SYNERGISTIC PHENOMENA IN POLYMER PHOTOSTABILIZATION

V.Ya. Shlyapintokh

Institute of Chemical Physics, Academy of Sciences of the
USSR, Kosygin street 4, Moscow USSR

Abstract – Investigation of the synergism between UV–absor-
bers (UVA) and antioxidants (A) for photostabilization of
polydienes and PP has revealed that synergism can be attri-
buted to diffusion of A from the deeper-lying layers of po-
lymer, protected from the action of light by UVA, towards
surface layers where the photoreaction takes place. With PP,
where additives are irregularly distributed in the amorphous
phase, the mixture of the same stabilizers may lead to a sy-
nergism effect due to UVA quenching the excited electronic
state of A, suppressing its photoinitiating effect. Also
considered is the synergism attributed to an increase in so-
lubility and a change in stabilizers distribution pattern
through introduction of low-molecular weight stabilizing or
non-stabilizing additives into polymers. A study of A light
protective function in the absence of UVA revealed that A
according to their influence on the induction period of pho-
tooxidation (T_{ind}), can be divided into groups by their ab-
sorption and photochemical activities. Typical experimental
relationships between T_{ind} and A for different groups of A
are explained.

1. INTRODUCTION

Synergism phenomena are widely used in practice for photostabilization of
polymers. To enhance the efficiency of synergistic mixtures and provide for
their rational selection it would be desirable to identify the mechanism of
their light protective action. Until recently, however, these mechanisms
have not been studied. Several hypotheses have been suggested to account
for these mechanisms, but they were not substantiated experimentally.
This paper presents the results of a study of synergistic mechanisms con-
ducted from 1976 in the laboratory headed by the author. This study has re-
vealed that the mechanism of the synergistic action of the mixtures most
commonly used in polymer photostabilization, i.e. mixtures of UV–absorbers
(UVA) and antioxidants (A), should be considered in terms of a diffusion
to the surface layer where the photo-oxidation of the polymer takes place
/1-5/. We have experimentally studied two other mechanisms of synergism,
namely (i) mechanism consisting in UV–absorber quenching the excited elec-
tronic state of the antioxidant, suppressing its photosensitizing effect;
(ii) mechanism of increasing the solubility and distribution pattern of a
stabilizer through various additives /6/.

2. SYNERGISM OF UV–ABSORBERS AND ANTIOXIDANTS

2.1. Diffusion mechanism

Figure 1 shows the distribution of light intensity in a polymer film of
thickness L containing a UVA (Curve 1). The photoreaction actually takes
place only in the narrow zone of thickness l adjacent to the irradiated
surface. As a result an antioxidant concentration gradient develops during
the photoprocess causing diffusion of the A from the deeper-lying layers of
polymer film towards the surface. It increases the duration of the induc-
tion period of the photoreaction and under favourable conditions the whole
amount of the A contained in the film can be consumed to inhibit the reac-
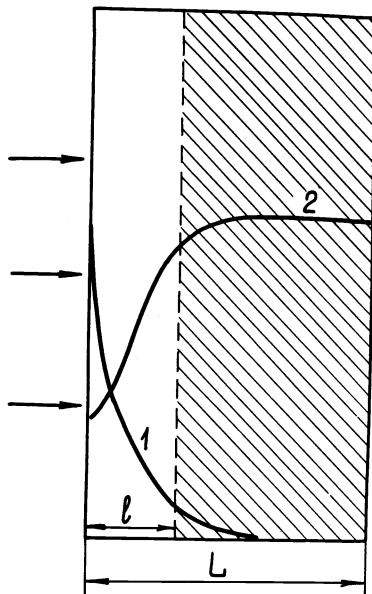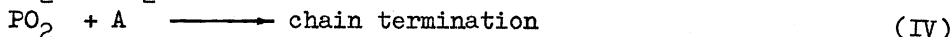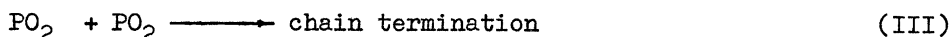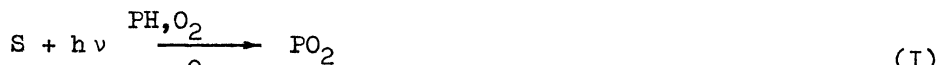tion in zone l. This is the diffusion mechanism of synergism.

