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NON-SULPHUR VULCANIZATION OF RUBBER – A BRIEF OVERVIEW

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Abstract. There are two types of non-sulphur vulcanization system for natural rubber (NR) that will be briefly disscussed here, peroxide vulcanization and urethane vulcanization. The peroxide and urethane systems do not offer a compromise, they have their own problems. They are alternative systems that are able to meet specific requirements. Outstanding characteristics of peroxide system are low permanent set and thermal stability. Urethane based vulcanisates provide the technologist with much improved fatigue on ageing, excellent bondability, chemically resistance and immune to temperature of cure where NR is called upon to meet the ever increasing demands put upon it by service conditions.

Keywords: vulcanization, crosslink, *Novor*, resistance, fatigue, ageing, modulus.

1.0 INTRODUCTION

Rubberlike materials have long been of extraordinary interest and importance. They find usage in items ranging from automobile tires to heart valves and gaskets in supersonic jet planes. The striking nature of their elastic properties and their relationships to molecular structure has attracted the attention of numerous chemists, physicists, technologists and engineers interested in structure-property relationships, particularly those involving polymeric materials.

Vulcanization is the process by which plastic rubber is converted into the elastic rubber or hard rubber state. The process, which is brought about by the linking of macromolecules at their reactive sites, is also known as crosslinking. Vulcanizing agents are substances that bring about the actual crosslinking process. The properties of the vulcanised rubber are influenced by the course of vulcanization. In particular the modulus, hardness, elastic properties and resistance to swelling are considerably modified during the course of vulcanization. The extent of the changes is governed by the choice of the vulcanization ingredients added to the rubber to bring about the vulcanization process and also by the vulcanization conditions. Other properties, such as tensile strength, gas permeability, low temperature flexibility and electrical resistance, change less with the degree of vulcanization. To obtain rubber products with the best possible properties, it is therefore always necessary to use the most suitable combination of vulcanization ingredients and the most suitable vulcanization conditions subjected to the application concerned.

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2.0 SULPHUR VULCANIZATION

It is well known that the properties of a vulcanizate depend on the crosslinking system but that, irrespective of the vulcanization system, the tensile strength of the network passes through a maximum as the crosslinking density is increased, Greensmith, Mullins and Thomas [1]. Over a wide ranges of crosslink densities, vulcanizates prepared by conventional vulcanization (CV) and containing mostly polysulphidic crosslinks, have higher tensile strengths than vulcanizates prepared by efficient vulcanization (EV) formulations and which contain mainly monosulphidic crosslinks.

CV system for natural rubber based on high accelerator and low sulphur levels give vulcanizates with excellent initial properties in terms of fatigue performance, but they also revert easily, especially at high temperatures, and they cannot be protected well against oxidative ageing, Baker [2]. Efficient vulcanization which considerably more reversion resistant and can be protected well against ageing, was introduced to overcome these disadvantages. However, these vulcanizates exhibit poor initial properties and are difficult to bond to metals.

In absence of any ideal all-around vulcanizing system, non-sulphur vulcanizing system have provided an acceptable compromise which could combine the high initial properties obtained from a conventional cure system with the reversion resistance and oxidative ageing of EV system.

3.0 PEROXIDE VULCANIZATION

In theory, peroxide vulcanization, giving simple carbon-carbon crosslinks, (Greensmith, Mullins and Thomas [1]) should provide a close to ideal crosslinking system with good heat resistance. However, in practice the system have a number of disadvantages such as scorch times are short and cure times are long. Furthermore, many antioxidants, particularly p-phenylenediamines, interfere with peroxide vulcanization such as reducing efficiency. A study shows that the better antioxidant cause the greatest reduction in crosslinking density, Baker [2]. Another disadvantage is in unaged vulcanizates properties, both tensile and tear strength are inferior to conventionally cured NR vulcanizates and tension fatigue lifetimes are slow.

