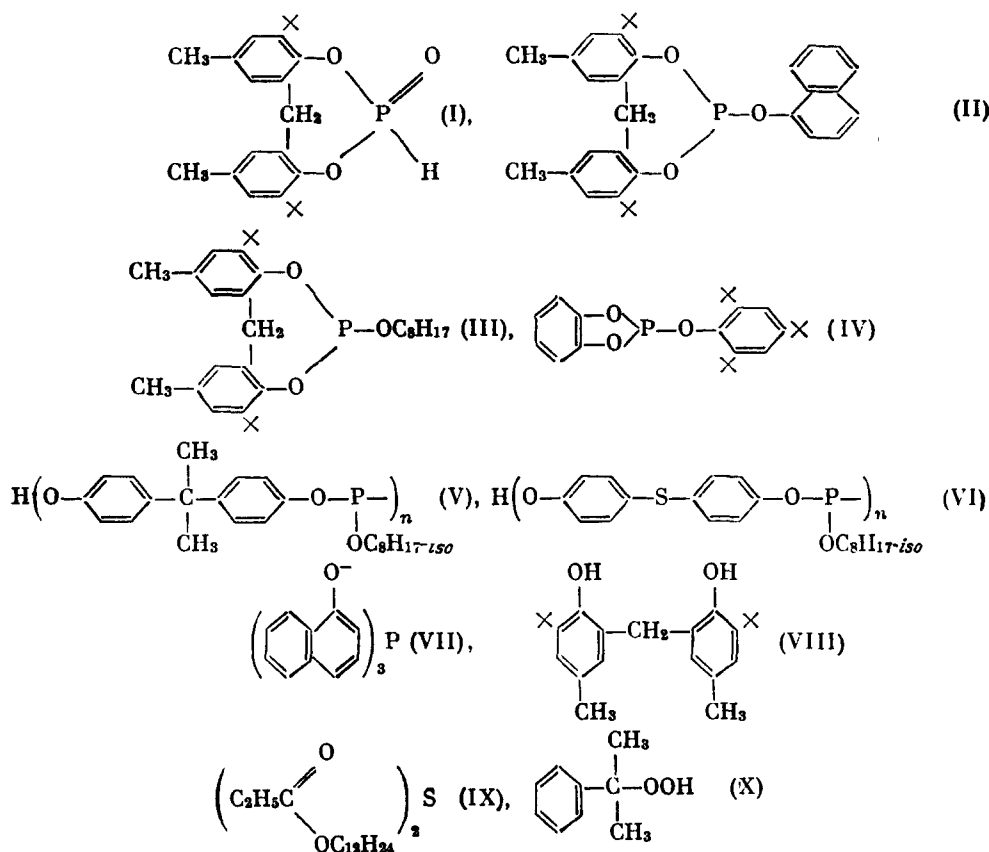


where RO' , $R'O'$ —an inactive resonance-stabilized radical, such as  (here and below $X = (CH_3)_3C$).

It was a reasonable supposition that some compositions consisting solely of phosphites acting at different levels might exhibit a non-additive action in the inhibition of polyolefins. Certainly we observed the synergism of mixtures based on different aromatic phosphites during the oxidation of low density polyethylene (200°, p_{O_2} = 250 torr). It was important to throw light on this effect, and to determine trends in the stabilizing behaviour of different phosphites. A further aim in our investigation was to estimate their ability to terminate kinetic chains, or suppress branching, in the light of our analysis of model "liquid phase" reactions of phosphites with stable nitroxyl radicals, or hydroperoxides, respectively.

EXPERIMENTAL

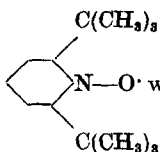
The following compounds were used as the starting materials*



The phosphites were synthesized by the known method, and before being used were purified by vacuum distillation or by recrystallization. Cumene hydroperoxide was purified by the usual method, and was used at a concentration of 99.8%. The bisphenol and the dilaurylthiodipronate were the commercial products.