Fig. 1. Distribution of light across the sample irradiated
in the presence of UVA (1), distribution of A after period
of time t from the reaction start (2). A dash line marks a
zone, where A is not exposed to light.

2.1.1. Synergism of UV-absorbers and radical scavengers:
The quantitative description of the diffusion mechanism involving radical
scavengers is given in /2,4/. Synergism relationships are obtained for the
photosensitized oxidation processes occuring via unbranched chain reac-
tions at a constant initiation rate

$$S + h\nu \xrightarrow[\text{O}_2]{\text{PH,O}_2} PO_2 \tag{I}$$

$$PO_2 + PH \xrightarrow{\text{O}_2} POOH + PO_2 \tag{II}$$

$$PO_2 + PO_2 \longrightarrow \text{chain termination} \tag{III}$$

$$PO_2 + A \longrightarrow \text{chain termination} \tag{IV}$$

where S is the sensitizer, PH is the polymer, PO_2 is the peroxide radical and
POOH is the peroxide. Solving the kinetic equations taking account of A dif-
fusion we obtain three characteristic regions corresponding to different
photoreaction modes.
The first region corresponds to the local reaction mode with $T_{ind} \ll (\tau_D)_1$,
where T_{ind} is the duration of the induction period, $(\tau_D)_1$ is the characteris-
tic time of diffusion to distance 1. This condition signifies that the dif-
fusion A during the period T_{ind} is too small and in each film layer the
antioxidant is used only in reaction with the radicals generated in the
layer. In the local mode

$$T_{ind} = a [A]_0 / I \tag{1}$$

where a is the constant, $[A]_0$ is the initial antioxidant concentration and I
is the light intensity. The second characteristic mode is that of fast diffu-
sion with $T_{ind} \ll (\tau_D)_L$, where $(\tau_D)_L$ is the time of diffusion to distance L.
Under this condition the diffusion of A proceeds at such a fast rate that the
antioxidant concentration is practically uniform throughout the sample thick-
ness. In this mode

$$T_{ind} = a [A]_0 (L/l)/I \tag{2}$$

and T_{ind} is (L/1) times greater than the corresponding T_{ind} in the local
mode. This is the greatest synergism effect.
In the local and fast diffusion modes the T_{ind} values are independent of
τ_D. In the intermediate - diffusion-controlled mode $(\tau_D)_1 < T_{ind} < (\tau_D)_L$.

In this case an exchange of antioxidant between adjacent layers takes place, affecting the oxidation rate. In the diffusion-controlled mode

$$T_{ind} = \pi D_A \left\{ 2.3f(\ [A]_o/l)\ \right\}^2 /4W_i^2 \qquad (3)$$

where D_A is the antioxidant diffusion coefficient, f is the inhibition coefficient and $W_i \sim I$ is the initiation rate.

2.1.2. Synergism of UV-absorbers and peroxide decomposers

The kinetic scheme of oxidation of a polymer containing a peroxide decomposing agent can be obtained by substituting eqn. (IV) by eqn. (V)

$$POOH + A \longrightarrow \text{stable products} \qquad (V)$$
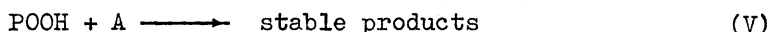
Solution of the kinetic equations taking account of the diffusion A permits to single out the same three characteristic modes determined by the ratio of T_{ind} and τ_D /3/. With peroxide decomposers in the local mode

$$T_{ind} \sim [A]_o / I^{1/2} \qquad (4)$$

in the diffusion-controlled mode

$$T_{ind} = \frac{2\pi D_A k_3}{W_i} \quad (\frac{\varepsilon [UVA][A]_o f}{2 k_2 [PH]})^2 \qquad (5)$$

i.e. $T_{ind} \sim 1/I$. In the fast diffusion mode

$$T_{ind} \sim [A]_o(\ L/l)/\ I^{1/2} \qquad (6)$$

From eqns. (4) and (6) it is seen that T_{ind} in the fast diffusion mode is L/l greater than that of the local mode. It means that the diffusion mechanism of synergism can be applied to describe the synergism of UVA and peroxide decomposers.

