WALDEMAR LIPIŃSKI[1)], JAN OGONOWSKI[2)], MARIA UHNIAT[1)]

# The stabilization of polyethylene with two-component stabilizing system

**Summary** — The results of investigations of PE-LD stabilization with two-component system consisting of commercial stabilizers: "Irganox 1010" and "Ultranox 626" are presented. The effect of molar ratio of components on the system efficiency has been determined. Stabilizing system efficiency was estimated on the basis of induction time values ($t_i$) of PE-LD oxidation process at temp. 210°C and 220°C. Induction time values have been determined from DTA measurements. On the basis of interaction coefficient (Θ) values calculated from equation (1) it has been found that the components of chosen stabilizing system show interaction synergism (Θ > 1) which significantly depends on molar ratio of the components. The optimal ratio is equal to 0.5.
**Key words:** polyethylene, two-component stabilizing system, "Irganox 1010", "Ultranox 626", interaction synergism.

The development of polymer chemistry, including polyethylene chemistry, and searching for new, technologically and economically attractive stabilizers causes that the field of science concerning polymer oxidation and stabilization processes is still in progress.

During the processing at the high temperature polyethylene can undergo the reactions of chain disruption, crosslinking and oxidation, which all may lead to the change of the end-product properties [1—3]. The addition of antioxidants prevents these reactions.

Scott divided antioxidants according to methods of their working [4]. Namely, antioxidants inhibit the process of the plastics oxidation through:

— the reduction of alkyl-peroxide and alcoxyl radicals,

— the hydroperoxides decomposition,

— the redox reactions including the alkyl radical destruction stage in macrochains by means of the acceptor form of the antioxidant, as well as the alkyl-peroxide radical destruction stage through the donor form of an antioxidant.

A lot of new anti-ageing agents that have a complex structure and unknown working mechanism appear in the market. Sometimes their industry applications are economically unfounded. An application of multi-component stabilizing systems, which protect polymers against simultaneous action of two or more destructive factors, is the cheaper method. When the stabilizing system contains at least two components, we can distinguish the following possibilities [5]:

— mutual attenuation of the action efficiency of components — antagonistic effect,

— mutual strengthening of the action of particular components — synergistic effect,

— summation of component action efficiencies — additive effect.

The Θ parameter, which can characterize the action of two components in the stabilizing system, is defined as:

$$\Theta = \frac{t_{i,1+2}}{t_{i,1} + t_{i,2}} \quad (1)$$

where: $t_{i,1}$ — *the induction time determined at temperature T for the stabilizer 1, at concentration* $C_1$; $t_{i,2}$ — *the induction time determined at temperature T for the stabilizer 2, at concentration* $C_2$; $t_{i,1+2}$ — *the induction time determined at temperature T for the stabilizing system containing stabilizers 1 and 2, at concentrations* $C_1$ *and* $C_2$.

Depending on the value of parameter Θ we may deal with:

