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SOME NEW ANTIOXIDANTS FOR NATURAL RUBBER*

By

A. COOMARASAMY, L. B. K. SILVA and R. C. SURANIMALA**

SUMMARY

The antioxidant activities of phenolic and amine antioxidants containing the maleimide group, determined by oxygen absorption measurements in cumene, cis 1, 4 *polyisoprene rubber and vulcanized natural rubber are a little lower compared to the antioxidant activities of 4 isopropylamino diphenyl amine and* 2,6 *ditert butyl* 4- *methyl phenol. The maleimide antioxidants were found to be less volatile than the two conventional antioxidants and may be suitable for high temperature applications. Stress relaxation measurements also showed that maleimide antioxidants perform better than the* 4-*isopropylamino diphenyl amine at* 100°C. *It has been shown that it is possible to bind antioxidants via the maleimide group to rubber with an efficiency of binding as high as* 48%. *The efficiency may be improved further by first modifying the rubber with maleic anhydride and by subsequently reacting the modified rubber with suitable compounds containing antioxidant functions.*

INTRODUCTION

Natural rubber (NR), in addition to the rubber hydrocarbon contains several non-rubber substances in small amounts. Some of these non-rubber substances protect the hydro carbon polymer from deterioration during the coagulation and drying process and thus there has been no necessity to add stabilizers in the preparation of raw NR as in the case of synthetic rubbers (Nadarajah *et al* 1971). In addition, the presence of naturally occurring antioxidants enables the use of latex in road construction, latex-cement mixes, adhesives and unvulcanised carpet backing and sole crepe as a consumer product without the addition of further stabilizers. The naturally occurring antioxidants are mainly phenols, tocotrienols, phospholipids, amino acids and betaines (Nadaraja *et al* 1971).

But after vulcanization, they have little effectiveness in preventing deterioration of the rubber under service conditions and this necessitates the incorporation of synthetic antioxidants during the manufacture of rubber products (Whitby, 1960).

The synthetic antioxidants used in rubber are mainly, relatively low molecular weight aryl amines and hindered phenols, which act by a chain breaking mechanism. Although the antioxidant activities of commercially available antioxidants are high, they could easily be lost either by volatilization or by leaching (by water or oils) especially from thin articles such as gloves, latex thread, cut thread, washers etc. and even from tyres.

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** Vidyodaya Campus, University of Sri Lanka, Gangodawila, Nugegoda, Sri Lanka. Presently at the Atomic Energy Authority, Colombo, Sri Lanka.

Cain *et al* (1972) have stated that, for satisfactory performance antioxidants must not only be designed for high activity against degradation but must also be resistant to physical loss from the article, a process which will depend on their physical properties. They made use of the high reactivity of rubber hydrocarbon towards nitroso compounds to bind amine and phenolic antioxidant functions, and were able to overcome the problem of leaching and volatilization. But there have been problems in making use of this route for binding antioxidants on a commercial scale (Dunn, 1974). Plant and Scott (1971) have studied the volatilities of phenolic and sulphur antioxidants of varying molecular weight in polypropylene and have found that the volatility could be reduced and the effectiveness of the antioxidant could be increased by the use of higher molecular weight antioxidants. Kay, Wright and Thomas (1972) have studied the effectiveness of 'Polymeric' antioxidants in fluoro elastomers and silicones. It has also been shown that the antioxidant groupings could be linked to the natural rubber chain by the use of vinyl groups (Amarapathy and Scott 1976) and thiol groups, (Fernando 1976). Natural rubber being an unsaturated hydrocarbon polymer with reactive methylenic groups, reacts readily with maleic anhydride and maleimides by thermal reaction, mechano-chemical reaction and radical initiated reaction, (Bacon and Farmer 1939; Pinazzi *et al* 1960). Tawney and Weinish (1965) have used maleimides containing carboxylic acid groups to introduce polar groups into the polymer.

The present work discusses the antioxidant activities of derivatives of maleic anhydride containing aryl amine and hindered phenolic functions and their reactivity with rubber and vinyl monomers.

EXPERIMENTAL METHODS

Evaluation of volatility

Volatilities of antioxidants were measured by using a simple yet easily reproducible method used by Russian workers (Wolkoba, 1975). 0.1000 g of the test material in finely divided form was placed in a petri dish in an air circulating oven at 100°C. The loss in weight was recorded at regular intervals. Percentage loss in weight is plotted against time for the different antioxidants.

Oxygen absorption measurements

Oxygen absorption provides very useful information on the oxidisability or the inhibition during accelerated ageing of a material in a closed system saturated with oxygen. The efficiency of inhibition or retardation of oxidation by the synthesised antioxidants were measured in purified cumene, solution of purified cis 1,4 polyisoprene (Natsyn 2200) in chlorobenzene and in vulcanised natural rubber films of 0.008" thickness. The oxygen absorption of the sample was followed continuously and automatically using an apparatus consisting of strain gauge type pressure transducers (pressure range ± 5 psi) manufactured by Pye Ether Co. Ltd., potentiometers of varying resistance to obtain the voltage required and multi-channel electronic recorder manufactured by Leeds & Northrup Ltd.