2.1.3. Dependence of synergism effect on the irradiation conditions

It follows from the diffusion mechanism that intermittent irradiation enhances the synergistic effect compared to continuous exposure, thus dark periods should contribute to the light stability since during that time the antioxidant's amount will be replenished due to diffusion.
A strict solution of the problem has revealed /7/ that under conditions of intermittent irradiation a pronounced increase in T_{ind} can be observed only with strongly absorbing samples. At the same time duration of the light periods (t_l) should be considerably lower than that of the dark periods (t_d).
Therefore in natural service conditions night breaks in irradiation do not strongly affect T_{ind} of the polymers, stabilized by mixtures of UVA and A.
The most pronounced effects can be expected in stabilization of photochromic and other systems irradiated periodically.

2.1.4. Results and discussion

To verify the diffusion mechanism quantitatively we have chosen a specific relationship between T_{ind} and I, predicted by the theory for the sensitized reaction. It follows from eqns. (1) and (2) that transition from the local to diffusion-controlled mode, which occurs at decreasing light intensity, should change relationship $T_{ind} \sim I^{-1}$ to $T_{ind} \sim I^{-2}$. With radical scavengers relationship $T_{ind} \sim I^{-1/2}$ is to be changed to $T_{ind} \sim I^{-1}$ (eqns.(4) and (5)). These dependences are confirmed by experimental results (Fig.2). In addition, the diffusion mechanism can be verified by determining D_A through eqns. (3) and (5), experimental results presented in Fig. 2, kinetic parameter $k_2/(2k_3)^{1/2}$ (literature data) and f/W_i values /4/. $D_A \simeq 5 \cdot 10^{-8}$ cm^2/s for Irganox 1010 in polybutadiene (PB) and for nickel dibutyldithiocarbamate in the block-copolymer of butadiene (70%) and styrene (30%), which corresponds to other known D_A values of antioxidants in polydienes. We also quantitatively verified the diffusion mechanism under intermittent illumination conditions (Fig.3). In our experiments T_{ind} under intermittent illumination increases by a factor of 2.3 which is in a good agreement with 2.5 value, predicted by theory.
Experimental results, obtained for the processes of photooxidation occurring as a branched chain reaction, are presented in Fig. 3 a,b for PB and Fig. 4 for PP /9/. They indicate that the predicted increase in the synergism
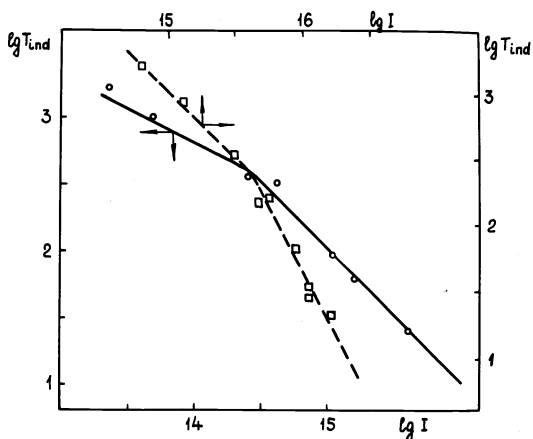
Fig. 2. Relationship between T_{ind} and intensity of the incident light with $\lambda = 365$ nm: a) photooxidation with benzyl as a sensitizer (0.13 mol/kg) of polybutadiene films (100 µm), containing Irganox 1010 (8.5×10^{-4} mol/kg) and Tinuvin P (4.4×10^{-2} mol/kg); b) photooxidation with benzyl as a sensitizer (0.1 mol/kg) of isoprene-styrene copolymer films (200 µm), containing nickel dibutyldithiocarbamate (0.002 mol/kg) and Tinuvin P (0.005 mol/kg).
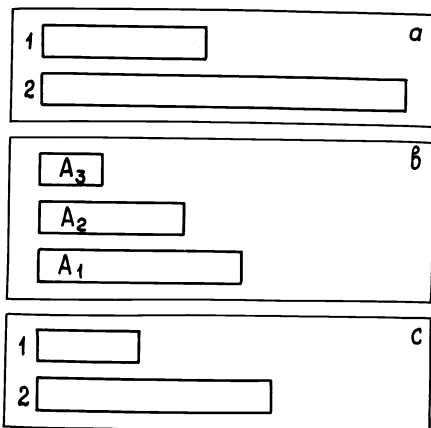