additive interaction effect — Θ = 1

synergistic effect — Θ > 1

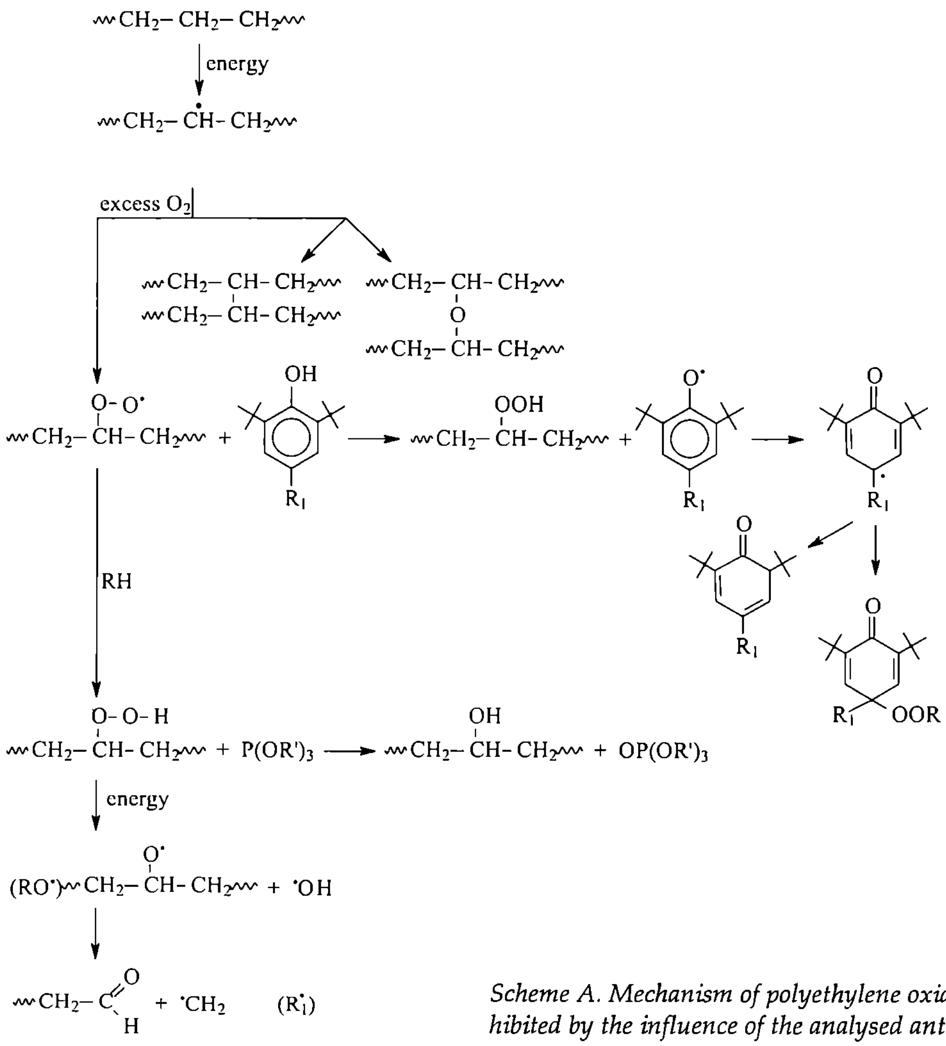
antagonistic effect — Θ < 1

From the point of view of the action mechanism of a stabilizing system, Scott distinguishes between two varieties of synergism, homo- and heterosynergism [4]. Homosynergism refers to stabilizers acting according to the same mechanisms but with different velocities, or on various stages of polymer destruction process. Heterosynergism concerns the action of two stabilizers acting according to different mechanisms.

[1)] Institute of Heavy Organic Synthesis, ul. Energetyków 9, 47-225 Kędzierzyn-Koźle, Poland.
[2)] Cracow University of Technology, ul. Warszawska 24, 31-155 Kraków, Poland.

The two-component stabilizing system, discussed in the paper, contains "Irganox 1010", which comprises phenylhydroxy-di-(*tert*-butyl) groups and is classified as a peroxide radical deactivator, and "Ultranox 626" — an organic ester of a phosphorous acid comprising phenyl-di-(*tert*-butyl) groups. The phosphorous acid's esters belong to the antioxidants' group reacting with hydroxyperoxides. In short the mechanism of polyethylene oxidation processes [6, 7] and the influence of the analyzed antioxidants' types [8—12] inhibiting them were presented in Scheme A. The system containing "Irganox 1010" + "Ultranox 626" and showing strong interaction synergism was the subject of our earlier research [13, 14]. That time the interaction synergism of the components existing in equal weight proportion 0.1:0.1% as well as the stabilizer consumption kinetics of two-component stabilizer were analyzed. In present paper the research results of "Irganox 1010" + "Ultranox 626" molar ratio influence upon the induction time of the oxidation process are described. Unfortunately we have not come across the similar research results in available literature. The knowledge concerning the optimal stabilizer components concentrations is crucial from the viewpoint of its action efficiency and economical substantiation of its application.

Differential Thermal Analysis method (DTA) is one of the methods allowing to determine the induction time $t_i$ [5, 15—19]. The method allows to determine the time in which the plastics oxidation velocity is changing from extremely small to big. This time is needed to initiate an autocatalyctic oxidation reaction in isothermal conditions. The $t_i$ value is the time of the first slow stage of inhibited oxidation reaction, during which the essential amount of antioxidant is used. [20, 21]; $t_i$ is also the time of stabilizer depletion, from the stabilizer initial concentration ($C_0$) to the critical value of the concentration ($C_{cr}$).




*Scheme A. Mechanism of polyethylene oxidation processes inhibited by the influence of the analysed antioxidant's types*

$C_{cr}$ is the concentration at which the stabilizer does not show the protective abilities against oxidation processes, at a given temperature.

It has been reported [5, 10] that for the proper evaluation of antioxidant action efficiency in various temperature it is beneficial to examine the dependency of the induction time $t_i$ on temperature.

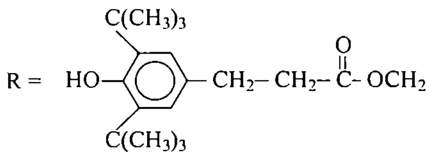
The analysis shows that one of the methods improving the action efficiency of anti-ageing agents is the application of stabilizing systems protecting polymers against simultaneous action of several destructive factors. Such a method allows to select a stabilizing system that is economically advantageous.

