J. nat. Rubb. Res., **2**(4), 246–254

Behaviour of Antioxidants Containing a Disulfide Bridge in Natural Rubber

MARIA GIURGINCA*, J. M. HERDAN** AND G. IVAN*

Antioxidants containing a -S-S- bridge have been synthesised and tested; it has been proved, they are able to be bonded on the elastomer backbone during processing and ensure a superior protection level by comparison to antioxidants with similar structure, but without a disulfide bridge. The obtained data from physico-chemical investigation are in good agreement with information obtained from physical tests carried out before and after ageing.

Antioxidants used in rubbers or rubber vulcanisates are consumed in reactions with oxidants present in environment or by reactions with various radical or molecular species resulting from the action of oxygen on the substrate. Thus, the antioxidants delay the start and/or diminish the rate of the destructive oxidative process. A significant amount of antioxidant is lost in inefficient ways — blooming, volatilisation, extraction (washing), *etc.* — and, in an attempt to avoid such losses, several researchers investigated the possibility of using antioxidants grafted on elastomer macro-molecules[1]. The immobilisation of the antioxidant on the polymer backbone ensures long-term efficiency, thus avoiding the inefficient consumption of the protecting agent[2,3]. Scott and his co-workers[4–13] have contributed greatly in the development of both theoretical and experimental bases of the protection by means of grafted antioxidants, using various methods for chemical bonding, indicating the possibility of mechanochemical grafting, as well as grafting in the presence of oxygen during processing or vulcanisation of the rubber. In order to carry out the grafting, the antioxidant molecule should contain at least one of the functional groups: nitroso[14–17], nitrone[11,13,18], phenol[11,13], thiol[11,19] and amine[20–23].

This paper presents a study of the behaviour of phenolic or secondary aromatic amine type of antioxidants containing a disulfide bridge, in a natural rubber (NR) matrix, taking also into account the above-presented data.

EXPERIMENTAL

The antioxidants synthesised in our laboratories and used in the present study are listed in *Table 1*. According to literature[24,25], the introduction of the disulfide bridge has been realised by the reaction of S_2Cl_2 with hindered phenols. A somewhat similar method was used in the reaction of S_2Cl_2 with secondary aromatic amines. The composition and structure of the resulting products, containing disulfide bridges, were established by spectroscopic and chromatographic techniques. The concentration of the disulfide bridge bearing antioxidants (as presented in *Table 1*) used to realise rubber protection was around 80% for phenolic antioxidants and around 85% for aminic antioxidants. Similar antioxidants containing monosulfide bridge *(Table 2)* were used as standard materials.

Initially, the influence of various substituents on the electronic spectra of the antioxidants was investigated. Following the introduction of the antioxidants in the NR matrix, their influence on thermo-oxidative degradation was investigated in the temperature range from 90°C to 120°C. The effect of degradation on physical characteristics of the vulcanised stan-

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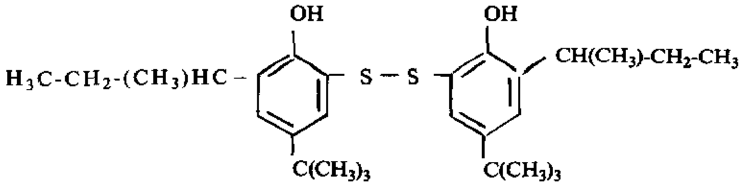
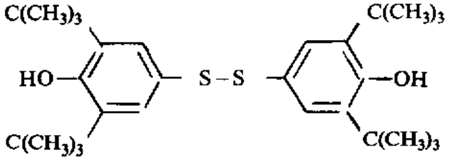
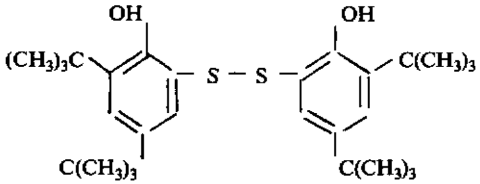
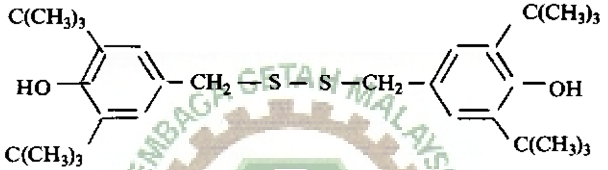
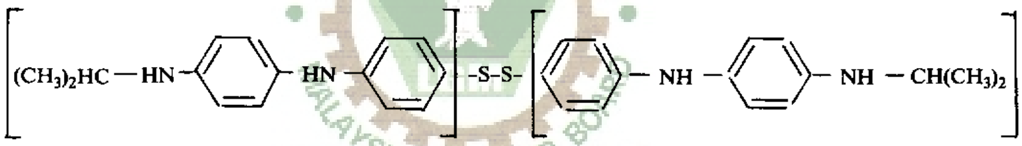
*Research Institute for Rubber and Plastics Processing, R-79628 Bucharest, Romania

