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RESEARCH AND THE IMPROVEMENT OF TYRE PERFORMANCE

By

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SUMMARY

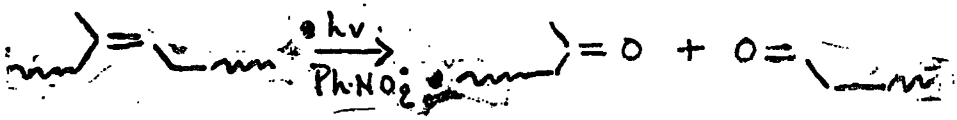
The impact of two new methods of vulcanization and other recent advances such as liquid rubbers and thermoplastic elastomers on tyre performance is considered. The development of a natural rubber tyre which has better grip and wear resistance on ice and hard packed snow than its synthetic rubber competitors is described.

The importance of tyres as a major outlet for natural rubber (NR) has long been recognised, and the study of tyres and the properties affecting their performance has always been part of the research programme of the Association. Tyres will continue to be the major market for NR for many years, and there remains much work to be done to ensure that the greatest possible share of this still rapidly expanding market is obtained by NR. The important properties for rubber in tyres are: wear, skid, heat build-up (*i.e.* the temperature attained in the interior of the tyre during running) and various forms of cutting and tearing behaviour. Their relative importance varies with the operating conditions and with different types of tyre. For example, with passenger car tyres the most important considerations are wear and skid resistance, but with large tyres heat build-up is the most important factor, and with off-the-road tyres in addition to heat build-up, failure is often caused by cutting, tearing and flaking. This paper gives a brief account is several aspects of research at MRPRA which are either directly or indirectly concerned with improving NR's position in the tyre field.

Liquid Rubber

Almost all the synthetic rubbers can be readily produced in a low-molecular-weight, liquid form by control of the polymerisation of the monomer. If at the same time terminal and/or pendent reactive groups such as—OH,—COOH,—NCO,—SH, or —Cl are introduced, these liquid polymers can be chain extended and crosslinked by the addition of suitable di-and poly-functional reagents to give vulcanizates. An obvious advantage of such methods would be the ready shaping of the vulcanizate by casting techniques. There is considerable interest in the "cast tyre" primarily from the economics of tyre manufacturing. Elimination of most of the traditional steps in tyre manufacture would be of considerable benefit to a tyre manufacturer, provided the materials used are economically viable. All tyre manufacturers (world wide) are doing some work in this area, because of the potential economic prize. The most advanced example is the Firestone cast tyre (FCT) (Alliger, 1972). Although Firestone have claimed that the FCT has many excellent qualities other tyre manufacturers do not as yet regard it as a serious threat to conventional methods of manufacture. Nevertheless although the FCT and liquid forms of the general purpose elastomers (Daniel, 1971) do not *at present* appear to offer a serious challenge to NR, (mainly because of their high cost and poor final properties) the MRPRA is exploring the possibility of having a liquid NR available should it ever be needed. Depolymerised NR, known for many years, does not have the regular pattern of functional groups needed for chain extension and when vulcanized by conventional methods has poor physical properties.

Advantage has been taken of a photochemically induced cleavage of the double bonds of NR by nitrobenzene to produce a material of average molecular weight as low as 3000 and terminated by carbonyl end groups.



The regular microstructure of the NR chain is retained and therefore chain extension with a bi-functional carbonyl reagent such as a bis-hydrazide followed by conventional crosslinking should, in theory, yield a vulcanizate with the normal excellent properties. In practice, chain scission has been efficiently achieved in solutions of NR and also, but more slowly, in latex. The resulting liquids have been chain extended to solid rubbers which in turn have given vulcanizates with reasonably satisfactory but not perfect physical properties (Saville & Cutts). Much development work would still be required to place the process on a viable commercial basis.

Thermoplastic Elastomers

Synthetic thermoplastic elastomers as their name implies are materials which flow at high temperatures and reform as "vulcanizates" on cooling. Such properties simplify processing since they eliminate compounding and of course reduce manufacturing costs. Thermoplastic elastomers are without exception block or graft polymers and owe their unique properties to the association of segments of their molecules into hard 'glass-like' domains to serve as physical crosslinks for the rubbery segments and to some extent as self-reinforcing filler particles. At high temperatures, these domains melt and allow the rubber to flow as a thermoplastic material but reform on cooling to the rubber again (Allport & James, 1973). Such materials are expensive (from 1.5 to 7 times the price of NR) and their properties are by no means ideal but should they undergo significant improvement they will undoubtedly encroach on conventionally processed elastomers in many applications.