The subject of the present work was the analysis of such systems. The $t_i$ value of oxidation, determined by isothermal method DTA [16, 17], has been adopted to estimate the stabilizing properties.

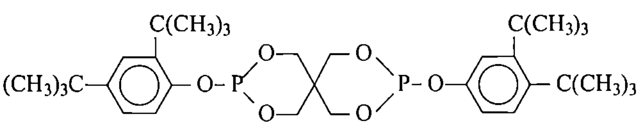
## EXPERIMENTAL

### Materials

Tetra{methylene 3-[3,5-(di-*tert*-butyl)-4-hydroxyphenyl]propionate}methane *i.e.* $C(R)_4$ [R see formula (I)] — "Irganox 1010" produced by Ciba-Geigy; bis[2,4-(di-*tert*-butyl)-phenyl]pentaerithritol diphosphite (formula (II)] — "Ultranox 626" produced by Borg-Warner




(I)




(II)

Chemicals Inc. and low density polyethylene PE-LD ($MFI$ = 0.3 g/10 min) — "Polyethylene GGNX 18-D003" produced by Poli-Chem Kędzierzyn Koźle were used.

### Sample preparation

The PE-LD mixture with stabilizers was prepared in a heated rolling mill at temperature 160°C. After the assumed rolling time (5 min), the hot mixture was placed into a forming frame. Next it was press-formed into 2 millimetre-thick plates. The samples for the further research were prepared through the grinding of the earlier formed plates, thus obtaining 0.1 mm-thick chips. The stabilizer concentrations and molar ratios of the examined PE-LD dual stabilizing system components are shown in Table 1.

**T a b l e 1. Characteristics of the stabilizing systems**

| Sample | Stabilizer | Concentration in PE | | Molar ratio 1:2 |
|---|---|---|---|---|
| | | component 1*) wt. % | component 2*) wt. % | |
| 1 | "Irganox 1010" | 0.1000 | — | — |
| 2 | "Irganox 1010" + "Ultranox 626" | 0.1000 | 0.2051 | 0.25 |
| 3 | "Irganox 1010" + "Ultranox 626" | 0.1000 | 0.1026 | 0.50 |
| 4 | "Irganox 1010" + "Ultranox 626" | 0.1000 | 0.0256 | 2.0 |
| 5 | "Irganox 1010" + "Ultranox 626" | 0.1000 | 0.0128 | 4.0 |
| 6 | "Ultranox 626" | — | 0.2051 | — |
| 7 | "Ultranox 626" | — | 0.1026 | — |
| 8 | "Ultranox 626" | — | 0.0256 | — |
| 9 | "Ultranox 626" | — | 0.0128 | — |

*) Component 1 — "Irganox 1010", component 2 — "Ultranox 626".

### Methods

The induction time $t_i$ was determined with using Unipan Thermal microcalorimeter DSC 605M type, which was programmed for a read-out of the induction time in oxidation process.

The influence of the components molar ratio on the dual stabilizing system action efficiency was investigated for mixtures of two stabilizers "Irganox 1010" + "Ultranox 626". The measurement of the oxidation induction time was carried out for the 3—6 mg sample of the stabilized PE-LD. The aluminum melting crucible with the sample was placed in the microcalorimeter chamber, at the proper temperature, in air atmosphere. During the measurement isothermal conditions were kept. The oxidation induction time ($t_i$) was defined as the time after which the exothermic effect of PE-LD oxidation became visible, at the fixed temperature.

## RESULTS AND DISCUSSIONS

The influence of the molar ratio of the components at the stabilizing systems consisting of "Irganox 1010" and "Ultranox 626" was studied at temperature 210 and 220°C. The stabilizers concentrations were similar to those which are used in traditional trading polyethylene applied for long-time exploitation products. The values of the oxidation induction time of PE-LD stabilized with single stabilizers and dual stabilizing systems are presented in Table 2.

**T a b l e 2. Results of the measurements of the oxidation induction time ($t_i$) of PE-LD stabilized by single stabilizers and dual stabilizing systems**

| Sample (acc. table 1) | Molar ratio 1:2 | Temperature of oxidation | |
|---|---|---|---|
| | | 210°C | 220°C |
| | | $t_i$, min | $t_i$, min |
| 1 | — | 22.65 | 7.9 |
| 2 | 0.25 | 64.2 | 50.4 |
| 3 | 0.5 | 73.2 | 60.65 |
| 4 | 2.0 | 67.8 | 52.15 |
| 5 | 4.0 | 45.3 | 18.05 |
| 6 | — | 6.0 | 0.0 |
| 7 | — | 0.0 | 0.0 |
| 8 | — | 0.0 | 0.0 |
| 9 | — | 0.0 | 0.0 |