Fig. 3. a) Relationship between the light intensity I and $(T_{ind})_{A + UVA} / (T_{ind})_A$ ratio : I = 1 - (1), I = 0.25 - (2) in photooxidation of PB films (60 µm) under the light of Hg-lamp DRSh-1000. A_1 - Ionol, UVA_1 - 2-hydroxy-4-heptoxy-benzophenone. b) Dependence of the induction period T_{ind} of photooxidation on the A molecular weight for mixtures of UVA_1 with various phenols (A_1), 2246 (A_2), Irganox 1010 (A_3). c) Influence of the breaks in irradiation at $t_1 : t_d = 1 : 60$ on T_{ind} in photooxidation of isoprene-styrene copolymer films (165 µm), sensitized by benzyl (0.13 mol/kg) and containing A_3 (2×10^{-3} mol/kg) and Tinuvin P (2×10^{-3} mol/kg). Continuous irradiation (1), intermittent (2), light with $\lambda = 365$ nm.

effect upon increasing L, D_A and decreasing I does take place. Thus we have quantitatively substantiated the diffusion mechanism in photooxidation occurring as an unbranched chain   reaction and demonstrated its qualitative va-

lidity in case of photooxidation through branched chain mechanism.
From the standpoint of the diffusion mechanism one can deduce the principle
for proper selection of synergetic mixtures to match the specific polymer
and service conditions. It also throws light on the requirements which
must be imposed on the sample thickness and light intensity under which ac-
celerated tests of light stability of the polymers stabilized with synerge-
tic mixtures should be carried out. The diffusion mechanism is valid only
within the range limited by condition $T_{ind} \geqslant \tau_D$. This range, however, can
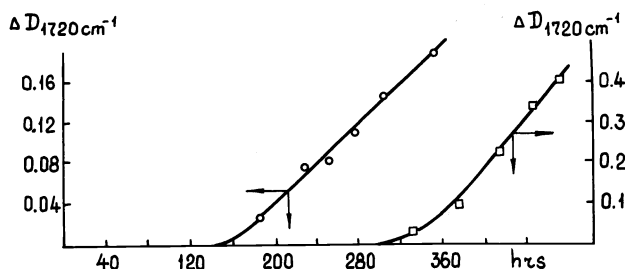be extended by increasing temperature or using plasticizers.

Fig. 4. Kinetic curves of carbonyl groups accumulation in
photooxidation of PP films with L=25 μm (I) and L = 100 μm
(2). The films contain 0.5% of sterically-hindered piperi-
dine and 0.4% of Tinuvin 326

For the first time an attempt was made to apply the diffusion mechanism in
order to increase photostability of some block-copolymers. Thus, for in-
stance, in block-copolymers of styrene and butadiene photoreaction mainly
occurs in PB. At the same time the antioxidant's light stability in PS is
higher than in PB. It is experimentally shown that in such copolymers an
increase in PS concentration enhances the light protective function of more
mobile antioxidants. This can be explained by diffusion of these antioxi-
dants in PB, where the reaction takes place.
In this context one can understand the observed drop in the efficiency of
less mobile antioxidants, which are better soluble in PS than in PB when we
increase the PS concentration. It can be assumed that the diffusion mecha-
nism is also applicable to increase the photostability of some homopoly-
mers, provided their oxidation is non-uniform.

2.2. Quenching mechanism
We started our work of investigating synergism with an attempt to explain
it in terms of the quenching mechanism. The experiments were performed on
thin, weakly absorbing films in order to eliminate the effects, connected
with light absorption. Under such conditions, however, there was no syner-
gism, although the experiments were conducted on synergistic mixtures known
from the literature. Therefore we made a conclusion that no synergism via
the quenching mechanism can be observed with traditional stabilizers at
commonly used concentrations. It became apparent that specific conditions
must be provided to obtain this effect, namely use very high concentrations
of quenchers (UVA) or select mixtures of stabilizers with great overlap of
A luminescence and UVA absorption spectra (in order to increase the dis-
tance of energy transfer to 3.5-4 nm), or search for systems with a non-
uniform distribution of additives, where distance of A to UVA would be lo-
wer than the average ones, corresponding to average concentrations. Fig. 5
shows the effect of synergism, obtained through a very high concentration
of the quencher. In this case the intensity of A luminescence and the rate
of its consumption decrease by a factor of 10. The obtained effect is due
entirely to the quenching mechanism. The diffusion mechanism in these condi-
tions does not work, since the quencher weakly absorbs light with $\lambda >360$ nm,
while A in the absence of a quencher acts as a sensitizer.
We selected a mixture (see Fig.5) with $R_0 = 1.9$ nm and corresponding criti-
cal UVA concentration $C_0 = 0.06$ mol/kg. With PP, where additives are irre-
gularly distributed in the amorphous phase /10/, the same mixture has the
following parameters $C_0 = 0.02$ mol/kg (after correction is made for the de-
gree of crystallinity) for $[A] = 6 \times 10^{-3}$ mol/kg and $C_0 = 0.002$ mol/kg for
$[A] = (1 - 2) \times 10^{-4}$ mol/kg. This effect is unusual and appears to be related