Stress relaxation measurements

Stress relaxation provides useful information on degradation of vulcanizates. Continuous stress relaxation of vulcanized rubber samples containing different antioxidants was carried out at 100°C, using Wallace Extension Stress Relaxometer and a Wallace Multicellular oven with air circulation.

Preparation of vulcanized rubber

Natural rubber (Pale Crepe IX) was masticated on a laboratory type two roll mill and the formulation used for the preparation of vulcanizates is given in Table 1.

Table 1. *Formulation*

Material	*Quantity by wt.*
Natural rubber	100·00
Stearic acid	2·00
Zinc oxide	5·00
CBS	0·50
Sulphur	2·50
Antioxidants	Variable

The curing characteristics of vulcanizates were determined using Monsanto oscillating disc rheometer. Samples were vulcanized at 140°C in an electrically heated press.

Reactions of maleic anhydride derivatives with rubber

Solution stage reaction

Maleimide compound and benzoyl peroxide were added and mixed with a solution of purified Cis 1,4 polyisoprene (Natsyn) in benzene and refluxed at 80^0 C for eighteen hours in an inert atmosphere, in a 500 ml two necked flask provided with gas inlet and a reflux condenser. After the reaction the rubber was precipitated from benzene solution with acetone and dried at about 40^{0}C in a vacuum oven. The dried samples were extracted using an azeotrope of acetone, methanol and chloroform, for 48 hours to remove the unreacted materials and dried at 40^{0}C in a vacuum oven. Percentage nitrogen present in the modified rubbers was estimated by the Kjeldhal method and the efficiency of binding was calculated. Oxygen absorption of the modified rubber was also measured.

Mechano – chemical reaction

Natural rubber (Pale Crepe IX) was masticated and 4-anilino phenyl maleimide was incorporated under tight nip using a laboratory mill in the presence and absence of benzoyl peroxide. After incorporation of the antioxidant, other vulcanizng chemicals were incorporated and vulcanized. Oxygen absorption of the vulcanizates was measured before and after extraction of unbound materials using an azeotrope of acetone methanol and chloroform.

Polymerization of maleic anhydride derivatives with vinyl monomers

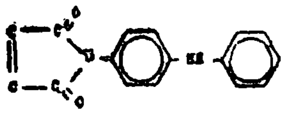
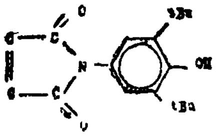
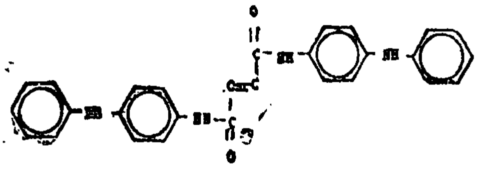
Maleic anhydride does not homopolymerise easily, but copolymerises readily with certain vinyl monomers. In this study the method of Tawany *et al* (*Chem.* Abs. 57) was used. Equimolar quantities of methyl methacrylate and maleimide compound dissolved in dioxan were heated to 60^{0}C in the presence of azo-bis-isobutyronitrile for four hours. After the reaction the solvent was removed. Solution viscosity measurements were made using solutions in acetone to determine the polymerisability.

The codes used for the antioxidants used are as follows:-

N-(4 anilino phenyl maleimide)	A. 0-1
N-(3,5 ditert butyl 4-hydroxy phenyl) maleimide	A. 0-2
N N Di (4-diphenyl amino) fumaramide	A. 0-3
4-(Isopropyl amino diphenyl amine) (Nonox ZA)	A. 0-4
2,6 Ditert butyl 4 methyl phenol (topanol OC)	A. 0-5

The Structural formulae of the maleimide and fumaramide antioxidants are given in Table 2.

Table 2. *Structural Formulae of Compounds Synthesised*

N-(4 anilion phenyl) maleinide		A.O. 1
N-(3,5 ditert. butyl 4-hydroxy phenyl) maleimide		A.O. 2
N,N′ Di (4 diphenyl amino) fumaramide		A.O. 3

Synthesis of N-(4-Anilino) phenyl maleimide (Antioxidant-1, A. O-1)

The above compound was prepared by a two stage process (Chem. Abs. 60). First maleic anyhydride was made to react with p-amino dephenyl amine to yield the corresponding maleamic acid which was then cyclised using sodium acetate and acetic anhydride.

