

# Formation of Inhibiting Active Products from Phenolic and Amino Antioxidants. II. Synergistic Interaction of Original and Thermally Treated Inhibitors\*

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The secondary induction period of oxidation of polymers inhibited with phenolic and amino antioxidants indicates that nonvolatile inhibiting active products are formed by oxidative transformations of inhibitors during the primary induction period. The shape of the curves of secondary induction period *vs.* the time of primary oxidation led to the supposition that the inhibiting active products can be formed by thermal treatment, and that the values of the secondary induction periods are influenced by synergistic interaction of original inhibitors with the products of their thermal degradation.

Investigations of inhibiting activity of mixtures of the original and thermally treated inhibitors [2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol) and *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine in the polyethylene as polymeric substrate] in various ratios show that while in the case of amino antioxidant, there is a considerable synergistic effect, on the other hand, in the case of phenolic antioxidant the effect is an additive one.

In our previous publications [1, 2] we pointed out that the products of direct reaction of 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol) (MPC) and *N,N'*-diphenyl-*p*-phenylenediamine (DPPD) with molecular oxygen may act as inhibitors of the oxidation of polymers even when the original inhibitors are completely consumed. From investigation of the effectiveness of particular components of oxidized inhibitors, we concluded that the products of oxidative transformations of aromatic amines and hindered phenols may not only act as inhibitors themselves, but also participate in mutual interactions and in interactions with the unconsumed original antioxidant.

The investigation of secondary induction periods of oxidation of polyethylene inhibited with phenolic and amino antioxidants, and of various polymeric substrates inhibited with MPC indicates that nonvolatile active products are formed early in the primary induction period [3]. The shapes of the curves of secondary induction periods led to the supposition that the inhibiting active products may be formed by pure thermal treatment and that the secondary induction periods are influenced by synergistic interaction of the original inhibitors with the products of their thermal degradation.

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In order to verify this view we tested the inhibiting activity of mixtures of the original and thermally treated inhibitors (MPC and *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine, IPPPD) in various ratios, using polyethylene as polymeric substrate.

### Experimental

Polyethylene was a product of ICI (Great Britain), Alkathene 20 precipitated by cooling from solution in hot toluene. Inhibitors were standard commercial grades of MPC and IPPPD, purified by recrystallization from acetone.

The thermal treatment of antioxidants was carried out by heating in nitrogen atmosphere (3 hours at 180°C) in the same apparatus as was used for oxygen absorption measurement.

In order to prepare the samples of polyethylene with mixtures of the original and thermally treated antioxidants, the solutions of polyethylene in hot toluene were mixed with solutions of antioxidants of corresponding concentrations and precipitated by cooling. After drying at room temperature a powdered product passing through 0.15 mm mesh sieve was obtained. The actual concentration of inhibitors was controlled in all cases by u.v. spectrophotometry.

The induction periods were estimated on the basis of oxygen absorption measurements. Apparatus, methods, and procedures for oxygen absorption (samples 10 mg) and estimation of actual concentration of inhibitors were used as in our previous publication [1]. For induction periods up to 5 hours a visual reading off of oxygen consumption, for longer induction periods, an automatically recording apparatus [4] was applied. The reported induction period data represented average values from at least four parallel oxygen absorption measurements.

### Results and Discussion

The interactions between original and thermally treated inhibitors were investigated on polyethylene, oxidized at 180°C, oxygen pressure 760 Torr, concentration of inhibitors being 0.05% w/w. Duration of the thermal treatment of inhibitors (3 hours at 180°C) corresponds approximately to the length of the induction periods of oxidation of polyethylene inhibited with MPC or IPPPD under the above-mentioned conditions.

It can be seen from Fig. 1 that the thermal treatment of MPC and IPPPD had no significant influence on their inhibiting activity — the induction periods are of the same values (within experimental error) as induction periods for untreated antioxidants.

The results of induction periods measurements of polyethylene oxidation inhibited with various ratios of thermally treated and original MPC and IPPPD (total concentration of both being 0.05%) are illustrated in Figs. 2 and 3.

From Fig. 2 it is evident that in the case of MPC no interaction could be detected under experimental conditions used. The experiments were then repeated with 10 times higher concentration of original and thermally treated MPC (0.5%, the upper curve in Fig. 2). The result was the same — the effect was an additive one.

Quite different picture is given by the measurements with IPPPD (Fig. 3). A considerable synergistic effect was found with maximum at 1 : 1 ratio of original and thermally treated inhibitor. The position of the maximum was controlled by repeated experiments with newly prepared polyethylene—IPPPD and polyethylene—thermally treated IPPPD samples. The results were the same, that means that the position of the maximum was estimated on the basis of twice four parallel oxygen absorption measurements.