When the "Irganox 1010" (component 1) concentration was 0.1 wt. % (sample 1), at the temperature 220°C the induction time of PE-LD oxidation $t_i$ was 7.9 minutes. In the similar conditions "Ultranox 626" (component 2) used in concentration 0.01—0.2 wt. % (samples 6—9) did not stabilize PE-LD (the oxidation induction time was zero). However, in the case of polyethylene samples containing 0.1 wt. % of "Irganox 1010" and various amounts of "Ultranox 626" (samples 2—5), the oxidation induction time was in the range from 18 to 60 minutes. Therefore, at temperature 220°C the addition of "Ultranox 626" influences the increase of the "Irganox 1010" $t_i$. When the molar ratio of "Irganox 1010":"Ultranox 626" increases, the oxidation induction time rises at the beginning and decreases afterwards.

At temperature 210°C $t_i$ values change in similar way: at the molar ratio 0.25 $t_i$ is equal to 64.2 minutes, at 0.5 ratio it reaches the highest value $t_i$ = 73.2 min and at the further growth of molar ratio up to 4.0 it drops again to 45.3 min. On the basis of these results the optimal molar ratio of "Irganox 1010":"Ultranox 626" was established as 0.5 for the range of stabilizers compositions investigated. When the molar ratio of 1:2 exceeds 0.5, $t_i$ becomes shorter.

**Table 3.** Values of Q coefficient for "Irganox 1010" + "Ultranox 626" systems at temperature 210 and 220°C

| Sample (acc. table 1) | Molar ratio 1:2 | Θ at temperature | |
|---|---|---|---|
| | | 210°C | 220°C |
| 2 | 0.25 | 2.2408 | 6.3797 |
| 3 | 0.50 | 3.2318 | 7.6772 |
| 4 | 2.00 | 2.9934 | 6.6013 |
| 5 | 4.00 | 2.0000 | 2.2848 |

Interaction synergism of examined dual stabilizing system was defined on the basis of the interaction coefficient (Θ). The values of Θ coefficient calculated for temperature 210 and 220°C according to equation (1), are presented in Table 3. Known from chemical literature interaction synergism of the components of the dual-stabilizing system "Irganox 1010" + "Ultranox 626" was confirmed. Values of Θ > 1 prove it.

REFERENCE


1. "Developments in polymer stabilization" (Ed. Scott G.), Vol. 7, Applied Science Publishers, London 1984.
2. Waldman W., De Paoli M.: *Polym. Degrad. Stab.* 1998, **60**, 301.
3. Habicher W. D. *et al.*: *Macromol. Symp.* 1997, **115**, 181.
4. "Developments in polymer stabilization" (Ed. Scott G.), Vol. 4, Applied Science Publishers, London 1982.
5. Latocha Cz., Uhniat M., Balcerowiak W.: *Polym. Deg Stab.* 1984, **7**, 189.
6. Decker C., Mayo F. R., Richardson H. J.: *J. Polym. Sci., Polym. Chem. Ed.* 1973, **11**, 2879.
7. Decker C., Mayo F. R., Richardson H. J.: *J. Polym. Sci., Polym. Chem. Ed.* 1973, **11**, 2848.
8. Ränby B., Rabek Ya. F.: "Photodestruction, Photooxidation, Photostabilization of Polymers" (*in Russian*), Mir, Moscov 1978.
9. "Developments in polymer stabilisation" (Ed. Scott G.), Vol. 1, Applied Science Publishers, Barking 1979.
10. Pospisil J.: *Adv. Polym. Sci.* 1980, **36**, 69.
11. Pospisil J., Klemchuk P. P.: "Oxidation Inhibition in Organic Materials", CRC Press, Boca—Raton—Ann Arbor—Boston 1990.
12. Schwetlick K.: *Pure Appl. Chem.* 1983, **55**, 1629.
13. Latocha C., Uhniat M.: *Polym. Degr. Stab.* 1992, **35**, 115.
14. Uhniat M., Latocha C.: *Polym Degr. Stab.* 1992, **35**, 163.
15. Howard J. B.: *Polym. Eng. Sci.* 1973, **13**, 429.
16. Marshall J. D. *et al.*: *Polym. Eng. Sci.* 1973, **13**, 415.
17. Wight F. R.: *Polym. Eng. Sci.* 1976, **16**, 652.
18. Latocha Cz., Uhniat M.: *Polimery* 1982, **2**, 67.
19. Latocha Cz., Uhniat M.: *Polym. Degr. Stab.* 1989, **23**, 193.
20. "Thermal characterization of polymeric materials" (Ed. Turi E.), Second Ed., John Wiley and Sons, New York 1996.
21. Hatekayama T., Quinn F. X.: "Thermal analysis" John Wiley and Sons, Chichester 1994.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