Q. Jl. Rubb. Res. Inst. Sri Lanka (Ceylon) (*1973*) **50**, **109—133**

NATURAL RUBBER IN THE CHANGING TECHNOLOGY OF THE RUBBER MANUFACTURING INDUSTRY

BY

LEONARD MULLINS

(*Director, Malaysian Rubber Producers' Research Association*)

SUMMARY

Natural rubber has an inherent potential far exceeding its present usage and there appears no reason why it should not in the future achieve a much larger consumption both in absolute and proportionate amounts. To do this demands a considerable increase in the growth rate of natural rubber production.

The development of new uses which generate new outlets for raw rubber has been happening continuously since the rubber industry started. Experience has shown that these have been far more successful commercially when they have resulted from a consumer demand. Recent examples of the development of new uses shows that even when successful they are likely to absorb only relatively modest tonnages of natural rubber.

Natural rubber is having to meet progressively more stringent demands for consistency, ease of handling and technical quality as industrial processes are increasingly automated and as final products are more critically judged in terms of technical performance. Recent developments have enabled significant improvements in performance to be realised, both during processing and of final articles in service. Exploitation of these developments is still only partial and the durability and performance of natural rubber in many applications would be still further improved by their fuller use.

Current interest in powdered, thermoplastic and liquid rubbers adds emphasis to the need for natural rubber to keep abreast of changing requirements in the consumer's factory. Already the basic technical elements to provide natural rubber satisfying many of these possible requirements are potentially available. However, it is clear that the bale will continue to be the principal form of natural rubber for many years to come.

SUPPLY AND DEMAND

Natural rubber has an inherent potential far exceeding its present usage. It possesses such a desirable balance of properties that if performance in the final product were the only criterion, and if sufficient natural rubber were available, it could satisfy at least 70% of total end use tonnage. There are relatively few end uses where performance requirements alone dictate any need to use one of the synthetics and in most mainstream products natural rubber can give excellent service to the end user.

The reason why natural rubber's share of the world rubber market today is so much lower, about 35%, is simply that there is not enough to go around. Its production rate since 1940 has been quite unable to meet world rubber demand and the balance has been progressively filled with synthetic rubbers (Fig. 1). In this period synthetic producers using cheap and abundant petroleum feedstocks have been able to fill the gap between natural rubber supply and total rubber demand in volume and at low cost.

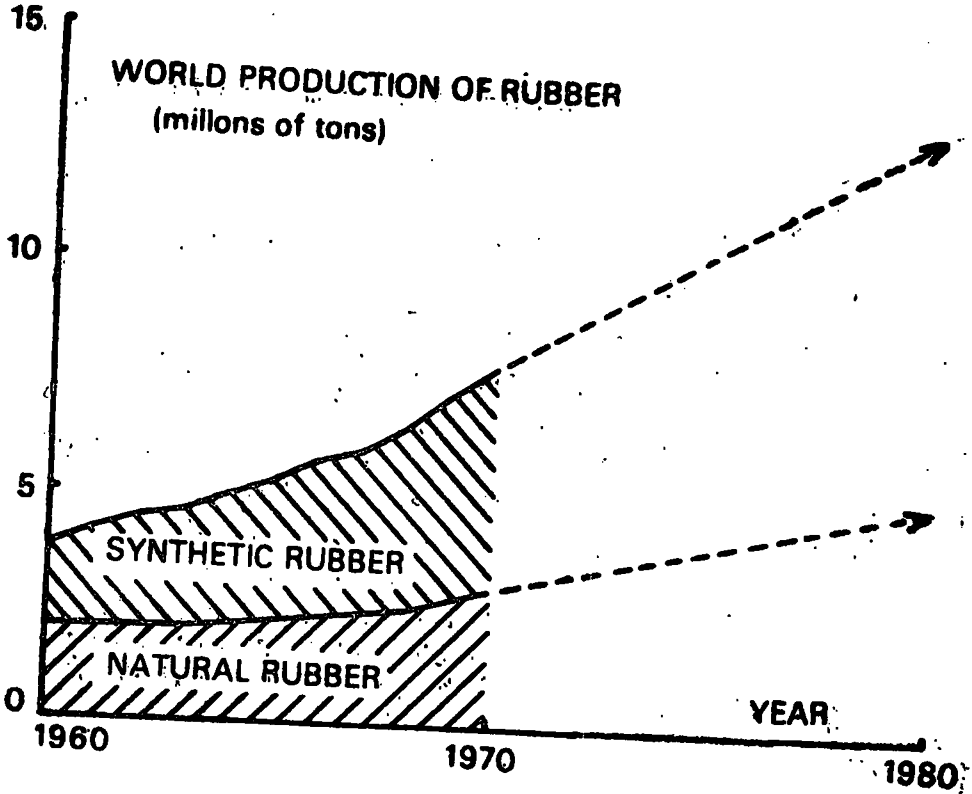

Fig. 1. World production of rubber.

There are signs that the past pattern is starting to change, and that the future will more and more lie with natural rubber. First its production rate is steadily increasing. During the past decade the average annual rate of increase has been just over 4%, more than twice the rate in the 1950's. This is mainly the result of the implementation of a massive and imaginative programme of replacement of old types of tree with newer high-yielding varieties. For the future, continued exploitation of improved trees plus the wider use of yield stimulants and a number of other agronomic techniques (*e.g.* crown budding, polybag collection) promise to provide the opportunity for the product to accelerate still faster.

Pessimists may argue that against the background of very low prices prevailing as recently as last year it is dangerous to contemplate expansion along such lines. This is to take too short and too narrow a view.

There is not the slightest doubt that these low prices were mainly due to an excess availability of synthetic rubber combined with the slow growth of the economies of a number of major rubber consuming countries. This led to price undercutting between synthetic rubber producers and to an international slump for all polymers including natural rubber. Synthetic rubber producers and natural rubber producers alike had to endure a savagely cold wind; there have been plant closures, production cut-backs, price discounts, and loss of profitability to a point near disaster for some companies. It is a sobering thought that the world's largest and most prestigious petrochemical companies have been unable to assess future demand with sufficient accuracy to adjust capacity growth. It is an even more sobering thought that the consequences of such miscalculations bear most heavily on those—rubber smallholders especially—who have no alternative form of livelihood to fall back on when times are hard.

However, world rubber demand increases rapidly, currently around 7% a year, and the excess capacity which bore so heavily on the market in 1971-1972 will soon be taken up, and further proliferation of synthetic rubber capacity has been discouraged —at least for the time being—by the slump in these recent years.

The situation exists in which many rubber product manufacturers use as little natural rubber as possible either because (a) they have a captive supply of synthetic rubber, or (b) they are able to buy synthetic rubber at attractive discounted prices, or (c) they dislike the marketing arrangements and lack of price stability for natural rubber, or (d) of government policy designed to encourage domestic industry or to save foreign exchange.

Thus with many manufacturers already using as little natural rubber as possible and with natural rubber production only increasing at about 4% a year the situation should rapidly arise where the demand for natural rubber will outrun supply. Several estimates of the total rubber requirements and the production of natural rubber in the next decade have been published and the figures given in Table 1 fall within the generally accepted range of values.

TABLE I

WORLD CONSUMPTION OF RUBBER (TONS)

Year	Total rubber consumption	Natural rubber consumption	Percentage natural rubber
1940	1,127,000	1,127,000	100
1950	2,339,000	1,750,000	75
1960	4,400,000	2,095,000	48
1970	8,600,000	2,992,000	35
1980	12,500,000	5,000,000	40

This and other forward projections of the consumption of natural rubber have involved conservative approaches undoubtedly influenced by the progressive fall in the percentage of total rubber requirements met by natural rubber over past years. There are now strong indications that the demand for natural rubber will increase in the 1970's not only in absolute but also in proportionate amounts—particularly in the tyre field where the transition towards tyres with radial construction places emphasis on qualities such as tack, green strength, resilience and fatigue life. Qualities which natural rubber possesses to a high degree. Nationalistic considerations apart there appears no reason why natural rubber should not achieve an even greater increase in its percentage share of world rubber consumption although to do this demands a very considerable increase in the growth rate of natural rubber production.