Abrasion resistance is also inferior to conventional sulphur cure and the used of dicumyl peroxide imparts unpleasant odour to the vulcanizates. The advantages of peroxide systems lie in excellent reversion resistance, good oxidative ageing resistance and improved high temperature set properties (Figure 1).

The problem of the slow vulcanization characteristic of peroxide can be overcome by increasing their concentration in the mix. Since the system is non-reverting, vulcanizates of the same modulus can be obtained by the used of increased concentration of dicumyl peroxide with shorter cure times. However, traces of peroxide that are still present in the vulcanizates capable of initiating oxidation, and lead to poor ageing performance. And at the same time, it will also have an effect on high temperature compression set, since it will continue to cure at $1000^o C$. Thus, it would be unsatisfactory to shorten cure time unless ageing and high temperature set properties are unimportant.

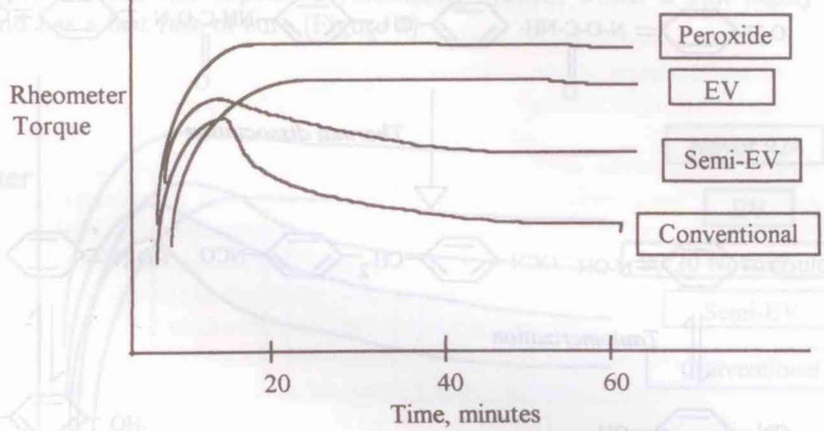

Fig. 1 Reversion resistance of peroxide vulcanisates at 180°C compared to sulphur systems

Studies, Baker [3] on the properties of 50 parts HAF black-filled vulcanizates with various concentration of dicumyl peroxide cured at 1 hour and 2 hour indicated a noticeable properties difference between cures. In initial properties this result in lower tensile strengths accompanied by several other minor changes such as reduced abrasion resistance at higher peroxide concentration, better heat build-up performance, and inferior compression set. It does improve ageing however with significantly better retention of tensile strength and modulus. Thus, if the optimum ageing performance is to be achieved with peroxide cures, longer cure times are desirable, but at the expense of initial vulcanizates properties. Many attempts (Greensmith, Mullins and Thomas [2], Elliot and Tield [4]) have been made at delayed action peroxide systems to minimize the scorch problem. One method to introduce a scorch delay is to use a suitable scavenges, such as a nitroso compound, which will remove reactive radical by converting them to the more unreactive nitroxides. But, the removal of radicals also reduces crosslink density.

4.0 URETHANE VULCANIZATION

The reagents are adducts of the oxime form of the p-nitrosophenol and a diisocyanate which at vulcanizing temperature dissociate in the rubber into their component species. The nitrosophenol so produced adds into the rubber chain to give pendant aminophenol groups which are linked up by the diisocyanate also generated, this is almost entirely via the amino group thus giving a thermally stable urea-urea type crosslink. The system that will be discussed here which using the urethane basic principle, is the new urethane or *Novor*, a technical acronym *from NitrosO Vulcanization* of Rubber system [5]. The basic principles of the urethane vulcanization system is shown in Figure 2.

