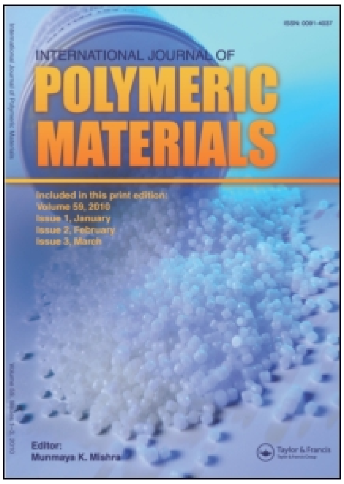


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

A New Class of Non-Staining Antiozonants for Elastomers

G. Ivan[a]; M. Giurginca[a]; J. -M. Herdan[b]
[a] Research Institute for Rubber and Plastics Processing, Bucharest, Romania [b] Research Institute for Petroleum Refining and Petrochemistry, Ploieşti, Romania

To cite this Article Ivan, G. , Giurginca, M. and Herdan, J. -M.(1992) 'A New Class of Non-Staining Antiozonants for Elastomers', International Journal of Polymeric Materials, 18: 1, 87 — 93
To link to this Article: DOI: 10.1080/00914039208034815
URL: http://dx.doi.org/10.1080/00914039208034815

Intern. J. Polymeric Mater., 1992, Vol. 18, pp. 87–93
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Great Britain

A New Class of Non-Staining Antiozonants for Elastomers

G. IVAN and M. GIURGINCA
Research Institute for Rubber and Plastics Processing, R-79628 Bucharest, Romania

and

J.-M. HERDAN
Research Institute for Petroleum Refining and Petrochemistry, R-2000 Ploieşti, Romania

(Received February 17, 1992)

General purpose rubbers containing double bonds in their backbone are particularly sensitive to ozone attack. The known antiozonants have some drawbacks and the search for new antiozonants is of interest. In present work a series of ethyl cyanoacetate, ethyl malonate and acetyl acetone derivatives containing, 3,5-dialkyl-4-hydroxybenzyl groups has been tested in isoprene rubbers as well as in their vulcanizates in order to evaluate their antiozonant capability. The most enhanced activity was observed for 3,5-di-*tert*-butyl-4-hydroxybenzyl cyanoacetate which exhibits an antiozonant capability comparable to N,N'-disubstituted p-phenylene diamines. Other tested derivatives containing *tert*-butyl substituents in positions 3 and 5 of the aromatic ring showed also antiozonant activity.

KEY WORDS Antiozonants, rubber, degradation, stabilization.

INTRODUCTION

Ozone reacts with virtually all organic materials and the rate of attack is particularly high on compounds containing C=C bonds. General purpose rubbers are polymers containing C=C bonds in their backbone and consequently such rubbers and their vulcanizates are particularly sensitive to ozone attack. The search for chemical antiozonants has led to a wide variety of substances with (dis)similar chemical structure being patented for this purpose.[1–5] The best known and widely used at the present is the class of N,N'-disubstituted p-phenylene diamines; although they are high in effectiveness as antiozonants, they have some drawbacks including interference with the vulcanization process, staining and discoloration, health hazards, volatility, solubility in fluids coming in contact with rubber products during service.

The present work is concerning with a class of chemicals which show an interesting antiozonant capability, and their synthesis[6] is rather easily allowing to control various characteristics important for practical purposes, including solubility and migration in elastomer matrix, volatility and solubility in various fluids, staining and discoloration.

EXPERIMENTAL

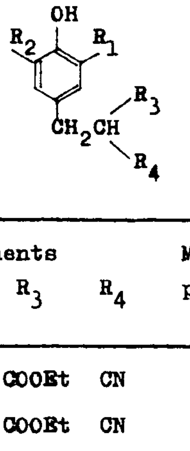
The new chemicals tested for their antiozonant capability are presented in Table I. Their synthesis was presented elsewhere[6] and their structure was checked by chemical analysis and confirmed by spectroscopic (infrared, ultraviolet-visible and NMR) methods.

In order to test their antiozonant capability, the synthesized substances were introduced in rubbers with isoprenic structure (natural rubber type RSS-1; synthetic polyisoprene containing 95.4 mole % of *cis*-1,4 units) as well as in their vulcanizates. The rubbers were carefully purified by successive extractions and precipitations conducted at room temperature, in order to eliminate natural/synthetic antidegradants contained in raw materials.