to a pattern of distribution. In case of a uniform distribution the quenching effect is independent of the energy donor concentration. Unfortunately, the efficiency of a quencher is the greatest at very low [A] , while at commonly used concentrations of A the effect is considerably lower. It limits the scope of application of synergistic mixtures working through the quenching mechanism for polymer photostabilization.
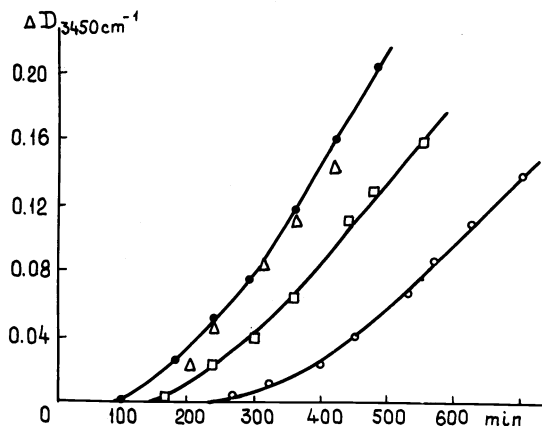

Fig. 5. Photooxidation kinetic curves for polyisoprene films (20 μm) containing 0.005 mol/kg of Neozon D (●), 0.19 mol/kg UV -531 (▲) and their mixture in the same concentrations (○), polyisoprene without additives (□), λ = 360 nm.

It is interesting to note that with PP despite stronger quenching we failed to obtain a synergistic effect in the mixtures on the basis of Neozon D, since this A is consumed within $t_c \ll T_{ind}$ time interval and therefore does not affect the T_{ind} value. It follows, that in order to obtain a synergistic effect via the quenching mechanism t_c must be comparable with T_{ind}. Taking this into account we selected as antioxidants phenols with considerably lower photochemical activity as compared to aromatic amines and mixture Irganox 1076 (1.2×10^{-2} mol/kg) - Tinuvin P and succeeded in obtaining a synergistic effect due to the quenching mechanism in PP. Thus a general conclusion to be made is that quenching mechanism is of a secondary importance, although it might well be that in some polymers where additives are distributed even more irregularly than in PP, specific mixtures of A-UVA will yield a tangible result.

3. RELATIONSHIP BETWEEN THE INDUCTION PERIOD OF PHOTOOXIDATION ON CONCENTRATION OF ANTIOXIDANT

Sometimes antioxidants act as photostabilizers even in the absence of UV-absorbers. In this connection the relationship between T_{ind} and [A] assumes great importance since it can be used for proper selection of the optimum A concentration. At the same time from the pattern of the relationship between T_{ind} and [A] one can draw conclusions concerning the mechanism of the A protective action, which is very important for identifying the means to increase the antioxidant's efficiency. Theoretical fundamentals of the relationship between T_{ind} and [A] in the processes of polymer photooxidation are not available in the literature. We made an attempt to obtain such a relationship on the basis of classifying antioxidants according to their photochemical and absorption activities.

3.1. Antioxidant is stable to the action of light and is weakly absorbing

The analysis has shown that the main difference in the action of antioxidants in branched chain processes of thermo- and photooxidation lies in the fact that with photooxidation reactions an increase in A concentration does not lead to critical phenomena. It is related to the fact that unlike thermooxidation processes the value of W_0 - rate of free radicals formation—for all of the reactions, except photodecomposition of peroxides, in photooxidation processes is considerably higher. Consequently, the crite-

rion of the critical phenomenon $(k_4/W_o) \geqslant 10^7$ l/mol /10/ is not reached. Therefore, in weakly absorbing antioxidants with low photochemical activity there should be no critical phenomenon and the following dependence $T_{ind} \sim [A]_o$ might be expected. Fig. 6 is an example of such an experimental relationship. No critical phenomenon is observed, although antioxidant critical concentration $[A]_{cr} \leqslant 0.01$ mol/kg can be determined through the known kinetic parameters /10/.

