Oxyluminescence – A Technique for the Study of Thermo-oxidative Destruction of Polyisoprene

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Thermo-oxidative destruction of natural rubber protected by different amino-antioxidants under normal conditions and after gamma irradiation is described. For this study the oxyluminescence technique was applied, and from experimental kinetic parameters a mechanism of oxyluminescence appearance is proposed.

Elastomers and their vulcanisates modify their initial properties under the influence of atmospheric factors with a destructive action which results in ageing with time. The modifications occurring in the destructive processes are mainly generated by simultaneous scission and crosslinking reactions which result in ageing. The isoprenic structures of elastomers, natural and synthetic, have been studied by means of various physico-chemical and physico-mechanical techniques[1]. The results obtained were used for the fundamental mecchanism involved in the destructive process. Nevertheless, the simulation of the whole assembly of the stress factors that occurred during storage and processing was not often successful. For this reason testing methods under accelerated ageing conditions that reveal the influence exerted Gby a certain aggressive factor were applied.

The techniques currently used for analysis of the thermo-oxidative destructive behaviour of elastomer included IR spectroscopy coupled with chromatographic analysis[2,3], differential thermal analysis[4,5], oxygen absorption measurement[6-8], EPR and NMR spectroscopy[1,9], and mechanical tests[10].

Oxyluminescence (OL), as a technique used for the investigation of the destructive process has been preponderantly applied to the study of polypropylene and other polyolefins[11-14] and only in a few cases to elastomer characterisation[15-17].

The present study deals with the application of OL technique to analyse thermo-oxidative destruction of natural rubber protected by means of amino-antioxidants, under normal conditions, and after gamma irradiation.

EXPERIMENTAL

In order to measure the OL signals, the OC-91 oxyluminograph designed and manufactured by ICPE, Bucharest, have been used. The apparatus runs in isothermal conditions, the OL emission detection being performed by means of a photomultiplying tube (Philips, XP-2008) with a sensitivity of 60 A/1m. Jipa *et al.*[18] in their paper have discussed the detailed presentation of this apparatus.

The resultant kinetic parameters from the processing of the oxyluminograms were of a typically sigmoid shape, and they were: the

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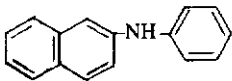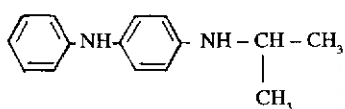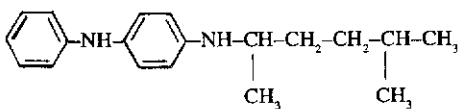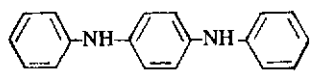***University of Bucharest, Faculty of Chemistry, Romania

induction period (t_i), the maximum oxidation rate (V_{ox}^{max}), the OL emission maximum intensity (I_{max}) and the time for reaching the OL emission maximum value (t_{max}).

The film samples (~40 mg) of natural rubber protected by the aromatic amine and diamine antioxidants *(Table 1)* were obtained and tested directly in the measuring-tray of the apparatus (area: 2.9 sq cm). In order to avoid mechano-chemical reactions, the incorporation of anti-oxidant at a concentration of 2% was performed on the rubber roll at a relatively low temperature (40°C). The films were obtained through the evaporation from the chloroform solution (2% concentration).

In order to shorten the experimental period the measurements were taken at temperatures ranging between 150°C–200°C. By using linear regression method, OL data were extrapolated to the temperature range of 40°C–100°C used for both the storage and some processing activities (lamination, milling and calendering) to which the natural rubber compositions are subjected.

TABLE 1. ANTIOXIDANTS USED FOR NATURAL RUBBER PROTECTION

Antioxidant structure	Chemical and commercial denomination	Molecular weight (g/mol)	Melting point (°C)	Symbol
	N-phenyl-2-naphtylamine PBN	219	105	A_1
$(H_3C - HC - H_2C - H_2C - HC - HN)_2 - C_6H_4$ with CH_3 substituents	N,N'-di-(1,4-dimethyl-penthyl) p-phenylene diamine *Santoflex-77*	304	–	A_2
	N-isopropyl, N'-phenyl-p-phenylenediamine *Santoflex-IP*	226	74	A_3
	N-(1,4-dimethyl-penthyl)-N'-phenyl-p-phenylene diamine *Santoflex-13*	282	46	A_4
	N,N'-diphenyl-p-phenylenediamine *Nonox-DPPD*	260	145	A_5

The effectiveness of the antioxidant protection was evaluated by means of the following parameters: relative activity (A_r) and relative stability (S_r), defined by the relations:

$$A_r = \frac{(t_i)_x - (t_i)_o}{(t_i)_s - (t_i)_o} \quad ;$$

$$S_r = \frac{(V_{ox}^{max})_x}{(V_{ox}^{max})_o} \qquad \ldots 1$$

where $(t_i)_x$ is the induction period of the protected elastomer

$(t_i)_s$ is the induction period of the standard protected elastomer

$(t_i)_o$ is the induction period of the unprotected elastomer

$(V_{ox}^{max})_x$ is the maximum oxidation rate of the protected elastomer

$V_{ox}^{max})_o$ is the maximum oxidation rate of the unprotected elastomer.

