## Synergy Effects of Binary and Ternary Mixtures of Inhibitors in the Process of Polypropylene Autooxidation

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# Synergy Effects of Binary and Ternary Mixtures of Inhibitors in the Process of Polypropylene Autooxidation

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The autooxidation of the solid isotactic polypropylene, inhibited with three different additives – phenol, amine and nitroxy radical as well as their binary and tertiary mixtures was investigated. Noticeable synergy effects were observed for inhibiting systems: phenol – amine and phenol – nitroxy radical; these effects were especially high in the region of low concentrations of inhibitors, in the so called subcritical region.

Mathematical model was proposed for the evaluation of contribution of each inhibitor to the induction period. Possibility of such description was confirmed by comparison of the experimental and calculated data.

*Keywords:* Isotactic polypropylene; autooxidation; inhibitors; phenol; amines; mixtures of inhibitors

## INTRODUCTION

Synergy effect in the process of inhibited oxidation of liquid and high-molecular hydrocarbons is rather well known. Different investigators observed this phenomenon for inhibiting composition phenol – amine, phenol – quinone, phenol – nitroxy radical [1 – 4]. The most detailed investigation was carried out for inhibited with amine – phenol mixtures initiated oxidation of liquid hydrocarbons [2 – 4]. To explain observed effects reaction between amine radical and phenol was

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proposed:

$$Am \cdot + PhOH \Leftrightarrow AmH + PhO \cdot \tag{1}$$
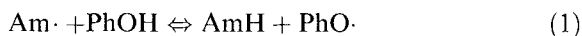
This reversible reaction leads to the amine regeneration and is competitive with possible side reaction of amine radical. In the case of sterically hindered phenols the reverse reaction is difficult and this fact increases efficiency of regeneration. For hydrocarbons with the weak O—H bond efficiency of this reaction is lower because of the competition with the process of H-atom abstraction by amine radical.

In the polymer systems the synergy effect of amine–phenol mixtures was also observed by different authors and in different polymers.

In polybutadiene synergy effect of phenyl-$\beta$-naphthylamine and 2,6-di-tert-butyl-4-methylphenol was observed in the temperature interval 100–150°C [5]. The maximum synergy effect was always observed regardless of summary concentration for 1:1 mixtures of inhibitors and its highest value was 1,8.

Synergy effect for system phenol–nitroxy radical was also observed in liquid phase [3], but because of high complexity of process no explanations of this fact were given. There are some other data and among them patents of the Uniroyal Chemical Company, that confirm the existence of the different inhibitors synergy effect in polymer [6, 7]. Rather interesting is result obtained for polyethylene: not only mixtures of aromatic amines with phenols but also with *N*-containing heterocycles give synergy effect during polymer oxidation [8]. In the work of Yu. A. Shlyapnikov with co-workers it was shown for the system phenyl-$\beta$-naphthylamine-tri-tert-butylphenol that if the concentration of amine is higher than critical one addition of phenol leads to shortening of induction period [9]. Besides in the work of J. Pospisil and L. Taimr synergy effect of phenol–amine mixture (initiated oxidation of squalene in chlorobenzene, 60°C, *N*-i-propyl-*N'*-phenyl-1,4-phenylenediamine–2,6-di-tert-butylphenol) was observed only in the presence of acid [10]. All these results show, that the problem of synergy of different inhibitors in polymer is rather complex and further investigations in this field are necessary.

This work was performed in order to investigate inhibiting activity in the process of autoxidation of polypropylene (130°C, air) of binary and ternary mixtures of three inhibitors of different classes: phenol–octadecyl-3,5-di-tert-butyl-4-hydroxycinnamate (1), aromatic amine–

4, 4'-di($\alpha$, $\alpha'$-dimethylbenzyl)diphenylamine (2) and nitroxy radical (3), obtained from this amine.
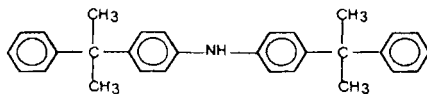


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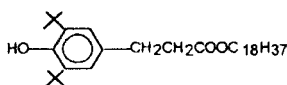


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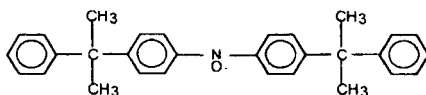


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## EXPERIMENTAL

Isotatic polypropylene in the form of powder (ProFax 6501 produced by Himont Co (USA) with the molecular mass $Mw = 164400$, $Mw/Mn = 38$) was used. Traces of inhibitor were washed out with benzene in the Soxhlet apparatus.