Synthesis of N-(4-Anilino phenyl) maleamic acid (1st stage)

Dioxan (100 ml) was added to p-aminodiphenyl amine (36·8 g, 0·2 moles) in a 500 ml flask. A solution of maleic anhydride (19·6 g) in benzene (50 ml) was added to the above solution whilst stirring and the orange-brown precipitate formed was filtered, washed with benzene and dried, (yield 70%). The product obtained was found to be suitable for next step without purification.

Synthesis of N-(4-Anilino phenyl) maleimide (2nd stage)

A mixture of N-(4-anilino phenyl) maleamic acid (25 g, 0·07 moles) sodium acetate (5.4 g) and acetic anhydride (90 ml) was heated at 70°C over ten minutes and then poured into water. The dark red precipitate obtained was washed with water, then with methyl alcohol and dried (yield 80%). It was recrystallised from diethyl ether (m. p. 160°C).

Synthesis of N -(3,5 ditert. butyl 4, hydroxy) phenyl *maleimide* (*Antioxidant - 2*, A.O – 2)

The above compound was prepared by a four stage process (Chandrasiri 1975). In the first step 2,6 ditert. butyl phenol was converted into the corresponding benzoquinone oxime. This was reduced to 3,5 ditert. butyl 4, hydroxy aniline, which was reacted with maleic anhydride to form N-(3,5 ditert. butyl 4, hydroxy) maleamic acid. The compound was cyclised to form the title compound using acetic anhydride and sodium acetate.

Preparation of 2,6 ditert. butyl 1,4 benzoquinone-4-oxime (1st stage)

Dilute hydrochloric acid was added gradually to a stirred, cooled suspension of sodium nitrite (10 g, 0·14 moles) and powdered sodium hydroxide (10 g, 0·25 moles) in an alcoholic solution of 2,6 ditert. butyl phenol (40 g, 0·19 moles) until a slight excess of acid was present in the solution. By dilution with water 2,6 ditert. butyl 1,4 benzoquinone-4-oxime was precipitated and isolated. The crude product (yield 80%) was recrystallised from chloroform; light petroleum ether (1:4) and then from ethyl alcohol (m. p. 218°C, yield 60%).

Reduction of 2,6 ditert. butyl 1,4 benzoquinone-4-oxime to 3,5 ditert. butyl 4, hydroxy aniline (2nd stage)

Granulated tin (30 g) and 2,6 ditert. butyl benzoquinone-4-oxime (20 g, 0·10 moles) were placed in a 500 ml capacity round bottomed flask fitted with a reflux condensor. Concentrated hydrochloric acid (150 ml) was added in three equal portions with thorough shaking after each addition. When vigorous reaction subsided the contents were heated under reflux on a water bath for 50 minutes, while shaking from time to time. Small quantity of ethyl alcohol was added to make the nitroso compound soluble. A 300% solution of sodium hydroxide solution was added to the cooled filtered solution until the precipitate of stannic hydroxide dissolved fully. The amine formed was extracted with ether and isolated by distilling off ether under vacuum (m. p. 104° C, yield 60%).

Preparation of N-(3,5 ditert. butyl 4-hydroxy) phenyl maleamic acid (3rd stage)

To maleic anhydride (5 g, 0·05 moles) in acetic acid (10 ml) was added dropwise to a solution containing 3,5 ditert. butyl 4-hydroxy aniline (10 g, 0·04 moles) in dimethyl fermamide (50 ml). The mixture was stirred at room temperature for one hour and then precipitated from ether to give N-(3,5 ditert. butyl 4-hydroxy) phenyl maleamic acid. This compound was recrystallised from benzene (m.p. 174°C, yield 60%).

Synthesis of N-(3,5 ditert. butyl 4–hydroxy) phenyl maleimide (4th Stage)

To N-(3,5 ditert. butyl 4-hydroxy) phenyl maleimic acid (5 g, 0·015 moles) were added. Acetic anhydride (50 ml) and sodium acetate (2 g; 0·025 moles) and the mixture was heated over a steam bath for one hour. The product was filtered while hot and poured over ice. The precipitated N-(3,5 ditertbutyl 4-hydroxy) phenyl maleimide was isolated and recrystallised from benzene (m. p. 217°C, yield 48%).

Synthesis of N,N′ Di(4 Diphenyl amino) fumaramide (Antioxidant 3, A.O – 3)

The above compound was prepared by reacting fumaryl chloride with 4 amino diphenyl amine. Fumaryl chloride was prepared by refluxing maleic acid (5·8 g, 0·05 mole) with thionyl chloride (12·0 g, 0·1 mole) in benzene (100 ml) for 48 hours. The acid chloride was added to a cooled solution of 4-amino diphenyl amine (18·5 g, 0·1 mole) in dry benzene and the precipitated compound was filtered and dried.

RESULTS AND DISCUSSION

Volatility

Volatility of the antioxidants was measured for four consecutive days at 100° C. The results obtained are given in Fig. 1.

