A STUDY OF THE EXPLOITATION OF THE PROPERTIES OF NATURAL RUBBER IN TYRES

by

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Summary

Tyres account for over 60 per cent of the world's total rubber usage. The distribution of rubbers used in tyres between natural and synthetic rubber varies from country to country. The trends in tyre development are indicated. The properties of natural rubber and the main synthetic rubbers used in tyres are described. Newer synthetic rubber types and new forms of natural rubber are also described. The suitability of the different rubbers for use in the various components of tyres is discussed. The other factors besides technological suitability are then taken up. These include availability and price. The manufacture of synthetic rubbers from petrochemical based materials is traced and the problems facing synthetic rubber manufacturers are discussed.

The dramatic changes in the world energy situation reflected in shortages and price escalation of petrochemical based materials since this research project was begun has led to rethinking on the choice of rubbers for use in tyres. The present low prices of natural rubber are a consequence of the economic recession following the world energy shortage. In the present confusion caused by the oil crisis, currency

fluctuations and balance of payment problems, it is not possible to paint a clear picture of the future of natural rubber in tyres. An attempt has been made to indicate the factors favouring and opposing a bright future of natural rubber in tyres. Motor cars provide an index for a country's prosperity. Tyre usage being tied to motor vehicle usage, the growth of tyre demand can only accompany increasing national and international prosperity.

It is not only the synthetic rubber used in tyres that are derived from petrochemical bases. Nylon (polyamide) and polyester tyre cord materials, carbon black, processing oils and the chemical ingredients used as accelerators, antidegradants and peptisers are all made from petrochemicals. The present oil crisis has created supply problems in all these materials. The position is particularly difficult for small tyre factories since research and development work on tyres is expensive. How expensive it is can be gauged from the section on testing of tyres and rubber compounds used in tyres. The need has arisen to evaluate new materials and re-evaluate older materials with a view to techno-economic optimisation of tyre manufacture. An exercise carried out as part of this project to obtain optimum levels of four compounding ingredients used in a natural rubber based truck tyre tread compound is described. The technique used was computer aided regression analysis in which regression equations are used to predict the cost and properties of a large number of different compounds and these predicted values are analysed to select the best levels of the ingredients.

The work described in this dissertation was carried out at the University of Aston in Birmingham and the Rubber and Plastics Research Association of Great Britain between June 1973 and January 1975.

It has been done independently and submitted for no other degree.

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A STUDY OF THE EXPLOITATION OF THE PROPERTIES OF NATURAL RUBBER IN TYRES

Introduction

1.1. The Importance of Tyres to Rubber Producers

The importance of tyres to producers of both natural and synthetic rubbers can be gauged from Table 1.1. which shows the quantities and percentages of rubber accounted for by tyres in the different countries. The U.S.A. which is by far the world's largest consumer of rubber used 64.5 per cent of its total rubber consumption in tyres. The data in the tables given in this section are obtained from the Rubber Statistical Bulletin (November 1974) published by the International Rubber Study Group (1)

Table 1.1. Raw Rubber used in Tyres and Tyre Products in 1973 in relation to total rubber consumption

'000 metric tons

(1) Country	(2) Total rubber consumption	(3) Rubber used in Tyres & Tyre Products	(4) (3) as percentage of (2)
U.S.A.	3,135.8	2,022.3	64.5
Japan	1,045.0	562.4	53.8
West Germany	613.6	274.0	44.6
France	466.9	297.7	63.8
U.K.	455.9	224.6	49.3

The proportion of natural to total raw rubber used in tyres varies from 25.5 per cent in the U.S.A. to 38 to 40 per cent for Japan, West Germany, France and U.K. as shown in Table 1.2. In 1971 in the U.S.A. the proportion of natural rubber in tyres was only 23.6 per cent. It will be noted that though the proportion of natural rubber to synthetics in tyres is low in the U.S.A. the actual quantity of the natural rubber used in tyres is much larger than that in any other country.

Table 1.2. Usage of Natural and Synthetic Rubber in Tyres

'000 metric tons

Country	NR	SR	Total rubber used in tyres	NR as per cent of total
U.S.A.	515.2	1,507.1	2,022.3	25.5
Japan	217.1	345.3	562.4	38.6
West Germany	106.8	167.2	274.0	39.0
France	119.6	178.1	297.7	40.2
U.K.	89.5	135.1	224.6	39.8

Table 1.3. shows the consumption of NR in different countries in relation to total world NR consumption while Table 1.4. shows the usage of NR in tyres in relation to total NR consumption in each country.

Table 1.3. Consumption of NR in different countries in relation to total world NR consumption - 1973

	NR Consumption	As per cent of Total World NR consumption
Total World	3,400.0	
U.S.A.	696.4	20.5
Japan	335.0	9.8
Germany	205.6	6.0
U.K.	173.1	5.1
France	162.3	4.8
Western Europe (total)	921.2	27.1
*Eastern Europe & China	700.0	20.6

*Estimated

Table 1.4. Usage of NR in tyres in relation to total NR consumption in the country - 1973

	Usage of NR in Tyres ('000 Metric Tons)	Total NR consumption	(1) as per cent of (2)
U.S.A.	515.2	696.4	74.0
Japan	217.1	335.0	64.8
West Germany	106.1	205.6	52.0
France	119.6	162.3	73.7
U.K.	89.5	173.1	51.7

No figures are available for the quantities of NR used in tyres in the countries of the Socialist bloc. It seems fair to assume that tyres account for more than 75 per cent of the total NR consumption on account of the much higher proportions of heavy vehicles to passenger car tyres. Larger tyres use high proportions of NR, while the proportion of NR in passenger car tyres is decidedly lower, as will be explained later.

The data presented so far stresses the importance of tyres to rubber producers. It explains why emphasis in rubber research and development work as well as in marketing of rubber is on tyres.

1.2. The choice of rubbers for use in tyres

The choice of rubbers (elastomers) for use in tyres is governed by the following factors:-

1. Availability.
2. Price.
3. Quality and uniformity.
4. Processing characteristics in the factory.

and 5. Performance in the finished tyre.

1. Availability

In the context of present day transportation rubber is a strategic raw material and adequate supplies of raw rubber are needed by every country to keep people and goods moving. Natural rubber plantations are concentrated in South East Asia which account for over 90 per cent of world production. During two world wars and in other times of international crisis natural rubber supplies have been denied to some countries. Rubber Restriction Schemes operated in the nineteen twenties and thirties have also artificially limited supplies to the world market.

2. Price

The restriction schemes were seen by non-rubber growing consumer countries as a means of forcing them to pay prices determined by the rubber growing interests. At other times too whenever the demand for rubber was strong manufacturers of rubber goods had to pay high prices for rubber. Two such occasions were the days of the Korean War early in the 'fifties and the months following the Middle East conflict of October 1973 when natural rubber prices rose to above £500 per metric ton. This was due more to speculation on the rubber market than to any real shortage of natural rubber. The activities of speculators on the natural rubber market have been decried by rubber producers and consumers alike. With their basic raw material showing such widely fluctuating prices rubber manufacturers face serious problems in planning production and pricing policies. Synthetic rubber prices had remained steady and shown a downward trend until the petrochemical shortage in 1973 forced price increases. Today general purpose synthetics rubbers are more costly than natural rubber.

3. Quality and Uniformity

Complaints of lack of uniformity and supplies below standard specification samples have been levelled against natural rubber particularly during times of shortage. The Rubber Manufacturers Association in the U.S. made a special appeal to rubber manufacturers against accepting sub-standard deliveries of natural rubber in 1951.

The claim was always made for synthetic rubber that there was a high degree of uniformity between lots.