The inhibitors (1) and (2) were supplied by Uniroyal Chemical Company, Inc. under the commerical names Naugard 445 and Naugard 76, correspondingly. Nitroxy radical was synthesised by Dr. A. B. Shapiro in the Semenov Institute of Chemical Physics, Russian Academy of Sciences. The low molecular additives were introduced into PP from their benzene solutions, in which the swollen polymer was kept during 3 hours. Thereafter the solvent was evaporated in air with constant stirring of the mixture.

Oxidation of polymer with additives was carried out in closed ampoules at the temperature $130 \pm 0, 5°C$. Samples of polymer were taken regularly and placed into the cell of sensitive capillary pressure gauge for measurement of the oxidation rate. Achievement of

oxidation rate value of $10^{-6}$ mole/kg.sec was considered as the end of induction period.

Synergy effects were calculated as

$$S = \tau_1/\tau_2 + \tau_3,$$

where $\tau_1$–induction period for binary inhibitors mixture,

$\tau_2$–induction period for the same concentration of the first inhibitor as in the binary mixture,

$\tau_3$–induction period for the same concentration of the second inhibitor as in the binary mixture.

Procedure of synergy effect evaluation for ternary mixtures was analogous to the one used for binary mixtures.

Mathematical processing of data was performed using multiple regression method. All calculations and figures were made by means of the computer program "Statistika". For such processing unified data file was organised which included practically all induction periods data obtained in the experiments with different concentrations of individual inhibitors and their binary and ternary combinations. Existence of such unified massive gave opportunity for analyse of whole experimental material in total and for evaluation of the contribution of each combination.

## RESULTS AND DISCUSSION

As a result of first state data for each one inhibitor were obtained (Tab. I).

These data were necessary for assessment of the synergy effect for mixtures of inhibitors.

Then experiments for binary systems were conducted. The summary concentration of components in all experiments was constant (as usually in the synergy experiments) $-5 \times 10^{-4}$ mole/kg. Results are given in the Tables II–IV.

It can be seen from these data that the best result can be obtained for binary mixtures containing $\sim 80\%$ of Irganox 76 and $\sim 26\%$ of other inhibitor. To be sure that this is true synergy effect the experiments were made with higher concentrations of Naugard 445 and Naugard 76 in PP. The following data were obtained:

TABLE I

| Inhibitor | Concentration mole/kg | Induction period, hrs (average of 3 meaurements) |
|---|---|---|
| Naugard 76 | .0001 | 4 |
| | .0002 | 11 |
| | .0003 | 18 |
| | .0004 | 27 |
| Naugard 445 | .0001 | 3 |
| | .0002 | 6 |
| | .0003 | 7 |
| | .0004 | 30 |
| Nitroxyl radical | .0001 | 4 |
| | .0002 | 6 |
| | .0003 | 15 |
| | .0004 | 22 |

TABLE II

| Naugard 76, mole/kg × $10^4$ | Naugard 445, mole/kg × $10^4$ | Induction period, hrs (average of 3 measurements) | Synergy effect |
|---|---|---|---|
| 1 | 4 | 30 | 0,9 |
| 2 | 3 | 49 | 2,7 |
| 2,5 | 2,5 | 62 | 3,0 |
| 3 | 2 | 79 | 3,3 |
| 4 | 1 | 108 | 3,6 |

TABLE III

| Naugard 76, mole/kg × $10^4$ | Nitroxy radical mole/kg × $10^4$ | Induction period, hrs (average of 3 measurements) | Synergy effect |
|---|---|---|---|
| 1 | 4 | 34 | 1,3 |
| 2 | 3 | 79 | 3,0 |
| 2,5 | 2,5 | 120 | 4,8 |
| 3 | 2 | 131 | 5,5 |
| 4 | 1 | 190 | 6,1 |

TABLE IV

| Nitroxy radical, mole/kg × $10^4$ | Naugard 445, mole/kg × $10^4$ | Induction period, hrs (average of 3 measurements) | Synergy effect |
|---|---|---|---|
| 1 | 4 | 18 | 0,53 |
| 2 | 3 | 13 | 1,0 |
| 2,5 | 2,5 | 26 | 1,5 |
| 3 | 2 | 22 | 1,05 |
| 4 | 1 | 42 | 1,7 |

.0005 mole/kg Naugard 445 – 500 hrs.
.0005 mole/kg Naugard 76 – 160 hrs.