Times are changing in yet another way. The ability of synthetic rubber producers to take advantage of low-cost starting materials—very cheap oil—and to take advantage of economies of scale by building bigger and bigger plants—are running out. Oil is getting more expensive and capital costs are steadily rising. Additional features causing problems for the petrochemical industry include anti-pollution measures and the current demands for lead-free gasoline which is disturbing the balance of refinery operations. On these and other counts the costs of producing synthetic rubbers are certain to increase. Thus, although in the future the price of natural rubber will undoubtedly go through fluctuations the signs are that it will be better able to meet the "troughs".

DEVELOPMENT OF NEW USES FOR NATURAL RUBBER

When the rubber market is depressed, attention is naturally directed to the subjects of stimulating consumption and developing new end-uses. In hard times it is important to seize any opportunity which is likely to result in the uptake of a reasonable tonnage. However, it is also important to recognize there is a serious danger of being over-optimistic in estimates of the likely impact of such activity.

Essential starting points in any discussion on new uses are the facts that (a) some 60% of total rubber consumption is in tyres, and (b) apart from tyres and a few other end uses (*i.e.* latex foam, hose, belting, footwear) there are few existing uses which individually absorb more than one per cent of total rubber consumption and most use substantially less. The history of the "new use" of rubberized road surfacings illustrates how the early optimism of a vast open-ended market for rubber has become, on more sober assessment, a realistic estimate of market size of some 25,000 tons/yr worldwide. Many will be surprised to learn that the familiar and also important use of rubber in car engine mountings consumes less than 3,000 tons/yr worldwide—however, all of this is natural rubber. In fact, apart from tyres, the total end use pattern of natural rubber is that of hundreds of individual end uses, most requiring rubber consumption in the range of 1 to 10,000 tons per yr. Recognition of this true scale of magnitude for rubber consumption in individual existing end uses helps to give the right perspective with which to approach the possibility of generating increased natural rubber consumption by the development of new uses.

Another important fact is that new uses for rubber are only of real and continuing value to the natural rubber producers if they correct possible supply/demand imbalances at the right price—a price not less than that at which natural rubber is sold in existing end uses. Otherwise these new uses will be rapidly satisfied by lower-cost synthetic rubbers. The new uses to be sought are those in which the distinctive properties of natural rubber: its high strength, high resilience, good processing and tack are put to good use, and are worth paying for. It is these qualities which have enabled natural rubber to retain its strong position in heavy duty tyres, heavy duty conveyor belting, suspension units, mountings and latex products. Within the natural rubber producing countries themselves there is an important difference. Here the development of rubber-based industries capable of supplying not only their own but other countries end-product needs is already growing, and, in these circumstances, choice between natural and synthetic rubber for any new or existing use should correctly favour natural rubber.

The development of new uses which generate new outlets for raw rubber has been happening continuously since the rubber industry started. Experience over the years has shown that these have been far more successful commercially when they have resulted from the consumer having a new specific end use requirement which can correctly be satisfied by the use of rubber. The promotion of rubber as a material giving improved performance in an application already satisfied by another material is a much more difficult and slower task.

Recent examples of the development of new uses in which MRPRA has been actively involved illustrate these conclusions that (a) the most successful new uses are likely to be found when the impetus comes from the end user and (b) they are likely to absorb relatively modest tonnages of natural rubber.

Bridge bearings: The modern natural rubber bridge bearing is a direct result of collaboration between MRPRA and a firm of engineering consultants who in 1955 suggested that "bridge designers would be interested in a new design of bearing with long life and no maintenance whatsoever". The first bearing to our new design was in service in 1956 and then after about five years commercial acceptance grew very rapidly. Now virtually all medium span bridges and a number of elevated motorways in the UK are mounted on natural rubber bearings and many other countries are following suit. This particular market of about 2,000 tons/yr is not vast but its importance is that it demonstrates in a way which no laboratory test does that natural rubber is tough, durable and designable. Proof of the value of such demonstration is that buildings are now being mounted on natural rubber (Figs. 2, 3 and 4).

Building mounts: The use of natural rubber building mounts to isolate noise and vibration was first suggested at an NRPRA Rubber in Engineersing Conference in 1956 when the design of bridge bearings was described, and is a direct spin-off from bridge bearings. By 1964 several successful natural rubber building mounts were available, their uses included television studios in London and Paris, there are several major buildings mounted on natural rubber in London, Paris, Sydney, Washington D.C., in these isolation from train vibrations has been of particular importance (Figs. 5 and 6). A new idea is to use natural rubber building mounts to reduce damage due to earthquakes. This is actively being investigated and if earthquakes can be catered for, the size of the market would be large (much more than 10,000 tons/yr). In this application and the use of rubber in bridge bearings the low creep of improved forms of natural rubber make natural rubber the preferred material.

Automotive anti-impact devices: Recent U.S.A. legislation required that by 1973 safety-related-systems in cars should sustain no damage on impact at specified speeds. Preliminary design considerations of a natural rubber energy absorbing device to meet this requirement were published by NRPRA in 1970/71. These were taken up by Fords and within two years their 1973 models were introduced containing natural rubber anti-impact devices. The size of this market is up to 10,000 tons/yr. It requires high quality rubber but there is strong pressure from synthetic rubber (*cis*-polyisoprene). Future demand will depend upon whether a cheaper device can be developed or whether more stringent impact requirements—needing a different approach—are introduced (Fig. 7).

The Ford Energy Absorbing Device is but one of a number of possible new uses for rubber in automobiles. Quite different approches are being considered, in conjunction with automobile manufactures, to limit damage due to impact. One of these is a complete "wrap-round" flexible bumper system, in this the injection moulding of large natural rubber units and the painting of natural rubber surfaces to give "cosmetic appeal" are problems which have had to be solved (Figs. 8 and 9). The market for these and other new automotive applications is potentially large, equivalent perhaps to that of a "Sixth wheel" on every car, but competition from other elastomeric materials is acute.

Winter tyres: This is not a new use for rubber, but the oil-extended natural rubber winter trye is an attempt to claw back a use currently met by synthetic rubber and so to create a new outlet for natural rubber. In 1967 the excellent wear and skid resistance of oil-extended natural rubber tyres at low temperatures was established by NRPRA and by 1970 it had been shown that under winter driving conditions involving snow and ice these tyres were often significantly better than conventional winter tyres (Fig. 10).

Importantly criticism and restriction of the use of studs in winter tyres has led to pressure for tyre manufacturers to develop unstudded tyres with better grip on ice and snow. A small Canadian manufacturer, Mansfield-Denman-General, led the way by introducing its "Big-Paw" winter tyre, labelled 80% natural rubber 20% polybutadiene in the winter of 1971 to 1972 and now one of the major tyre manufacturers is introducing a new improved winter tyre based on NR and it is anticipated that it will be closely followed by another of the biggest tyre manufacturers. The market at stake is about 80,000 to 100,000 tons/yr (Fig. 11).

Hovercraft skirts: Hovercraft only became a practical proposition with the development of a skirt to provide a flexible seal to contain the cushion of air below the vehicle. Most successful systems involve a segmented skirt of rubber coated fabric to enable uneven surface contours to be followed (Fig. 12). The development of satisfactory segments or fingers has been a major problem due to rapid abrasion and tearing, but coating compounds containing a high proportion of natural rubber have been developed and shown to give satisfactory performance and should permit the forecast of widespread use of this new method of transport.