The sample irradiation was performed in the air at room temperature, by using a ^{60}Co gamma source with the activity of 500 Ci. The irradiation doses were determined by means of PVC foil dosimeters previously calibrated by means of the Fricke dosimeter[19].

RESULTS AND DISCUSSION

Effect of Film Thickness

Figure 1 shows the oxyluminograms of some natural rubber films with various thicknesses recorded at 170°C. The oxyluminogram processing led to the determination of the characteristic parameters presented in *Table 2*, emphasising the following:

● Increase of the elastomer film thickness generates an increase in the induction period and of the time for reaching the maximum value of OL emission.

● Decrease of OL maximum intensity with the increase of the tested film thickness.

The logarithmic variation of the above mentioned OL parameters as a function of the film thickness led to straight lines with correlation coefficients of 0.980 – 0.996. Extrapolating these results by means of linear regression, values of the induction periods for various thicknesses currently used in practice were obtained. One can thus exemplify the values: $t_i = 3.6 \times 10^3$ min for the thickness of 0.5 mm and $t_i = 1.5 \times 10^5$ min for the thickness of 1 mm, both for 170°C. The dependence of the kinetic parameters of the OL process on the elastomer film thickness suggests that the phenomenon is controlled by oxygen diffusion; the results obtained being in good agreement with the data from oxygen absorption[20].

Effect of Antioxidant Protection

Figure 2 shows the oxyluminograms of natural rubber at 190°C stabilised with antioxidants. The kinetic data from oxyluminogram processing are presented in *Table 3*. As shown in *Figure 2*, the presence of the antioxidant in the elastomer matrix generates a considerable increase in the induction period due to the blocking of the peroxy radicals involved in the OL emission. The antioxidant depletion in the sample is accompanied by a sharp increase in the emission as a result of the acceleration of reactions generating OL.

The analysis of these data leads to the conclusion that antioxidants A_4 and A_5 offer effective protection, evaluation is based on the induction period and from the time necessary for reaching the maximum intensity value of OL. For the same antioxidants one can notice the low values of parameter I_{max}; this is explained by the low content of oxygenated groups formed during thermal oxidative destruction.