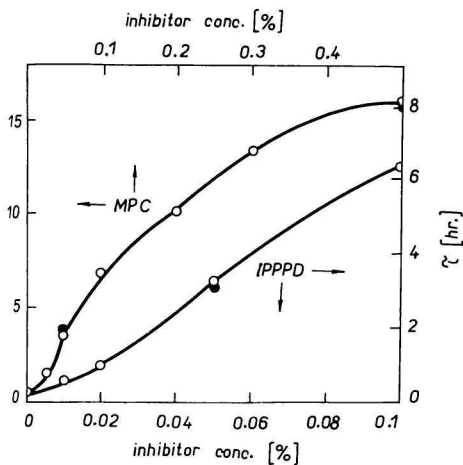


Fig. 1. The dependence of induction period on inhibitor concentration: (○) original inhibitors; (●) thermally treated inhibitors. Oxidation of polyethylene at 180°C.

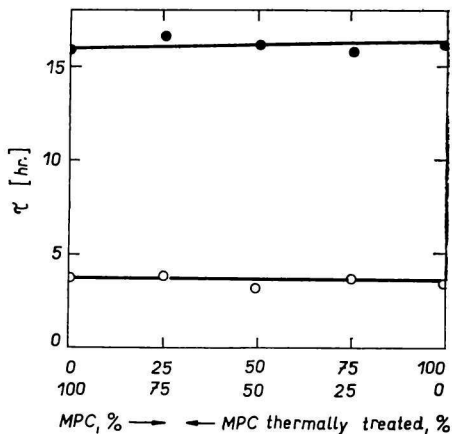


Fig. 2. The dependence of induction period on ratio of original and thermally treated MPC. Oxidation of polyethylene at 180°C. (○) total concentration 0.05%; (●) total concentration 0.5%.

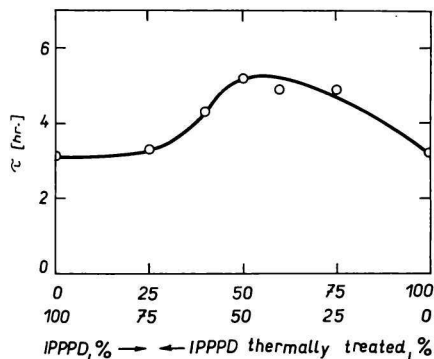
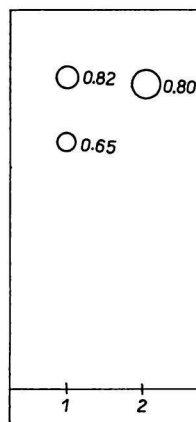


Fig. 3. The dependence of induction period on ratio of original and thermally treated IPPPD. Oxidation of polyethylene at 180°C. Total concentration 0.05%.

Fig. 4. Chromatographic analysis of original (2) and thermally treated (1) MPC on alumina thin layer. The mobile phase petroleum ether—ethylacetate (10 : 2). Detection u.v. light. Violet spot ( $R_F$  0.82), reddish spot ( $R_F$  0.80), pale brown spot ( $R_F$  0.65).



The investigation of chemical changes of MPC and IPPPD caused by the thermal treatment [5] is not an object of this communication, but it is not without interest to point out some estimated facts: the u.v. spectra of the original and thermally treated

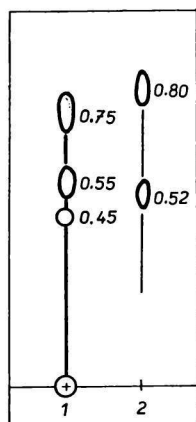


Fig. 5. Chromatographic analysis of original (2) and thermally treated (1) IPPPD on alumina thin layer. The mobile phase benzene—carbon tetrachloride (8 : 2). Detection u.v. light. Dark violet spots ( $R_F$  values as given in the figure).

inhibitors are identical with the exception of absorbance increase in absorption minima (70% at 250 nm in the case of MPC and 4% at 225 nm in the case of IPPPD) what means that more significant change was found for MPC.

The same conclusion can be deduced from chromatographic behaviour of the thermally treated inhibitors. The chromatography of thermally treated MPC using various chromatographic systems shows a considerable change in chemical structure (a typical chromatogram is in Fig. 4). On the other hand, by the chromatographic analysis, using silica as adsorbent, mobile phases of different polarity and several types of detection could not be detected significant difference between the original and thermally treated IPPPD. The formation of products of thermal degradation of IPPPD was proved only by chromatographic system shown in Fig. 5.

These results indicate that the components of thermally treated IPPPD are of similar chemical type as the original inhibitor.

The results of induction periods measurements clearly establish the possibility of synergistic interactions between original inhibitor and the products of its thermal degradation, as we assumed from the curves of secondary induction periods [3]. This possibility is a further phenomenon that is to be considered in the study of the mechanism of antioxidant function.

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### References

1. Gömörý I., Štímel J., Reya R., Gömörýová A., *J. Polym. Sci. C*, **16**, 451 (1967).
2. Gömörý I., Gömörýová A., Reya R., Štímel J., *Eur. Polym. J., Suppl.* **5**, 545 (1969).
3. Gömörý I., *Eur. Polym. J.* **6**, 1047 (1970).
4. Štímel J., Reya R., *EKT* **23**, 225 (1970).
5. Gömörýová A., Reya R., Gömörý I., unpublished results.

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