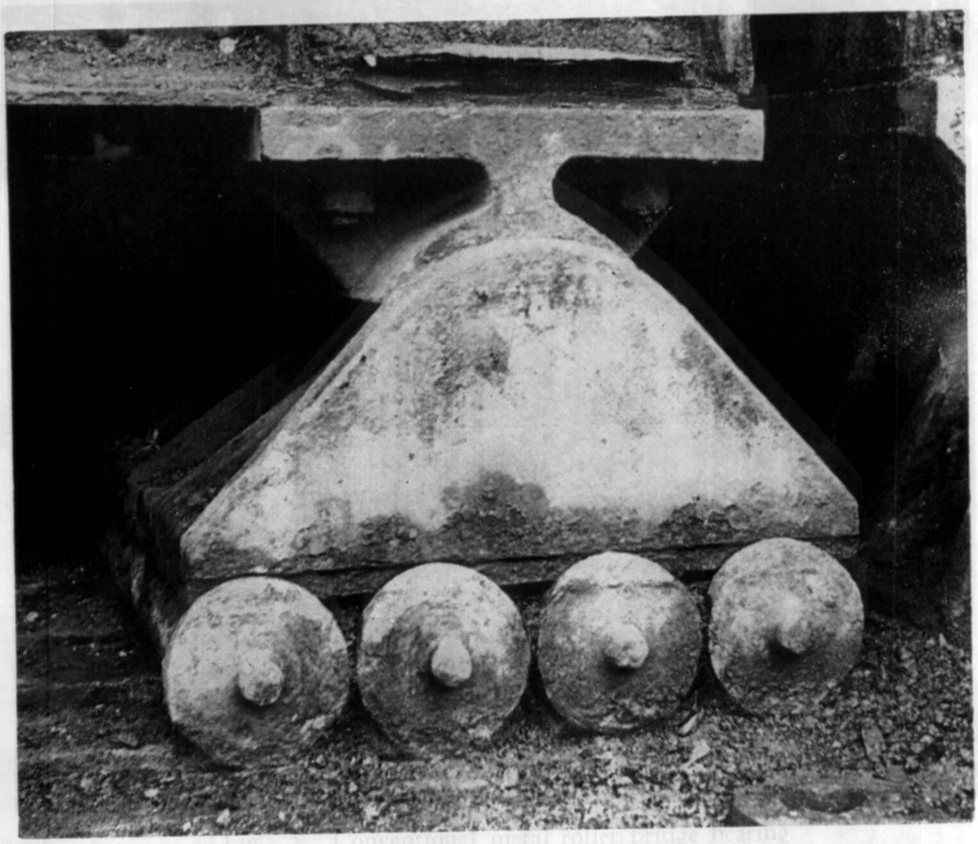

Fig. 2. Conventional metal roller bridge bearing

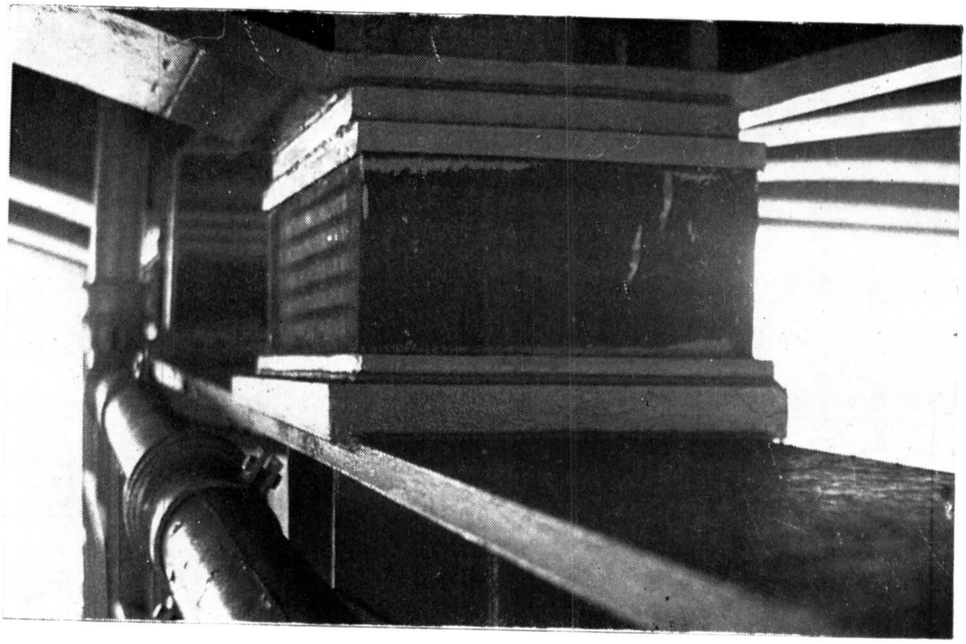

Fig. 3. Modern natural rubber bridge bearing

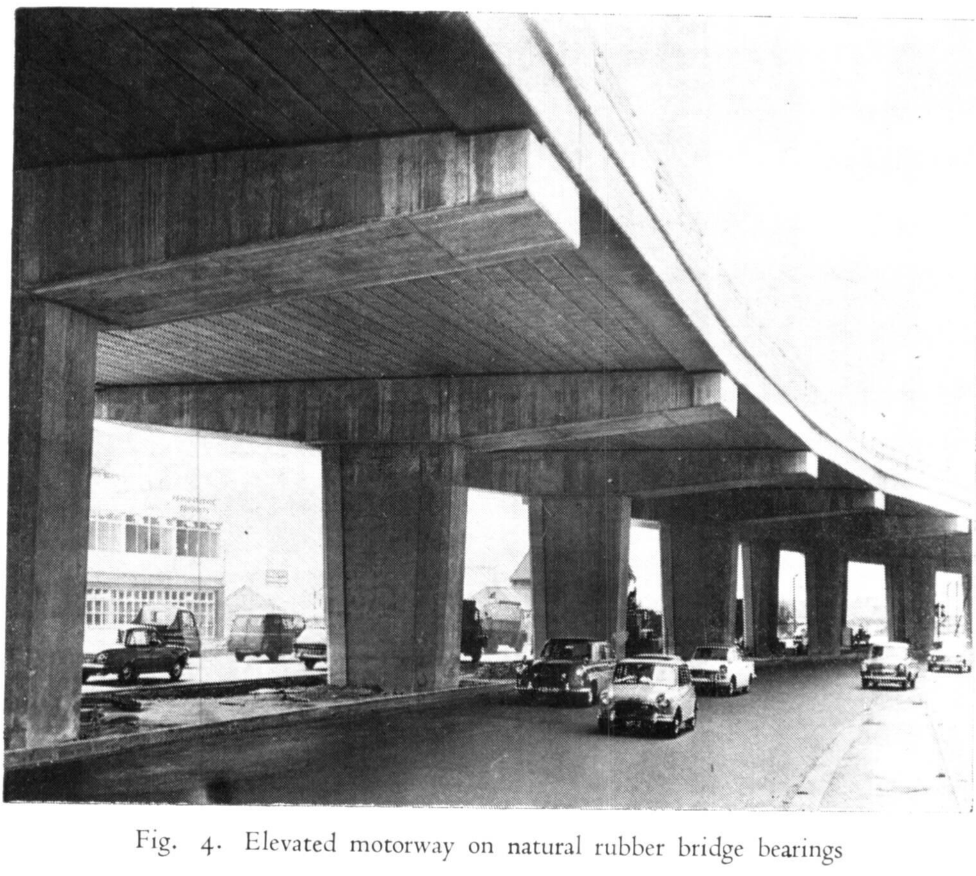

Fig. 4. Elevated motorway on natural rubber bridge bearings

