J. Rubb. Res. Inst. Malaysia, **26(2)**, 76–84

Synergistic Combinations of Antioxidants for Natural Rubber Vulcanisates

MD. SALLEH NORDIN

Three combinations of antioxidants were observed to show synergistic effects in gum stock vulcanisates. The retention of tensile strength with these synergistic combinations was found to be better than that achieved by individual antioxidants after three days ageing at 100°C. The successful combinations investigated are: zinc 2-mercaptobenzimidazole with N,N'-diphenyl-p-phenylenediamine; 6-dodecyl-1,2-dihydro-2,2,4-trimethyl-quinoline with N-isopropyl-N'-phenyl-p-phenylenediamine; and 2,6-di-tert butyl-p-cresol with 4,4'-dihydroxydiphenyl.

Many factors, namely, oxygen, heat fatigue, metal catalysts, light and ozone cause deterioration in properties during ageing of unprotected natural rubber (NR). Among these factors, attack by oxygen is the most common and can lead, in extreme cases, to severe breakdown of the rubber. The oxidation process is normally initiated by either heat or light radiation and it can result in rapid deterioration of physical and chemical properties of the vulcanisates. Mechanically, the oxidation process involves three stages[1–4]:

Initiation

$$R\bullet \xrightarrow{+\,O_2} ROO\bullet$$

Propagation

$$ROO\bullet + RH \longrightarrow ROOH + R\bullet$$
$$R\bullet \xrightarrow{+\,O_2} ROO\bullet$$

Termination

$$ROO\bullet + ROO\bullet \longrightarrow \text{Non-radical products}$$
$$ROO\bullet + R\bullet \longrightarrow \text{Non-radical products}$$

Oxidation can be inhibited or retarded by antioxidants. The preventive antioxidants retard the formation of free radicals in the initiation step while chain-breaking antioxidants interrupt the propagation cycle by reacting with R● or ROO● radicals and thus introducing a new termination reaction. When the rubber article is subjected to high temperature, scission of both the network crosslinks and main chains can take place. In most cases, however, the NR vulcanisate is more susceptible to chain-scission reactions with resultant decreases in tensile strength.

Antioxidants are normally added to protect rubber products against oxidation. One useful way to increase the efficiency of antioxidants is to use mixtures of antioxidants to produce 'synergistic', *i.e.* greater than additive, effects. Furthermore, these antioxidants are normally expensive; the use of synergistic combinations gives increased protection at lower costs. This paper presents three such useful synergistic combinations of antioxidants and their efficiencies in relation to the individual components.

EXPERIMENTAL

In this work, gum mixes based on SMR 5 and a fast curing conventional system of the general formulation shown in *Table 1* were used to test the efficiency of the antioxidants.

Mixing was conducted on a heated two-roll mill (60°C–70°C) and the vulcanisates were cured to 90% cure at 140°C. The oxidisabilities/ageing of the mixes were

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TABLE 1. GENERAL FORMULATION OF GUM STOCK

Ingredient	Amount (p.h.r.)
SMR 5	100
ZnO	5
Stearic acid	1
MBTS[a]	0.75
DPG[b]	0.75
Sulphur	2.5
Antioxidant A	Variable
Antioxidant B	Variable

[a]2,2'-Dibenzothiazyl disulphide
[b]N,N'-Diphenylguanidine

studied using the percentage retention of tensile strength of the vulcanisates after they were subjected to 100°C ageing for three days. The pairs of antioxidants chosen for the study are shown in *Table 2*.

RESULTS AND DISCUSSION

Among the twelve combinations of antioxidants shown in *Table 2* only three pairs were found to give synergism in terms of tensile strength retention after three days ageing at 100°C. These are discussed in detail.

Imidazyl with Para-phenylenediamine Derivative

Zinc 2-mercaptobenzimidazole is a non-discolouring antioxidant and has the ability to protect NR vulcanisates against heat degradation. It can be easily dispersed in NR mixes and has a moderately powerful antioxidant action. N,N-Diphenyl-para-phenylenediamine is a powerful antioxidant particularly for retention of heat and flex cracking resistance but has the disadvantage of blooming.