An amount of tested substances (2 mass parts for 100 mass parts of rubber) was added in benzenic solution of rubber. Films were obtained by casting on spectral

TABLE I

Substances tested as antiozonants



Symbol	Substituents				Melting point, °C	Boiling point, °C (pressure, Torr)
	R_1	R_2	R_3	R_4		
AO-1	t-Bu	t-Bu	COOEt	CN	207-208	
AO-2	Me	Me	COOEt	CN	187-189	
AO-3	Me	t-Bu	COOEt	CN		225-228 (5)
AO-4	t-Bu	t-Bu	COOEt	COOEt		192-195 (2)
AO-5	Me	Me	COOEt	COOEt	190-192	
AO-6	Me	t-Bu	COOEt	COOEt		205-208 (4)
AO-7	t-Bu	t-Bu	COMe	COMe	148-149	
AO-8	Me	Me	COMe	COMe		160-163 (2)
AO-9	Me	t-Bu	COMe	COMe		180-183 (3)

window and their infrared spectra were recorded using a Perkin-Elmer 577 (U.S.A.) spectrograph, before and after exposure to ozone.

The antiozonant capability was tested also in vulcanizates. Formulations for testing have been selected as simple as possible (mass parts): 100 rubber, 40 HAF carbon black, 5 zinc oxide, 2 stearic acid, 1 cyclohexyl benzothiazyl sulfenamide, 3 sulfur, 2 antiozonant (various).

For exposure to ozone, a MAST ozone test chamber type 700-1 (with controlled temperature and ozone concentration) was used. The period of exposure in ozone cabinet was extended up to 144 hours.

RESULTS AND DISCUSSION

Behaviour of Protected Raw Rubbers on Ozone Exposure

The films of protected rubbers have been exposed in ozone cabinet at 25 and 50°C and 50 pphm O_3. The infrared spectrum of each sample was recorded at time intervals allowing to observe the modifications appearing in the elastomer structure. These modifications are characterized by appearance and increase of the content of oxygen-bearing groups like carbonyl/carboxyl (ν_{CO} 1720 cm^{-1}) and hydroxyl (ν_{OH} 3450 cm^{-1}) accompanied by decrease of double bond content ($\nu_{isoprenyl}$ 840 cm^{-1}). For the unprotected elastomer, the appearance of the oxygen-bearing groups is observable even during first hour of ozone exposure. The protected elastomers exhibit a stability to ozone varying with the structure of the groups linked at the benzylic carbon (R_3, R_4), with the nature of the substituents on the aromatic ring (R_1, R_2), as well as with testing temperature. The results are grouped in Table II, where the data for the same polymer protected by N,N'-diphenyl-*p*-phenylene diamine (DPPD) or by N-isopropyl-N'-phenyl-*p*-phenylene diamine (IPPD) are presented also for comparison. The presented data allow for the following remarks: (i) all tested compounds exhibit an antiozonant capability but at a rather different level, depending on the nature of the substituents; (ii) the compound AO-1 containing two *tert*-butyl substituents vicinal to the phenolic OH, a CN and a COOEt groups on the benzylic carbon atom exhibit an antiozonant protection comparable with IPPD; (iii) in the second position, but not too far from the first, there are compounds AO-4 and AO-7 with the same *tert*-butyl substituents on the aromatic ring and symetrical COOEt or COMe substituents on the tertiary carbon atom; they are followed by derivatives having a *tert*-butyl replaced by a methyl group on the aromatic ring; (iv) the other tested substances exhibit also an antiozonant capability which is indeed inferior to N,N'-disubstituted p-phenylene diamines but it is net superior in comparison with hindered phenols customary used as non-staining antioxidants; (v) as a rough rule it can be observed also, that synthetic polyisoprene exhibits a lower resistance to ozone attack in comparison with natural rubber.