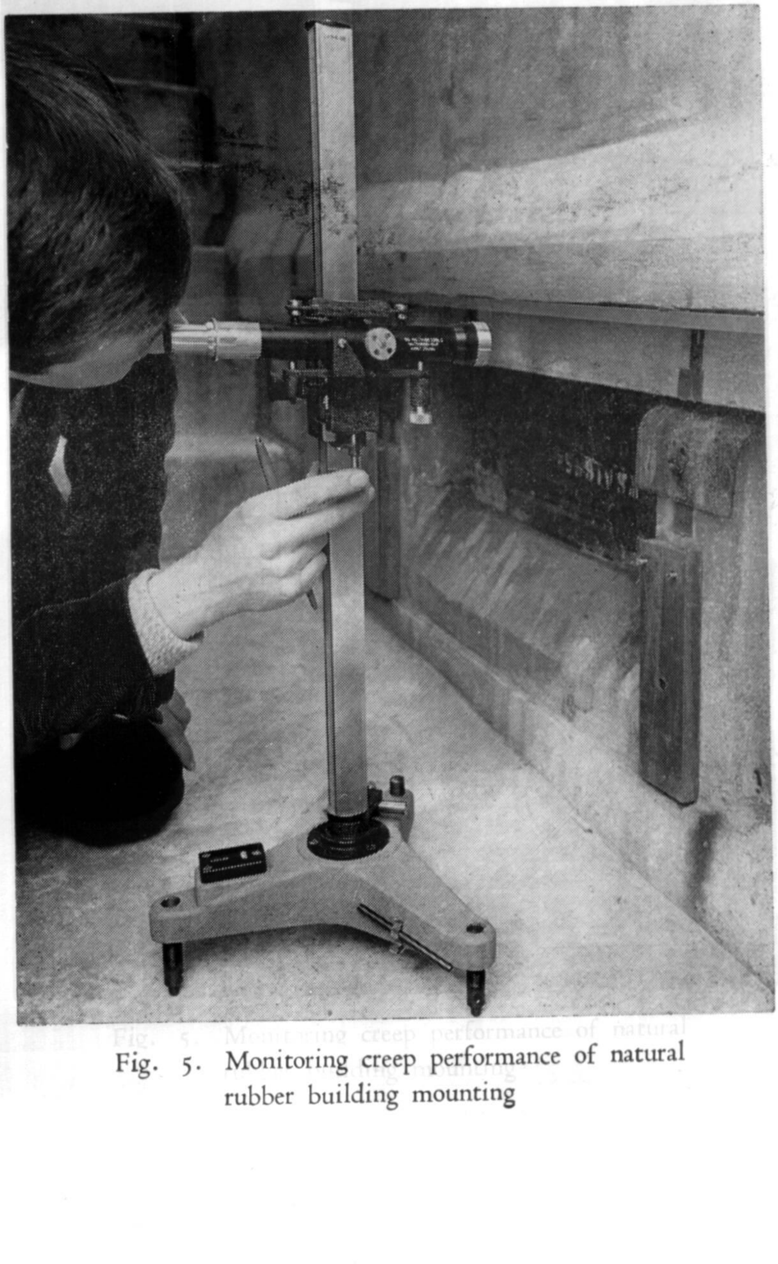

Fig. 5. Monitoring creep performance of natural rubber building mounting

Fig. 6. Albany Court an early example of building supported on natural rubber

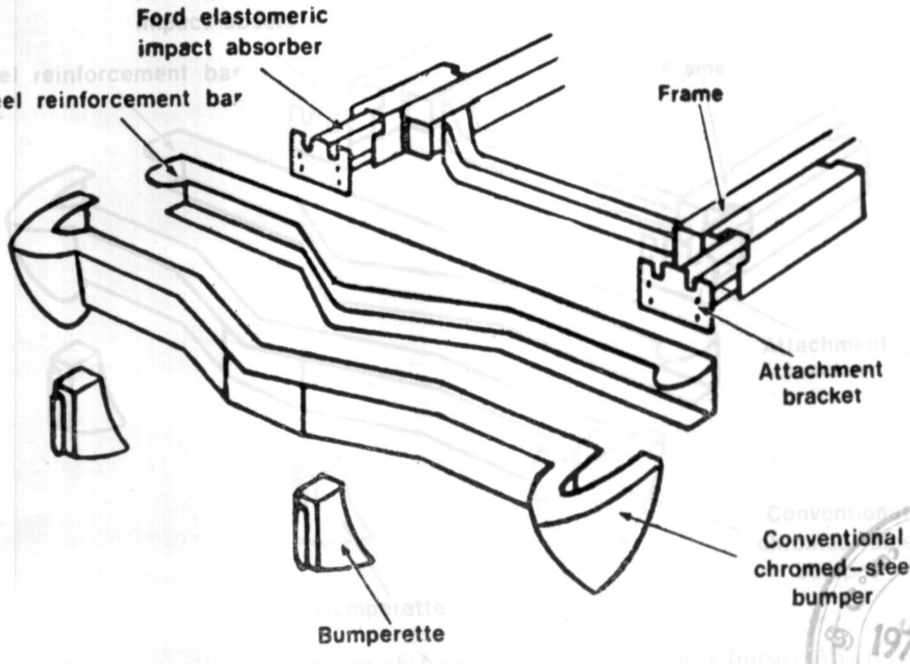

Fig. 7 Diagrammatic representation of New Ford Natural Rubber Impact Absorber.