It is a challenging problem to produce a thermoplastic NR as the sophisticated molecular engineering used in the polymerisation of the synthetic materials is not possible with a pre-formed natural polymer. MRPRA chemists have formulated a quite new concept—that of vulcanizing NR by special types of crosslinks which are strong ('closed') at ambient temperature but which break ('open') at high temperature and reform as the temperature falls. This would allow the desired reversible transformation from elastic to plastic state and should have the advantage of giving vulcanizates of NR possessing quite normal physical properties at service temperatures. Good progress has been made towards this target and a crosslink having the correct dependence on temperature for breaking and reformation has been achieved together with an, at present, slightly inefficient method of modifying NR with the necessary pendent groups for crosslink attachment (Campbell, 1973). Crosslinking efficiency is high and the vulcanizates have a degree of remouldability limited by the intrusion of permanent crosslinks arising in an unknown manner at remoulding temperatures. The science has advanced sufficiently far to say that the ideal technology is conceptually possible. Clearly, this would demand that the attachment of reactive pendent groups to NR and the introduction of thermally labile crosslinks be carried out in latex within the cost margins allowed by the price of synthetic thermoplastic elastomers and the product sold as a free-flowing vulcanizate ready for remoudling by the consumer.

Urethane Vulcanization

In this method of vulcanization, no sulphur compounds are involved, the vulcanizing agent is a urethane, formed from a nitrosophenol and a di-or polyisocyanate (Baker *et al.*, 1970). The chemical principle of its operation is as depicted below (Fig. 1). These di-urethanes are stable, light-coloured solids which can readily be incorporated into rubber using conventional techniques. Under vulcanizing conditions, preferably at 140-160°C, the di-urethane dissociates into its two components. The free nitrosophenol reacts with the rubber chains forming pendent aminophenol groups which are then crosslinked by the di-isocyanate. The physical properties of the vulcanizates generally similar to those obtained from the best sulphur systems (Table 1). The advantage lies in the high stability of the crosslinks so that very little modulus reversion takes place, even on extreme overcure and resistance to oxidative ageing is excellent. In some properties, for example, dynamic fatigue resistance urethane vulcanizates appear to be superior to all types of sulphur vulcanizates.

Urethane vulcanization is now in its final stages of development. Licences for the world-wide manufacture and sale of the vulcanizing reagents have been granted to Hughson Chemical Co., U.S.A. and to Sumitomo Chemical Co., Japan, and these licencees are themselves putting a considerable effort into the exploitation of the many variations of which the system is capable. The urethanes can be used to vulcanize some synthetic rubbers but it is to NR that they impart special advantages and a further competitive edge over rival materials. They may prove beneficial in several areas an important one which is described later is in the carcass and tread base of heavy-duty tyres—an application in which much NR is used.

Winter Tyres and Ice Friction

The friction between tyres and the road is adequate for most driving conditions on dry or wet roads. On ice covered surfaces however, the friction coefficient is frequently only one tenth of that on dry roads. Mechanical aids such as chains and studs have been used for many years to improve grip but chains are inconvenient to fit and give a rough ride on roads not covered by snow, and studs are made from very hard materials which cause serious damage to road surfaces. The problem is so acute that studs have been banned in some areas of Canada and U.S.A., and they are a growing problem in Europe. There is, therefore, a real need for tyres with improved friction on ice and they would make a significant contribution to road safety. Our approach to the problem of increasing the friction between tyres and ice has been to investigate the effect of the type of rubber in the tread on the friction coefficient. We have not been concerned with improving tread design because tyre manufacturers have concentrated their efforts in this area and any improvement is likely to affect all rubber compounds equally.

Skid was first studied in our laboratory using a Pendulum skid tester(Giles, 1965). Typical results are shown in Fig. 2 where it can be seen that NR has the highest friction on ice followed by oil extended natural rubber (OENR), and oil extended styrene butadiene rubber blended with butadiene rubber (OESBR/BR) of the type normally used in winter tyres. On wet concrete the ranking is changed—NR is worst and the other two compounds are almost identical (Southern, 1973). A good compromise is the OENR which is as good as the synthetic blend on wet concrete and better than the synthetic blend on ice. This illustrates an important feature which often arises when developing new tyre compounds. Due regard must be given to changes which occur in other important properties. A compromise is necessary, in this case to ensure good wet skid resistance and good ice skid resistance. These results led to three full scale trials (2 in Sweden and 1 in Norway) during the last few winters, using tyres with NR treads. From these results it was concluded that the grip of OENR tyres whether of cross ply or of radial construction on ice and hard packed snow, is superior to that of conventional OESBR/BR treads. The most recent and comprehensive set of data using a variety of methods, show an average improvement of 15% for OENR over OESBR/BR (Fig. 3). This was the result of over 200 tests on each compound, each test consisting of several measurements of the coefficient of friction; these large numbers of tests are necessary because of the variability of ice. In some circumstances the OENR tyre without studs may be better than an OESBR/BR tyre with studs, although studs can be beneficial to all compounds (Grosch, 1967). Furthermore, the wear resistance of OENR treads is better than that of OESBR/BR treads at low tyre surface temperatures, such as are encountered under winter conditions (Grosch, 1967; Schallamach, 1968). Thus NR has two important advantages over SR under winter conditions, and there is no doubt that winter driving would be safer if the tread compound is made from OENR.