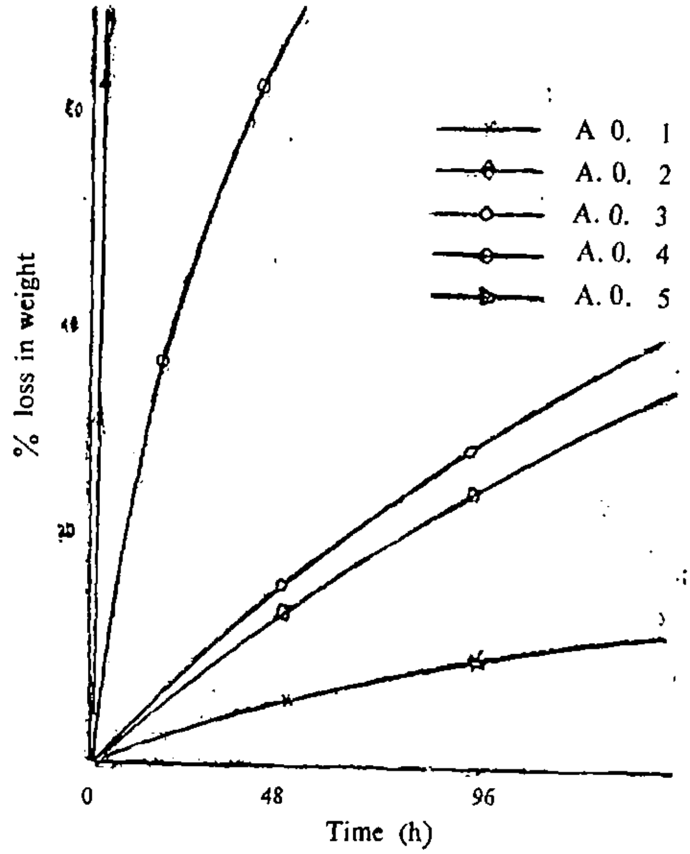


Fig. 1. *Volatility of antioxidants at 100°C*

2,6 Ditert. butyl 4 methyl phenol (Topanol OC) volatilized completely within a few minutes. 4-Isopropyl amino diphenyl amine (Nonox ZA) showed partial decomposition. There was also a colour change in the N,N′di-(4 diphenyl amino) fumaramide sample. The maleimide antioxidants were less volatile and were more stable compared to the commercial antioxidants under the condition used.

Antioxidant activity in cumene

Antioxidant activity in cumene was measured by carrying out oxygen absorption measurements at 100°C. The results obtained are given in Fig. 2.

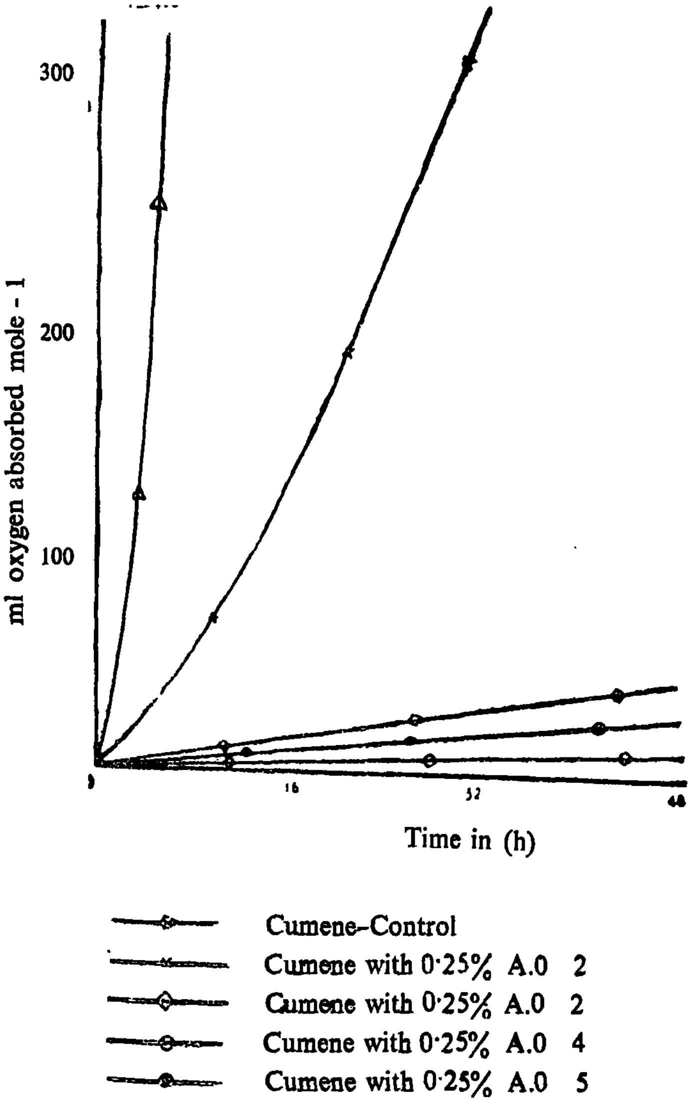


Fig. 2. *Oxygen absorption of cumene in the presence of antioxidants (100°C)*

The antioxidant activity of N-(3,5 ditertiary butyl 4-hydroxy) phenyl maleimide is comparable to the commercial antioxidants Topanol OC and Nonox ZA. The actiivity of N-(4 anilino phenyl) maleimide is found to be low in this medium.