Thus, around concentrations 0,0004 – 0,0005 for these two inhibitors values of induction periods increase sharply. Such effect usually can be seen near critical concentration of inhibitor, and it seemed possible, that sharp increasing of induction periods for the mixtures with 80% Naugard 76 and 20% of other inhibitor was a result of transition over the critical concentration rather than synergy effect. For checking this point the experiments were made with other summary concentration $-4 \times 10^{-4}$ mole/kg. These experimental data are given below in the Tables V – VII. Only one experiment was done for system Naugard 445 – NR because synergy effect for it was very low.

From all these data it is obvious that in the region far from critical values the best results can be obtained for the mixtures of inhibitors with roughly equal concentrations of both inhibitors. As to the

TABLE V

| Naugard 76, mole/kg $\times 10^4$ | Naugard 445, mole/kg $\times 10^4$ | Induction period, hrs (average of 3 measurements) | Synergy effect |
|---|---|---|---|
| 1 | 3 | 29 | 2, 6 |
| 2 | 2 | 46 | 2, 7 |
| 3 | 1 | 24 | 1, 1 |
| 3, 5 | 0, 5 | 24 | 1, 0 |

TABLE VI

| Naugard 76, mole/kg $\times 10^4$ | NR, mole/kg $\times 10^4$ | Induction period, hrs (average of 3 measurements) | Synergy effect |
|---|---|---|---|
| 1 | 3 | 23 | 1, 2 |
| 2 | 2 | 103 | 6, 1 |
| 3 | 1 | 50 | 2, 3 |
| 3, 5 | 0, 5 | 52 | 2, 1 |

TABLE VII

| NR, mole/kg $\times 10^4$ | Naugard 445, mole/kg $\times 10^4$ | Induction period, hrs (average of 3 measurements) | Synergy effect |
|---|---|---|---|
| 2 | 2 | 22 | 1, 8 |

mixture Naugard 445 – NR its synergy effect is rather small and may be even lies in the range of experiments accuracy. But these data indicate that synergy is not a result of nitroxy radical reaction with alkyl radical, and this conclusion is very important one from the standpoint of mechanism understanding.

Besides specially made kinetic calculations also show, that stationary concentration of alkyl radicals in the oxidising PP is very low and reactions with these species practically cannot influence the process.

Data about optimal 1:1 proportion of inhibiting components in the mixture are in good agreement with data of other investigators. The most obvious explanation of this fact is formation of some 1:1 complex from both compounds that is more effective towards active radicals. Kinetic calculation made with this assumption shows that in this case even if rate constant of such complex is only one order of magnitude higher than the constants of both inhibitors even small deviations from 1:1 proportion have to lead to the shortening of induction period. But reaction (1) or cross-disproportionation also can not be excluded, because in contrast to liquid phase in the polymers levelling of rate constants of different inhibitors takes place and optimal proportion of inhibitors can be other than in the liquid phase. Even in the liquid phase mechanism of inhibiting action of phenol – nitroxy radical mixture was not determined because of its evident complexity. It is not enough to know inhibiting activity of mixtures for understanding of mechanism. It is clear that additional experiments are necessary with usage of ESR method particularly for the phenol-radical mixture.

Simple analyse of data for binary mixtures leads to conclusion that ternary system cannot give result much better, than binary one because of the practical absence of effect for the mixture amine – nitroxy radical. Possibility of better result for ternary mixture can arise only as a result of some additional triple interaction in the system.

On the next stage data for 5 ternary mixtures were obtained.