On the other hand, the maximum oxidation rate gets accentuated values, except for the
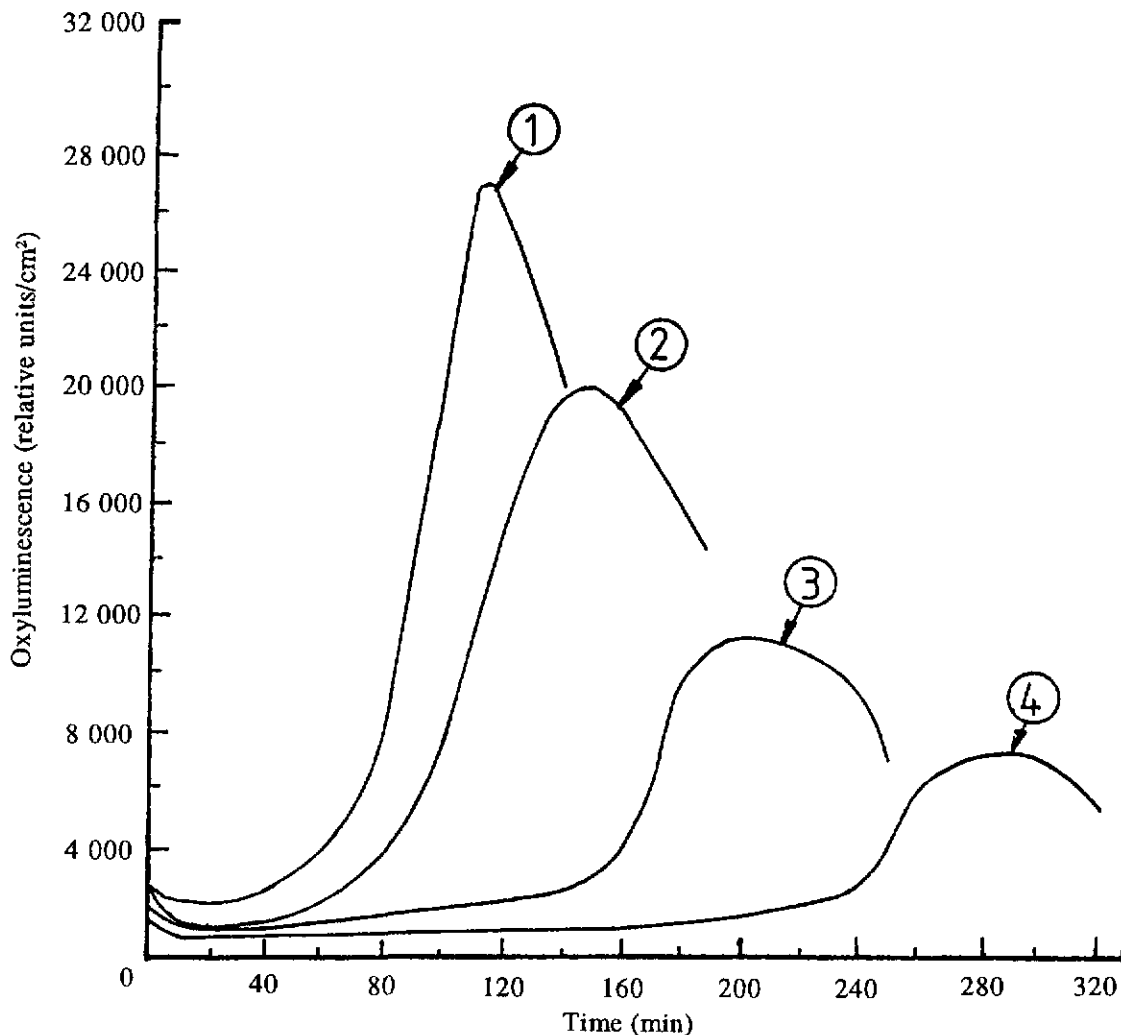
Figure 1. Sample thickness effect on natural rubber isothermal oxyluminescence emission (170°C).

elastomer protected by antioxidant A_5. This suggests the participation in the autocatalytic stage of either the amine/radicals of some other aromatic amine transformation products–compounds with extended conjugation and high molecular weights, having some pro-oxidant activity at this temperature[21].

The registration of typical OL parameters at several temperatures ranging between 150°C–200°C and the application of the Arrhenius treatment led to the activation energies shown in *Table 4*. The correlation coefficients varied within the limits 0.967 – 0.998.

TABLE 2. INFLUENCE OF NATURAL
RUBBER FILM THICKNESS ON THE
OXYLUMINESCENCE PARAMETERS

Sample	Thickness (μm)	t_i (min)	I_{max} (rel. units/g)	t_{max} (min)
1	9.8	92	26 861	114
2	23	111	20 118	147
3	86	173	11 450	201
4	142	250	7 075	269

The activation energy corresponding to the induction stage gives the following order of protection activity:

$$A_1 > A_3 > A_4 > A_5 > NR > A_2$$

The fact that the product A_2 cannot prove its protective effectiveness can be explained by the increased temperature range used for the testing, with consequences on volatilisation.

In the autocatalytic stage of the process, the order of effectiveness evaluated by parameter I_{max} is:

$$A_5 > A_4 > A_2 > A_1 > A_3 = NR$$

This order is in agreement with the data obtained by the oxygen absorption method[8,22].

The activation energies for this stage are 1.5 – 3.0 times lower than those calculated for the induction stage, and could be the result of the evolution of some radical species in the system[23].

The extrapolation of the induction periods to the temperature range of 24°C – 100°C led to the results presented in *Table 5*. The analysis of these data indicates certain changes in effective protection at these temperatures.

If the antioxidant A_3 is taken as a standard, with the activity equal to the unit, then, according to the relative activity *(Table 6)*, the order of effectiveness for the induction period is modified with the temperature with increasing activity of aromatic diamines A_4 and A_5 and a decreasing activity of secondary amine A_1. The diamine A_2 presents a remarkable increase in the activity over 40°C and, then, a gradual diminution at over 80°C; this is contributed by an increase in volatility.

In the autocatalytic stage, the relative diamine stability is superior to the aromatic amine; at this stage, the diamine A_4 *(Table 7)* shows special effectiveness.