Behaviour of Protected Vulcanizates on Ozone Exposure

The vulcanizates based on natural rubber or synthetic polyisoprene have been exposed in the ozone testing chamber at 50 pphm O_3, temperatures 25 and 50°C, with previous elongation of 20%, in static and dynamic conditions. The protected

TABLE II

Behaviour of protected raw rubbers on ozone exposure

Systems	Time up to observation of carbonyl/carboxyl groups, h at temperature	
	25 °C	50 °C
Natural rubber, unprotected	2.0	1.0
cis-1,4-Polyisoprene, unprotected	1.5	0.6
Natural rubber + AO-1	100	85
AO-2	24	16
AO-3	42	24
AO-4	54	30
AO-5	18	7
AO-6	8	6
AO-7	46	36
AO-8	18	6
AO-9	24	7
IPPD	120	100
DPPD	90	80
cis-1,4-Polyisoprene		
+ AO-1	92	82
AO-2	20	17
AO-3	35	20
AO-4	42	16
AO-7	36	20
IPPD	95	72
DPPD	62	54

samples were exposed as obtained by curing or after an accelerated aging in a cell oven for 3 days at 90°C. The results are grouped in Table III allowing to remark that the product AO-1 exhibits again an antiozonant capability comparable to N,N′-disubstituted p-phenylene diamines as well as in static and dynamic testing. After accelerated aging of vulcanizates, the antiozonant efficiency of the compound AO-1 drops in comparison with IPPD but remains at a level comparable with DPPD. A near antiozonant activity exhibit the compounds AO-4 and AO-7; the other tested substances show a low antiozonant capability, comparable to the usual phenolic antioxidants.

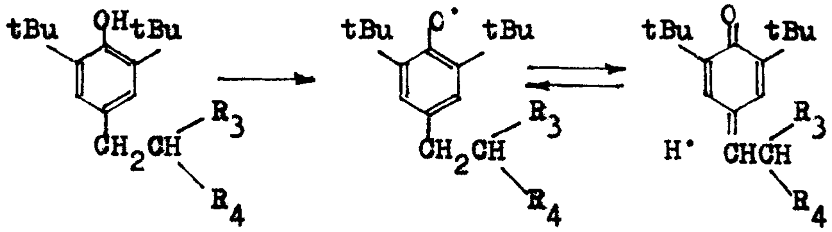
The Mechanism of Antiozonant Activity

The examination of the literature data[1-4,7] leads to the remark that there is not an agreement about the mechanism by which chemical antiozonants impart protection.

TABLE III

Behaviour of protected vulcanizates on ozone exposure

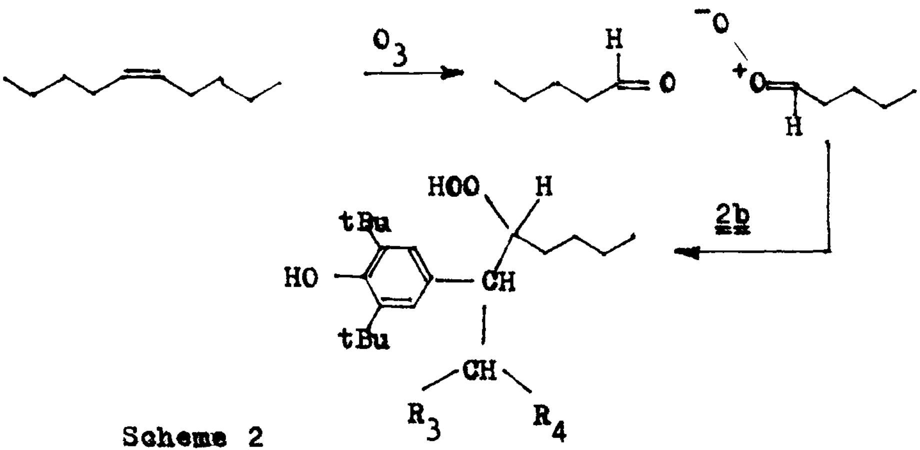
	Static testing, *h*				Dynamic testing, *h*			
	Initial		After ageing		Initial		After ageing	
Recipes	25°C	50°C	25°C	50°C	25°C	50°C	25°C	50°C
Natural Rubber								
+ AO-1	94	46	72	47	75	32	72	20
AO-2	6	4	8	5	8	2	6	2
AO-3	12	9	15	8	12	8	18	10
AO-4	72	54	54	72	24	22	24	20
AO-5	8	6	4	4	8	4	6	2
AO-6	6	6	4	3	8	4	6	3
AO-7	72	54	72	54	54	46	24	21
AO-8	6	6	8	4	8	6	8	6
AO-9	6	6	6	4	3	2	3	2
IPPD	96	54	90	42	88	60	75	68
DPPD	55	35	30	18	62	42	42	28
cis-1,4-Polyisoprene								
+ AO-1	86	56	78	32	62	24	72	12
AO-2	7	3	6	2	4	2	3	2
AO-3	18	7	20	4	16	4	8	3
AO-4	48	36	40	24	24	16	20	16
AO-5	6	4	4	4	6	4	4	2
AO-6	6	6	4	2	6	4	6	2
AO-7	48	32	36	24	36	18	30	16
AO-8	6	4	6	6	6	4	4	2
AO-9	8	6	8	4	6	2	4	2
IPPD	78	62	60	44	56	32	48	24
DPPD	42	24	24	18	42	20	24	10