Synergism was observed in the mixture of zinc-mercaptobenzimidazole and N,N-diphenyl-para-phenylenediamine as illustrated in *Figure 1*. The degree of protection in terms of retention of tensile strength was improved by more than 25% at the maximum level of protection in comparison to the total amount of retention of tensile strength by the individual antioxidants. N,N-diphenyl-para-phenylenediamine gave better protection than zinc 2-mercaptobenzimidazole but the level used was much higher than the blooming limit (0.35 p.h.r.) and any excessive dosages of antioxidant used are also uneconomical. However reduction in dosage of N,N-diphenyl-para-phenylenediamine of up to 0.5 p.h.r. at constant concentration of zinc 2-mercaptobenzimidazole (*i.e.* 1.0 p.h.r.) also resulted in successful retention of synergistic properties as illustrated in *Figure 2*. The synergistic effect displayed depended on the concentration of N,N-diphenyl-para-phenylenediamine but at 0.5 p.h.r. tensile strength retention was above 60%. There was slight blooming but this could be tolerated particularly in the case of black-filled compounds. When the physical appearance of the rubber articles is not important, N,N-diphenyl-para-phenylenediamine level may be increased. For light coloured compounds it is advisable to use a higher level of zinc 2-mercaptobenzimidazole.

Ketone/Amine Condensate with Para-phenylenediamine Derivative

A ketone-amine condensate which is an excellent antioxidant in respect of flex cracking resistance is 6-dodecyl-1,2-dihydro-2,2-4-trimethyl-quinoline. It is often used for dynamic applications e.g. in tyre compounding, belting, hoses; and, for mechanical goods and footwear. N-Isopropyl-N'-phenyl-p-phenylenediamine gives excellent protection against oxidation particularly against crack formation and crack growth. Rubber goods which are often subjected to dynamic stress and permanent exposure to weathering

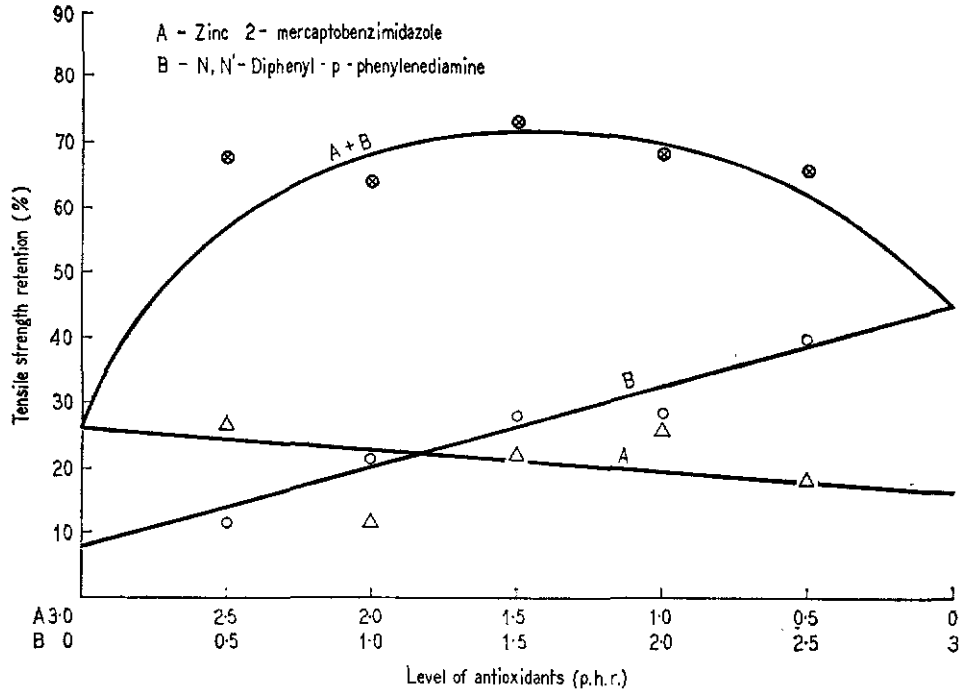


Figure 1. Synergistic combination of imidazyl with para-phenylenediamine derivative.