Tyres made to our formulations have been tested for the past two winters on car fleets in Canada, the U.S.A. and Europe. Furthermore, we know that as a result of our work, many of the worlds tyre manufacturers have carried out their own winter tyre tests with OENR. Last year one small manufacturer (Mansfield, Denman & General in Canada) commenced marketing OENR winter tyres. Next year we know that a large manufacturer in Europe is going to produce OENR winter tyres. Tyre factories in Eastern Europe (Poland, East Germany and Czechoslovakia) are producing tyres from OENR and retreaders in Italy are using OENR for winter tyres. Thirty five million winter tyres were sold in the U.S.A. last year, and the potential world market is about 80,000 tons of rubber per annum.

Future Developments in Ice-Friction

Although it now appears that some sectors of the tyre industry will be making winter tyres from OENR, nevertheless we are not satisfied that our OENR formulation is the best that can be obtained from NR in this respect. Consequently we are continuing to carry out research on ice-friction, and recent laboratory work (Southern & Walker, 1972) has shown that the friction of rubber on ice is not necessarily as low as common experience suggests. Unfilled rubbers were used in these experiments which were designed to elucidate the mechanism of the friction of rubber on ice. It was found that the nature of the ice has a profound effect on the results. Initially, the results on fresh ice are not very reproducible but eventually, if the tests are continued, the results become more consistent. A tentative explanation of the phenomenon is that fresh ice is too weak to support the shear stresses imposed by the sliding rubber. Repeated stressing, work hardens the surface so that shearing of the ice does not occur and the viscoelastic properties of the rubber are utilized. The variable nature of the results on fresh ice could account for some of the variability observed in full scale tyre trials. The maximum coefficient of friction which can be attained on old ice is similar to that obtained for rubber on other smooth surfaces (Grosch, 1973), being about 3 or 4.

It should be emphasized that the rubber used in these experiments is not a typical tyre tread compound but the results show that it may be possible in the future to produce tyres which have substantially better grip on ice than the best that is currently available.

Heat Build-up

The deformation of a tyre rolling through its contact area with the road leads to mechanical energy losses because of the imperfect elasticity of all tyre components. These losses manifest themselves as rolling resistance and heat build-up the latter is the more serious effect because it can produce catastrophic failure. The problem of heat build-up increases with increasing tyre size, and with large truck tyres it can lead to tread separation and blow-out (Fig. 4). The amount of heat build-up depends on the dynamic properties of the tyre components and may, in the first instance, be related to the resilience of the materials. The high resilience of NR, uniquely combined with building tack and high green strength, makes its use in carcasses indispensable, the proportion used rising as the tyres become larger. With large tyres the tread makes a significant (∽ 60%) contribution to the total heat build-up, and accordingly the proportion of NR used here must also be increased with increasing tyre size (Collins *et al.*, 1964). For example, in the most popular size of truck tyre (10.00-20) the amount of NR relative to SR (in the whole tyre) is 65:35 in a crossply, and 95:5 in a radial, (cf. a 5.60-13 passenger car tyre, crossply 10:90; radial 36:64), while large earthmover tyres (up to 27.00-49) are entirely NR (Diamond, 1973). The problems confronting NR here are both concerned with vulcanization. Firstly, there is a need in the manufacture of large tyres to ensure that the state of cure is homogeneous and optimal throughout the tyre. This limits vulcanizing conditions to long cure times at relatively low temperatures because of the low rate of heat transfer in rubber, the size of the mouldings, and the reversion behaviour of the currently used conventional accelerated sulphur recipes. Secondly, there is a need to maintain the vulcanizates chemical structure and crosslink density during running in service, when internal temperatures can be > 150 °C. Indeed direct experiment has demonstrated that incipient failure in service, and actual failure in rig-testing of lorry tyres, are associated with chemical changes in the rubber compound (Cunneen & Russell, 1969). It is quite possible that these two needs will be satisfied by soluble compounding which was referred to in the previous paper, and by the urethane method of vulcanization; because laboratory scale heat build-up tests have shown promise with both systems (Fig. 5), and it is known that tyre manufacturers are currently evaluating these compounds. These needs, however, are *not* satisfied by blending with polybutadiene (BR). The merits of blending BR with NR in tread compounds are well-known, *i.e.* improvement of abrasion resistance and of resistance to groove cracking, but NR/BR blends are also used by some tyre manufacturers in the non-tread regions of tyres. Our investigations have shown that the reversion resistance (maintenance of modulus and resilience at curing temperature) of NR can be significantly improved by blending with BR but only for a conventional curative system; negligible improvement is apparent when a semi-EV cure is used and NR with a semi-EV cure is better than a 70/30, NR/BR blend with a conventional cure. Furthermore, anaerobic ageing stability at 100°C, subsequent to cure, typifying service conditions of many large truck tyres, is not improved by blending NR with BR even for a conventional cure system. Goodrich heat build-up tests on the blends showed considerably higher temperature rises than on NR, and dynamic testing indicated that the heat generation of NR/BR blends would be higher than NR under constant stress, constant strain, or constant stored energy deformations. Therefore, because of the inferior heat build-up and vulcanizate stability of NR/BR blends, 100% NR should be preferred for the carcass regions of tyres (Bristow & Metherell, 1973).