Oxygen absorption of natsyn in chlorobenzene solution

Measurements made with 3% Natsyn solution containing 0.5 phr antioxidants at 80°C are given in Fig. 3.

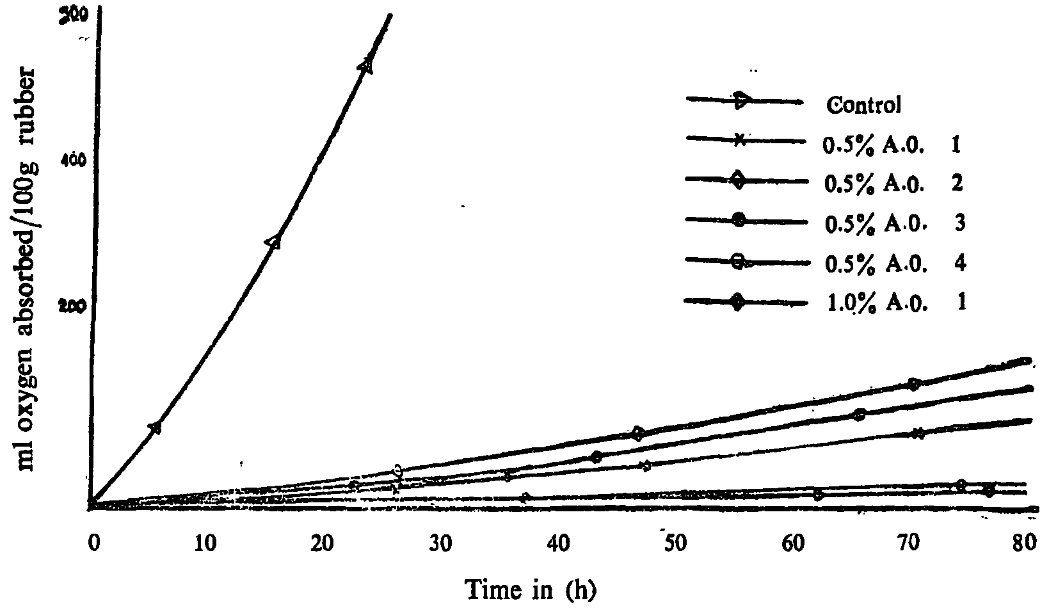


Fig. 3. *Oxygen absorption in natsyn solution*

The maleimide and fumaramide antioxidants seem to have similar activity. Nonox ZA is found to be the best of the compounds studied.

Vulcanization characteristics

The scorch time, time to reach 90% cure, maximum torque and cure rate for samples containing different antioxidants were obtained using a Monsanto Rheometer (Model R-100) operated at 140°C and are given in Table 3.

Table 3. *Vulcanization characteristics*

Type of antioxidant	*Scorch time min.*	*90%Cure time min.*	*Max. torque NM.*	*Cure rate index*
Control - on antioxidant	7·5	19·5	4·86	8·3
1% N-(4 Anilino phenyl) maleimide	12·0	32·0	4·62	5·0
1% N-(3,5 ditert'butyl 4 hydroxy phenyl) maleimide	9·5	24·0	4·86	6·9
1% NN Di (4diphenyl amino) fumaramide	8·5	26·5	5·48	5·6
1% Nonox ZA	8·5	22·0	5·47	6·6

The maleimide and fumaramide antioxidants seem to reduce the rate of cure. The vulcanizing formulation could be adjusted if faster rate of cure is desired.

Oxygen absorption of vulcanized rubber

The oxygen absorption at 85°C of the control sample and samples containing 1 phr of antioxidants are given in Fig. 4.