* The numbering of the products shown above corresponds to the numbers appearing in the diagrams.

A static oxidizing apparatus was used for investigation of the stabilizing properties of the phosphites and the mixtures based on them. As a criterion of efficiency we took the length of the oxidation induction period τ . In investigations of the model reactions of cumene hydroperoxide with aromatic phosphites the radical acceptors method was used [4];

free nitroxyl radicals  were used as counters of free radicals formed in the

model reactions. The rate of decay of the nitroxyl radicals was determined from changes in the EPR signal with time; a sample of Mn^{2+} in MgO crystal was used as the reference sample. Reactions of the nitroxyl radical with cyclic acid I were run in ampoules from which air had been removed up to a residual pressure of $\sim 5 \times 10^{-4}$ torr.

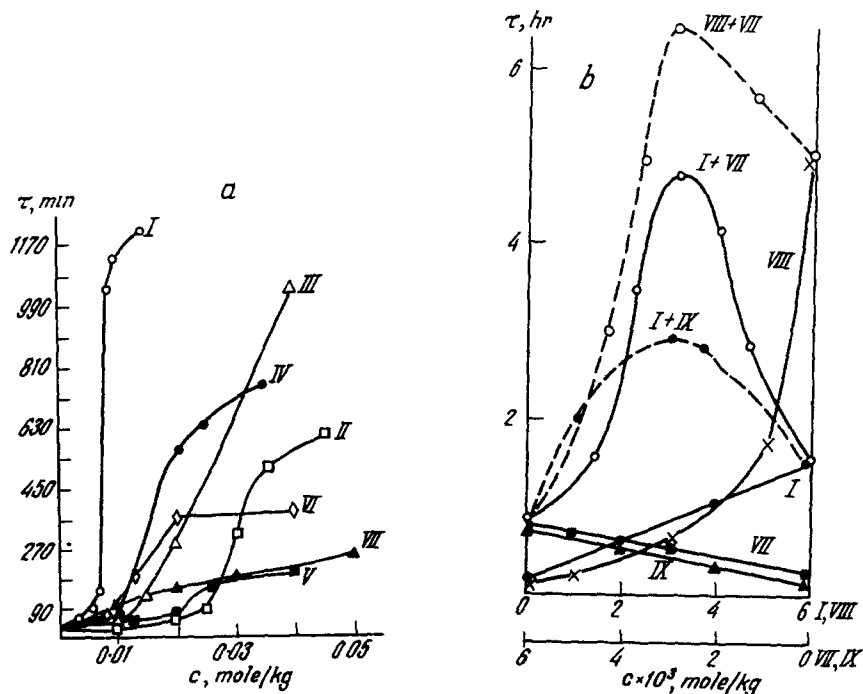


Fig. 1. Plot of τ for PELD vs. phosphite concentration (a) and concentration of the mixture of inhibitors (b).

DISCUSSION OF RESULTS

Investigation of the induction period in the oxidation of low-density polyethylene (PELD) relative to phosphite concentration (Fig. 1a) show that the phosphites differ in regard to their antioxidative properties. Most of the studied phosphites are characterized by the existence of upper and lower critical concentrations (I–VI), which puts them in the category of medium-strength antioxidants [7]. At the same time trinaphthylphosphite VII, which did not exhibit

any critical concentration, is a weak antioxidant. These data on the antioxidative properties of phosphoric acid esters provided a basis for the selection of components of the binary stabilizing mixtures.