**Institute of Technological Engineering, Research and Refinery Design, R-2000, Ploiesti, Romania

Paper presented at the Seminar 'Progress in Polymer Processing', Bucharest, 23–24 October 1986.

TABLE 1. STUDIED ANTIOXIDANTS

Symbol	Chemical structure
S1	
S2	
S3	
S4	
S5	

dard compounds containing studied antioxidants was put in evidence.

Previously, NR was purified by successive extractions and precipitations, followed by dissolution in 1% concentration of benzene and addition of 2 p.h.r. antioxidants. Each solution was used to cast films needed to record infrared spectra ant initial time and then, after degradation for various times at different temperatures, following the accumulation of the oxigenated groups from the development of the band $\bar{\nu}_{C=O}$ at 1720 cm^{-1}.

Physical tests were conducted on simplified recipe presented in *Table 3,* noticing the variation of the main tensile characteristics, after exposure of the samples in circumstances of

TABLE 2. REFERENCE ANTIOXIDANTS

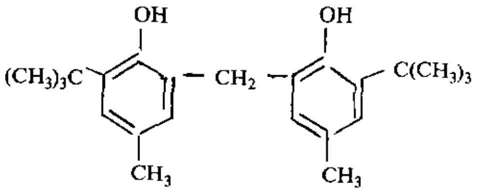
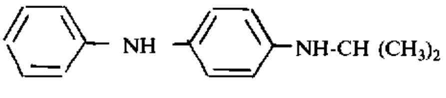
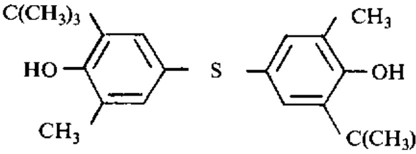
Symbol	Chemical structure
E1	
E2	
E3	

TABLE 3. RECIPE FOR TESTING THE ANTIOXIDANTS IN VULCANISED COMPOUNDS

Components	p.h.r.
NR	100
Zinc oxide	5
Stearic acid	2
CBS accelerator	1
Sulfur	3
Antioxidant	2

thermo-oxidative degradation, in ozone chamber, or after water extraction.

The above-mentioned data were completed with the determination of free and total sulfur by the Schoniger method[26], as well as by determination of free and bound antioxidant using spectroscopic techniques in infrared, ultraviolet-visible[27] and near infrared[28] domains. For these purposes, a Perkin-Elmer 577 (Perkin-Elmer, USA), a Specord UV-VIS and a Specord NIR (Carl Zeiss, GDR) spectrophotometers were used.

RESULTS AND DISCUSSION

Substituent Effect

The studied substances *(Table 1)* contain structurally chromophore groups (three- and four-substituted benzene rings) realising an absorption assigned to a $\pi \rightarrow \pi^*$ transition, as well as auxochrome groups consisting of phenol, amine and disulfide bridge containing a loan pair of electrons able to interact with π electrons of the benzene ring leading, in this way, to $n \rightarrow \pi^*$ transitions. As reference structures for ascertaining the effects induced by substituents on the chromophore, the substances listed in *Table 2* have been used.

Table 4 presents the main spectral characteristics of the studied antioxidants. The obtained data reveal that the replacement of the methylene bridge (in *E*1) by a heteroatom (in *E*3) leads to an important bathochromic displacement of the $\pi \rightarrow \pi^*$ band, as well as for the $n \rightarrow \pi^*$ band ($\Delta\lambda$ = 28 nm, and $\Delta\lambda$ = 12 nm respectively)[29]. Then, the introduction of the second sulfur atom (substance *S*1) enhances this bathochrome displacement, even