1 2a 2b

Scheme 1

Although a major part of the chemistry of polydienes' degradation by ozone has been interpreted in ionic terms, the production and involvement of several different kinds of peroxidic species would certainly indicate that some free-radical chemistry could take place. Long time ago, it was reported[8,9] that a significant amount of p-phenylene diamine derivatives become unextractible after exposure of the protected vulcanizates in ozone cabinet and this experimental fact was accepted as an argument for the reaction of the antiozonant (or its derivative) with the zwitter ions, ozonides or aldehydes resulting in reaction of rubber macromolecules with ozone. For the class of antiozonants discussed in present paper, the succession of reactions can be presented as in Scheme 1. The structure of phenoxyl radicals (**2a**) is supported by ESR data even it seems to be less stable (more reactive).[6] In their



Scheme 2

turn, the species **2a** are potential donors of hydrogen atoms for peroxy radicals resulting in formation of p-quinone methide structues **2b**. On another way, the species **2b** can react with zwitter ion **3**, as presented in Scheme 2, interfering with ozonide formation in ozonant degradation of the elastomer. The both ways involve an increased reactivity of the benzylic hydrogen which is assisted by substituents R_3 and R_4.

At the same time, the hindered phenolic group present in structure **1** can be involved in reactions with radicalic species playing its classical role of antioxidant.

CONCLUSION

A series of ethyl cyanoacetate, ethyl malonate and acetyl acetone derivatives containing 3,5-dialkyl-4-hydroxybenzyl groups has been tested in isoprenic rubbers as well as in their vulcanizates in order to evaluate their antiozonant capability. The most enhanced activity was observed for 3,5-di*tert*-butyl-4-hydroxybenzyl cyanoacetate (AO-1) which exhibits an antiozonant activity comparable to N,N'-disubstituted p-phenylene diamines in the circumstances of our experiments. Other tested derivatives containing *tert*-butyl substituents in positions 3 and 5 of the aromatic ring showed also antiozonant activity, even it was not at the level of the compound AO-1.

References

1. R. W. Murray, "Prevention of Degradation by Ozone," Chap. 5 in *Polymer Stabilization* edited by W. L. Hawkins (Wiley-Interscience, New York, 1972), p. 215; R. W. Layer and R. P. Lattimer, *Rubber Chem. Technol.*, **63**, 426 (1990).
2. G. Bertrand, paper presented at *International Rubber Conference*, Moscow 1984.
3. D. Brück, H. Königshofen and L. Ruetz, *Rubber Chem. Technol.* **58**, 728 (1985).
4. H. Fries, *Gummi Fasern Kunstst.* **40**, 238 (1987).
5. S. K. Rakovski, D. R. Cherneva and G. E. Zaikov, *Inter. J. Polymeric Mater.* **14**, 21 (1990).

6. J.-M. Herdan, V. Dinoiu, A. Meghea, M. D. Gheorghiu, A. Schiketanz, M. Giurginca and A. T. Balaban, *Revue Roumaine Chim.* (Bucharest) **35**, 407 (1990).
7. J. Pospišil, paper presented at 1st microsymposium "Ozone Destruction of Polymers," Sofia 1984; *Communications of the Dept. of Chemistry,* Bulgarian Academy of Science, **18**, 277 (1985).
8. M. Braden and N. A. Gent, *J. Appl. Polym. Sci.* **6**, 449 (1962).
9. O. Lorenz and C. R. Parks, *Rubber Chem. Technol.* **36**, 194 (1963).