As may be seen from Fig. 1b, a considerable synergetic effect was observed for the mixture of cyclic acid I with trinaphthylphosphite VII. Similar results were observed on replacing VII with a typical decomposer of hydroperoxides, dilaurylthiodipropionate IX, or on replacing I with a typical inhibitor of free-radical action, A-22-46, keeping the total concentrations identical. This points to similarity of the stabilizing action of dilaurylthiodipropionate and trinaphthylphosphite, on the one hand, and of A-22-46 and the cyclic acid on the other hand. The proposed mechanism of the synergetic action of the mixture in question is also confirmed from a kinetic standpoint by the displacement of the critical concentration of I in the presence of hydroperoxide decomposers VII and IX (Fig. 2). Finally, the fact that the cyclic acid interacts with the model substance in the liquid phase means that this phosphite is capable of participa-

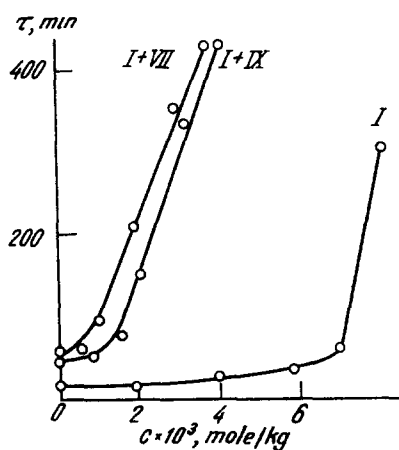


FIG. 2. Displacement of the critical concentration of I in the presence of VII and IX.

ting in radical reactions of abstraction of a hydrogen atom. It was found that the reaction of acid I with the radical in toluene obeys a kinetic equation that is first order in respect to the components, and the temperature dependence of the rate constant of this interaction (in the range 50 to 100°) is expressed as

$$k = 6.6 \times 10^6 \exp(-14,700/RT), \text{ l./mole} \cdot \text{sec}^* \quad (3)$$

* It was found that with phosphite concentrations of ~ 0.15 mole/l. the rate of interaction of the phosphite with the radical was not a function of the starting concentration of the phosphite, which means that self-solvation by the phosphite [7] may be disregarded.

This value for the activation energy is close to the activation energies for the abstraction of a hydrogen by nitroxyl radicals from phenols in the liquid phase [9].

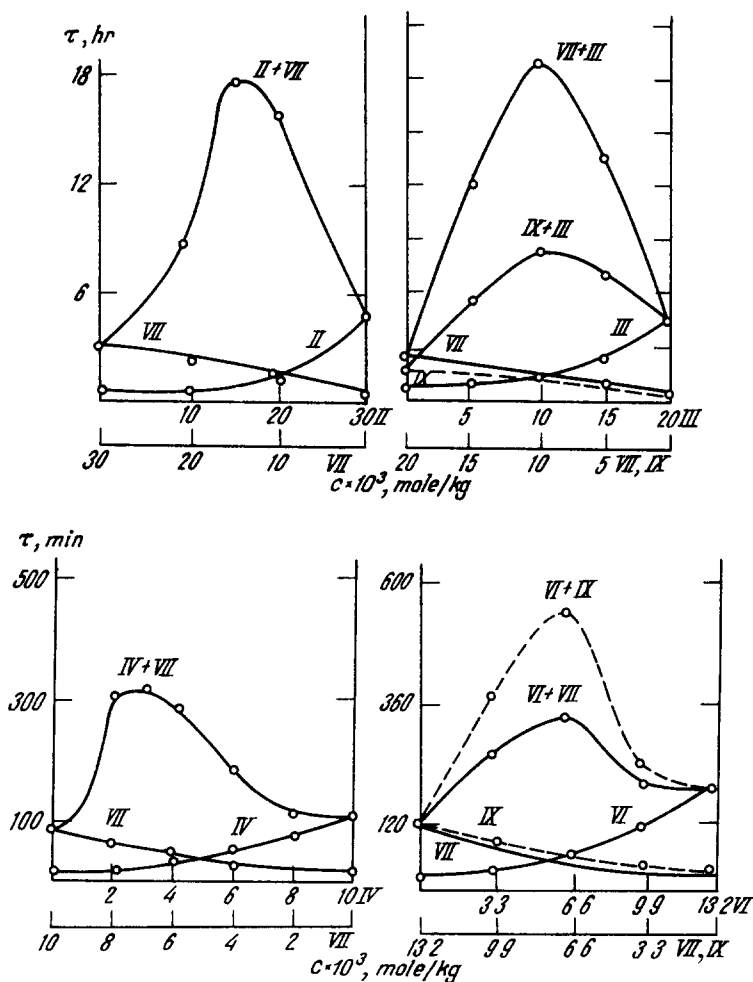


FIG. 3. Plots of τ vs. ratio of the components of mixtures.