It is necessary to say that such significant synergy effects as 6, 1 and 8, 5 most probably can be observed only in the transition region from non-stationary process to the stationary one. At higher concentrations of mixture components the regularities most likely will be the same ones but synergy values will be much lower. It is right not only for this

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TABLE VIII

| Naugard 76, mole/kg × 10⁴ | Naugard 445, mole/kg × 10⁴ | NR, g × 10⁴ | Induction period, hrs (average of 3 measurements) | Synergy effect |
|---|---|---|---|---|
| 2 | 1, 5 | 0, 5 | 54 | 3, 2 |
| 2 | 0, 5 | 1, 5 | 153 | 8, 5 |
| 2 | 1 | 1 | 92 | 4, 6 |
| 3 | 0, 5 | 0, 5 | 49 | 2, 3 |
| 1 | 2 | 1 | 31 | 2, 2 |

series of experiments, but for all accelerated testing methods which mostly use non-stationary conditions.

For processing of the all experimental data file methods of linear as well as non-linear multiple analyses were used.

In the first case function (1) was under consideration:

$$f(x1, x2, x3) = a0 + a1 \times x1 + a2 \times x2 + a3 \times x3, \qquad (1)$$

where $x1$, $x2$ and $x3$ are the concentrations of three different inhibitors, $f(x1, x2, x3)$ is induction period and $a1$, $a2$, $a3$ – coefficients.

By means of multiple linear regression coefficients $ai$ in this equation were determined and their statistical errors and confidence levels of regression coefficients ($p$) were evaluated.

From obtained data it was clear that the most significant contribution to the induction period at such approach gave inhibitors Naugard 76 and NR (nitroxy radical) ($p < 0.000002$ and $p < 0.002$ correspondingly). Multiple regression coefficient ($R$) value is 0.7, and this gives significance level $p < 0.000013$. This result means that system in all can be quite adequately described with the multiple linear regression and this method can be used for further analyse and prognosis.

Multiple linear regression has to be linear only to parameters, so some latitude exists for the choice of functional dependence for each inhibitor. This gives chance for significant improvement of description quality. Results of calculation for the case when dependence of each member in the Eq. (1) was regarded as exponential one showed that in this case multiple regression coefficient was higher ($R = 0.86$) and significance level for all coefficients increased to at least $p < 10^{-3}$.

Figure 1 illustrated agreement between observed and calculated induction period values for linear approximation without values which most probably belong to the overcritical range ( > 100 hrs).

Obtained results made possible adequate enough description of experiment but without selection of contribution of binary and ternary systems to formation of induction period because every reagent concentration in the equation was to power 1.

For quantitative evaluation of inhibitors mixtures contributions calculation were made with non-linear regression method which gave possibility to take into account interactions between variables. However it was clear that some arbitrariness arose in the choice of the non-linearity type. We took into consideration the simplest variant of cross-terms in the Eq. (2):

$$f(x1, x2, x3) = a \times x1 + b \times x2 + c \times x3$$
$$+ ab \times x1x2 + ac \times x2x3 + bc \times x1x3 + abc \times x1x2x3$$

$$(2)$$

where $a$, $b$, $c$, $ab$, $ac$, $bc$, $abc$ – corresponding coefficients.

Fitting of this equation parameters with least square method made possible evaluation of contributions of the each inhibitors combina-
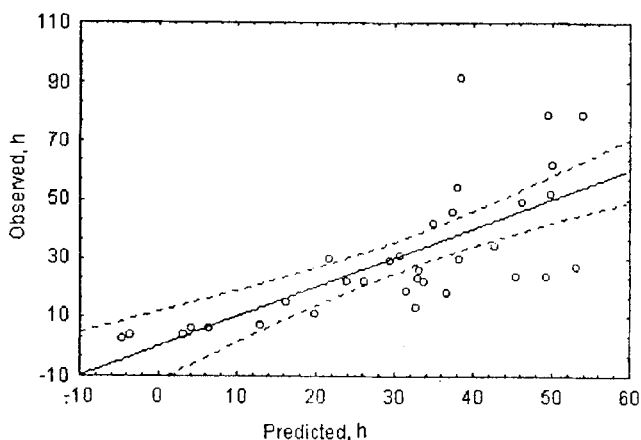


FIGURE 1 Observed values of induction periods *versus* predicted ones. Linear regression for the points < 100. Correlation: $r = .92082$. Dotted lines set limits of confidential borders for regression lines (95%).

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tion to the total induction period value by means of coefficient followed by corresponding term.

In the Table IX values of these coefficients are given for two data files: including all experimental data and without overcritical values ($< 100$ hrs).