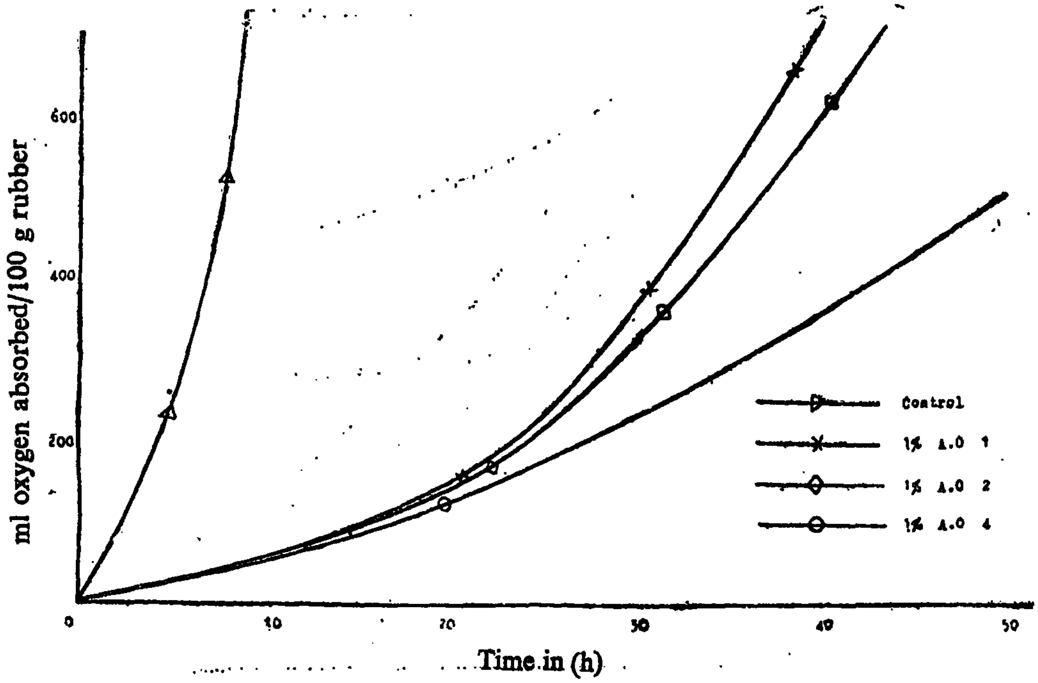


Fig. 4. *Oxygen absorption in vulcanized rubber*

Nonox ZA is found to be a little more effective in retarding the oxidation of rubber compared to the maleimide antioxidants, showing that the antioxidant activity of Nonox ZA is high compared to those of maleimide anitoxidants.

Stress relaxation.

Continuous stress relaxation measurements of vulcanized rubber samples containing 1 phr antioxidants, made at 100°C are given in Fig. 5.

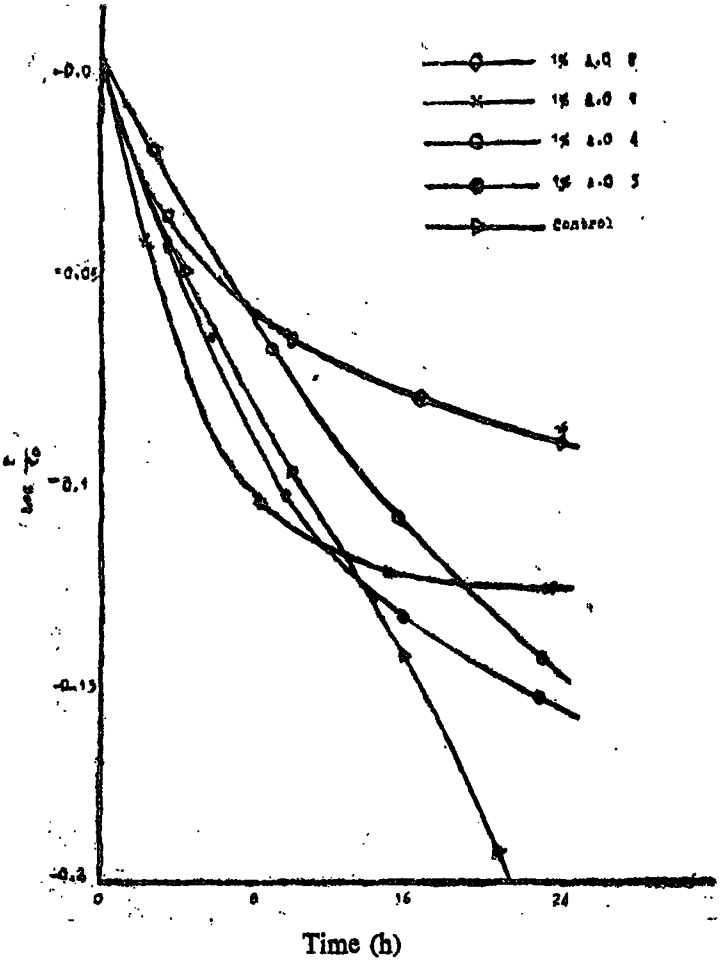


Fig. 5. *Stress relaxation of vulcanizd rubber*

The maleimide antioxidants are found to be better than Nonox ZA under the conditions used. The lower effectiveness of Nonox ZA may be due to the physical loss of this antioxidant by volatilization and decomposition at this temperature. These results could be correlated to the results obtained on volatility and indicate that the maleimide antioxidants may be suitable for high temperature applications.