The difference in behaviour of the antioxidants in the major destruction stages is

TABLE 3. INFLUENCE OF ANTIOXIDANT STRUCTURE ON OXYLUMINESCENCE

Protection	Temperature (°C)	t_i (min)	V_{ox}^{max} (%/min)	I_{max} (rel.units/g)	t_{max} (min)
NR	190	40	3.65	148	54
NR + A_1	190	24	13.03	171	32
NR + A_2	190	112	3.22	155	126
NR + A_3	187	30	6.89	257	38
NR + A_4	190	276	4.76	85	289
NR + A_5	190	201	2.39	94	220

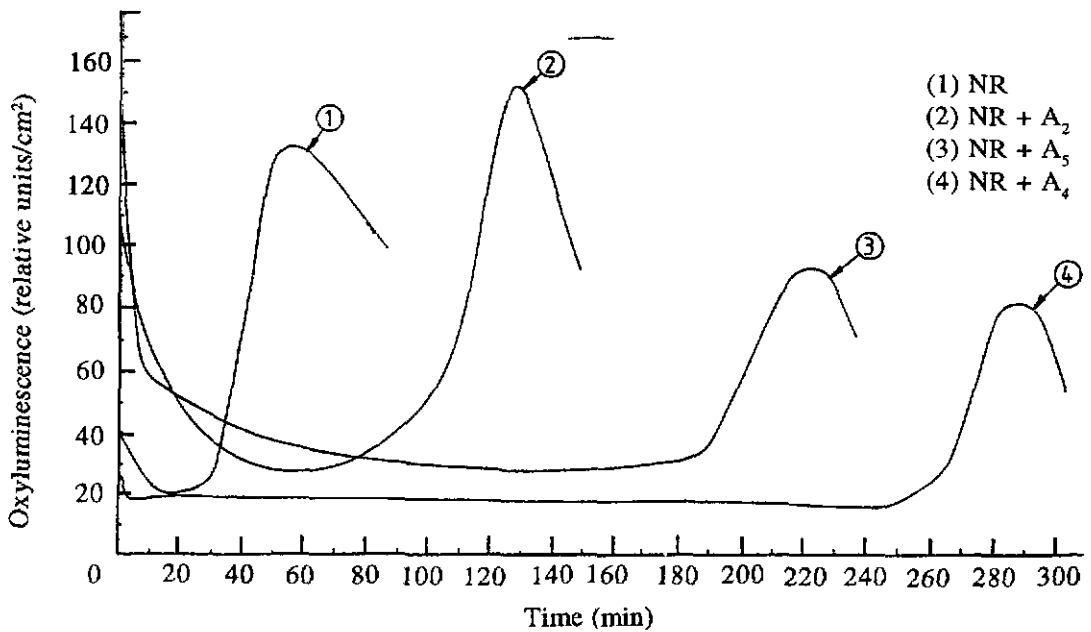*Figure 2. Antioxidant influence on natural rubber isothermal oxyluminescence emission (190°C).*
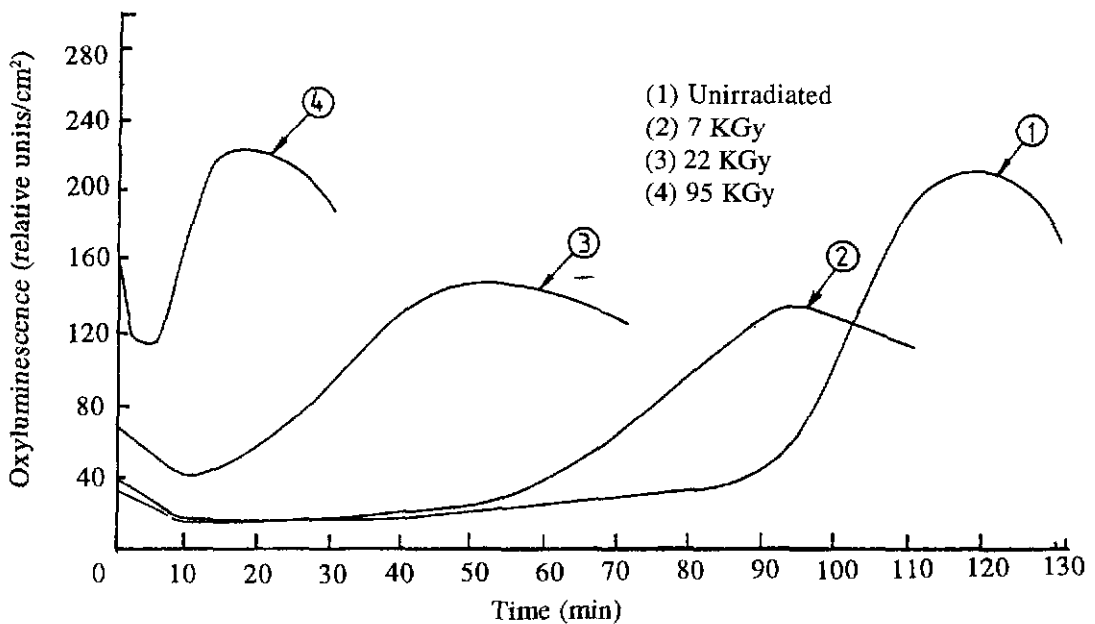

Figure 3. Gamma irradiation effect on natural rubber isothermal oxyluminescence emission (180°C).