3.2. Antioxidant is stable to the action of light and is strongly absorbing

In the case due to the reasons mentioned above we also observe no critical phenomenon. Since the antioxidant is a strongly absorbing one the distribution of light intensity across the sample is similar to that obtained with a UVA. Consequently, the presence of such an A will lead to the diffusion synergism. It follows from (2) that in the fast diffusion mode $T_{ind} \sim [A]_o^2$, since $1 = 1/\varepsilon_{UVA}[\,UVA\,]$, while in this case A and UVA is one and the same compound. Fig. 6 shows the corresponding relationship. We selected a photostable azo dye with sufficiently strong antioxidative function as an A. The experiments have confirmed the theoretical dependence.
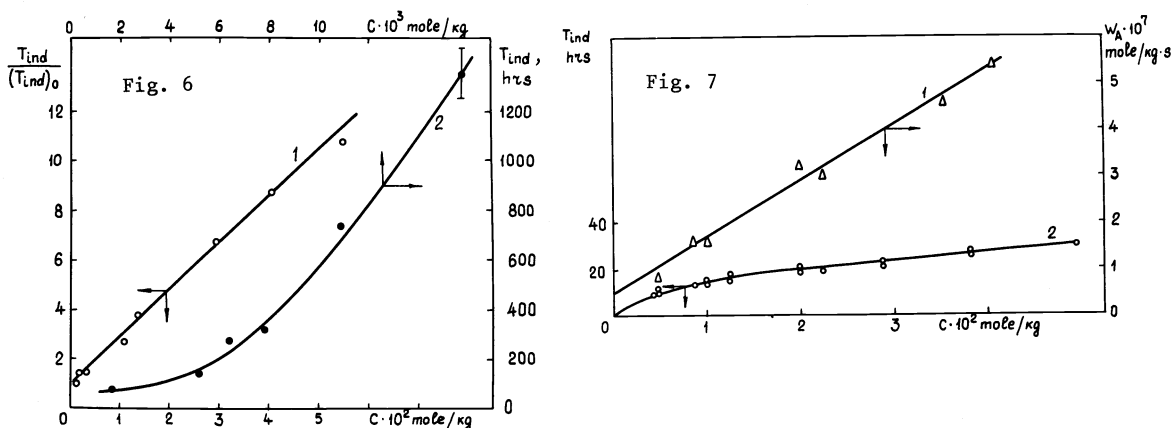

Fig. 6. Dependence of the relative value T_{ind} of butadiene-styrene rubber film (170 μm) on 2,2,6,6-tetramethyl-4-benzoylhydroxypiperidine-1-oxyl (I); dependence of T_{ind} of isoprene-styrene film photooxidation (350 μm) on 3-methyl-4-oxyphenylazobenzene concentration (2); λ >300 nm.

Fig. 7. Dependence of the initial consumption rate of Ionol (1), T_{ind} of isoprene-styrene rubber film photooxidation (170 μm) (2) on Ionol concentration. λ > 300 nm.

3.3. Antioxidant is photochemically active and weakly absorbing

In this case the kinetic scheme of inhibited oxidation (reactions I-IV) should be supplemented by reaction

$$A + h\nu \xrightarrow{\text{PH, } O_2} PO_2 \qquad (V)$$
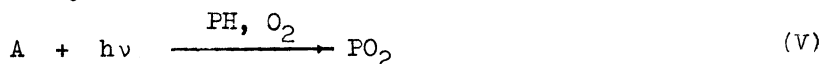
which is a major reaction of radical formation during the induction period. The distinguishing feature of such an A is that fast consumption of A is observed from the very start of the reaction. At large antioxidant concentrations T_{ind} becomes independent of $[A]$, since further increase in $[A]$ enhances W_i and antioxidative function simultaneously. These features are presented in Fig. 7. Our interpretation of the process is confirmed by the fact that from curves (1) and (2) we succeeded to obtain similar values of the rate constants for reaction V:

$$7 \times 10^{-5} \text{ s}^{-1} \text{ from (1) and } 5 \times 10^{-5} \text{ s}^{-1} \text{ from (2)}$$

Experimental relationships T_{ind} - [A] similar to those, presented in Figs. 6, 7 were repeatedly obtained by many scientists and they may be considered as typical ones for photooxidation processes. It follows from these specula- tions that the main experimental relationships can be explained on the basis of antioxidant's absorption and photochemical activity.