Reaction of antioxidants with rubber

Table 4 shows the results obtained on solution stage reactions.

Table 4. *Reaction of maleimide antioxidants with natsyn*

Molar ratio of antioxidants to rubber isoprene units	*Percentage benzoyl peroxide*	*Percentage bound antioxidant on rubber*	*Percentage binding on antioxidant used*
N(4-Anilino phenyl) maleimide			
1 : 40	6	1·6	16·6
1 : 80	6	1·5	30·2
N (3,5 ditert-butyl 4-hydroxy phenyl) maleimide			
1 : 40	6	3·0	27·5
1 : 80	6	2.62	48·0

It is seen that the phenolic antioxidant gets bound a little more easily than the amino antioxidant. With lower percentage of catalyst, the binding efficiency was found to be still lower. The binding efficiency is reduced when the amount of antioxidant to rubber is in-creased. No observable cross linking occurred during the reaction. The oxygen absorption curve obtained with modified rubber is shown in Fig 6.

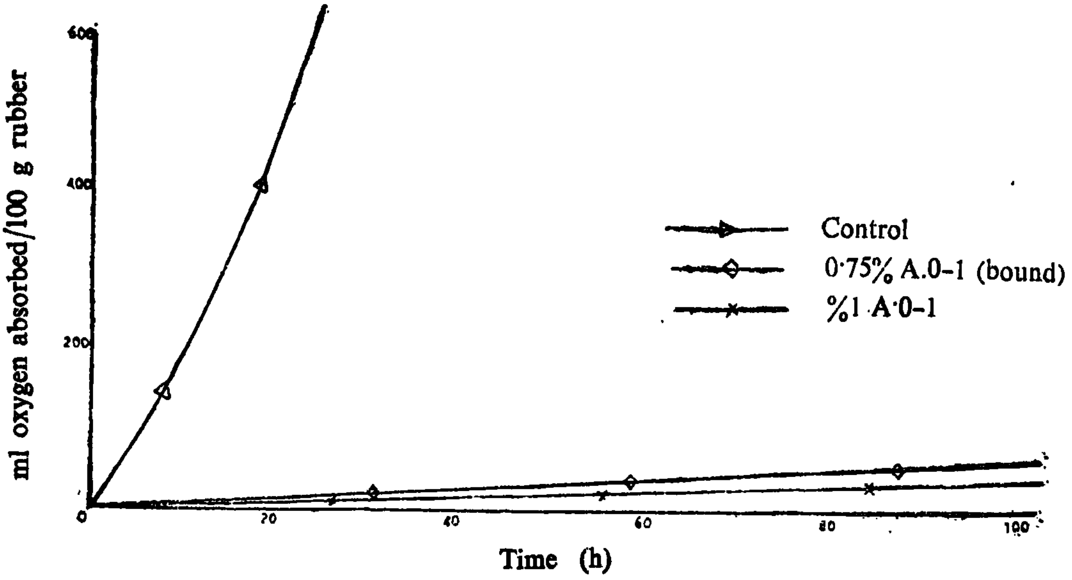


Fig. 6. *Oxygen absorption of natsyn with bound antioxidant after extraction*

These results clearly indicate that the bound antioxidant at 0.75% is quite effective in regarding the uptake of oxygen by rubber.

Further work is being carried out to find the optimum conditions for binding. Chandrasiri (1975) has shown that it is possible to bind N-(3,5 ditert. butyl 4-hydroxy phenyl) maleimide on to natural rubber by solution stage reaction and a Sri Lanka Patent application has been filed for using unsaturated groups present in maleimides and related compounds as the linking group to bind antioxidants to plolymers (Coomarasamy and Chandrasiri 1975).

Mechano-chemical reaction

The oxygen absorption curves obtained for rubber milled with N (4anilino phenyl) maleimide and subsequently vulcanized are given in Fig. 7.