4. Processing characteristics in the factory

The increasing emphasis on greater productivity in the factory requires materials which need less processing. In a tyre factory the demand would be for raw rubber which needs no warming, little or no mastication and shorter mixing times. Fast extrusion and calendering rates are also desired.

5. Performance in the finished tyre

The rubber compounds used in tyre components should ensure good performance of the components and the whole tyre.

The choice of raw rubber for tyre production is made on the basis of techno-economic evaluation of these factors. These parameters as applied to different materials are however subject to change as evidenced by the recent escalation of the prices of all petroleum based materials. It then becomes necessary to evaluate new materials and re-evaluate older materials with a view to techno-economic optimisation of tyre manufacture.

1.3. Scope of the Present Project

Smaller tyre factories like the one in Sri Lanka are badly affected by disruption of the supply pattern. Higher prices of certain raw materials and difficulties in obtaining adequate supplies of others make it necessary to carry out optimisation studies of rubber compounds with cost as one of the variable characteristics. However, before the subject of optimisation studies can be discussed present trends in tyre development and the suitability of the available rubbers for use in the different components of passenger car and truck tyres must be assessed. The methods used to evaluate the performance of different rubber compositions in tyre service are then critically described.

The experimental work consisted of an exercise aimed at predicting optimum levels of four compounding ingredients used in a natural rubber based truck tyre tread compound by the technique of computer aided regression analysis.

2. TRENDS IN TYRE DEVELOPMENTS

2.1. Tyre Design and Construction

The basic function of the tyre is that of an envelope for the air that actually carried the load of the vehicle. The envelope is the fabric body or carcass of the tyre which is surrounded by a cushion of rubber compound. The tyre tread provides traction against the road surface while the bead anchors the tyre to the wheel of the vehicle. In tubeless tyres the inner liner hinders diffusion of air into the carcass plies which then tend to separate. Figure 2.1. is a cross sectional drawing of a radial passenger car tyre and Figure 2.2. that of a large truck tyre. The structure of a tyre and the principles underlying it are explained by Gough (2).

There are two basic tyre constructions, cross ply or bias-ply and radial ply. The belted-bias construction is a hybrid of these two. In the cross ply the tyre cords run at an angle from bead to bead, the cords in alternate layers running in opposite directions. In the radial ply tyre the cords run at right angles to the bead. The radial ply tyre has additionally one or more layers of fabric constituting the rigid breaker belt which are restricted to the tread area. Belted-bias tyres have cross ply carcass construction with a rigid belt. Figure 2.3. shows the three different constructions.

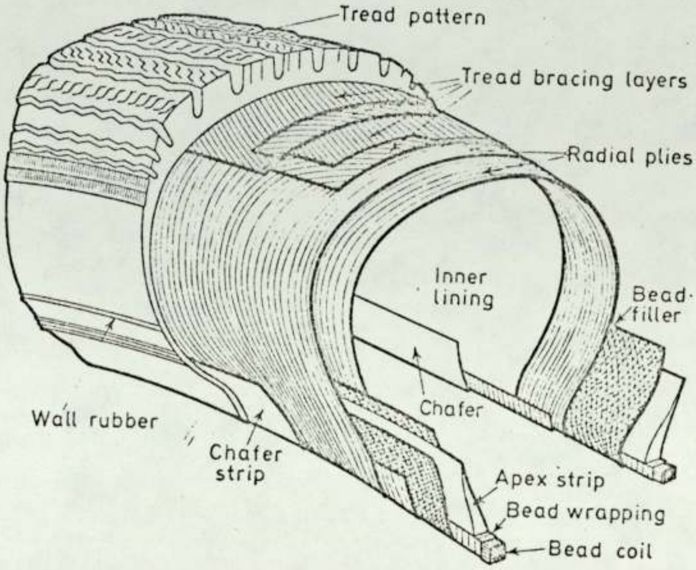


Fig. 2.1 *Radial ply tyre (two-ply construction), tubeless*

Source Blow:

Source: Blow : Rubber Technology and Manufacture
Butterworths, London 1971

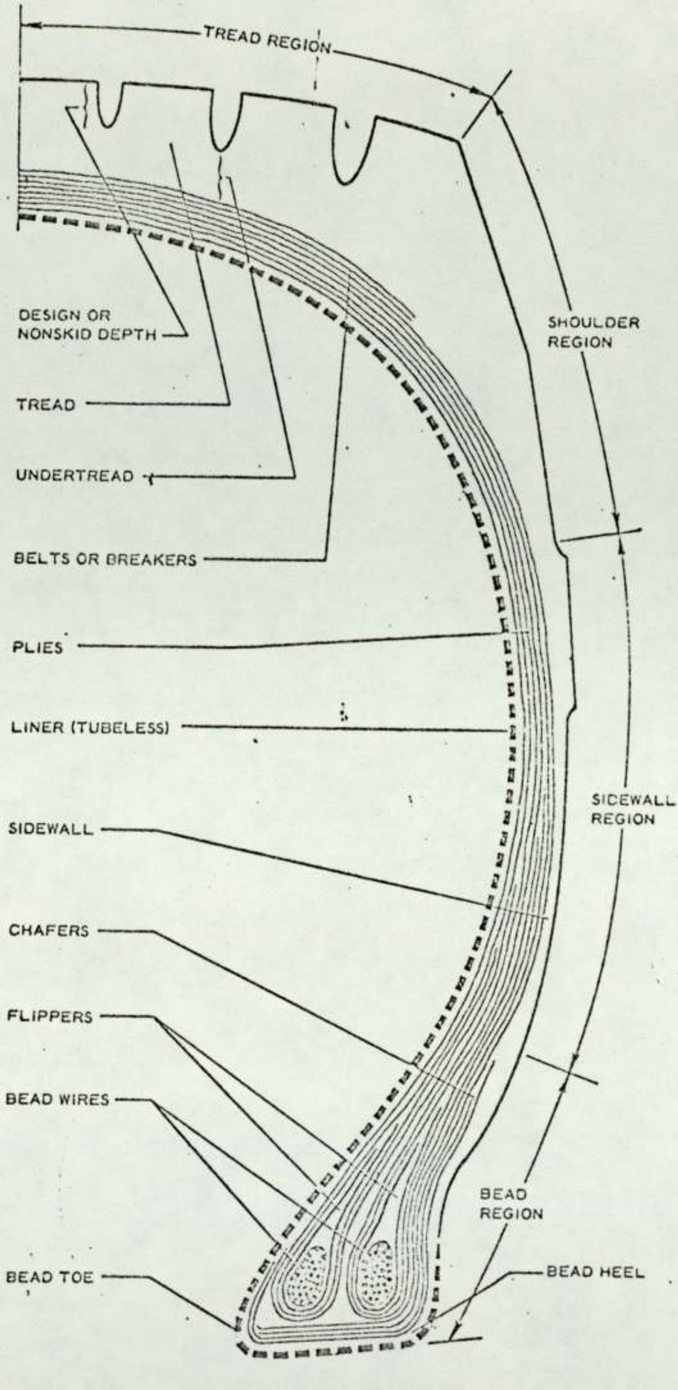


Fig. 2.2. Components of a truck tyre

Fig. 2.3a Basic Tyre Constructions

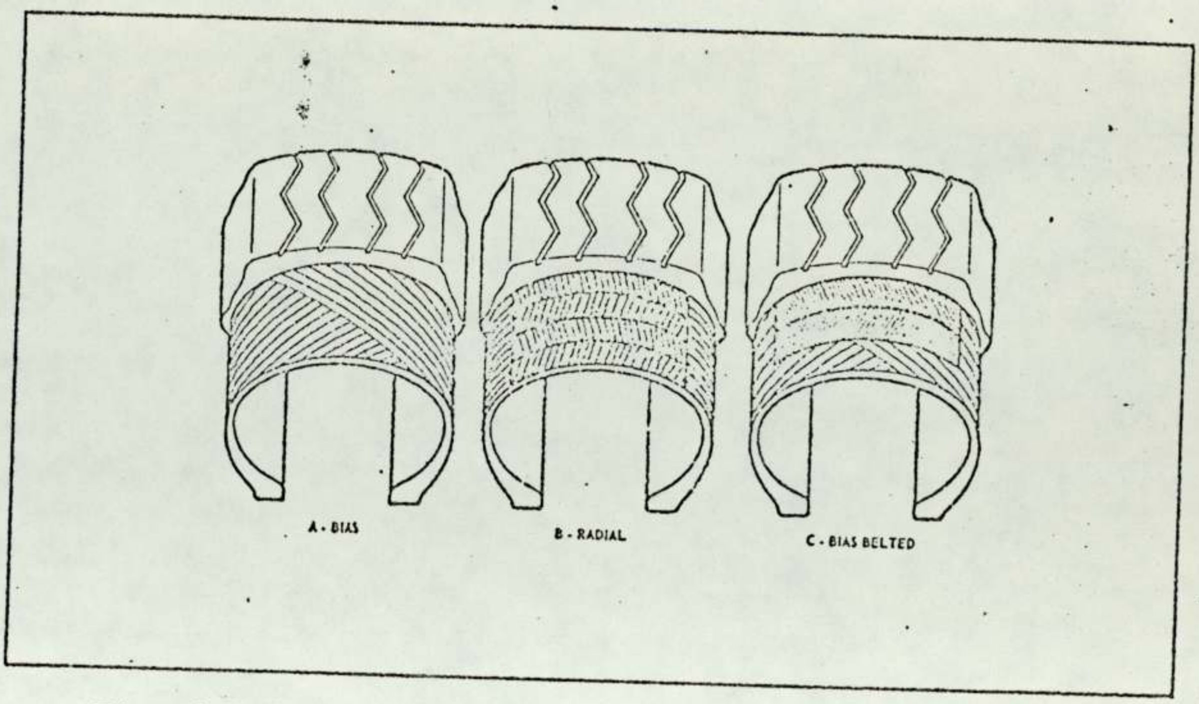
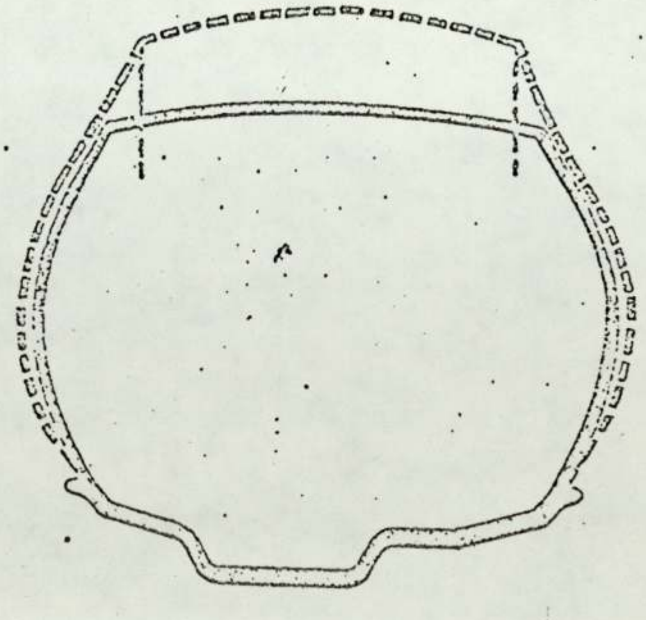


Fig. 2.3a Basic Tire Constructions

Knill and Urbon (14)

Fig. 2.3b Standard Tyre versus Low Profile Tyre



15° Tubeless Rim

Shearer (7)

It has been explained (3) that "The guiding principle in development of rubber compositions for tires is to achieve the best balance of properties for a particular type of tire service. Since a tire is a mechanical structure a rubber component should be judged on how it functions in the system rather than on its individual properties or performance capabilities".

2.2. General trends in tyre development

Tyre developments are largely determined by vehicle developments. Vehicle development is in turn influenced by socio-economic factors like the state of the economy, environmental legislation and the energy crisis which has led to shortages and high prices of petroleum-based products. It is relevant to stress here that nearly all the raw materials used in the tyre industry including the synthetic rubbers, carbon blacks, polyamide (nylon) and polyester tyre cord materials, processing oils, peptisers, accelerators, retarders and antidegradants are petrochemical based.

The directions that tyre development takes will greatly influence which polymers (rubbers) and other raw materials the industry will use. Radial ply tyres for instance require higher proportions of natural rubber. Technologically it is not only the properties conferred by a material on the finished tyre that are important. As factory processes continue to become more streamlined the ease of processing becomes more important. Natural rubber is the preferred material in radial ply tyre carcasses because its high strength in the unvulcanised state ("green strength") enables it to resist the more exacting stresses imposed during the operation of assembling a radial ply tyre. The economic considerations of price and availability are also of paramount importance.

The following trends are predicted for both passenger car tyres and heavy vehicle tyres in this decade. (6,7,8)

1. A pronounced shift to radial construction.
2. A move towards progressively lower aspect ratios. (ASPECT RATIO is defined as the tyre section height divided by its width).
3. Greater emphasis on safety.
4. Increased importance of comfort in riding. NVH - Noise, Vibration, Harshness - characteristics of tyres are receiving greater attention as they do in motor vehicles.
5. Greater use of steel as the tyre cord material. Competitors include polyester, du Pont's Kevlar an Aramid fibre, and glass fibre.

2.2.1. The Radial Ply Tyre

The conventional cross-ply or bias ply tyre has the cords of the tyre carcass running from bead to bead at an angle, the cords in alternate layers running in opposite directions. It is not braced by an inextensible belt. In the radial ply the carcass cords lie at right angles to the tyre bead and are reinforced by an outer rigid belt. A British patent granted to Gray and Sloper in 1913-14 (9) stated "the tyre cover comprises in combination radially disposed flexible inextensible cords which constitute the sole restraining means at the sides of the tyre, and a girder belt of flexible material inextensible in directions oblique to the circumferential direction of the tyre .... to prevent rolling". Though rayon was first used as the material of the rigid breaker belt, steel cord and glass fibre are the present front runners.

The greatly improved performance of the radial tyre is due to the separate functioning of the tread and sidewall. In the cross-ply tyre the same tyre cords reinforce both the tread and the sidewall so that when the sidewall flexes the tread is distorted. The presence of the additional layer of rigid breaker belt in the radial ply tyre prevents this distortion ("squirming") of the tyre tread, so that it remains flat while the sidewall flexes in response to cornering, braking or road surface irregularities.

2.2.1.1. Comparison of radial ply and conventional cross ply tyres

Gough, Jones and Udall (9) have explained the differences in performance between the radial ply tyre and the conventional cross ply tyre.

Advantages of radial ply tyres

1. Much longer tread life

The initial motivation for using radial ply tyres was the greatly increased tread life of radials. Tread wear depends on a variety of factors as will be shown later. Gough (9) estimated that the tread life of radials is 60 to 120 per cent better than that of cross ply tyres. It is generally accepted today that a radial tyre will show 100 per cent better tread wear than a cross-ply tyre would. The radial ply tyre, it is pointed out, (9) represents the greatest breakthrough in increased treadwear resistance since the introduction of carbon black into tyre tread compounds. Gough (10) has shown that the tread breaker belt acts as a beam supported on the elastic foundation provided by the radial casing.