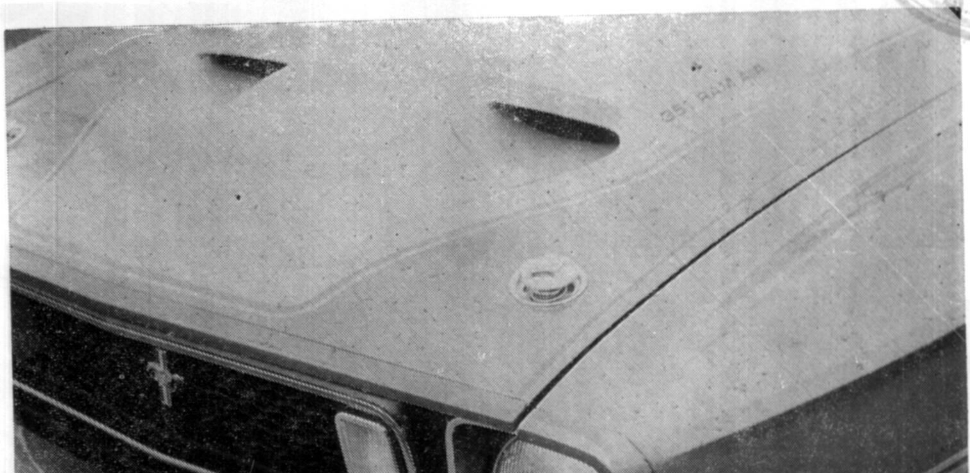

Fig. 8 The 1973 Ford Mustang with painted rubber bumper and sight shield

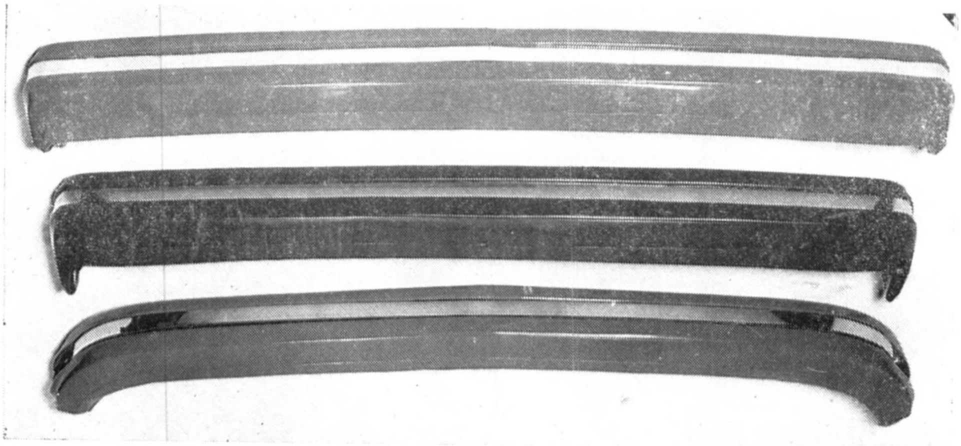

Fig. 9 Natural rubber injection moulded bumpers with glossy polyurethane finish

Fig. 10 Winter tyre trials in Sweden

Fig. 11 First commercial oil-extended natural rubber winter tyres

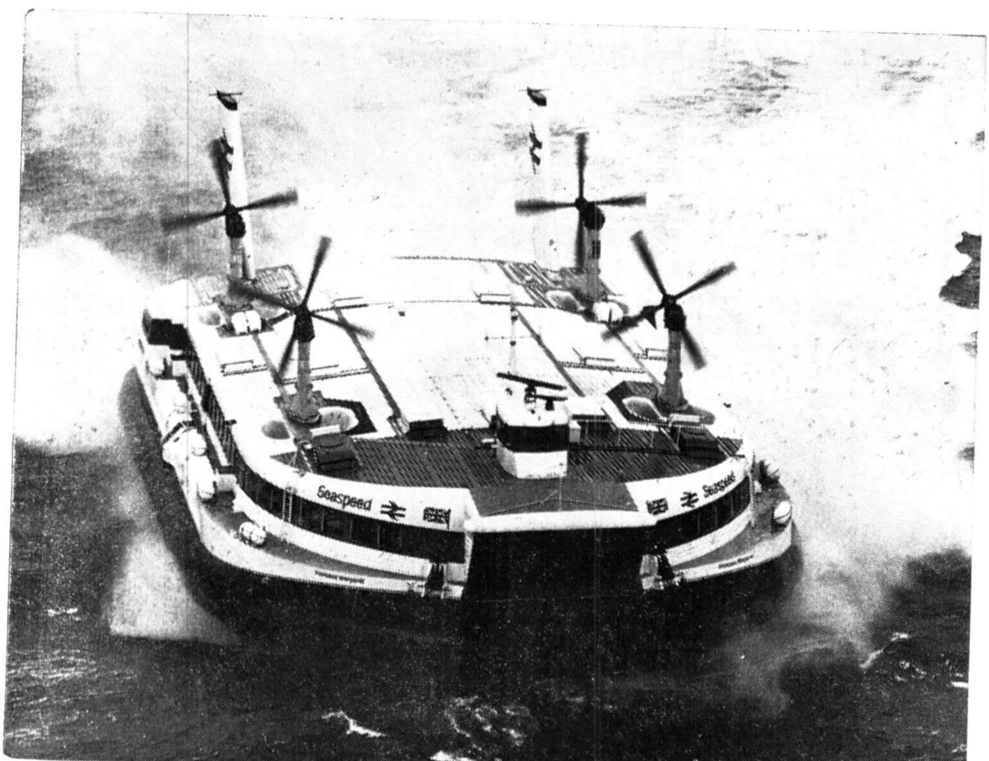

Fig. 12 Hovercraft with rubberized skirts

Carpet backings: The rapid growth in the popularity of tufted carpets in the last 15 years has provided a major new use for latices (Fig. 13). At first conventional natural rubber latex vulcanizing formulations were used but by the mid 1960's they were challenged by a specially developed type of SR latex. It was cheap, easy to use and did not require vulcanizing. An urgent defensive operation at MRPRA was manned and a satisfactory natural rubber latex formulation developed and the choice between natural and synthetic latex then rested mainly on the price of the latex. Further recent advances in synthetic rubber technology have necessitated the development of new natural rubber non-gel formulations (Fig. 14). The market involved is large about 250,000 tons/yr for both synthetic and natural rubber latex; for high-quality carpets natural rubber is preferred but with cheap synthetic latices available, natural rubber commands approximately a quarter of the total market (Fig. 15).

Flexible plaster: Flexible plaster made from natural rubber latex and gypsum is a novel material developed specifically for the National Coal Board for use as a sealant for walls and ceilings in mines to assist in ventilation control. Unfortunately, in 1967 when a suitable material was developed the use of organic based sealants for underground use was banned by the NCB. Outlets for flexible plaster in the building industry appear promising and large but the market is difficult and slow to develop (Fig. 16). Here there is a parallel with the next item.

Rubber in road surfacings: This idea dates back many years and current usage is quite modest. It has been very difficult to persuade road engineers of the advantages of using rubberized road surfacings, but it is fair to express a cautious hope for faster growth in the future. Up to now the impetus has been entirely from the rubber producers, but now with growth of traffic densities, increased costs of road-maintenance and recognition of the cost of traffic delays resulting from road repairs, road engineers are becoming much more conscious of the benefit/cost implications of longer lasting roads. The potential market is estimated at about 30,000 to 50,000 tons/yr but synthetic rubber will be in strong competition.

These examples of new uses have been selected from those in which MRPRA is actively involved. Manufacturers of rubber articles are, of course, continously alert to the development of possible new markets and there is a steady flow of new uses from this source.

In his choice of the type of rubber for a particular end use the manufacturer is influenced by many factors. Some are technical: there are service requirements and probably performance specifications to meet. Some are economic: these include price and price stability of the rubber, coupled with assurance of supply, marketing efficiency and ease of handling complaints, while technical factors affecting ease of processing directly influence the cost of production. Some are special to the individual consumer: previous experience, company policy (captive synthetic rubber plants), government policy, scarcity of foreign exchange, may all constrain the freedom of choice. The remainder of this contribution is concerned with the steps being taken to strengthen natural rubber's technical position and so to stimulate its consumption in a changing technological scene.

IMPROVEMENTS IN PERFORMANCE OF NATURAL RUBBER PROCESSING

A major requirement of consumers is that their raw materials should be uniform and consistent, that they should be easy to handle and that they should process easily and cheaply in increasingly automated factory operations. The recently introduced improved methods of production and marketing of natural rubber which involve the production of natural rubber in polythene wrapped small bales and their marketing to technical specifications have already gone a long way to satisfying these requirements. They provide not only close control of technical quality necessary to enable the rubber to move smoothly through highly automated factories, but, importantly, new forms of packaging eliminates the need to guillotine bales of rubber, control of dirt eliminates the need for straining, control of viscosity at suitable low levels eliminates the need to plasticise by premastication. In this way the natural rubber producing industry has redeemed those features in which natural rubber has in the past been at a disadvantage to synthetic rubbers.

Technology does not stand still and it is essential that natural rubber can adapt to the changes which inevitably lie ahead. What then of the future? A recent attempt to predict this sees the highly automated factory of the 1980's moving out of the "stone age", of current power-consuming mixing techniques using mills and Banburys to simpler processes involving free flowing powered or granulated rubbers precompounded with vulcanizing ingredients, fillers, and protective chemicals and ready for direct injection moulding. Even more radical changes in processing methods would follow from the introduction of liquid rubbers, to allow simple casting techniques to be used in which the rubber is transformed to the finished article by chain extension and crosslinking in one step; or from the use of so-called thermoplastic rubbers which behave as if they were vulcanized when cold but as a thermoplastic when hot, thus enabling moulding to be carried out in the way used for the processing of thermoplastics without the need for mixing or vulcanization stages.

Such ideas are not daydreams.

Powdered rubbers based on nitrile and high-styrene rubbers are already commercially available, and processes for the production of powdered natural and general purpose synthetic rubbers have already been established and there could now be a move towards new processing technology based on powdered rubbers.

Commercial production of liquid rubbers is around 250,000 tons a year, these are mainly for polyurethane foams, but in 1971 the market for solid cast applications (non-foam) was over 15,000 tons/yr. In the context of this paper the most important development is the Firestone cast tyre, however it appears that generally the required quality is not fully attained and whether this can be accomplished is not clear. It will take some while before there is a sizeable breakthrough, and even if it is possible to meet quality requirements the switch over will involve high capital investment.

A number of types of thermoplastic rubbers are currently available and production is about 50,000 tons/yr.

How then is natural rubber placed to meet these challenges?

Powdered or pelletized natural rubber: The possibility of producing a free-flowing rubber powder from natural rubber latex has long been in people's minds and many have been produced commercially. The unvulcanized powders have included large proportions of fine earth to stop agglomeration and caking of the rubber powder, while in other cases the free flowing characteristics have been preserved by vulcanizing the powder. However neither of these types of powder are suitable as base raw materials for the rubber manufacturing industry.