Taking into account the inhibiting properties of other phosphites (cyclic esters, polyphosphites and pyrocatechinphosphorous acid esters (II–VI) (the appearance of critical concentrations, displacement of the latter in presence of decomposers of hydroperoxides) a study was made of the effectiveness of mixtures of mixtures of these phosphites with dilaurylthiodipropionate and trinaphthylphosphite in relation to the concentrations of these mixtures. As one would expect, the studied compositions exhibit a marked synergistic effect under the conditions of the experiments. For instance, with a mixture of the octyl ester

of cyclic acid III and trinaphthylphosphite VII, the maximum length of the induction period determined at a total concentration of 2×10^{-2} mole/kg exceeds 18 hr.

The fact that for some of the phosphites (I, II, III, VI) the critical concentrations (0.007, 0.025, 0.013 and 0.008 mole/kg respectively) are much lower in the presence of decomposers of hydroperoxides—dilaurylthiodipropionate

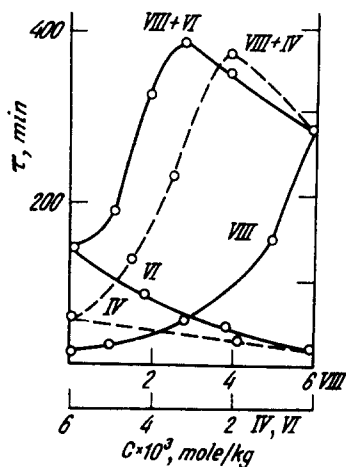


Fig. 4. Plot of τ vs. concentration of inhibitor mixtures.

and trinaphthylphosphite (in amounts of up to 0.001–0.002 mole/kg) shows that these phosphites probably participate in interactions with the hydroperoxide of the polymer. Moreover, it is known [10] that it is in fact this reaction that may provide an additional source of free radicals. Certainly direct investigations based on the radical acceptor method which were carried out to determine the character of the reaction of a model hydroperoxide X with the phosphites showed that it proceeds through free radicals, and that the yield of free radicals is much higher for the pyrocatechinphosphite IV (3.9×10^{-2}) than for the trinaphthylphosphite (0.6×10^{-2}) or the dilaurylthiodipropionate (0.9×10^{-4}). Taking these values one may now proceed to analyse factors underlying the displacement of the lower critical concentration for the remainder of the medium strength inhibitors.

In addition it was found that a synergetic effect likewise appears (Fig. 4) when some of the medium activity inhibitors (pyrocatechinphosphites and polyphosphites) are combined with bisphenol A-22-46, i.e. with a stronger inhibitor. This shows that in addition to causing termination of kinetics chains of oxidation, these phosphites may also suppress degenerate branching. The competing synergetic forces will decide which of the two tendencies in the stabilizing behaviour of these phosphites will prevail.

In the light of these results one can now subdivide the phosphorous acid

esters into the following groups: 1) phosphites that are inhibitors of kinetic chains of oxidation (the presence of critical concentrations, and displacement of the latter in the presence of decomposers of hydroperoxides, interaction with a model stable radical); 2) phosphites that are highly effective in suppressing degenerate branching (low probability of free radical yields in reactions with a model hydroperoxide; the absence of any critical concentrations); 3) phosphites exhibiting a twin role in the stabilization of polymers, i. e. inhibiting oxidation and suppressing degenerate branching.

Correct assessment of the antioxidative properties of the phosphites should provide a basis for more precise and effective selection of stabilizing compositions for polymers using the studied materials

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