2. Better steering characteristics

The better steering characteristics of radial tyre are explained on the basis of higher cornering power and lower aligning torque.

3. Greater stability at high speeds

The radial ply tyre is more stable at high speeds than the cross ply tyre. The difference in stability is explained in terms of the ripple effect, the wave like distortion noticed in tyres operating at high speed. (11) This effect is variously known as ripple, standing wave, stationary wave and traction wave.

4. Better wet skid resistance

Gough and others (9) point out that the rigid breaker belt in radial ply tyres enables a wide variety of tread designs and polymers to be used, resulting in high resistance to skidding in both braking and cornering. A possible explanation is the ability of the tread of the radial tyre to flatten to the road configuration without difficulty. The cross ply tyre tread can only do so with tread distortion. The belt like flexibility of the breaker layer and the high flexibility of the sidewall of radials gives a slightly longer contact patch and higher contact pressure than is obtained with cross ply tyres. 10 to 20 per cent greater traction is developed. Figure 2.4 (9) shows the relative grip of the two types of tyres on a traffic polished smooth surface.

5. Cooler running at high loads or low pressures

This is due to the lower level of distortion of the radial tyre.

6. Lower noise generation and transmission

The tendency of radial ply tyres to reduce road roar on rough road surfaces is reported (9) to be a major reason why some vehicle engineers prefer radials.

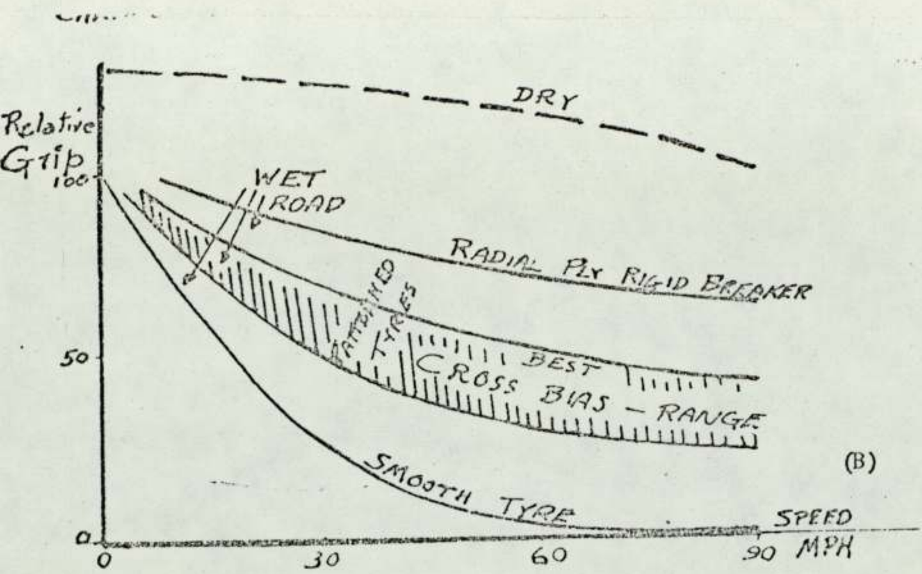


Fig. 2.4 Relative grip of tires on traffic polished smooth road.

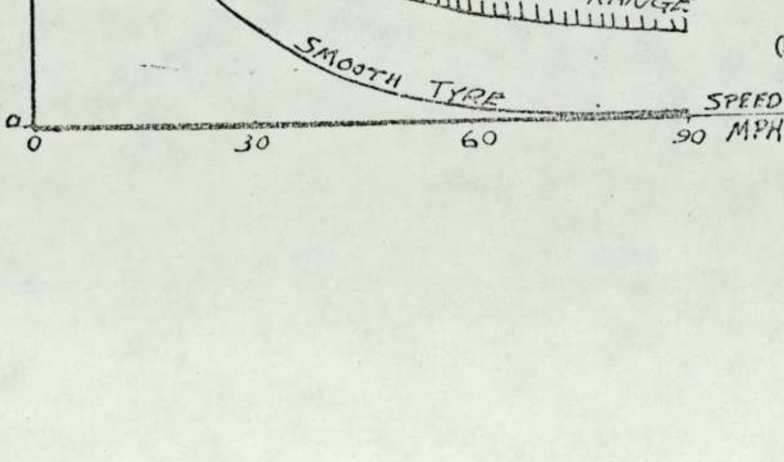


Fig. 2.5 Rolling resistance data for radial ply and conventional tires

7. Lower rolling resistance leading to lower fuel consumption

The radial tyre has a lower rolling resistance than a cross-ply tyre. Figure 2.5 (9) gives a comparison between the two types. Rolling resistance multiplied by speed gives the power consumption. It is now known that rolling resistance is little influenced by speed so that it is a convenient index of the power consumption of a tyre (11). Fuel consumption is influenced by the conditions of operation of the vehicles. It is extimated that for conditions existing in England, the use of radials can reduce the fuel consumption of trucks by 5 per cent and of passenger cars by 2 per cent. Fuel consumption is listed as a secondary feature in Gough's summary of performance of radial and cross ply tyres reproduced at the end of this section but today it is an important factor.

The disadvantages of radial tyres

1. Radials cost half as much more as cross-ply tyres Their higher manufacturing cost is due to the additional processes involved in their manufacture, the expensive equipment needed, and the greater degree of precision and supervision required in the manufacturing operations. The increase of 50 per cent in cost must however be balanced against the 100 per cent or so increase in tread life alone.

The effects of tyre design, particularly radial, on production equipment are described by Isaksson (12). He points out that accurate dimensional control of all parts of a radial tyre during manufacture is an absolute necessity for high quality and that the placement of components in their appropriate places without distortion during handling is the key to quality tyre assembly. Special dispensers or servicing machines, tyre assembly machines and vulcanising machines are described. They are much more sophisticated, more precise and more expensive than the equipment used for cross-ply tyres. Graham (13) describes "on-stage" tyre building machines, segmented tyre moulds, cable bead machines and other other special equipment designed for radial tyre manufacture.

2. At speeds below about 40 m.p.h. radials give a harsher ride. This is caused by the reaction of the rigid breaker belt to irregularities on the road surface. Such harshness can be corrected by "tuning" the transmission characteristics of the vehicle suspension system.

3. The radial ply tyre is less robust than the cross ply tyre and is more susceptible to accidental damage on poor roads.

4. The remouldability of cross-ply tyres is greater than that of radials.

5. At very high cornering intensities caused by high speeds or sharp corners one or more of the tyres can skid. With cross ply tyres the feel on the steering wheel changes giving warning of a likely skid. In radials, particularly steel belted ones, breakaway is

sudden and with no warning that most drivers can recognise.

Table 2.1. is a tabulated summary of the comparison of radial ply and cross-ply tyres made by Gough and others (9).