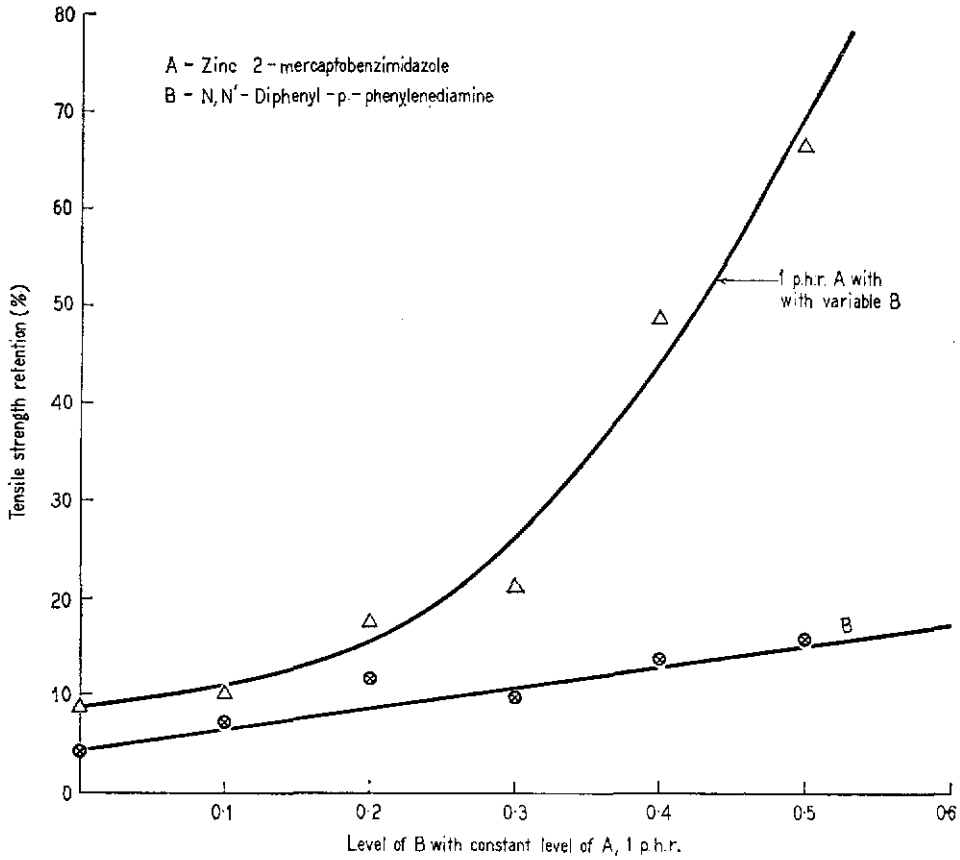


Figure 2. Synergistic combination of imidazyl with para-phenylenediamine derivative.

TABLE 2. PAIRS OF ANTIOXIDANTS STUDIED

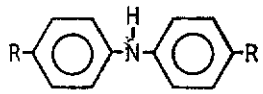
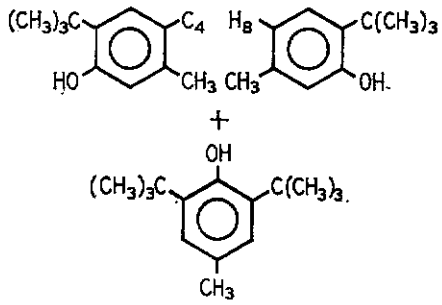
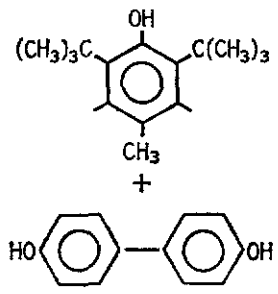
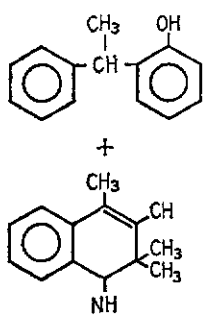
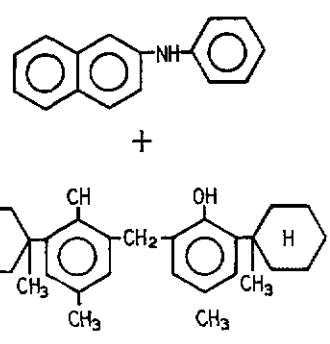
Combination of antioxidants	Molecular structure
Polycarbodiimide + Diphenylamine-derivative	
4,4'-Butylidene-bis-(2-tert butyl, 5-methyl phenol) + 2,6-Di-tert butyl-p-cresol	
2,6-Di-tert butyl-p-cresol + 4-4'-Dihydroxydiphenyl	
Styrenated phenol + Polymerised 2,2,4-trimethyl-1,2-dihydroquinoline	
Phenyl-beta-naphthylamine + 2,2-Methylene-bis-/6-(alpha-methyl cyclohexyl)-p-cresol	

TABLE 2. PAIRS OF ANTIOXIDANTS STUDIED (CONTD.)