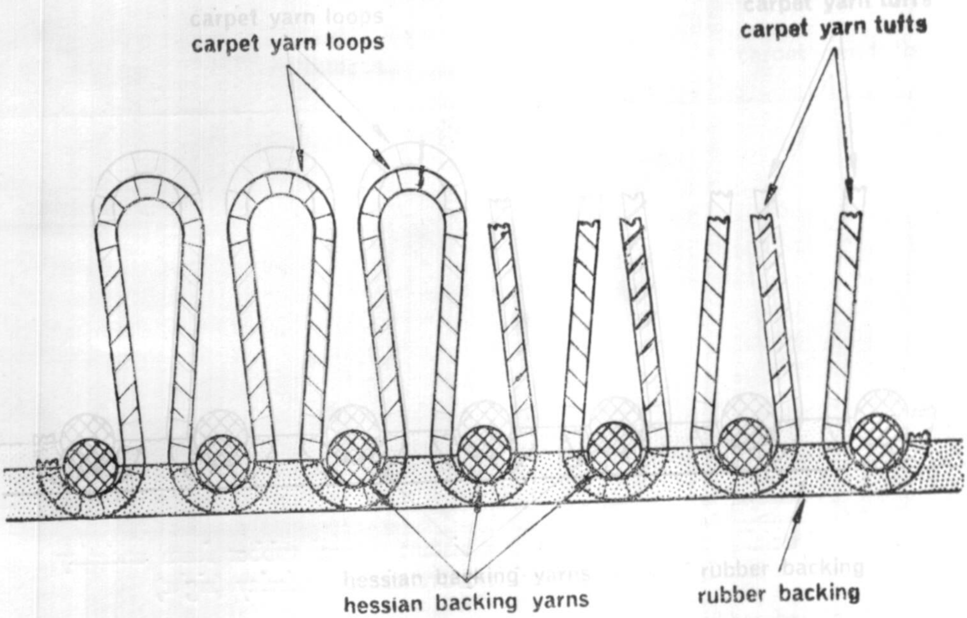

Fig. 13 Structure of tufted carpets

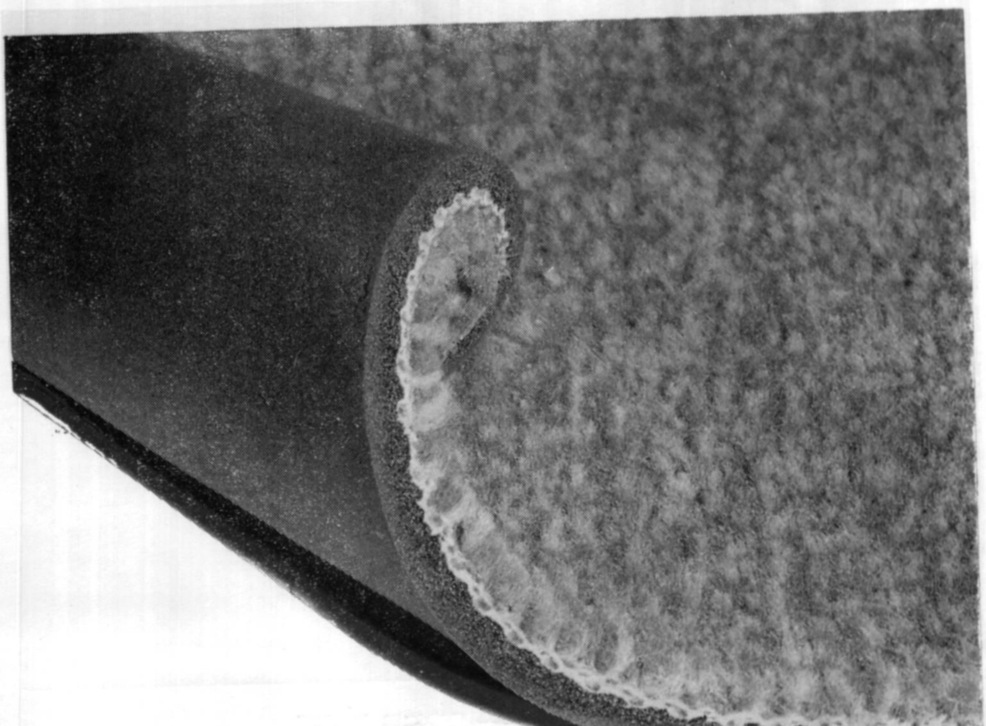

Fig. 14 Tufted carpet with no-gel foam underlay

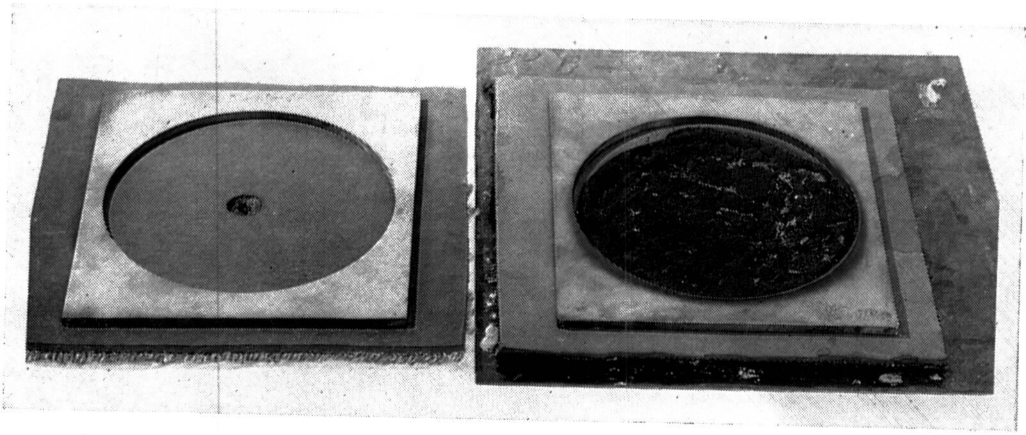

Fig. 15 Specially compounded flame resistant natural rubber foam underlay (left) compared with conventional underlay (right)

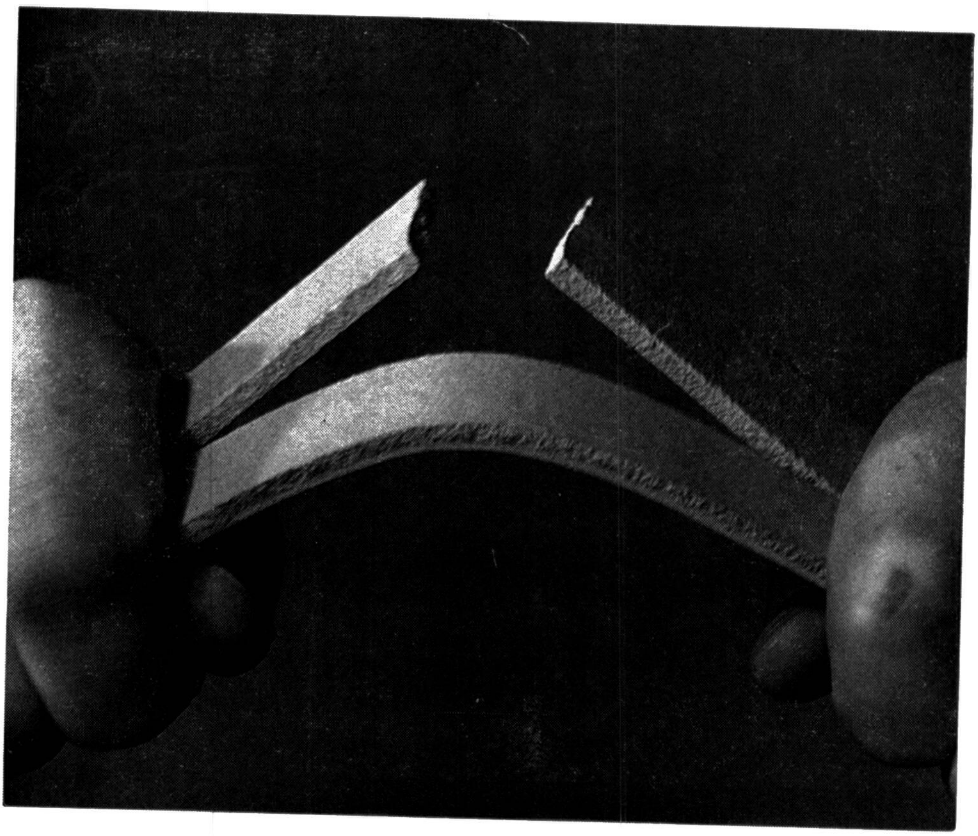

Fig. 16 Rubberized gypsum plaster

A process for marking excellent pre-compounded gum or lightly-filled natural rubber from latex for engineering uses was developed some years ago at MRPRA. In this the vulcanizing ingredients were ball milled into latex, the resulting compound was stable for extended periods at room temperature and when vulcanized gave excellent strength properties and consistency of properties much greater than normally obtained using conventional dry mixing methods. The process could be readily adapted to the production of powdered or granulated rubber, by spray drying the pre-compounded latex, crumbing of the wet coagulum or mechanical comminution of the dried product and using and anti-cohesion agent such as silica powder.