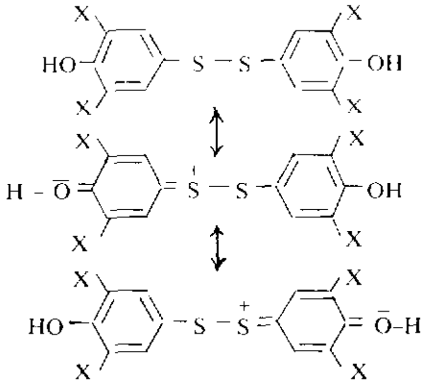
TABLE 4. SPECTRAL CHARACTERISTICS OF THE STUDIED ANTIOXIDANTS

Symbol	Absorption bands in ultraviolet-visible spectrum (nm)	Absorption bands in infrared spectrum (cm $^{-1}$)
S1	278; 322	3 600; 3 450
S2	275; 425	3 625
S3	295; 325	3 450
S4	278; 425; 455 (sh)	3 625
S5	295; 590	3 350
E1	222; 274	3 600
E2	247; 292	3 400
E3	250; 286	3 500; 3 300

by comparison with reference substance containing methylene bridge (*E*1), as well as with the substance containing thioether bridge (*E*3). The bathochrome displacement is given by the increase of the interaction of the π electrons of the chromophore with the loan pair of electrons of the sulfur, leading to a lower transition energy level. On the other hand, it may be supposed to be a plane structure of the disulfide bridge, thus favouring the extension of the conjugation and in turn leading to the noticed enhanced bathochrome displacement[30,31].

The other substances containing disulfide bridge (*S*2 – *S*4) exhibit $\pi \rightarrow \pi^*$ transitions at a wavelength near to the value noticed for the substance *S*1. The $n \rightarrow \pi^*$ transition appears unmodified for the product containing the disulfide bridge in position 2,2′ (substance *S*3) and exhibits bathochrome displacement for substances *S*2 and *S*4 with disulfide bridge in position 4,4′. This fact suggests a stronger interaction of the heteroatom with aromatic ring in compounds of 4,4′-type by comparison with the compounds of 2,2′-type. Furthermore, this observation is in good agreement with the data supplied by infrared spectra of the same compounds, particularly for the bands situated in the range from 3700 cm^{-1} to 3200 cm^{-1}. For the products with disulfide bridge in position 2,2′ (*S*1 and *S*3) a strong absorption is recorded at 3450 cm^{-1} accompanied by a weak band at 3600 cm^{-1}. The 3450 cm^{-1} band may be assigned to the associated OH groups and the 3600 cm^{-1} band may be attributed to the dimerisation by hydrogen bonds. In the spectra of the compounds *S*2 and *S*4 a rather strong absorption band appears at 3625 cm^{-1}, assigned to the free (unassociated) OH group.

The presented data lead to the assertion that the products *S*2 and *S*4 having unassociated OH groups (because *o*- and *o*′-positions are occupied by bulky *tert*-butyl groups) exhibit an enhanced efficiency, as a result of the increased ability to participate in typical thermo-oxidative processes as chain-breaking reactants. For the compound *S*2, the absorption band present at 425 nm might be an indication for a weak conjugation of the aromatic ring with the bridge, hence the formation of a partially double bond of the sulfur atom with aromatic ring which may be symbolised by the limit structures:



...1

...2

The product *S*5 results from the reference structure *E*2 introducing the disulfide bridge and, by comparison, exhibits a significant bathochrome displacement for the bands assigned to both transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ ($\Delta\lambda$ = 48 nm and $\Delta\lambda$ = 298 nm respectively). This fact is correlated with the observation concerning the displacement of the ν_{NH} band from 3400 cm^{-1} to 3350 cm^{-1} allowing the supposition that the bridge is formed between the aromatic rings. Similar behaviour is also to be expected for the structure resulting from insertion of the disulfide bridge between two nitrogen atoms, but the data supplied by infrared and electronic spectra, unfortunately, are not able to discriminate between the two possible structures.

Behaviour of the System Elastomer + Antioxidant on Thermo-oxidative Degradation

The antioxidant capability of the studied protecting agents was investigated using purified NR as a matrix. Introducing of the antioxidant in rubber was carried out in two ways:

(a) The antioxidant was solved in benzene solution of the rubber, which was then used to cast the films necessary for recording of the spectra, after various oxidation times; for an eventual bonding of the antioxidant on the macromolecules, the film was heated for 5 min at 160°C before starting the oxidation experiments.

(b) Incorporation of the antioxidants by mixing in a Brabender Plastograph (Brabender OHG, FRG) type PI 3S, provided with mixing chamber and cam rotors (type N50), at 50°C, with a rotor speed of 50 r.p.m., the mixing cycle was 10 minutes.