Cutting, Tearing and Flaking

Adventitious cutting by sharp objects, such as broken glass or jagged metal, is an important form of 'hazards' failure for tyres across the whole range of sizes from small solid tyres on the one hand, to giant earthmover tyres on the other. If it is severe, cutting alone can render a tyre unserviceable; alternatively, cutting may accelerate other forms of failure in which chunks or flakes of rubber are removed from a tyre tread, so that the rate of wear is greatly increased.

In order to make soundly-based recommendations for improvements in tyre compounds an understanding of the primary factors affecting cutting and related phenomena is desirable. Although certain *ad hoc* tests have been developed, there is at present little basic understanding of these types of failure. Work is, therefore, in progress to rectify this position and this has shown that two distinct cutting processes can occur; one is slow, time-dependent cutting and the other is rapid, 'catastrophic' cutting. Effects of type of elastomer and compounding variables on these processes are being studied (Lake & Yeoh,).

Abrasion and Wear

Tyre wear is one of the most important of the tyre properties to the user because it is easy to assess the life of one tyre relative to another. Somewhat paradoxically tyre life is extremely difficult to predict accurately from short term measurements. Tyre companies spend large amounts of money using a fleet of cars to obtain an accurate assessment of tyre life. The difficulties arise because a large number of factors such as type of road surface, temperature, acceleration and braking, all influence the rate of wear of the tyre and it is necessary that all the tyres being tested are subjected to the same "average" conditions so that a meaningful comparison is made.

Numerous laboratory abrasion machines have been proposed but none give results which correlate with full scale road tests on tyres. Good correlations have been claimed in the past but careful examination of the data reveals that either inadequate testing has been carried out or the compounding changes are limited to one variable so that a correlation is almost inevitable. So misleading are the laboratory abrasion results that some tyre companies do not use them even for preliminary screening of compounds.

MRPRA has developed a method of testing full size tyres which is economical and relatively quick. The equipment uses a two-wheeled trailer towed by a car. The test tyres are fitted to the trailer in normal operation but check measurements on the car wheels are also carried out. The rate of tyre wear is increased by having the trailer wheels inclined at a small angle (between 1 and 4°) to the direction of travel. The wheels are switched from the toe in to toe out position every mile to make the wear uniform.

It has been found the relative wear of one compound to another depends mainly on the tyre surface temperature during running. Factors such as ambient temperature, type of road surface, acceleration and braking all influence the tyre surface temperature so that the ratio of the wear rate of one compound to another can simply be plotted against tyre surface temperature (Grosch, 1967; Schallamach, 1968). The relationship for NR and styrene butadiene rubbers is shown in Fig. 6 where it can be seen that at high tyre surface temperatures SBR is better than NR, but at low tyre surface temperatures NR is better. The tyre surface temperature at which both rubbers have equal wear is 35° C and this occurs at an ambient temperature of 5°C for an average driver. Under winter conditions the NR compound will wear less than the synthetic but in summer the reverse is the case. Small compounding differences do not affect the cross-over temperature but blending 20% of BR with NR gives improved high temperature wear properties (Grosch, 1967; Schallamach, 1968). Experiments have also been carried out using light truck tyres and similar results have been obtained.

It can readily be appreciated that NR based compounds will show improved wear characteristics over SBR compounds in applications where the tyre surface temperature under normal operating conditions is relatively low. A good example has been given earlier—winter tyres operate under ideal conditions for NR and fleet trials in Canada have shown NR to be 30% better than SBR in the coldest winter months.