TABLE 4. OXYLUMINESCENCE
ACTIVATION ENERGY CALCULATED FROM
DIFFERENT KINETIC PARAMETERS

Protection	Activation energy (kJ/mol)			
	t_i	V_{ox}^{max}	I_{max}	t_{max}
NR	121.4	100.0	39.9	107.9
NR + A$_1$	141.5	141.5	51.7	131.5
NR + A$_2$	119.3	69.3	53.8	117.6
NR + A$_3$	130.6	68.0	40.0	113.0
NR + A$_4$	127.3	58.8	55.4	115.9
NR + A$_5$	121.0	57.5	71.4	115.5

obviously dependent on the physical state of the aggregation, the molecular weight and the vapour pressure at various temperatures[24].

Effect of Gamma Radiation

Figure 3 presents the oxyluminograms of natural rubber at 180°C irradiated at various doses of gamma radiations. The oxylumino-gram analysis *(Table 8)* indicated the following:

- increase in irradiation dose caused an increase in the initial OL signal (I_o) and a decrease in parameters t_i and t_{max}

- maximum oxidation rate and maximum intensity of OL emission have the highest values at the lowest doses, after which they be come stationary.

Radio-induced changes of OL parameters were also observed in the case of natural rubber protected by diaryl-*p*-phenylenediamine (A$_5$) with the indication that the irradiation effect was largely diminished by the presence of antioxidant *(Table 9).*

For the unstabilised sample, the dependence (correlation coefficient: 0.979) of the OL parameters t_i and t_{max} on the irradiation dose can be expressed in the following form:

$$\frac{1}{P} = \frac{K \cdot D^{0.3} + 1}{P_o} \qquad \dots 2$$

where P is the OL parameter at the dose D
 P_o is the OL parameter at the dose $D = 0$
 K is proportionality constant.

The parameter I_o varies with the irradiation dose (correlation coefficient: 0.957) according to the relation:

$$I_o = K \cdot D^{0.7} + I_o \qquad \dots 3$$

where I_o is the parameter at the dose $D = 0$.

TABLE 5. INDUCTION PERIOD (MIN) OF STABILISED NATURAL RUBBER (24°C-100°C)

Protection	Temperature (°C)				
	24	40	60	80	100
NR	3.3×10^9	2.5×10^8	1.5×10^7	1.2×10^6	1.3×10^5
NR + A$_1$	2.0×10^{10}	1.1×10^9	4.1×10^8	2.3×10^6	1.7×10^5
NR + A$_2$	3.9×10^9	3.3×10^8	2.1×10^7	1.9×10^7	2.1×10^5
NR + A$_3$	5.8×10^9	3.9×10^8	1.9×10^7	1.4×10^6	1.4×10^5
NR + A$_4$	2.9×10^{10}	2.1×10^9	1.1×10^8	8.5×10^6	8.4×10^5
NR + A$_5$	9.5×10^9	7.8×10^8	4.8×10^7	4.1×10^6	4.5×10^5

TABLE 6. ANTIOXIDANT RELATIVE
ACTIVITY AT DIFFERENT TEMPERATURES

Protection	Temperature (°C)		
	40	80	100
NR + A_1	6.1	5.5	4.0
NR + A_2	0.6	8.5	8.0
NR + A_3	1.0	1.0	1.0
NR + A_4	13.2	36.5	71.0
NR + A_5	3.8	14.5	32.0

TABLE 7. ANTIOXIDANT RELATIVE
STABILITY AT DIFFERENT TEMPERATURES

Protection	Temperature (°C)		
	40	80	100
NR + A_1	0.3	0.8	1.1
NR + A_2	57	15	9.0
NR + A_3	104	26	14.0
NR + A_4	59 407	1 600	353.0
NR + A_5	122	19	9.0