(a) *Kinetic features put in evidence* by recording the formation and development of the carbonyl/carboxyl groups, revealed by the 1720 cm^{-1} absorption band are presented in *Table 5*. The values of the induction and propagation steps reveal a superior antioxidant efficiency of the products *S*2 and *S*5 at low and high temperatures by comparison with all other products, including reference compounds. The relative activity of the antioxidants in the elastomer + antioxidant systems was computed using the relation[32]:

$$A = \frac{t_x - t_o}{t_s - t_o} \qquad \ldots 3$$

TABLE 5. KINETIC FEATURES EVALUATED FROM INFRARED SPECTROSCOPIC DATA FOR THERMO-OXIDATIVE DEGRADATION OF THE SYSTEMS NR + ANTIOXIDANT

Symbol of antioxidant	Induction period (h)		Propagation period (h)		Relative activity	
	100°C	120°C	100°C	120°C	100°C	120°C
NR purified	15	6	6	2	—	—
S1	95	25	45	20	0.76	0.66
S2	250	45	50	40	2.24	1.34
S3	30	10	20	7	0.14	0.14
S4	90	14	40	13	0.72	0.27
S5	420	80	155	110	3.86	2.55
E1[a]	120	35	30	15	1.00	1.00
E2	155	100	80	60	1.33	3.36
E3	80	30	30	20	0.62	0.83

[a] Reference antioxidant for the calculation of the relative activity

where t_x is the induction period for the system elastomer + antioxidant; t_s is the induction period for the system elastomer + reference antioxidant; t_o is the induction period for the oxidation of unprotected elastomer. The compound *E*1 has been used as reference antioxidant. For most of the tested antioxidants, a rather long propagation step has been noticed (see *Table 5*) and this observation is particularly valid for the compounds *S*2 and *S*5; this fact supports the hypothesis that the new substances, resulting from transformation of the initial antioxidant during the oxidative degradation process, are able to participate as protecting agents as well in this step (by reaction with oxygen, peroxides, and/or hydroperoxides).

(b) NR samples containing the antioxidants incorporated by mechanochemical method (mixing in Brabender Plastograph), after a 24 h rest, were introduced again in the mixing chamber of the Plastograph for mechanochemical destruction by processing for 20 min, with a rotor speed of 80 r.p.m. at 100°C. The evolution of the torque value during the experiments was used to calculate the processability index (I_p) and the destruction index (I_d)[33]; the obtained values are presented in *Table 6.* The tabulated data suggest that the processability index is unaffected in the presence of studied antioxidants, while the destruction index appears to be improved by all antioxidants. The most enhanced favourable effect was noticed for the antioxidants *S*2 and *S*5 which were able to suppress the destruction at a level comparable or better than the effect obtained in the presence of the reference compound *E*2.

TABLE 6. BEHAVIOUR OF NR CONTAINING VARIOUS ANTIOXIDANTS BY PROCESSING IN BRABENDER PLASTOGRAPH

Symbol of antioxidant	Processability index[a]	Destruction index[a]
NR purified	0.41	37.5
S1	0.47	42.5
S2	0.46	70.0
S3	0.45	42.5
S4	0.42	46.3
S5	0.49	65.0
E1	0.50	41.0
E2	0.61	67.5
E3	0.48	42.0

[a]After Ivan and Bugaru[33]

Samples of the elastomer containing the antioxidant incorporated by mechanochemical method prelevated before and after mechanochemical destruction were used to measure the total sulfur content and the sulfur content in acetone extract respectively. The obtained data *(Table 7)* show that a certain amount of the sulfur is unextractable. These experimental findings lead to the supposition that, in experimental circumstances, a certain amount of the disulfide bridged antioxidants undergo the cleavage of the S-S bond

$$\text{In-S-S-In} \xrightarrow{t_o} 2\ \text{In-S}^{\cdot} \qquad \ldots 4$$

and the resulting thiyl radicals are grafted on the macromolecules by addition to the double bonds[5,18], or by reaction with macroradicals generated either in mechanochemcial destruction or in thermo-oxidative degradation process of the rubber.