5.0 *NOVOR* 924

The *Novor* 924 formulation in general used, (Chen and Yeoh [5]) contains 6.7 parts *Novor*, 2 parts zinc dialkyl dithiocarbamate, 3-5 parts calcium oxide drying agent and 2:2 parts ZMBI:TMQ protect system. The dithiocarbamate acts as a catalyst for the nitroso addition reaction and a calcium oxide type drying agent ensures that there is a hydrolysis of the

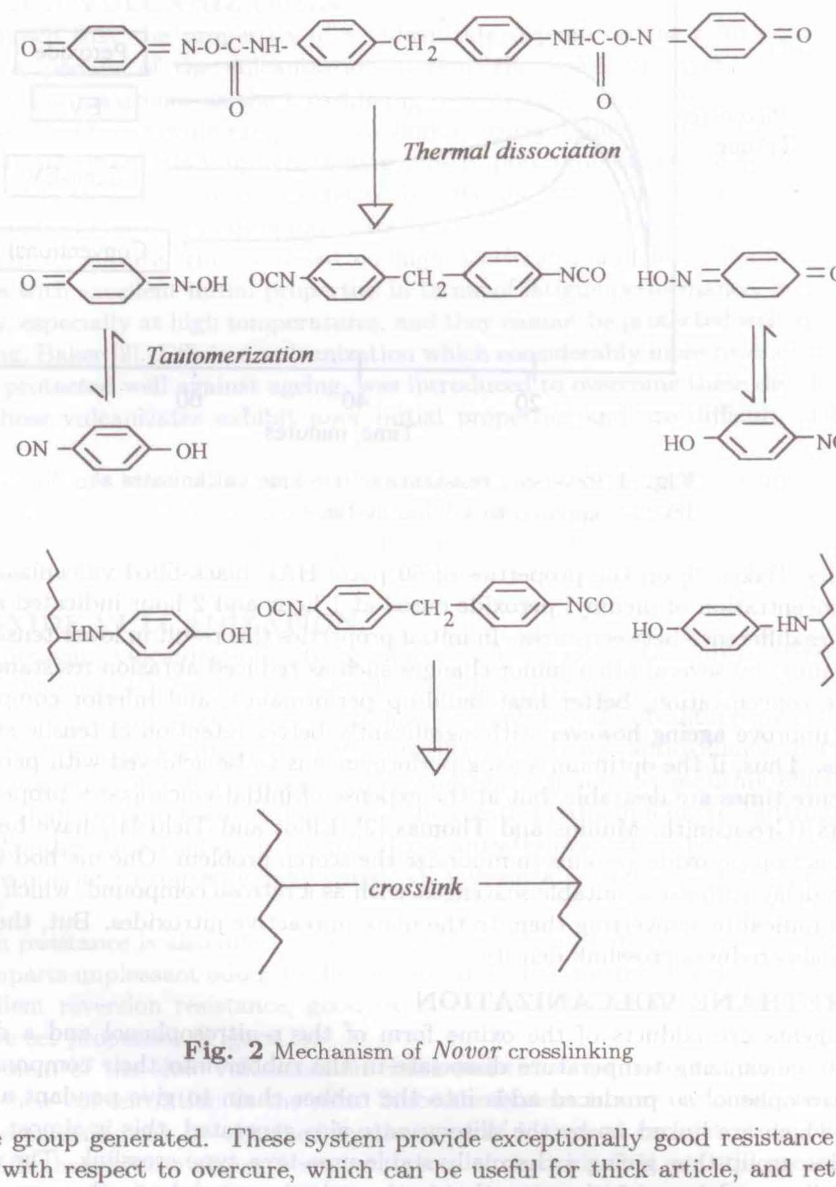

Fig. 2 Mechanism of *Novor* crosslinking

isocyanate group generated. These system provide exceptionally good resistance to heat, especially with respect to overcure, which can be useful for thick article, and retain their properties well on air oven ageing or in service, with an added advantage of improved fatigue with time. The unaged fatigue of *Novor* vulcanizate usually lies between that of EV and semi-EV systems, Baker [3] but on ageing show an improvement with no change in modulus. Therefore, the *Novor* system may be of particular use in application where a combination of heat resistance and fatigue performance is important.