TABLE 8. INFLUENCE OF GAMMA IRRADIATION ON OXYLUMINESCENCE
PARAMETERS OF NR SAMPLE

Irradiation dose (KGy)	t_i (min)	V_{ox}^{max} (%/min)	l_{max} (rel. units/cm²)	t_{max} (min)	l_o (rel. units/cm²)
0	101.0	4.4	214	118	30
2	75.0	2.5	157	90	39
7	72.0	2.4	135	94	43
22	30.5	2.6	151	50	73
51	32.0	1.9	156	48	92
95	9.8	-	155	18	197
154	8.4	-	155	14	187

The last equation confirms the largest part of the·energy used for irradiation is spent in the formation of peroxy radicals responsible for the appearance of initial OL signal; the rest of the energy leads to the formation of other radical species which, in the thermal oxidation process, influence the evolution of hydroperoxides involved in the further emission of OL.

The antioxidant A_5 has an anti-radiation effect, limiting the radio-induced destruction effect for a while.

For all the samples tested, in the first minute of the isothermal measurement of OL signal, one can observe a decrease of parameter I_o, this demonstrates the pre-existence of some radical species formed in the very stages of synthesis, processing and storage. The analysis

TABLE 9. INFLUENCE OF GAMMA IRRADIA-
TION ON OXYLUMINESCENCE
PARAMETERS OF NR + A_5 SAMPLE

Irradiation dose (KGy)	t_i (min.)	t_{max} (min.)	l_o (rel. units/cm²)
0	178	135	25
7	115	105	27
51	72	100	29
95	50	95	25
154	45	70	23
30	43	68	30

of variation $I_o = f(t)$ has led to the conclusion that the process which takes place is a radiative bimolecular recombination of peroxy radicals; the reaction developing with an activation energy of 5 kJ/mol.
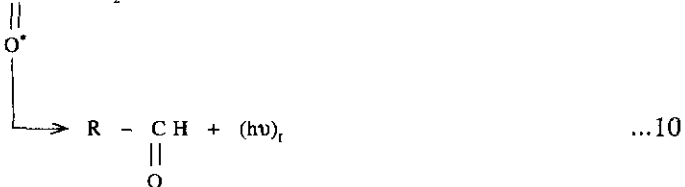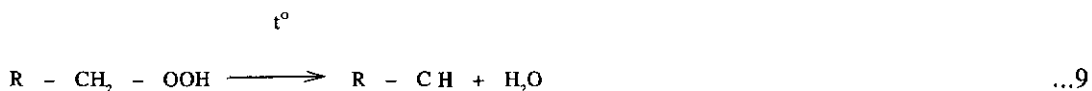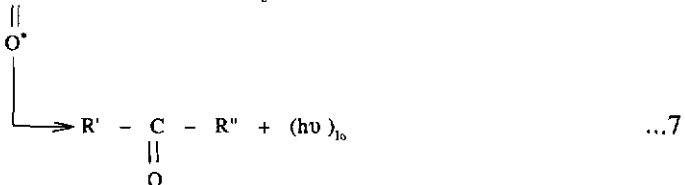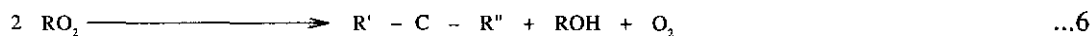
The results of the study lead to the following possible mechanisms consisting of OL signal in the thermal-destruction and radio-thermal-destruction processes *(Scheme 1, Equations 4 to 10)*.

The initial OL signal of intensity I_o results from the recombination of radio-induced peroxy radicals at the ambient temperature *(Equations 4-7)*. The emission is due to the phosphorescence of the ketone triplet state resulting from the recombination reaction

(Equation 7). Consequently, the initial OL intensity will be proportional to the peroxy radical concentration. The appearance of the intense OL signal after induction period can be the result of the thermal decomposition of hydroperoxides generated during the experiment *(Equations 8 – 10)*.

In the presence of antioxidant A_5, the following reactions can take place *(Scheme 2, Equations 11 and 12)*.

This mechanism requires the formation of diamine-peroxy radical complex in the first stage followed by its stabilisation through the transfer of a proton and/or through the reaction with another peroxy radical. The forming of quinone-diamines in the thermal oxidation

$$RH \quad \xrightarrow{\text{t}° \text{ or } \gamma} \quad R \qquad \qquad \dots 4$$

$$R + O_2 \quad \longrightarrow \quad RO_2 \qquad \qquad \dots 5$$

$$2\ RO_2 \quad \longrightarrow \quad R' - \underset{\underset{O^\bullet}{\|}}{C} - R'' + ROH + O_2 \qquad \dots 6$$

$$\longrightarrow R' - \underset{\underset{O}{\|}}{C} - R'' + (h\upsilon)_{I_o} \qquad \dots 7$$

$$RO_2 + RH \quad \longrightarrow \quad ROOH + \overset{\bullet}{R} \qquad \dots 8$$

$$R - CH_2 - OOH \quad \xrightarrow{\text{t}°} \quad R - \underset{\underset{O^\bullet}{\|}}{C}H + H_2O \qquad \dots 9$$