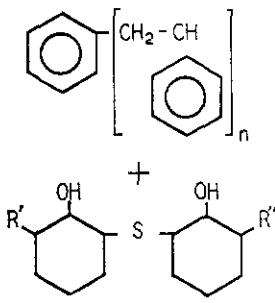
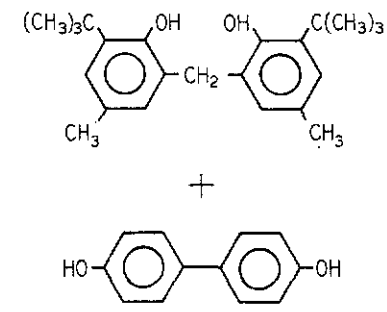
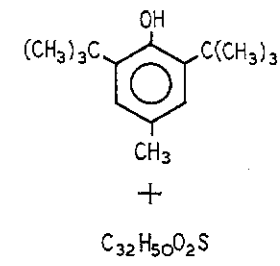
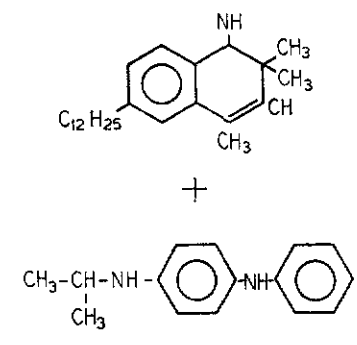
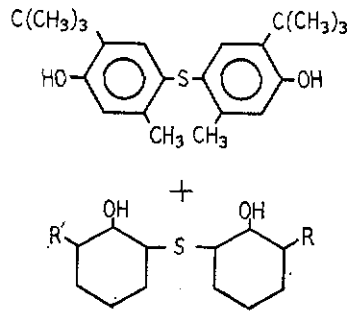
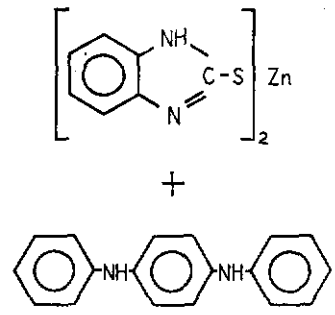
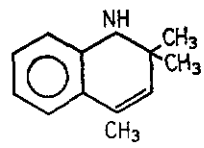
Combination of antioxidants	Molecular structure
Mixture of styrenated phenol + Phenolic sulphide	
2,2'-Methylene-bis-(4-methyl,6-tert butyl phenol) + 4,4'-Dihydroxy diphenyl	
2,6-Di-tert butyl-p-cresol + 4,4'-Thio-bis(di-sec-amyl phenol)	
6-Dodecyl-1,2-dihydro-2,2,4-trimethyl-quinoline + N-Isopropyl-N'-phenyl-p-phenylenediamine	

TABLE 2. PAIRS OF ANTIOXIDANTS STUDIED (CONTD.)

Combination of antioxidants	Molecluar structure
4-4'-Thio-bis-(6-tert butyl-m-cresol) + Phenolic sulphide	
Zinc 2-mercaptobenzimidazole + N,N'-Diphenyl-p-phenylenediamine	
Polymerised 2,2,4-trimethyl-1,2-dihydroquinoline + Benzofurane derivative	

and ozone can be efficiently protected by N-isopropyl-N-phenylenediamine.

Individually they do not give very good resistance to heat ageing as shown by the tensile strength retention which does not exceed 10%. Satisfactory synergistic effects against heat ageing were clearly displayed by 0.75/0.75 and 0.5/1.0, 6-dodecyl-1,2-dihydro- 2,2,4-trimethyl-quinoline/N-isopropyl-N-phenyl-p-phenylenediamine as illustrated in *Figure 3*. With equal parts of these two antioxidants the heat ageing resistance measured by tensile strength retention improved dramatically (50% retention of tensile strength as against 10% for the individual components).