TABLE 7. CONTENT OF TOTAL SULFUR AND EXTRACTABLE SULFUR IN THE SYSTEMS NR + ANTIOXIDANT

Symbol of antioxidant	Total sulfur (%)	Extractable sulfur (%)
S1	0.27	0.13
S2	0.27	0.02
S3	0.27	0.05
S4	0.25	0.10
S5	0.27	0.01
E1	—	—
E2	—	—
E3	0.18	0.14

The determination of the free antioxidant content *(Table 8)* also makes evident that a certain amount of the antioxidant becomes

TABLE 8. CONTENT OF FREE AND BOUND ANTIOXIDANTS IN THE SYSTEMS NR + ANTIOXIDANT

Symbol of antioxidant	Free antioxidant (%)[a]	Bound antioxidant (%)[a]
S1	47	53
S2	27	73
S3	66	34
S4	51	49
S5	23	77
E1	93	7
E2	53	47
E3	78	22

[a] Free antioxidant + bound antioxidant = 100%

unextractable as a result of bonding with the polymer. The highest percentage of the bound antioxidant (against total antioxidant content) is noticed for products *S*2 and *S*5, while for products *S*1, *S*3 and *S*4 the attained level is comparable to the value determined for the reference compound *E*2. Moreover, all antioxidants containing monosulfide or disulfide bridge appear to be able to form bound antioxidants, but the grafting capability is higher for the disulfide bridge-bearing antioxidants.

Influence of Some Physical Characteristics

Physical characterisation consisting in evaluation of Mooney viscosity, cure behaviour (using a Monsanto Rheometer type TR 100), and tensile test, was accomplished for a simplified recipe *(Table 3)*. The results grouped in *Table 9* show that these characteristics are less influenced by the chemical nature of the antioxidant. Stress-strain values at room temperature *(Table 10)* are also comparable for all stocks, irrespective of the antioxidants used.

The stability at thermo-oxidative degradation, evaluated on the basis of the variation of main tensile characteristics after exposure of the samples to thermo-oxidative degradation, shows that the antioxidants with disulfide bridge ensure a superior level of protection by comparison with reference antioxidants. The product *S*5 exhibits the highest protection capability among the studied antioxidants, ensuring the highest level for conservation of tensile strength, of elongation at break for the entire studied domain of temperature. In addition, after prolonged water extraction (six days at 30°C in Soxhlet extractor) followed by air ageing (three days at 70°C) it was noticed that compounds protected by antioxidants with disulfide bridges preserved their physical characteristics at a higher level compared with compounds protected by other antioxidants, and these experimental data support the assertion that disulfide bridged antioxidants are able to form bound antioxidants.

TABLE 9. VISCOSITIES AND CURE CHARACTERISTICS OF NR COMPOUNDS CONTAINING VARIOUS ANTIOXIDANTS

Symbol of antioxidant	Mooney viscosity ML_{1+4}(100°C)	Mooney scorch time at 130°C (min)	Rheometer scorch time at 160°C (min)	Rheometer optimal vulcanisation time at 160°C (min)
S1	36	27	4.00	7.25
S2	38	24.7	4.00	6.90
S3	37	30.5	4.25	7.00
S4	36	28.2	4.15	7.20
S5	36	25.5	3.15	6.50
E1	38	26.5	4.25	7.50
E2	36	26.2	4.00	7.00
E3	37	27.0	4.20	7.25

TABLE 10. PHYSICAL CHARACTERISTICS OF STANDARD COMPOUNDS CONTAINING VARIOUS ANTIOXIDANTS BEFORE AND AFTER AGEING IN DIFFERENT CONDITIONS

Symbol of anti-oxidant	Initial physical characteristics		Tensile strength preserved after ageing (%)			Elongation at break preserved after ageing (%)		
	Tensile strengh (MPa)	Elongation at break (%)	I	II	III	I	II	III
S1	21.2	690	92	65	60	83	52	55
S2	24.1	670	95	80	65	88	67	70
S3	23.5	700	87	72	58	75	58	52
S4	22.8	700	90	67	65	78	65	60
S5	24.8	690	97	92	73	92	80	71
E1	22.8	700	84	67	65	82	70	56
E2	24.2	690	90	75	30	73	55	35
E3	23.0	700	82	70	65	80	62	60

I = Thermo-oxidative ageing for three days at 70°C
II = Thermo-oxidative ageing for three days at 90°C
III = Thermo-oxidative ageing for three days at 70°C, after water extraction on six days at 30°C

CONCLUSIONS

The antioxidants containing a disulfide bridge synthesised in the framework of the present study are able to be bond on the elastomer backbone during processing and ensure a superior protection level by comparison to the antioxidants with similar structure, but without a -S-S- group. The obtained data from physico-chemical investigation are in good agreement with the information obtained from physical tests carried out before and after thermo-oxidative ageing.