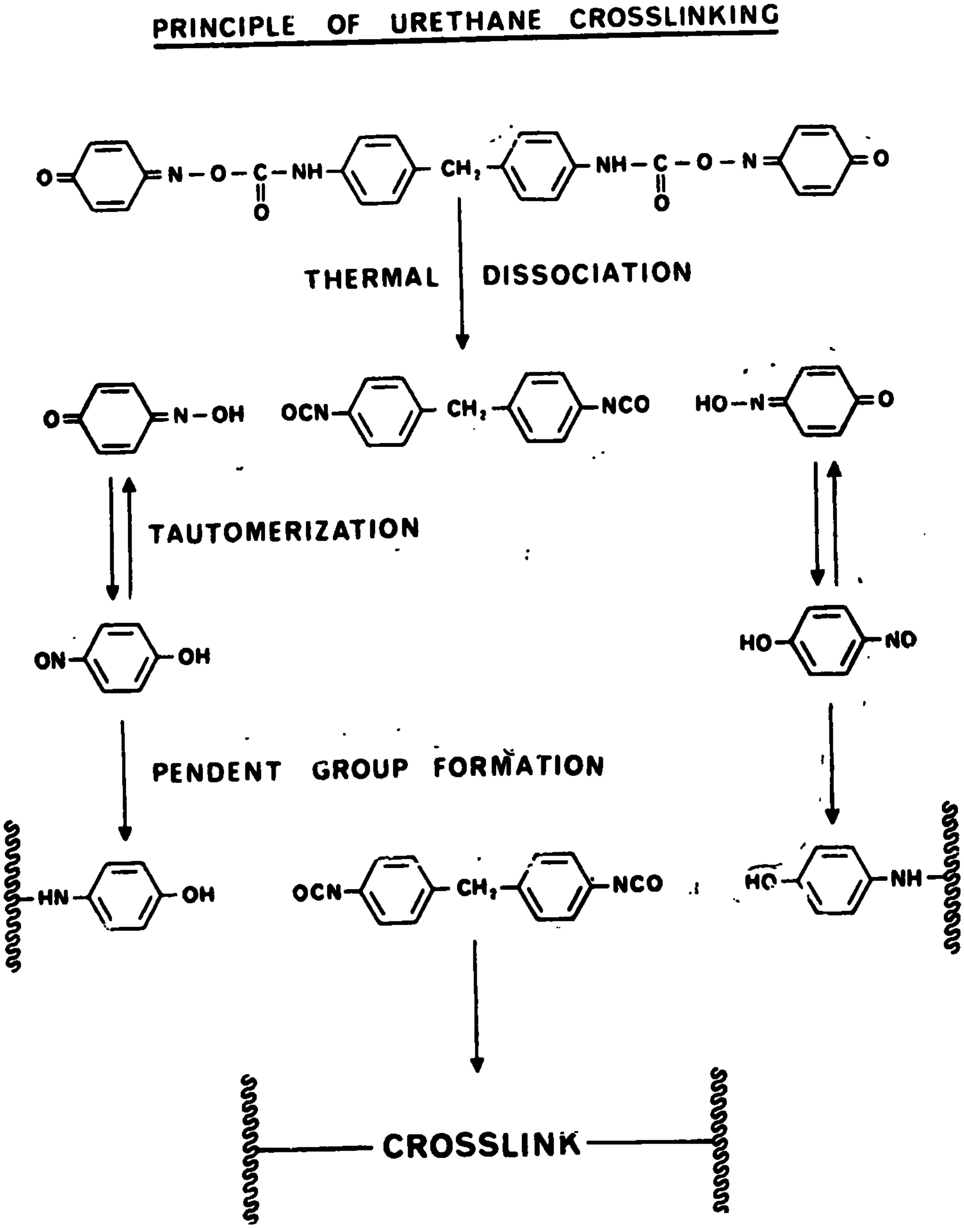


Fig. 1 Principle of Urethane Crosslinking

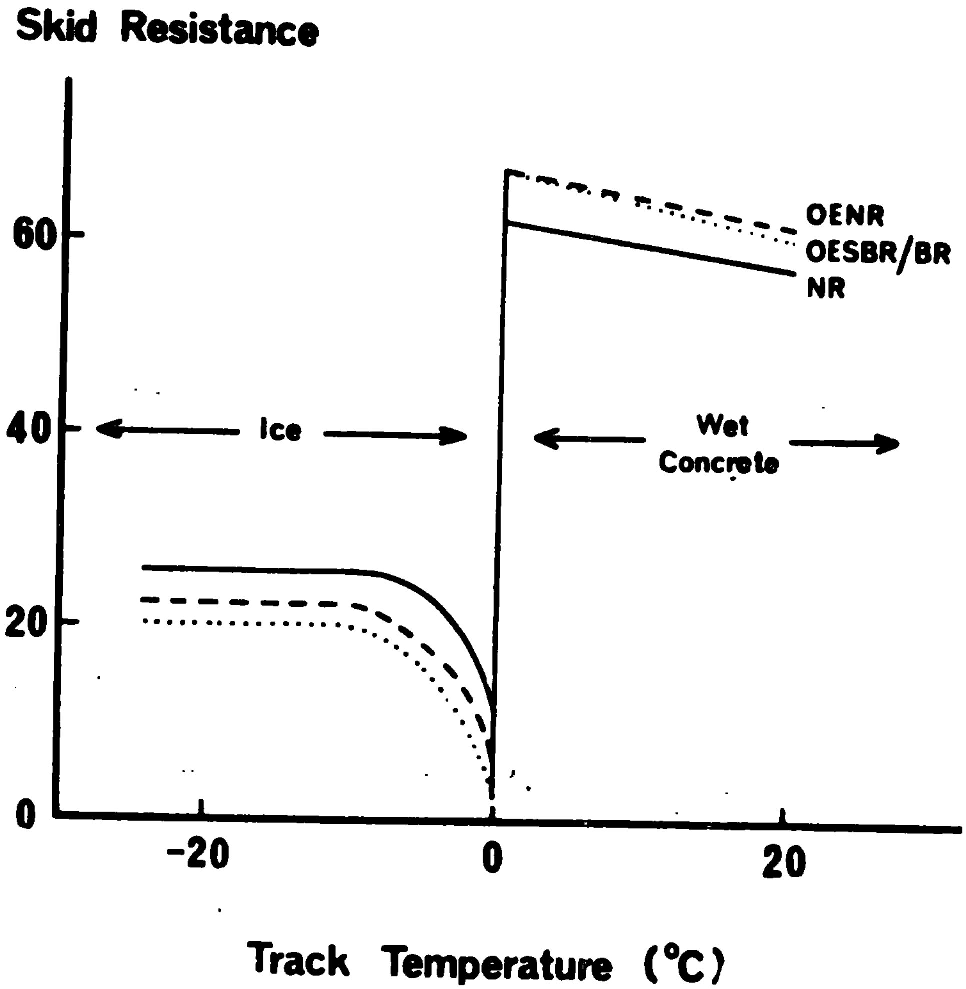


Fig. 2 Skid resistance