Table 2 - Conventional Cross Bias Tires Versus Radial Ply Rigid Breaker Tires
(Merit Ratings Given from Consideration of Basic Concept Only)

Major Features	Cross Bias Tires	Radial Ply Tires	Comments
Tread Wear	100	160^+	This feature dependent on individual design.
Noise Suppression	100	+ Superior to Conventional	Substantial reduction in road roar frequencies (100-300 cps) on noise exciting surfaces.
Ridging/Wander	100	+ Superior to Conventional	Radial ply tires better even when compared with conventional tires with wrap round shoulder designs; also, still maintain good properties when worn.
Ride			
Low-Speed Hardness up to 40 Mph	100	80-90	Vehicle suspension factors important in assessing these properties.
High-Speed Ride	100	125	Radial ply tire a "natural" for European cars at motorway speeds.
Secondary Features			
Fuel Economy	100	Up to 105	Small but positive saving in fuel consumption for radial ply tires.
Car Control and Handling	100	95-105	Radial ply tires generally good on constant bend corners but slightly inferior on transitional effects; also dependent on car.
Tire/Road Adhesion	100	100+	Satisfactory for both types with modern tread material and patterns, but more scope with radial ply tires for radically new tread designs.
Parking Torque	100	90	Radial ply tires inherently heavier in parking than cross bias tires; this feature to be watched in medium sized cars without power assisted steering.
Endurance	100	100 on Good Roads 95 on Unmade Roads	Radial ply downgraded slightly because of higher susceptibility to wall damage by loose boulders, etc.

2.3. Trends in Passenger Car Tyre Development

The following trends are noticeable in passenger car tyre development.

1. The average size of tyres will be smaller, following the move towards lighter cars as a result of escalating prices of motor fuels.

2. The switch to radial construction will be accelerated because of the greater economy in fuel and wear characteristics. The relative performances of bias-ply (cross-ply), bias-belted and radial ply passenger car tyres are shown in Table 2.2. below prepared by Knill and Urbon (14).

Table 2.2

Performance of the three Tyre Constructions in 78 series

PERFORMANCE RATINGS

Construction	Bias	Bias-belted		Radial	
Carcass Belt	Polyester -	Polyester Fiber-glass	Polyester Steel	Polyester Rayon	Polyester Steel
Treadwear	100	140	165	200	240
High Speed	110	115	115	120	115
Wet Skid	100	110	112	112	115
Ride					
low speed	100	98	96	96	94
high speed	100	99	98	100	100
Fuel consumption	100	99	100	104	104

(Ref. Knill and Urbon : "Future Trends in Tyre Technology (7)

Forecasts for the distribution of the passenger car tyre market in Europe and the U.S.A. (Tables 2.3 and 2.4) (15) (16) show that Europe is far ahead of the U.S.A. in the switch to radials.

Table 6

Percentage Share of the U.S.A. passenger car tyre market-by construction

	Original Equipment Market				Replacement Sales			
	1972	1973	1974	1975	1972	1973	1974	1975
Radial	06	18	41	61	8	13	19	24
Bias-belted	78	64	46	30	38	42	39	38
Bias-ply (cross-ply)	16	18	13	9	54	45	42	38

Ref. (15) Modern Tyre Dealer January 1974 p.54

Table 7

Percentage Share of passenger car tyre market in Europe for radial ply tyres

	Original Equipment		Replacement Sales	
	1970	1975	1970	1975
U.K.	35	90 to 100	38	80
France	95	100	95	100
W. Germany	35	100	40	90
Italy	100	100	50	85

Ref. (10) PRT Polymer Age : May 1973 p.173 : Wind of Change in Tyre Design

It is interesting to note that the tyre specified by General Motors for their new cars is a radial.

3. Tyre aspect ratios will be reduced towards 70 and 60. Lower aspect ratios apart from giving car designers more opportunity to improve the aesthetics of the vehicle are said to give the following technical advantages:-

"... the contact patch becomes shorter and wider, the tyre has a lower rolling resistance, it is less distorted in manoeuvre, and of course its vertical stiffness is greater." The disadvantages of lower aspect ratios are "harder riding especially on vehicles with standard suspensions, harder to steer when parking, greater difficulties in manufacturing and higher costs". (12)

The low aspect ratio tyre not only improves tyre mileage but also vehicle stability and permits the use of a wheel with a larger internal diameter, thereby permitting larger brakes. (7) (17) Figure 2.3. (b)

4. Polyester is the likely tyre cord material in the U.S. for bias belted tyres in the 1970s. In Europe rayon is the favoured material for tyre cord, polyester being used to any extent only in Britain. The advantages of steel cord, particularly its resistance to cutting and its cooler running properties are recognised, but special expensive equipment is needed to process it. This investment is gradually being made and it is expected that steel cord will be the predominant tyre cord material towards the end of this decade. All-steel radials have been manufactured for many years by Michelin. Most passenger car radial tyres

in the U.S. now have an all steel construction. Competing with steel will be glass fibre and organic fibres like du Pont's Kevlar. Their claims are based on their lower costs, their lower specific gravity, their ability to be processed on existing equipment and their comparative performance. Three U.S. tyre companies have put out all glass radial tyres priced 20 per cent lower than an all-steel one, claiming it duplicates the performance of the steel radial and in addition gives a softer ride.

5. The rigid breaker belt of radial ply tyres will be made of steel in Europe. In the U.S. it will be of steel or fibreglass.

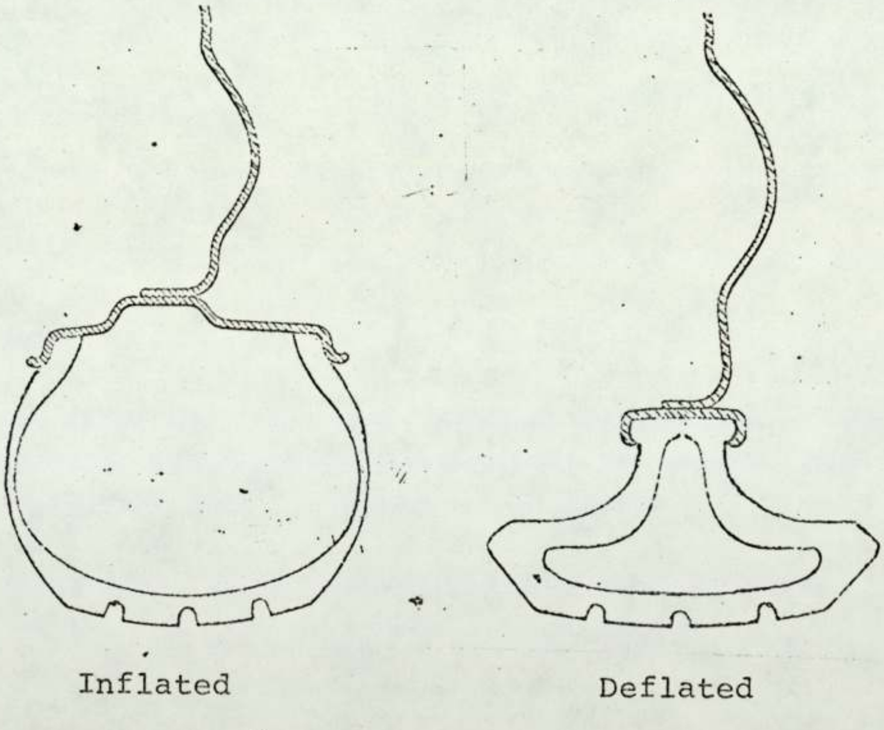
6. Motor car manufacturers are anxious to dispense with the spare tyre to provide more usable space in the car and greater freedom for the car designer. Run flat tyres while satisfying these needs would also assure the motorist greater safety and less inconvenience in the event of a puncture.