One large producer, Harrison and Crosfield, has announced the availability, *via* a latex process, of a free-flowing raw or pre-compounded natural rubber which is suitable for injection moulding and is proceeding to large scale production in Malaysia.

The problems still to be solved are (a) how to achieve an indefinite storage life of the compound, (b) how to incorporate reinforcing fillers into latex, and (c) how to overcome certain processing problems due to the very high molecular weight of the rubber.

Although there are undoubted attractions in the use of powdered/pelletized rubber in allowing automatic handling and weighing and, if pre-compounded; eliminating the need for mixing, the economic advantages are by no means certain. Mixing compounds in latex is not necessarily less expensive than Banbury mixing, and the need to install handling and storage equipment for powders must be offset by saving of investment in mixing equipment.

Liquid natural rubber: Almost all the synthetic rubbers can be readily produced in a low molecular weight liquid form by control of the polymerisation of 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 a more or less normal vulcanizate. The advantages lie mainly in the ready shaping of the vulcanizate by casting techniques or by curing *in situ* for gaskets and seals. Disadvantages include high cost, poor physical properties due to loss of micro structure of the backbone polymer and to imperfection of the network-forming process, and the difficulty of adding reinforcing fillers and of handling the resulting sticky materials. Only the poly-urethanes stand apart since they offer high strength properties and are essentially self-reinforcing although they are expensive at *ca.* 0.7 to 0.9 U.S. $ per lb.

The challenge from liquid forms of the general purpose elastomers is at present not serious but MRPRA chemists have exploited 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. Much development work would still be required to place the process on a viable commercial basis.

Thermoplastic natural rubber: The synthetic thermoplastics are without exception block or graft copolymers and owe their unique properties to the association of segments of their molecules into hard 'crystalline' 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 'crosslink' the rubber again. Such materials are expensive (from 1.5 to 7 times the price of natural rubber) 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 natural rubber. 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 cross link 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. 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 thermoplastics and the product sold as a free-flowing vulcanizate ready for remoulding by the consumer.

VULCANIZATION

After mixing the rubber compound and moulding it into the desired shape the final stage in the manufacture of a rubber article involves vulcanization—a process which chemically binds the rubber chain-like molecules into a strong three-dimensional network. This was originally accomplished by heating with sulphur and even today sulphur and its compounds are the prime agents for vulcanizing natural rubber. Their main advantages are their cheapness, ease of control of processing safety, and the exceptionally good strength and dynamic properties of rubbers vulcanized in this way. Their disadvantages lie in a rather poor resistance of their vulcanizates to oxidative ageing and to reversion. Reversion is, according to many consumers, the major deficiency of natural rubber compared with its synthetic competitors. It results from destruction of the crosslinks introduced during vulcanization of further exposure to high temperature and shows itself by softening and loss of strength.

Unfortunately reversion is particularly important in those articles, such as heavy duty and giant tyres, which for good technical reasons constitute a major market for natural rubber. In such articles high temperatures are generated during service and in the vulcanization of thick sections, rubber is kept at high temperatures for long periods to allow heat transfer. With current emphasis on increased productivity the practice of vulcanizing for long periods at low temperatures to limit reversion with a consequent low rate of production is no longer considered acceptable.

Efficient vulcanization and semi efficient vulcanization systems: Recent investigations at MRPRA have shown that superior resistance both to ageing and reversion can be obtained by reducing the amount of free sulphur to a minimum. Such "efficient vulcanization" (E.V.) systems are not suitable for all types of use—they are not quite as strong as conventional sulphur vulcanizates. However, "semi-E.V." systems with sulphur levels intermediate between those of the conventional and "E.V." systems have been shown to combine greatly superior ageing and reversion resistance with equivalent fatigue properties to those of conventional systems. These improved systems are increasingly being adopted by the rubber manufacturing industry.

Urethane systems: It is increasingly evident that sulphur vulcanization systems have been exploited nearly to the limit and if dramatic improvements are to come about it is necessary to look in other directions and to explore entirely novel ways of vulcanizing rubber. One such system for natural rubber has been developed. This produces vulcanizates with physical properties as good or better than those obtained using sulphur vulcanization but in addition they have excellent resistance to reversion which was the major target.

It involves a novel chemical compound formed by the reaction of para nitrosophenol and difunctional isocyanates which can be mixed with the rubber in the normal way. At vulcanizing temperatures it breaks up to attach reactive groups along the rubber chain and diisocyanates which form crosslinks between these reactive groups. Additionally heat build-up characteristics and resistance to oxidative ageing are as good as with the E.V. system and much superior to those of conventional sulphur vulcanizates while the dynamic fatigue properties are equivalent to the best obtained from conventional sulphur vulcanizates. Thus the "best of both worlds" has been obtained. Urethane vulcanization, as it is called, should find application in premium uses of natural rubber such as engineering components, heavy duty and giant tyres and bulky articles. It is now in its final stages of development and well protected by patent coverage. A licence for world-wide manufacture and sale has been granted to Hughson Chemical Co., U.S.A. and options to license to Sumitomo Chemical Co., Japan and Robinson Bros. Ltd., U.K.

Although this system can be used to vulcanize some synthetic rubbers it is of special applicability to natural rubber and it improves its acceptibility in respect of important features of ageing and reversion. The technical exploitation of this development promises to further the competitive edge of natural rubber over its rivals (Fig. 17).

Compounding natural rubber for low creep and improved dynamic performance: Although natural rubber has achieved a dominant position amongst rubbers used for engineering purposes, improvement in its consistency and precision of stiffness, reduction in its creep and dynamic loss would encourage its much wider use in applications currently satisfied by steel springs. Two developments at MRPRA with these objectives have brought enthusiastic response from industry.

Sulphur and accelerators are only partially soluble at normal temperatures and becomes more soluble at mixing temperatures. As the compound cools these ingredients may be redeposited often as large crystals leading to coarsened dispersion and local overcrosslinking with a variable and deterimental effect on strength and modulus. A simple solution has been found in which the various vulcanizing ingredients are carefully selected so that they are fully soluble at normal temperatures. Another essential constituent of a sulphur vulcanizing system is a zinc soap, conventionally this is zinc stearate formed *in situ* by the reaction of zinc oxide with stearic acid, this also is only slightly soluble at normal temperatures and is now recognized as an important source of modulus variation. A rubber soluble zinc soap, zinc 2-ethylhexanoate has been found and fully soluble E.V systems (FSEV) are available which possess all of the attributes of the normal E.V. systems together with particular advantages in the precision of modulus, resilience and creep of its vulcanizates (Table 2).

TABLE 2

MODULUS PRECISION

Cure system	Soap	Rubber	Initial 95% limits	Change in 18 months
Conv. S/CBS	ZnSt	RSS	± 13%	+ 3%
Sol EV	ZnSt	RSS	± 4%	+ 3%
Sol EV	ZEH	DPNR	± 2%	0%

The second development involves deproteinized natural rubber which when used in conjunction with the fully soluble EV system enhances properties still further. Natural rubber has a very low affinity for water but it normally contains small but significant amounts of protein and inorganic salts and water adsorption is increased and may vary from batch to batch. Adsorption of water can have a number of consequences: it can affect the rate of vulcanization and the efficiency of crosslinking thus giving rise to loss of processing safety and modulus variability: it can also adversely affect resilience, creep and stress relaxation (Table 3).

TABLE 3

THE EFFECT OF MOISTURE ON THE MODULUS OF VULCANIZATES MADE FROM NATURAL RUBBER WITH DIFFERENT NON-RUBBER CONTENTS

Raw rubber	Non-rubber content	Change in Modulus*
Field latex total Solids	very high	15%
RSS 1	normal	5%
DPNR	very low	1%

* % Change in M_{R100} between equilibration of vulcanizate at 10% relative humidity and 80% relative humidity.