Applications are where the very best reversion resistant NR compound are required, for example curing bags and heating pads, engine mounts and in bushes and flexible couplings where the heat resistance fatigue combination is needed. It has been found ([Baker [2], Baker

[3]) that when *Novor* systems are mixed with sulphur systems a high degree of synergism occurs to give a much less expensive vulcanizing system, which is still highly reversion resistant and has a fast rate of cure (Figure 3).

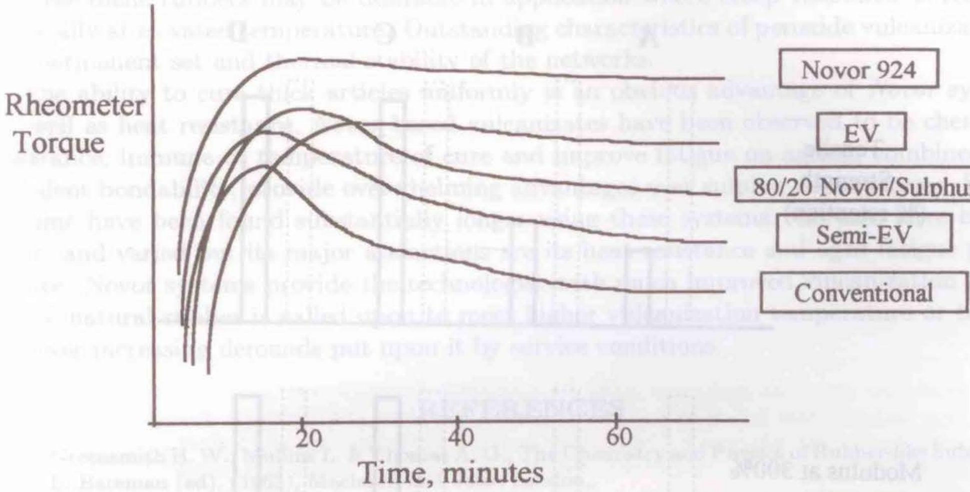

Fig. 3 Reversion resistance of 80/120 mixed sulphur vulcanizates at 180^oC compared to all-*Novor* 924 and sulphur systems

6.0 MIXED *NOVOR*-SULPHUR SYSTEMS

Novor/sulphur systems can be blended in any proportion from 90:10 to 10:90 *Novor*:sulphur according to the degree of reversion resistance and rate of cure required. However it has been found, (Chen and Yeoh [5] and Baker [6]) that ageing resistance is virtually unaltered by blending with the sulphur system with an 80:20 system. This has virtually identical retention of tensile strength as the all-*Novor* system, and shows a small modulus increase as against the slight loss with the *Novor*, (McClune [7]). These systems offer a high degree of reversion resistance, excellent ageing and faster rate of cure at a much reduced cost. Another advantages of the mixed systems are improvement in fatigue on ageing, and is immune to temperature of cure (Figure 3 and 4).

By far, the most widespread use (Willis [8]) of *Novor*/sulphur mixed system is in engineering applications. Thus, *Novor*/sulphur mixed systems are very suitable for the general field of bushes, coupling, and mounts. With the ever increasing demand by motor manufacturers for engine and exhaust mounts with better heat resistance the *Novor* systems offer a new spectrum of formulations for such applications. Many of these applications utilize injection moulding on account of their immunity to temperature cure. Another major application area is in a solid tyres on account of their tendency to give vulcanizates with higher hardness. *Novor* system has the ability to cure thick article uniformly on account of reversion resistance. And finally *Novor* mixed system can be used in various belting application.