In February, 1972, Dunlop announced the development of a run-flat tyre. Originally called the Total Mobility Tyre its name has since been changed to DENOVO. The Denovo is a tubeless radial tyre and it was made possible because of the development of the radial ply concept and the lowering of tyre aspect ratios. The concept of this tyre it is stated, differed from earlier attempts to prevent a puncture from immobilising the tyre in that the flattened condition of the tyre was accepted as the starting point for this development. The Denovo idea comprises not only the tyre but also a special wheel and a special lubricant. The tyre is a low aspect ratio, tubeless radial. The wheel is in two sections and the drum is flat as in aircraft wheels. The lubricant is contained in special dispensers that are located round the circumference of the wheel. It is automatically released from the dispensers when the air pressure drops in the tyre. The lubricant serves 3 purposes. It acts as a lubricant preventing chafing of the inside of the tyre when deflated. It contains a sealant that plugs small punctures and it liberates a vapour that maintains a pressure of 5 p.s.i. It is claimed that the tyre in this condition (5 p.s.i.) can be driven 100 miles at 50 m.p.h. The claims made for the Denovo include, apart from the convenience of getting to one's destination in time, easy fitment, elimination of the spare wheel and jack,and freedom from the danger of the driver losing control over the car. The likelihood of damage to the tyre by running flat is also minimised. Natural rubber is the favoured polymer for such applications. (6) The Denovo has great economic potential as both a safety tyre and a run flat tyre. The drawbacks are that repairs to Denovo can be carried out only by specialists,and its high cost. The cost of fitting four Denovos to a Rover 2000 has been estimated to be between £200 and £500 compared with £50 for five steel belted radials. (18)

Wide tread, with narrow rim which automatically runs centrally, when tyre flat

Eliminate internal destructive friction by use of suitable lubricant (Tyre aquaplanes <u>internally</u>)

Fig.. 2.6(a) The Dunlop Denovo tyre (section)



Inflated

Deflated

Fig. 2.6(b) The Pirelli D

The Firestone ACT (Advanced Concept Tyre) is constructed like the Denovo. The radial carcass which can be made of rayon, nylon or polyester is encased in two belt plies of steel. The sidewalls are thicker than an ordinary radial and the tyre is said to settle straight down on the run in the event of a puncture. A water soluble lubricant introduced into the tyre through the valve stem is said to keep the tyre running cool and partly inflated when a puncture occurs. A car with a deflated ACT is reported to have travelled the 266 miles from Akron to Detroit at an average speed of 55 m.p.h. (19)

7. Progress has been made towards making a tyre without any fabric at all or the fabric restricted to the breaker belt for tread reinforcement. Such tyres would lend themselves to be manufactured by direct moulding methods using simpler equipment. Examples are the Pirelli DIP tyre and the Firestone cordless tyre.

The Pirelli Tyre Company continuing the Dunlop development further arrived at the Pirelli DIP (Development Integrated Project) tyre. (19) The Pirelli DIP tyre is a belted tyre with a triangular cross-section a third wider than the normal radial ply tyre and twice as wide as it high. It is described as having two breaker belts but no carcass layers, chafer strips or bead wires. The tyre is said to retain its shape because -

1. It has two thick beads (without bead wires) which almost touch each other owing to the very narrow rim.
2. The breaker belts restrain distortion except in the tyre rolling plane.

The tyre sidewalls are built in compression so that they act as compression springs.

Shearer (7) notes that in the Pirelli DIP tyre "the total shape of the tyre has been modified to ensure that the rubber remains in compression under all operating conditions, thereby eliminating the need for sidewall reinforcement."

The run flat characteristics of the Pirelli DIP tyre are described as spectacular. Road grip is claimed to be improved and hydroplaning reduced. It is said to offer the possibilities of manufacture by injection moulding, centrifugal casting or being built of annular extrusions.

This tyre is still at the development stage and awaits the solution to certain problems before being launched commercially. The question of materials of construction is one such problem. Natural rubber is presently favoured because of its high resistance to fatigue. Commercial production of the Pirelli DIP tyre is not expected before 1980.

In January 1970 Firestone Tyre Company announced that they had succeeded in making by a process of liquid casting a cordless tyre with only two bead wires and the polymer but no textile reinforcement at all or with the textile reinforcement restricted to the tread area. The cast tyre has long been a dream of tyre manufacturers both for its simplicity of production and its uniformity in performance. The preparation of the special polyurethane elastomer and the details of the process of centrifugal casting are described in the patent. (20) A pre polymer made from a polyalkylene glycol and a diisocyanate is reacted with a diamine. Firestone claim that "moulding with the high strength rubber produces a cordless tyre with large cornering stiffness, low resonance frequency, a strong carcass and commercially accepted endurance". (21), (22) Should this venture be a success, Firestone say, tyre plants of the future will be essentially automated moulds, transfer equipment and warming room, eliminating 90 per cent of today's tyre manufacturing equipment. Firestone's competitors and other authorities in the tyre industry feel that this claim is premature, and that the cast tyre is not likely to be a reality in this decade.

G. Shearer (7) Tyre Technical Director of Dunlop makes the following predictions about the tyre in general use in 1984:

"The tyre will still be pneumatic and will have an ultra low profile of about 40 per cent height to width ratio.

The tread section will be wide and will be reinforced by a belt of non-woven material. There will be no textile reinforcement in the sidewall and the method of location between the tyre and rim will be c changed to eliminate the bead wire principle.

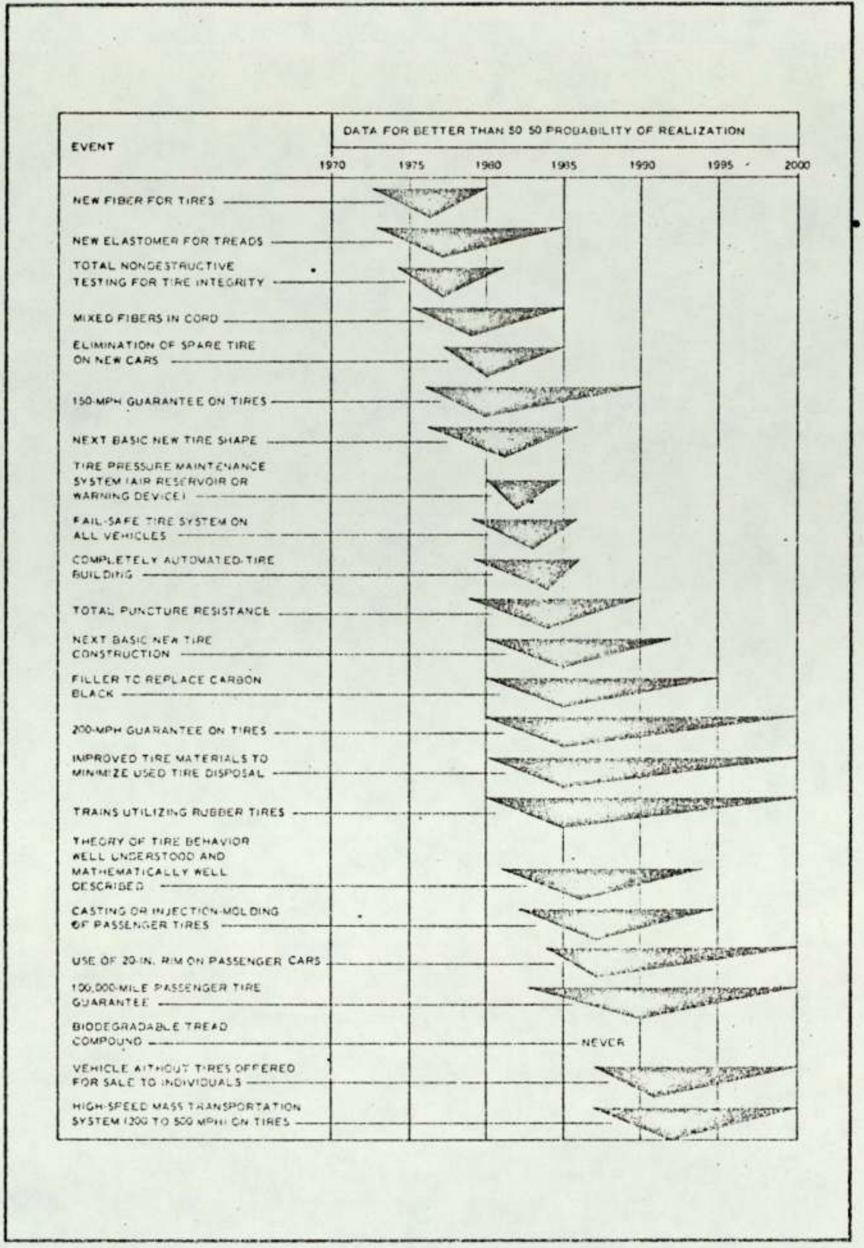


Figure 2.7 Delphi Probe on Tires

Source: Kovac: Tire Technology

Goodyear Tire Company 1973

The structure will have a greater load carrying capacity than at present and, therefore, could be of reduced diameter providing, of course, the vehicle stylists agree.