4. SYNERGISTIC ACTION OF ADDITIVES, WHICH INCREASE THE SOLUBILITY OF THE STABILIZER AND CHANGE THE PATTERN OF ITS DISTRIBUTION IN THE POLYMER

In a general case the induction period of photooxidation depends on A con- centration. Therefore, a change in A concentration as well as A solvatation by other additives may influence the efficiency of the A protective func- tion. Let us consider as an example the relationship of T_{ind} in the process of polyisoprene photooxidation (Fig. 8) on the composition of a mixture of stabilizers - zinc and bismuth diethyldithiocarbamates /6/. These stabili- zers mutually increase the solubility of each other. The synergism effect
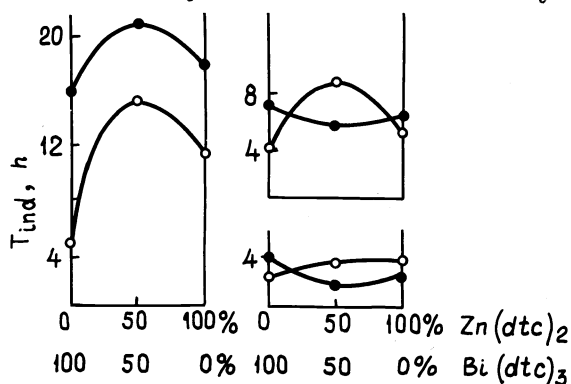

Fig. 8. Dependence of T_{ind} of isoprene- styrene rubber films photooxidation on $Zn(dtc)_2$-$Bi(dtc)_3$ mixture concentration at total concentration of stabilizers 2% (a), 0.5% (b), and 0.2% (c), 1 - in the absence, 2 - in the presence of 3% surface - active compound.

is observed as one passes from total concentration 0.2% to 0.5% concentra- tion. As the concentration increases to 2% (open circles) the effect is enhanced. The influence of the 3% additive of a surface-active compound - oxyethylated cetyl alcohol $C_{16}H_{33}O(CH_2CH_2O)_{40}H$ is shown by full circles. This compound acts as an antagonist at $Bi(dtc)_3:Zn(dtc)_2$ ratio 1:1 at a low concentration and as a synergist at a high concentration, while the surface-active compound alone practically does not affect the induction pe- riod. It can be concluded that introduction of stabilizers into micelles reduces their stabilizing action and that the observed synergism in the range of high stabilizer concentrations is related to the considerable in- crease in their solubility.

The synergistic mechanism considered may bring about considerable effects at commonly used concentrations of stabilizers. Perhaps, the greatest ef- fect can be achieved with difficultly soluble stabilizers, for instance, with polar stabilizers in non-polar polymers.

REFERENCES

1. V.B. Ivanov, N.A.Rozenboym, L.G. Angert and V.Ya. Shlyapintokh, Dokl. AN SSSR, 242, 449–452 (1978).
2. V.B. Ivanov, S.F. Bulatsky, N.A. Rozenboym and V.Ya. Shlyapintokh, Eur. Polym.J., 16, 65–72 (1980).
3. V.B. Ivanov, E.L.Lozovskaya and V.Ya. Shlyapintokh, Polym.Photochem., 2, 55–63 (1982).
4. V.B. Ivanov, N.A. Rozenboym and L.G. Angert, Vysokomol.Soed. B, 24, 234–236 (1982).
5. V.Ya. Shlyapintokh, Photochemical Conversions and Stabilization of Po- lymers (in Russian), Khimiya Press, Moscow (1979).
6. A.F.Efremkin and V.B. Ivanov, Vysokomol.Soed. B, 24, 622–625 (1982).
7. E.L.Lozovskaya and V.Ya. Shlyapintokh, Polym. Photochem. (in press).
8. V.B. Ivanov, S.G.Burkova, Yu.L.Morozov and V.Ya.Shlyapintokh, Kinet. i Kataliz, 20, 1330–1333 (1979).
9. A.A. Efimov, V.B. Ivanov, G.V. Kutimova, E.L. Lozovskaya and V.Ya. Shlyapintokh, Polym.Photochem. (in press).
10. N.M. Emanuel, and A.B.Gagarina, Uspekhi Khimii, 35, 618–655 (1966).