of Tyre tread compounds

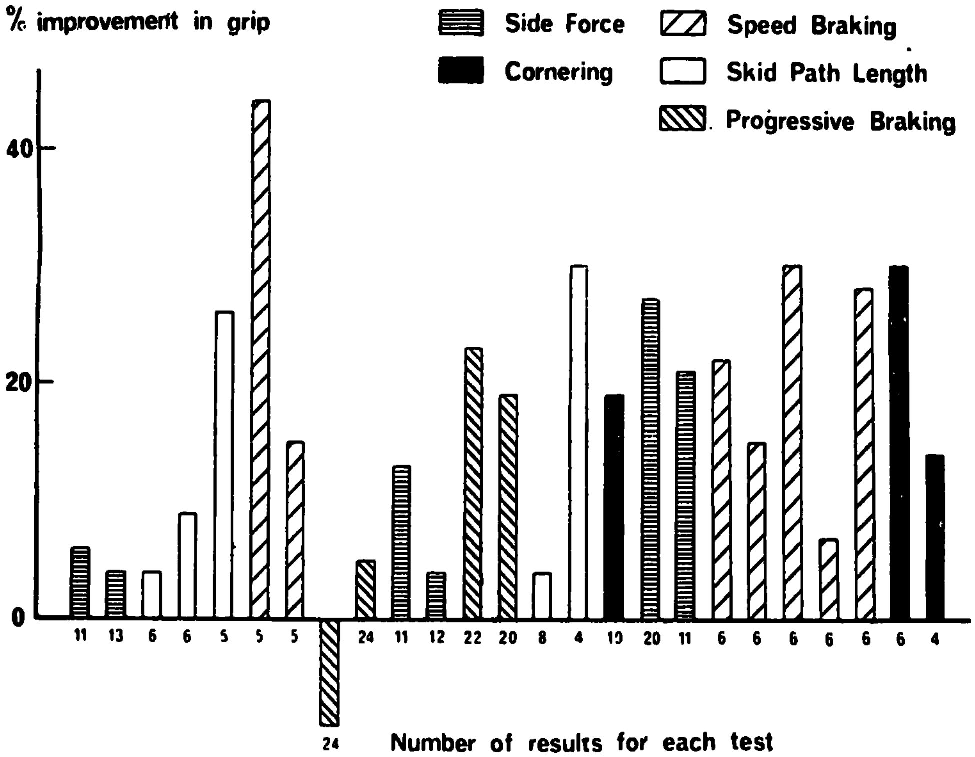


Fig. 3 Improvement in grip for OENR relative to OESBR/BR for different test methods