Rubber will be the main material and the whole structure will be produced by injection or transfer moulding methods."

The Pirelli DIP tyre would thus be the prototype for the tyre of 1984. Adoption of a tyre of this type would make the tyre building machines and the heavy vulcanising presses of today redundant. Little use (for breaker only) would be found for the fabric processing equipment including heavy calenders.

The predictions of a Delphi probe on possible tyre developments reproduced in Fig. 2.7 are interesting

2.4. Development Trends in Truck Tyre Technology

Hale and Haskell (8) have estimated that tyres account for about 8 per cent of the cost of a new truck compared with only 4 to 5 per cent in the case of a car. Tyres account for 10 per cent of truck operating costs and fuel for 40 per cent. Shearer (7) stresses that what matters in truck tyre technology is reduced cost per operating mile. He lists 4 ways of achieving this.

1. Improved tread life.
2. A reduction in tyre and wheel assembly weight permitting the carriage of an equivalent pay load.

3. A reduction in tyre rolling resistance and, therefore, fuel consumption.
4. Tyre reliability.

Shearer estimates that an improvement of 20 per cent in each of the first 3 factors could improve the operating margin of a trucker by 2 to 3 per cent, but points out that this margin of profit could be lost by the vehicle being off the road for just two days in a year through tyre failure. Hence the importance of tyre reliability.

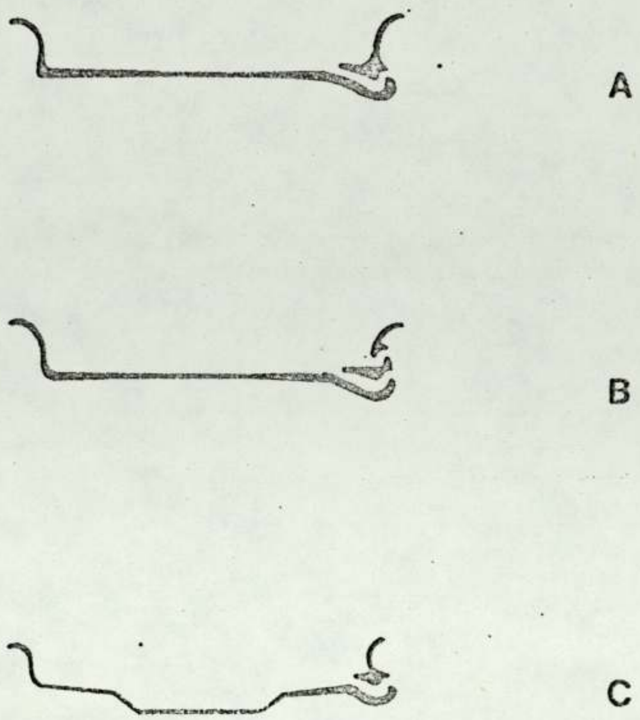
The advantages of radial ply truck tyres over conventional cross ply tyres are:-

1. Increased tread life.

2. A saving in fuel of about 5 per cent. Fuel, as already pointed out, accounts for 40 per cent of truck operating costs.

3. Reduced heat generation permitting higher cruising speeds.

4. A saving in weight of the wheel assembly amounting to 10 to 12 per cent is possible with radials as they are well suited for the single 15° drop centre wheel, eliminating the multipiece wheel, tube and flap. This wheel also provides improved brake ventilation. Figure 2.8 D (8) shows the single drop centre wheel. A, B and C are different types of multipiece wheels used with tubed tyres mainly in 16 in. and 20 in. diameters.



Multipiece wheels

Single drop centre wheel

Fig. 2.8

Truck Tyre Rims

French and Hofferbeth (24) point out that the radial tyre is less robust than the cross-ply and presents more problems in remoulding.

Aspect ratios of radial truck tyres are expected to progressively decrease effecting further weight reduction, savings in fuel consumption, longer tread life and increase in vehicle stability. Radial truck tyres with 70 per cent aspect ratios are reported to have shown longer treadlife as well as savings in fuel consumption. It is stated that trucks are being designed in Britain and on the continent to use these 70 series radials. (25)

Lower noise and vibration levels for driver comfort are being sought for by vehicle manufacturers. Greater emphasis is also being placed on tyre uniformity and balance.

The European Rubber Journal of May 1973 predicts that "by 1975 82 per cent of the 19 million-odd CV (commercial vehicle) tyres will be radial". The progress of radials in the U.S. is expected to be much slower. Beindorff (23) gives only 16 to 17 per cent of the market in 1977 to radials.

Table 8

Forecast of Truck Tyre Construction in the U.S.A. (per cent)

	Light Truck Tyres (8 ply & under)			Heavy Truck Tyres (10 ply & over)	
Year	Cross-ply	Belted Bias	Radial	Cross-ply	Radial
1972	98	1	1	98-100	0-2
1977	80	4	16	83	17
1982	55	5	40	66	34

2.5. Earthmover Tyre Developments

Earthmover tyres represent a segment of enormous growth potential. Earthmoving operations are carried out on a large scale at present in North America and Africa, and are likely to be a feature in Asia in the future. Two different types of earthmover vehicle are in operation - the working machines (loaders) which load the earth and the haulage machines which move it away. Both types of machine operate on rough terrain and carry heavy loads. Working machines carry heavier loads but operate over short distances and at speeds aroung 5 m.p.h. The loads for haulage are also heavy though not so heavy as for working machines. Haulage machines are being developed which can carry 300 tons for distances up to 20 miles at speeds up to 50 m.p.h. Nunn (87) has pointed out that development is towards heavier machines of both types and that the strains imposed on the tyres will increase. In Shearer's view (7) earthmoving machinery is the one area where tyre performance falls behind vehicle requirements.

Earthmover tyres are of special interest to natural rubber producers because it is an area where natural rubber predominates. It is estimated that 85 per cent of the 600 lb. of rubber used in an earthmover tyre is natural rubber. (26) It is the polymer that has high tear and cut resistance to operate on rough terrain and the low heat build-up characteristics to resist deterioration of the thick tyre sections through heat failure caused by carrying heavy loads.

Earthmover tyres have been made larger and larger to dissipate the heat generated in them and the limit in size has now been reached, because earthmover machines are assembled on site. It is stated that it would be impossible to transport larger tyres by conventional road or rail means. (7) Therefore greater performance is demanded from tyres with the present dimensions. The demands are listed as (i) high load capacity (ii) increased resistance to concussion failure (iii) cut resistant tread compounds and (iv) low aspect ratios. (6)

Shearer emphasizes the urgent need to switch to radial construction in earthmover tyre manufacture.