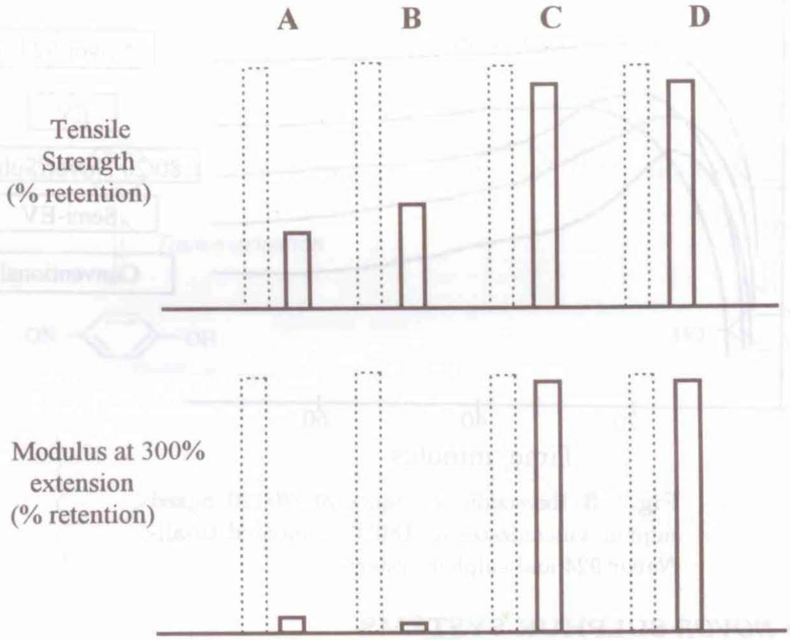

Fig. 4 Air-oven ageing performance 80/20 mixed *Novor*/-sulphur vulcanisates at 100^oC compared to all-*Novor* and sulphur systems; Unaged Aged 7 days at 100^oC. (A) Conventional sulphur (B) Semi-EV (C) *Novor*/Sulphur 80/20 and (D) *Novor* 924

7.0 *NOVOR* 950

The possible detection of toluene diisocyanate (TDI) from *Novor* 924 cures brought about the developement of a new *Novor* crosslinker based on methylene bis(4-phenylisocyanate) or MDI, as the diisocyanate moiety in the urethane adduct (Baker [2], Baker [6]). As well as exhibiting a very substantially lower vapour pressure than that of TDI, the MDI present in the adduct is stoichiometric amount for the crosslinking step, and thus has no cause to become eliminated in the reaction. In the preliminary testing in all-*Novor* system Baker [6], no significant difference could be detected between the *Novor* 924 and 950 in terms of scorch, efficiency and ageing in the standard HAF black fomulation.

Moreover, it was found that the reversion resistance is identical to the TDI adduct. Following this discovery, *Novor* 950 has been extensively examined in a series of formulation for commercial use, and a completely satisfactory results were obtained with a direct substitution of *Novor* 950 for *Novor* 924.

8.0 SUMMARY

Peroxides are importance mainly because of their ability to crosslink elastomers that contain no sites for attack by other types of vulcanizing agents. Elastomers derived from isoprene and butadiene are readily crosslinked by peroxides. However many properties are inferior to those of vulcanizates cured by accelerated sulphur. Nevertheless, peroxide vulcanizates of these diene rubbers may be desirable in application where creep resistance is required, especially at elevated temperature. Outstanding characteristics of peroxide vulcanizates are low permanent set and thermal stability of the networks.

The ability to cure thick articles uniformly is an obvious advantage of *Novor* systems. As well as heat resistance, *Novor* based vulcanizates have been observed to be chemically resistance, immune to temperature of cure and improve fatigue on ageing, combined with excellent bondability, provide overwhelming advantages over sulphur cure systems. Service lifetime have been found substantially longer using these systems. Its uses have become many and varied but its major attractions are its heat resistance and aged fatigue performance. Novor systems provide the technologist with much improved vulcanization system where natural rubber is called upon to meet higher vulcanization temperature or to meet the ever increasing demands put upon it by service conditions.

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