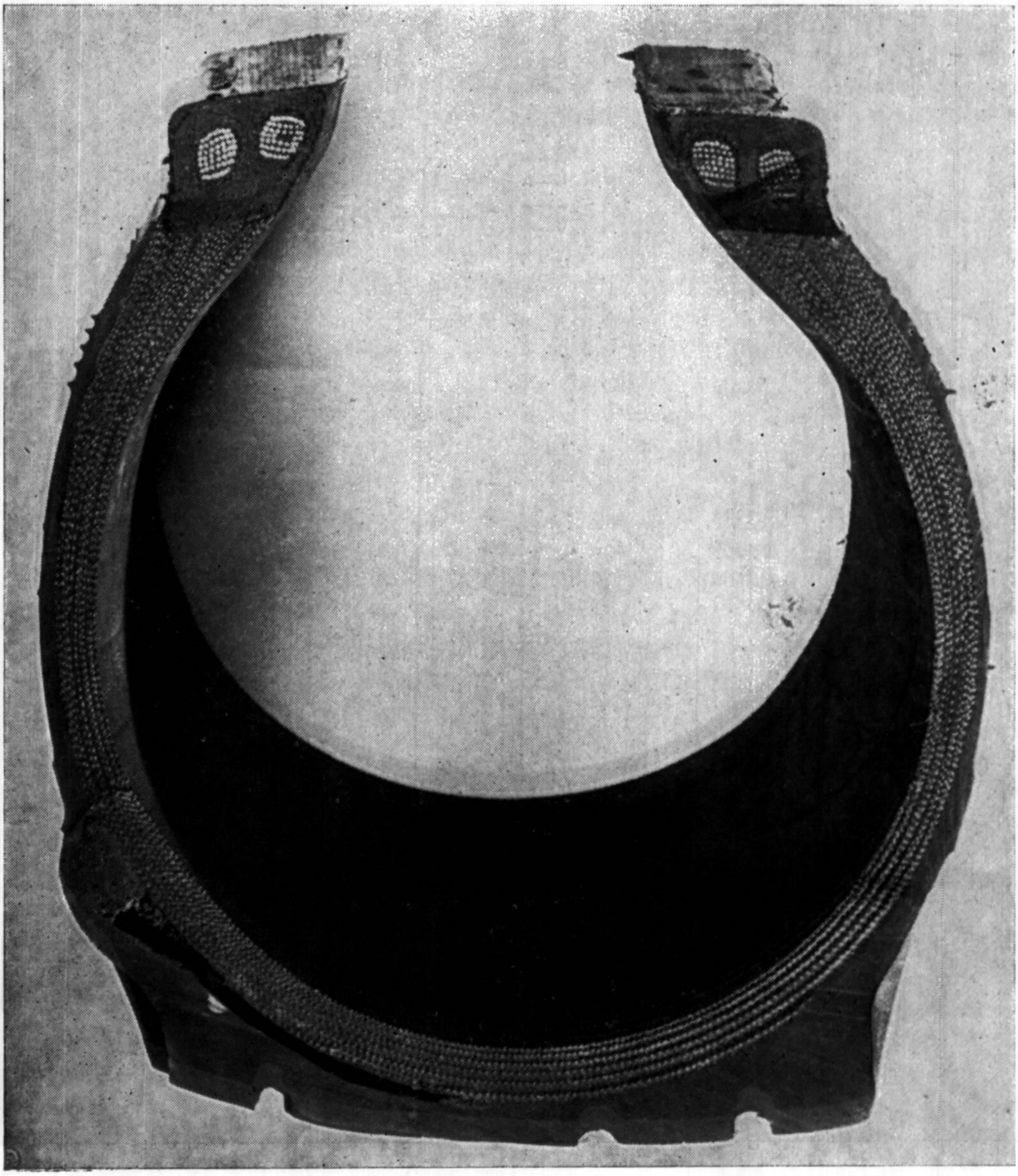


Fig. 4 Section of a truck tyre showing tread lift after Rig Testing

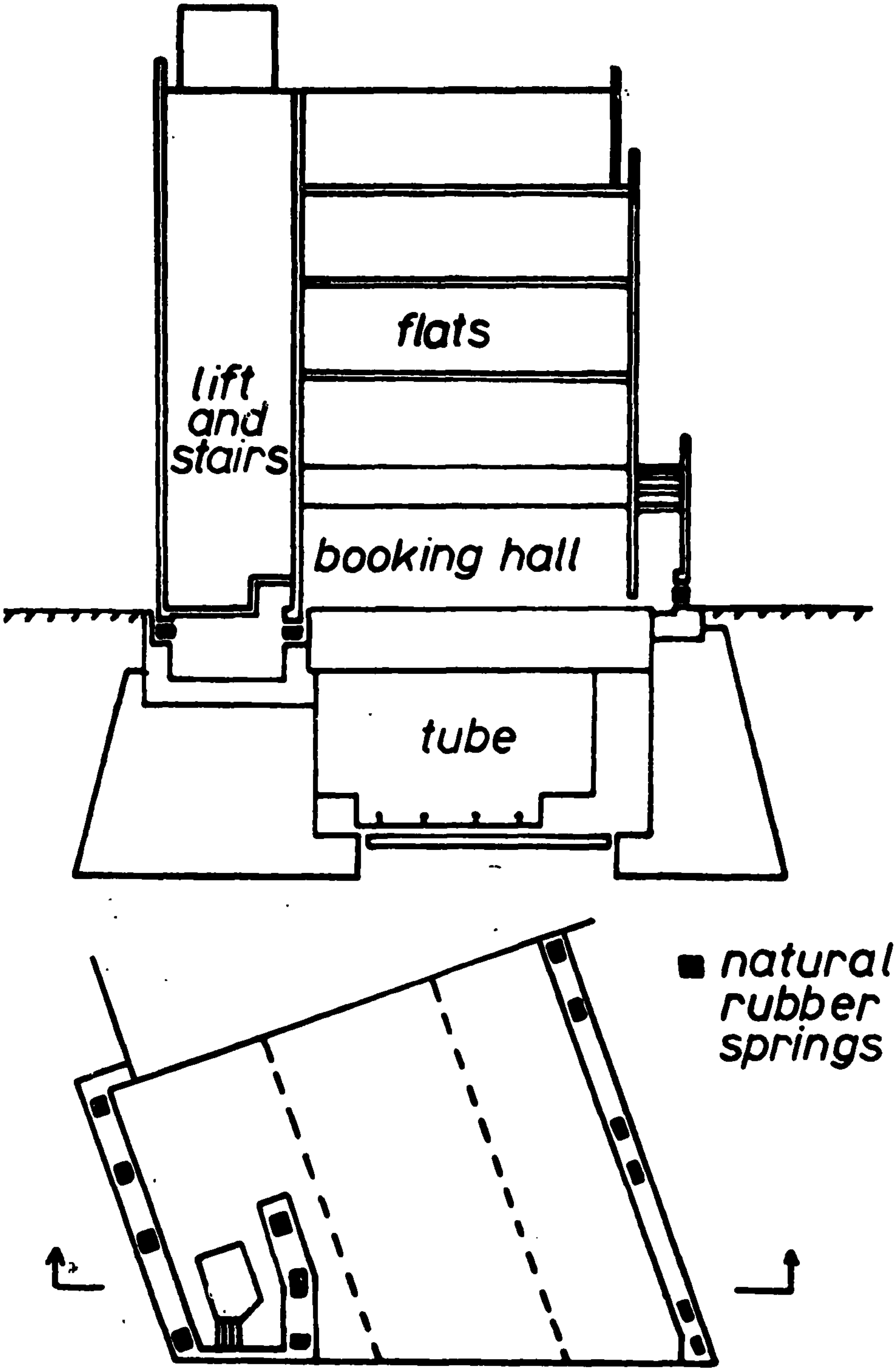


Fig. 5 Block of Flats in London mounted on NR springs

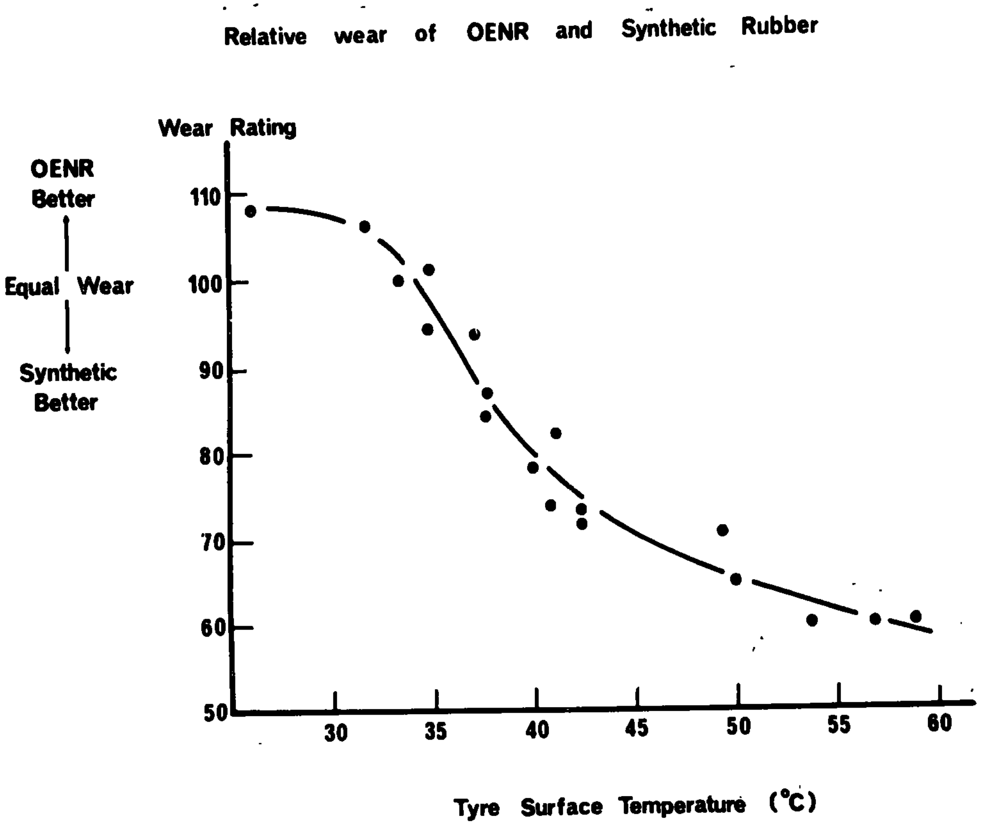


Fig. 6 Relative wear of OENR and OESBR

TABLE 1

NR TREAD COMPOUNDS, PHYSICAL PROPERTIES AT 21°C.

	Conventional with antioxidant	Urethane No antioxidant	Urethane with antioxidant
Hardness°BS,	68	72	68
M300 kg/cm^2	192	158	134
Tensile strength kg/cm^2	290	260	234
Elongation at Break %	429	453	453
Tear kg/mm	1.70	2.29	2.08
Dunlop Resilience %	74.6	68.8	67.9
Ring Fatigue 100% Extn kcs	113	104	85
Heat Build-Up (Goodrich flexometer)ΔT°c	38.5	44	41
Permanent Set%	3.7	3.8	4.1
Compression Set (25%, 24 h at 70°C)	31	25	27
Tension Set (75% EB, 10′ at 21°C),%	17	10	6

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