Mechanistically, 6-dodecyl-1,2-dihydro-2, 2, 4-trimethyl-quinoline is capable of slowing the initiation process and N-isopropyl-N-phenyl-p-phenylenediamine of reacting with either RO or ROO free radicals to interrupt the propagation cycle and thus retard the oxidation process. The synergism is probably the consequence of these two reactions[1,5]. Blooming was not observed, thus this combination is ideal for coloured

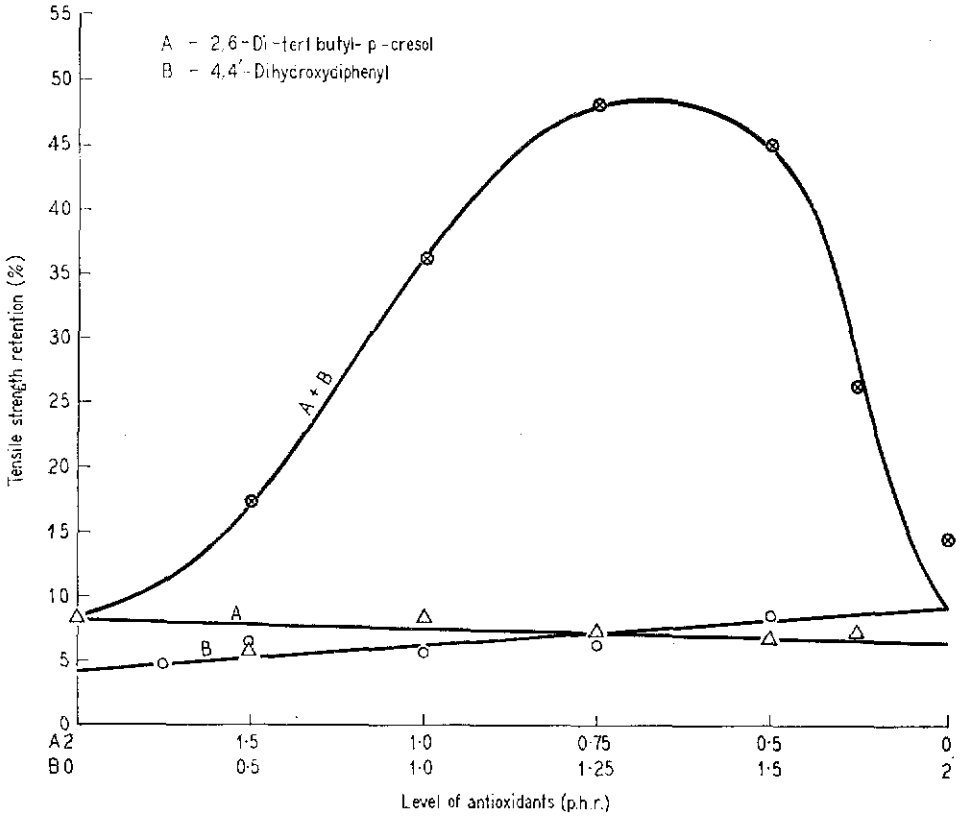


Figure 3. Synergistic combination of ketone/amine condensate with para-phenylenediamine derivative.

articles used under static and dynamic conditions.

Two Substituted Phenols

The degree of protection with phenolic antioxidants compared with amine antioxidants is much less in many aspects of degradation. Phenolic antioxidants are mainly suitable for latex and coloured products where staining and blooming are usually not tolerable. 2-6-Di-tert butyl-p-cresol is a non-staining antioxidant and is harmless when in contact with foodstuff. 4,4-dihydroxydiphenyl is an odourless and also non-staining antioxidant and is suitable for stocks which come into contact with foodstuff. It is also suitable for latex goods and sulphur chloride vulcanisates for providing resistance against oxidation and minimising overcure effects. It is recommended for NR articles such as mechanical rubber goods and fabric coating.

The combination of 2,6-di-tert butyl-p-cresol with 4,4-dihydroxydiphenyl showed a significant synergistic effect as illustrated in *Figure 4*. The synergistic effect seems to be prominent at 0.75 2,6-di-tert butyl-p-cresol to 1.25 4,4-dihydroxydiphenyl. 4,4-dihydroxydiphenyl is a non-hindered phenolic antioxidant which could donate a hydrogen