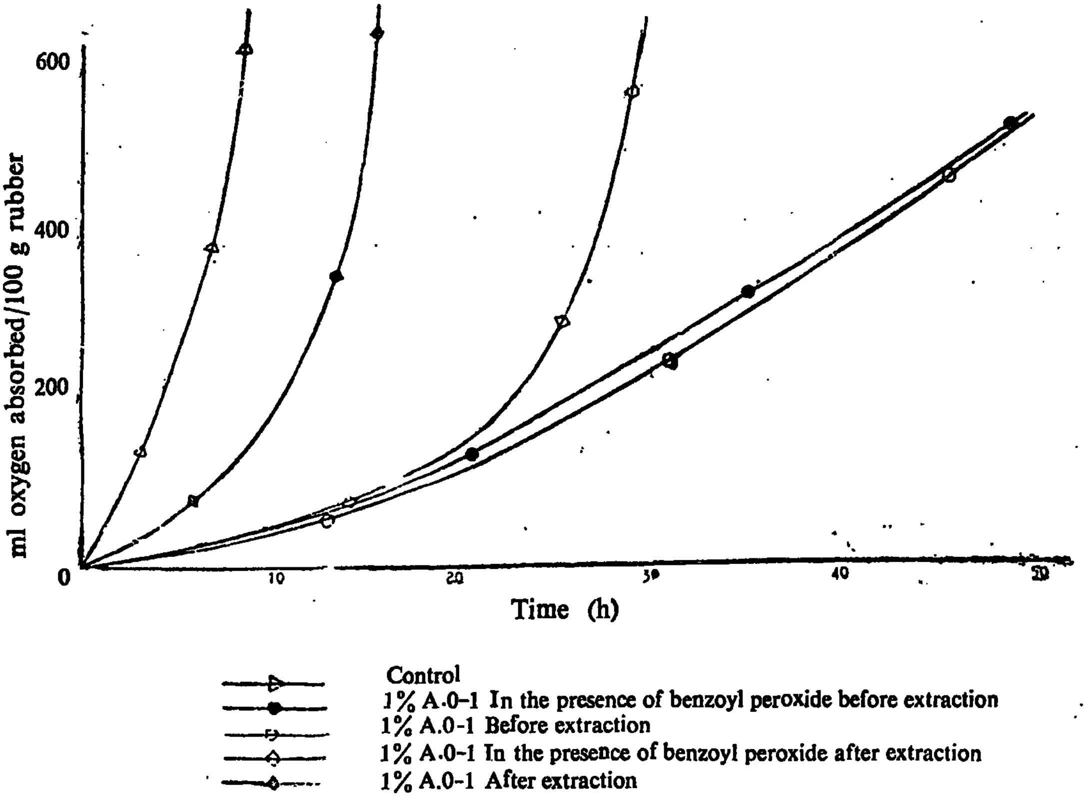


Fig. 7. *Oxygen absorption in vulcanized rubber in the presence of antioxidant 1.*

There is definite evidence of binding of antioxidant to the polymer in the presence of benzoyl peroxide. The sample prepared without the addition of benzoyl peroxide during incorporation of the antioxidant, after extraction shows very little stabilising effect.

Polymerization with methyl methacrylate

Maleic anhydride, N phenyl maleimide and N-(4 anilino phenyl) maleimide were used for polymerization with methyl methacrylate. The flow time for soulutions in acetone of the polymerization products obtained was measured using Ubbelhode suspended level viscometer. These results are given in Table 5.

Table 5. *Flow time measurement of polymerization products*

Materials used for polymerization	*Flow time*	
	3.3% solution	*10% soulution*
MMA and maleic anhydride	64 sec.	4. min. 15. Sec.
MMA and N-phenyl maleimide	47 sec.	1 min. 29 . Sec.
MMA and N-(4 anilino phenyl) maleimide	48 sec.	—
Acetone (solvent)	38 sec.	—

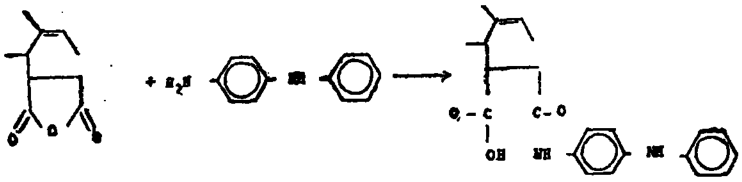
The nature of the reaction products were not fully analysed. The above solution viscosity measurements show that N-phenyl maleimide and N-(4 anilino phenyl) maleimide retarded the polymerization drastically. Work is in progress on the polymerization of these compounds with other vinyl monomers such as styrene.

Conclusions

From the results obtained it may be concluded that the inherent antioxidant activity of the antioxidants containing maleimide group are a little lower than the activity of conventional antioxidants such as 4 isopropyl amino diphenyl amine (Nonox ZA); and 2,6 ditert. butyl 4 methyl phenol (Topanol OC).

The volatilities of the maleimide antioxidants are lower compared to those of Nonox ZA and Topanol OC and therefore may be preferable for high temperature applications. Stress relaxation measurements also show that at high temperature the performance of maleimide antioxidants are better compared to the conventional antioxidants used in this study.

The results obtained on binding shows that the efficiency of binding is low especially in the case of N-(4 anilino phenyl maleimide). In a previous study, (Machado, 1975) it had been shown that maleic anhydride reacts with rubber with 80-90% conversion. One approach to increase the efficiency of binding of antioxidant grouping would be to use maleic anhydride modified rubber to attach the antioxidant functions by the following reaction (Scheme - 1).



Scheme 1. *Binding of antioxidant to modified rubber*

Similar type of reaction could also be used for the preparation of polymeric antioxidants, using copolymers of maleic anhydride and vinyl monomers.

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