Dependence between two set of coefficients can be satisfactorily linearised in the double logarithmic co-ordinates (Fig. 2), which fact indicates power character of this dependence. This plot illustrates changing of parameters of the system after exception of over 100 hrs values. It is clear that after such exception part of NR increases significantly, coefficient following by its concentration increases 36 times; that means that the part of nitroxy radical becomes less

TABLE IX

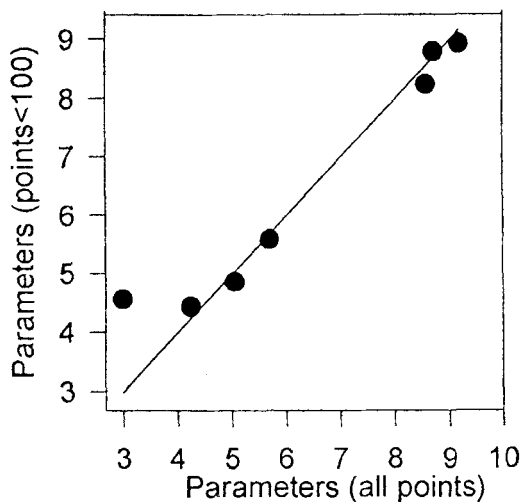|  | All data | Data < 100 |  |
|---|---|---|---|
| a | 1.13e + 5 | 7.12e + 4 | Naugard 76 |
| b | 1.75e + 4 | 2.70e + 4 | Naugard 445 |
| c | 9.80e + 2 | 3.57e + 4 | NR |
| ab | 5.20e + 8 | 6.01e + 8 | |
| ac | 1.55e + 9 | 8.13e + 8 | |
| bc | 3.78e + 8 | 1.70e + 8 | |
| abc | 4.95e + 5 | 3.83e + 5 | |



FIGURE 2 Correlation between two set of parameters: for all points and for the points < 100 hours (double logarithmic correlation).

important after transition over critical values. Variations of other parameters were unessential.

The most important part in formation of induction period evidently play two main reagents: Naugard 76 and nitroxy radical. Using calculated values of coefficients following by this reagents concentrations for individual and binary systems it is possible to make some prognosis (three-dimensional interpolation surface of response) and arranging experimental values for ternary mixtures on this surface visually evaluate contribution of ternary combinations to the induction period. In the Figure 3 these results are given. It is clear, that practically ternary combinations do not lead to the substantial increasing of induction period. It is necessary to mention that during these calculations over-critical values of induction periods were excluded. The same conclusion about rather little effect of the third component addition can be made also as a result of comparison of different coefficients values in the Eq. (2) (See Tab. IX).
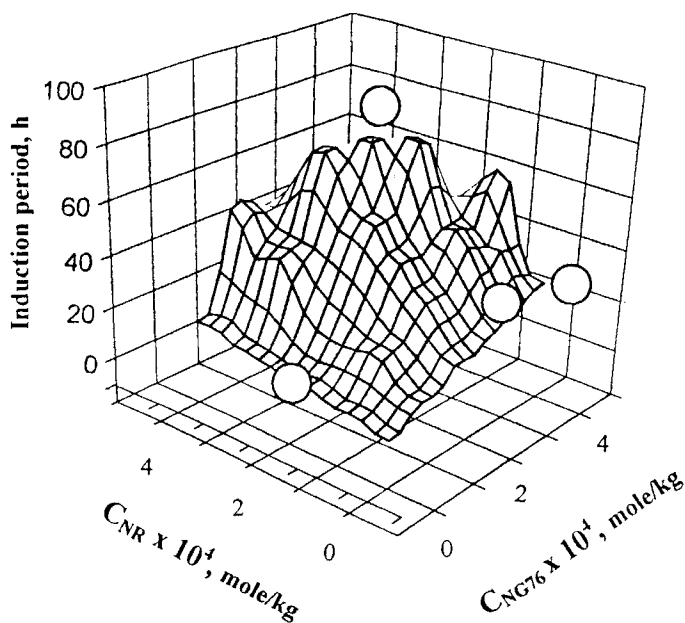


FIGURE 3   Three-dimensional interpolation surface of response (prognosis). Points correspond to experimental values for ternary system.

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