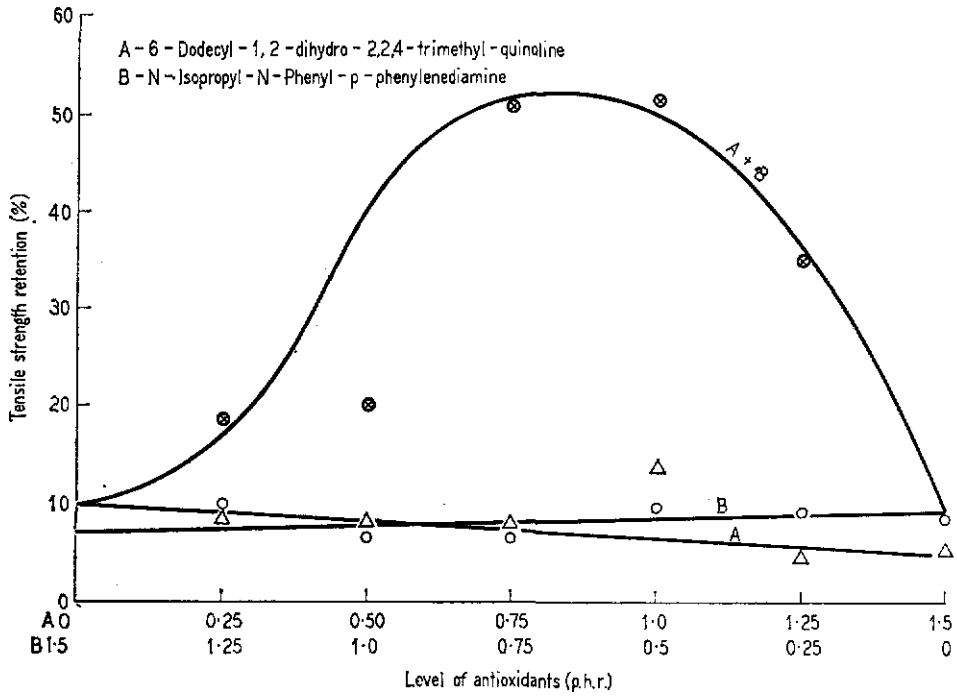
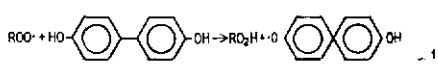


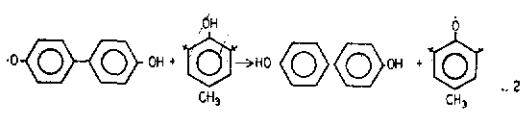
Figure 4. Synergistic combination of two substituted phenols.

atom to the radicals propagating the oxidation process:



...1

2,6-Di-tert butyl-p-cresol is a hindered phenolic antioxidant which can react with the non-hindered phenolic antioxidant radical and regenerate the non-hindered phenolic antioxidant:



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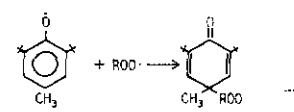
The hindered phenoxy radical can then react rapidly with a second ROO● to give a 2,6-di-tert-butyl-4-alkylperoxycyclo-hexdienone:



...3

Synergism occurs because the steady-state concentration of the non-hindered phenoxy radical is reduced and the non-hindered phenolic antioxidant is regenerated by reaction with the hindered phenol[5].

CONCLUSION

Three combinations of antioxidants which showed synergistic effect were: an imidzyl and ketone/amine condensate with para-phenylenediamine and a pair of two substituted phenols. The combination of imidazyl

and para-phenylenediamine derivative war the most effective compared with the othes two combinations in terms of retention of tensile strength during oven ageing. There was a disadvantage of blooming in the case of para-phenylenediamine. The protection given by individual phenolic antioxidants is too low; the retention of tensile strength after ageing is less than 10%. Combination of two particular phenolic antioxidants can successfully give at least 45% retention in tensile strength.

ACKNOWLEDGEMENT

The author would like to thank Dr C.T. Loo for his guidance and help during the work and in the preparation of this paper. A special word of appreciation is due to Mr D. Ganeson for assisting in most of the experimental work.

Rubber Research Institute of Malaysia
Kuala Lumpur *August 1978*

REFERENCES

1. PARKS, C.R. AND SPACHT, R.B. (1977) Antioxidants in Compounding. *Elastomerics*, **109(5)**, 25.
2. REID SHELTON, J. (1972) Review of Basic Oxidation Processes in Elastomers. *Rubb. Chem. Technol.*, **45**, 359.
3. DUNN, J.R. (1974) Review of Unsolved Problems in the Protection of Rubber Against Oxidative Degradation. *Rubb. Chem. Technol.*, **47**, 960.
4. BELL, C.L.M., CAIN, M.E., ELLIOTT, D.J. AND SVAILLE, B. (1966) Recent Studies in the Aging of Natural Rubber. *Kautsch Gummi*, **19**, 133.
5. HOWARD, J.A. (1974) Autoxidation and Antioxidant Basic Principles and New Developments. *Rubb. Chem. Technol.*, **47**, 976.