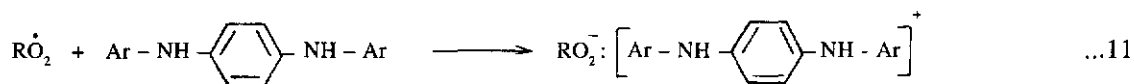$$\longrightarrow R - \underset{\underset{O}{\|}}{C}H + (h\upsilon)_I \qquad \dots 10$$

Scheme 1

processes was confirmed by various techniques[25,26], the diamine having the capacity of deactivating two peroxy radicals. Besides this, quinone-diamine can react with a segment of the elastomer chain restoring the initial diamine and developing a grafted amine area (rubber-bound antidegradant[27]) that explains the expansion of A_5 antioxidant activity[28] as shown in *Scheme 3, Equation 13*.

The protective effect of antioxidant A_5 appears both in the case of sample, thermally stressed and on its irradiation with ionising radiations (anti-radiation effect).
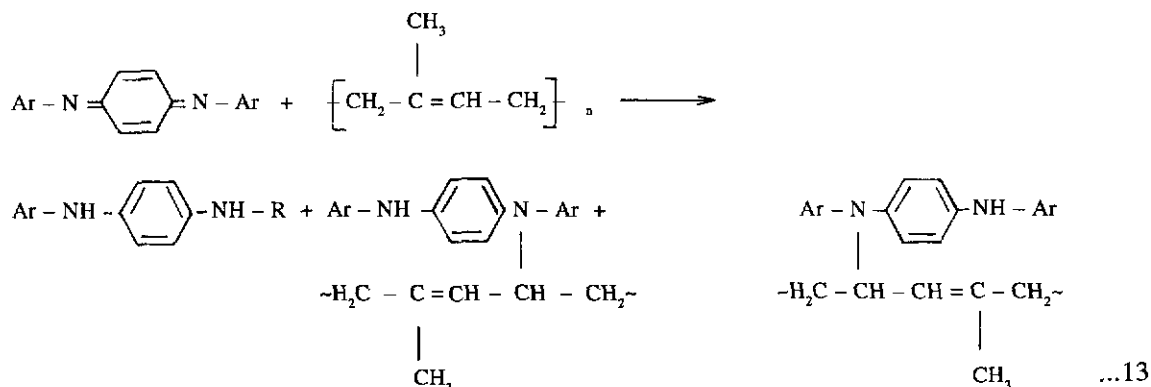
CONCLUSION

Studying the destructive thermal- and radio-induced processes occurring in natural rubber by the OL technique, the following conclusions can be drawn:

- Film thickness influences the kinetic parameters; this phenomenon is controlled by oxygen diffusion.

- Antioxidants can be quantitatively evaluated by their protection effectiveness against degradation and by increase of the material resistance to the above mentioned stress factors.

$$R\overset{\bullet}{O}_2 + Ar-NH \overset{}{\underset{}{\bigcirc}} NH-Ar \longrightarrow RO_2^- : \left[Ar-NH \overset{}{\underset{}{\bigcirc}} NH-Ar \right]^+ \qquad ...11$$

$$RO_2^- : \left[Ar-NH \overset{}{\underset{}{\bigcirc}} NH-Ar \right]^+ + R\overset{\bullet}{O}_2 \longrightarrow Ar N = \overset{}{\underset{}{\bigcirc}} = NAr + 2ROOH \qquad ...12$$

Scheme 2

$$Ar-N= \overset{}{\underset{}{\bigcirc}} =N-Ar + \left[CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2 \right]_n \longrightarrow$$

$$Ar-NH \overset{}{\underset{}{\bigcirc}} -NH-R + Ar-NH \overset{}{\underset{}{\bigcirc}} \underset{\underset{\displaystyle CH_3}{|}}{\overset{|}{N}}-Ar + \qquad\qquad Ar-N \overset{}{\underset{}{\bigcirc}} -NH-Ar$$

$$\sim H_2C-\underset{}{C}=CH-CH-CH_2\sim \qquad\qquad -H_2C-CH-CH=C-CH_2\sim$$

$$CH_3 \qquad\qquad\qquad CH_3 \qquad ...13$$

Scheme 3

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- Previous irradiation of elastomers leads to some changes in the kinetic parameters and this depends on absorbed dose.