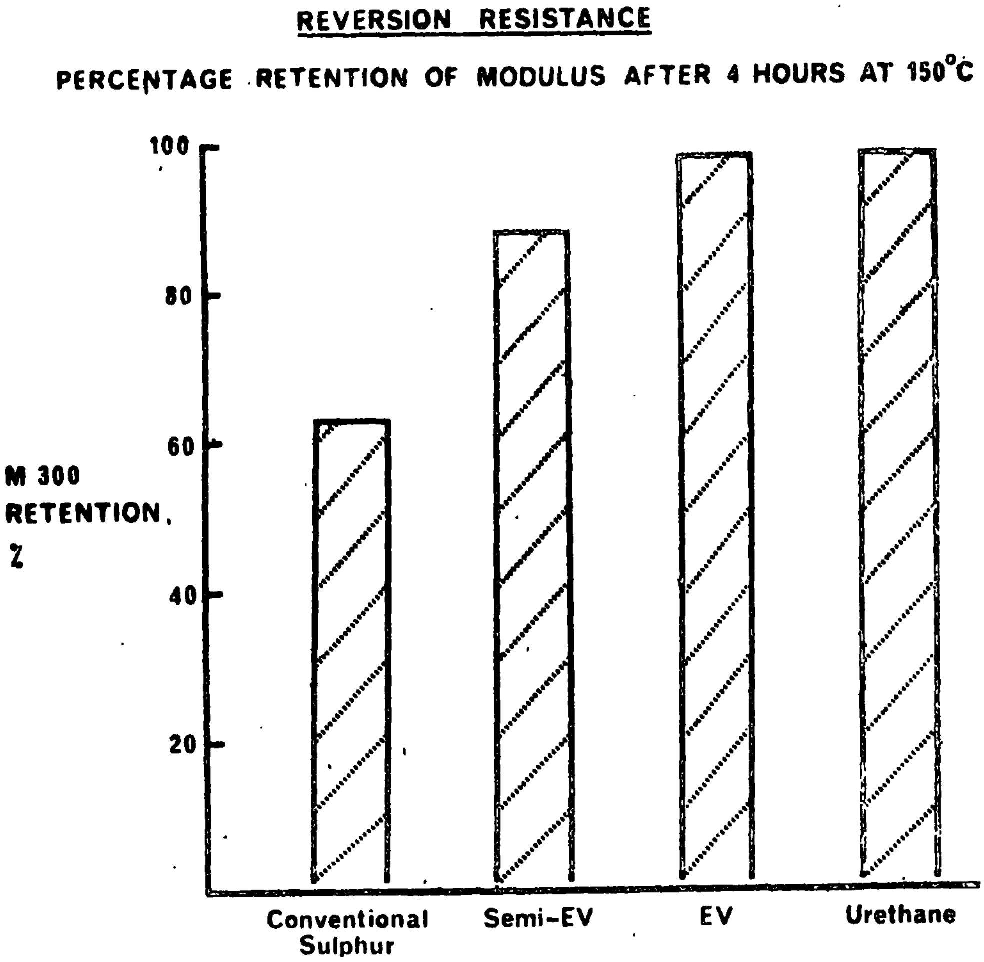

Fig. 17. Showing excellent reversion resistance of 'Efficiently vulcanized' (EV) and urethane vulcanizing systems.

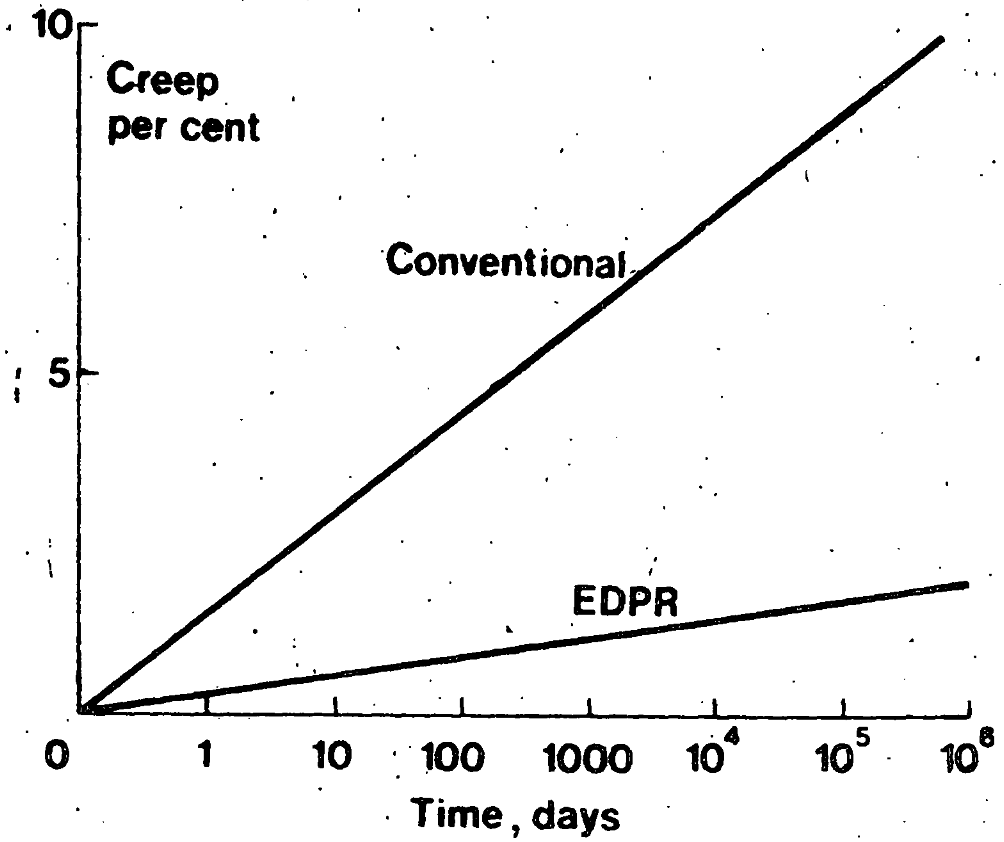

Fig. 18 Exceptionally low creep rates shown by soluble compounded enzyme deproteinized natural rubber

An efficient process for the removal of protein and inorganic salts has now been developed and production is being scaled up to a commercial level by the RRIM. This provides natural rubber of extra high performance which is particularly suitable for applications such as engineering components where its main advantages are superior creep, resilience and better consistency (Fig. 18). Already a number of manufacturers are examining its use in conjunction with soluble compounding principles in applications such as vehicle suspensions, engine mountings, washing machine gaskets *etc*. One vehicle manufacturer has reported a 50 fold increase in service life of a particular component.

AGEING

The life of a rubber component in service is almost always limited by deterioration of the rubber due to ageing. Fortunately natural rubber, unlike its synthetic counterpart is well endowed by nature with antioxidants which protect it very efficiently as raw rubber and to some extent after vulcanization. Advances by manufacturers of antidegradants have enabled the protection of natural rubber against ageing to keep ahead of the increasing severity of service conditions. Two recent developments at MRPRA promise still further to strengthen the position.

The first is the development of antioxidants which can be chemically bound to natural rubber so that they are not lost through volatility at high temperature or by leaching through contact with water or solvents. As yet their commercial uptake has been limited by a darkening which is unacceptable in light coloured articles such as garments containing rubber thread or foam and where dry cleaning or laundering rapidly leaches out conventional antioxidants.

The second is the development of a new class of antiozonants which does not incur the penalties of poor processing safety and loss of crosslinking efficiency—shown by the best of modern antiozonants and yet at the same time afford unimpaired protection against ozone cracking.

At the outset of this paper it was stated that natural rubber had an inherent potential far exceeding its present usage. To achieve and maintain this potential and in the changing technological scene calls for continuous effort on the part of the producing industry to tailor natural rubber to meet the precise needs of the manufacturing industry. The developments described will assist in improving the performance of articles made from natural rubber and ensure that it can meet the demands placed on it.