REFERENCES

1. KUCZKOWSKI, J.A. AND GILLICK, J.G. (1984) *Rubb. Chem. Technol.*, **57**, 621.
2. WOLFE, J.R. (1981) *Rubb. Chem. Technol.*, **54**, 988.
3. BADRAN, B.M., SHERIF, S. AND FAHMY, M.M. (1981) Elastomerics, **113(9)**, 31.
4. SCOTT, G. (1978) *Gummi Asbest Kunstst.*, **31**, 934.
5. KULARATNE, K.W. AND SCOTT, G. (1978) *Eur. Polym. J.*, **14**, 835.
6. FERNANDO, W.S.E. AND SCOTT, G. (1980) *Eur. Polym. J.*, **16**, 971.
7. COORAY, B.B. AND SCOTT, G. (1981) *Eur. Polym. J.*, **17**, 379.
8. CHAKRABORTY, K.B. AND SCOTT, G. (1977) *Eur. Polym. J.*, **13**, 731.
9. CHAKRABORTY , K.B. AND SCOTT, G. (1980) *Polymer*, **21**, 252.
10. KATBAB, A.A. AND SCOTT, G. (1981) *Eur. Polym. J.*, **17**, 559.
11. SCOTT, G. (1978) *Gummi Asbest Kunstst.*, **31**, **966**.
12. AJIBOVE, O. AND SCOTT, G. (1982) *Polym. Degrad. Stab.*, **4**, 415.
13. EVANS, B.W. AND SCOTT, G. (1974) *Eur. Polym. J.*, **10**, 454.
14. BARNARD, D., CAIN, M.E., GAZELEY, K.F., KNIGHT, G.T. (1971) *Pat. England 1 255 645;* (1972) *CA*, **77**, P 6979n.
15. KOGAN, L.M., MONASTYRSKAYA, N.B., DAVYDOVA, L.M., KROPATSCHEVA, E.N., BELGORODSKIY, I.M., BELGORODSKAYA, O.L., BOLKHOVETS, B.M. AND GAGIN, A.V. (1976) *Pat. FRG 26-444395* (1977) *CA*, **87**, P 54337e.
16. CAIN, M.E., GAZELEY, K.F., GELLING, I.J. AND LEWIS, P.M. (1972) *Rubb. Chem. Technol.*, **45**, 204.
17. CAIN, M.E., KNIGHT, G.T., LEWIS, P.M. AND SAVILLE, B.J. (1969) *J. Rubb. Res. Inst. Malaya*, **22**, 289.

18. SCOTT, G. (1977) *Plast. Rubb. Process.*, **2**, 41.

19. WEINSTEIN, A.H. (1977) *Rubb. Chem. Technol.*, **50**, 614 and 650.

20. KOTANI, T., TAKEMURO, Y. AND MIGABASHI, S. (1980) *Pat. FRG 3 018 841;* (1981) *CA*, **94**, P 104704q.

21. DUNN, J.R. (1974) *Rubb. Chem. Technol.*, **47**, 960.

22. KIRPICHEV, V.P., PIOTROVSKIY, K.B. AND YAKUBCHIK, A.I. (1973) *Kauchuk i rezina No. 7*, 20.

23. FARZALIEV, V.M., FERNANDO, W.S.E. AND SCOTT, G. (1978) *Eur. Rubb. J.*, **14**, 785.

24. FUDJISAWA, T. AND YAMAMOTO, T., (1977) *Pat. Japan 52-33101;* (1978) *Ref. zhur. Khimiya*, 7H174.

25. EXXON RES. ENG. CO. (1975) *Pat. France 22-48270;* (1976) *CA*, **84**, 16947.

26. *ASTM D297* (1976).

27. *ASTM D1416* (1980).

28. MEGHEA, A., GIURGINCA, M. AND VASILESCU, S.D. (1986) *Industria usoară (Bucharest)*, **33**, 542.

29. IVAN, G. AND GIURGINCA, M. (1986) *Revista de chimie (Bucharest)*, **37**, 287.

30. JAFFÉ, H.H. AND ORCHIN, M. (1962) *Theory and Application of Ultraviolet Spectroscopy*. New York: Wiley.

31. SVERDLOVA, O.V. (1973) *Elektronnye spektry v organiceskoi khimii*. Leningrad: Khimiya.

32. JIRAKOVA, L. AND POSPIŠIL, J. (1973) *Eur. Polym. J.*, **9**, 71.

33. IVAN, G. AND BUGARU, E. (1973) *Industria usoară (Bucharest)*, **20**, 521.