- Diaryl-*p*-phenylenediamine used in this study reveals the effect of antioxidant and antirad.

- The above mechanism of the OL appearance is proposed and sustained on the base of the experimental kinetic parameters.

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REFERENCES

1. RABEK, J.F. (1980) *Experimental Methods in Polymer Chemistry.* New York: Wiley.

2. BEVILACQUA, E.M., ENGLISH, E.S., GALL, J.S. AND NORLING, J. (1964) *J. Appl. Polym. Sci.,* **8,** 1029.

3. MORAND, J.L. (1974) *Rubb. Chem. Technol.,* **47,** 1094.

4. REICH, L. AND STIVALA, S. (1971) *Elements of Polymer Degradation.* New York: McGraw-Hill.

5. BUDRUGEAC, P. (1992) *Polym. Degrad. Stab.,* **38,** 165.

6. REICHENBACH, D. AND SCHEELE, W. (1970) *Kaut. Gummi Kunst.,* **23,** 141.

7. VOIGHT, H.U. AND SCHEELE, W. (1970) *Kaut. Gummi Kunst.,* **23,** 359.

8. GIURGINCA, M., TUDOR, E. AND IVAN, G. (1982) *Industria Usoara, Bucharest,* **29,** 67.

9. RANBY, B. AND RABEK, J.F. (1977) *ESR Spectroscopy in Polymer Research.* Berlin: Springer Verlag.

10. CLOUGH, R.L. AND GILLEN, K.T. (1990) *Polym. Degrad. Stab.,* **30,** 309.

11. GEORGE, G.A., EGGLESTONE, G.T. AND RIDDELL, S.Z. (1983) *Polym. Eng. Sci.,* **23,** 412.

12. BILLIN GHAM, N.C., O'KOEFE, E.S. AND THEN, E.T. (1988) *Polym. Mater. Sci. Eng.,* **58,** 431.

13. AUDOMIN-JIRACKOVA, L. AND VERDU, J. (1987) *J. Polym. Sci. Polym. Chem.,* **A25,** 1205.

14. MATISOVA-RYCHLA, L., RYCHLY, J. AND VEVREKOVA, M. (1978) *Eur. Polym. J.,* **14,** 1033.

15. DE KOCK, R.J. AND HOL, P.A.H.M. (1969) *4th International Synthetic Rubber Symp., London.*

16. ITO, M. (1989) *Proc. Int. Symp. Radiation Degradation of Polymer and Radiation Resistant Materials, Takasaki.*

17. KADIR, Z.A., YOSHII, F., HOSOI, F., MAKUUCHI, K. AND ISHIGAKI, I. (1990) *J. Appl. Polym. Sci.,* **40,** 799.

18. JIPA, S., SETNESCU, T., SETNESCU, R., CAZAC, C. AND MIHALCEA, I. (1993) *Revista de Chimie (Bucharest),* **44,** 65.

19. FITI, M. (1973) *Dozimetria Chimica a Radiatiilor Ionizante.* Bucuresti: Ed. Acad., 100.

20. HORUN, S. AND SEBE, Q. (1983) *Degradarea si Stabilizarea Polimerilor, Bucuresti: Ed. Tehnica,* 44.

21. DUCHACEK, V., KUTA, A., SOSKOVA, L., ROTSCHOVA, J. AND POSPISIL, J. (1990) *Polym. Degrad. Stab.,* **29,** 217.

22. GIURGINCA, M. AND IVAN, G. (1979) *Industria Usoara (Bucharest),* **26,** 251.

23. EMANUEL, N.M. AND BUCEACENKO, A.L. (1982) *Khimicheskaia Physika Stareniya i Stabilizatzii Polymerov Moskow: Nauka.*

24. SHLEAPNIKOV, Yu. A., KIRYUSHKIN, S.G. AND MARIIN, A.P. (1986) *Antiokislitel' naya Stabilizatsiya Polymerov Moskow: Khimiya.*

25. CAIN, M.E., GELLING, I.A., KNIGHT, G.T. AND LEWIS, P.M. (1975) *Rubb. Ind., 9,* 216.

26. GIURGINCA, M. (1981) *Industria Usoara (Bucharest), 28,* 543.

27. GIURGINCA, M., IVAN, G. AND ALBERT, F.M. (1992) *Materiale plastice (Bucharest), 29,* 51.

28. VOLINTIRU, T., GIURGINCA, M., ALBERT, F.M. AND IVAN, G. (1990) *Revue Roum. Chim., 35,* 791.