3. TECHNICAL ASPECTS OF THE USAGE OF ELASTOMERS IN TYRES

3.1. Historical

Natural Rubber had reigned supreme in the field of tyres until World War Two. Styrene-butadiene rubber was used as a substitute for NR when Japan overran S.E. Asia. These tyres however were much poorer in quality than those made from NR. SBR's rise to eminence as a tyre rubber was due to three reasons:-

1. The development of fine furnace blacks.
2. The discovery of low temperature polymerisation that gave "cold" rubber, and
3. The discovery of oil extension.

Oil extended SBR has held the region of car tyre tread compounds since the early 1950s. The high resilience and low heat build-up properties of NR made its use essential in all tyre carcass compounds and in all components of large tyres. In the period 1955 - 1960 following the discovery of the Ziegler-Natta catalysts for stereo-specific polymerisation first cis 1,4 polybutadiene and then 1,4 cis poly-isoprene the homologue of natural rubber were synthesized. Cis 1,4 polybutadiene has a resilience even greater than that of natural rubber. Fear of a serious shortage of NR in the 1960s prompted determined efforts to make poly-isoprene rubber (IR). The fight by NR for its existence started in the early

1960s. The proportion of NR used in tyres has progressively dropped but the actual quantities used have increased because the industry has been expanding. The advent of the radial tyre in the latter half of the sixties demanded higher proportions of NR but this was thought to be only a temporary reprieve for NR as synthetics modified to meet the requirements of the radial tyre were expected to be soon developed.

The situation for NR was none too bright until the late months of 1972 when the price of SBR began to rise and it became more difficult to obtain. The shortage was due to benzene being used in place of lead compounds in gasoline in the U.S.A. and also to a large increase in demand for polystyrene. With first the discounts on SBR being removed and then the price itself going up, NR prices rose in sympathy. Prices for RSS I (Spot) were: £144 per ton in September 1972, £193 in December 1972, £294 in June 1973 and £372 in August 1973. The Middle East War only aggravated an already bad situation. NR prices climbed steadily to peak values of over £500 per metric ton in January and February of 1974 partly due to speculative buying. They have shown a steady decline since and are now below the £300 per ton mark while the SBR list price is around £380 per ton. The recession in the motor industry has adversely affected all rubbers and the present world rubber situation is confused.

3.2. General

The technical properties of an elastomer may be classified under two main headings: processing properties and vulcanizate properties.

Under the term "processing" are included all the operations leading to the production of the finished tyre. It includes compound mixing and the operations preceding it (warming and mastication of the polymer), extrusion, calendering, tyre assembly and vulcanization.

In the present developed stage of the industry with tight operating margins, savings accruing from greater streamlining of processing operations become more important. The emphasis is therefore towards reduction in the number of processing steps and the simplification of the operations involved. Also easier materials handling, continuous and automated operation sequences and the use of materials that lend themselves to smooth and easy processing. The form of packing, bale size, technical specifications, variations between batches, etc. today receive much greater attention than they used to. The technical properties which contribute to processing - plasticity and other rheological properties, tack, green strength, tendency of the compounded rubber to scorch and the rate of cure - also receive serious attention.

The advent of the radial tyre has made the demands on tyre polymers even more exacting. Allard (28) describes the situation as follows:- "The conversion of the tire industry to radial tyres further complicates the needs placed on polymers because of the higher order of stable properties required by these much more precise constructions. This degree of sophistication dictates a whole order of magnitude of improvement in polymer uniformity, particularly rheological uniformity. This is an area in which our older standard test procedures are proving inadequate."

3.3 THE TECHNICAL PROPERTIES OF NATURAL RUBBER RELEVANT TO ITS USE AS TYRE POLYMER

3.3.1. General

Natural Rubber has been able to remain competitive with the synthetics because of a combination of several properties. Beach and Todd (29) have listed the more important of these as:

1. High raw polymer tack
2. High compounded gum strength (green strength)
3. Equally good hot tensile and hot tear strength
4. Excellent hysteresis properties.

To this must be added

5. Excellent dispersion of compounding ingredients

3.3.2. Processing Properties

If we follow through the sequence of operations involved in the processing of natural rubber, we can see some of the advantages and disadvantages of using NR.

3.3.2. 1. Storage Hardening

Bales of NR are found to harden on long storage, the Mooney Viscosity rising from 50 - 70 units to 100 - 130 Mooney units. This hardening has been traced to the presence of aldehyde groups on the rubber molecule. It has been shown that storage hardening can be suppressed by the addition of materials like hydroxylamine which block the aldehyde groups by reacting with them. This finding has enabled NR to be offered as Constant Viscosity (CV) and Low Viscosity (LV) forms. (30)

3.3.2. 2. Crystallisation

NR crystallises at low temperatures and warming of crystallised bales is a necessary step before mastication. Decrystallisation is a slow process since rubber is a poor conductor of heat. This problem will be more serious with palletisation of rubber, the palletised bales being larger than the present bales of RSS.

3.3.2. 3. Plastication

Raw NR must first be broken down by milling, reducing its viscosity before the compounding ingredients can be added. This process has been termed mastication, plastication, plastification and plasticisation. Synthetic rubber can be had in grades of any desired viscosity and does not need to be plasticated. NR is also now being offered in forms like low viscosity rubber that do not need mastication, e.g. SMR 5 LV.

3.3.2. 4. Dispersion of Compounding Ingredients

Compounding ingredients are more uniformly dispersed in NR than in any other polymer. This is explained on the basis of the high shear involved in milling NR owing to its high "nerve", a consequence of its high molecular weight.

3.3.2. 5. Dimensional tolerances of NR compounds

NR compounds can be calendered and extruded to close dimensional tolerances.

3.3.2. 6. Tack (Autohesion)

NR compounds have high tack (or Autohesion). This leads to strong joints at spliced junctions and at built-up interfaces, as in the plies of tyre carcasses.

3.3.2. 7. Compounded Gum Strength (Green Strength)

NR has very high compounded gum strength, more commonly referred to as green strength . The high tack and green strength of NR are two properties that its synthetic counterpart cis poly-isoprene has not yet been able to match. Tack and green strength are important in calendering, extrusion and component assembly. Green strength is particularly important in the building of radial ply tyres where the cord body is expanded under pressure. Inadequate green strength leads to distortion of the rubber compound leading in turn to displacement of the cords of the carcass plies.

3.3.2. 8. Scorch

NR compounds have a greater tendency to scorch than SBR compounds. Consequently SBR compound have greater latitude in processing operations. Processing temperatures are therefore lower for NR compounds. Reprocessing of NR compounds is also more limited than with SBR compounds.

3.3.3. THE PROPERTIES OF NATURAL RUBBER VULCANISATES

3.3.3. 1. Tensile Strength

NR has high tensile strength in both pure gum and reinforced compounds, much higher than any of the synthetics. Equally important is the fact that these tensile properties are maintained at relatively high temperatures. Modulus and ultimate elongation are in line with the tensile strength.

3.3.3. 2. Tear Strength

NR not only has excellent tear strength but also maintains it at high temperatures. The high tear strength also gives it high resistance to cutting and chunking. This makes NR the preferred polymer for use in off the road tyres.

3.3.3. 3. Abrasion Resistance

MRPRA workers have shown the factor determining wear of a tyre tread on a given road surface is the tyre surface temperature (TST). The TST reflects the ambient temperature, the severity of service, and wetness of the road. As pointed out by Schallamach (34) NR passenger car tyre treads wear less than SBR treads at low temperatures, and faster at higher temperatures, their ranking reversing at an ambient temperature about 14°C. Using a theory of slipping wheels Schallamach (35), (36) has worked out the equations -

$$A = \gamma \rho f s^2 = \gamma \rho F^2/f$$

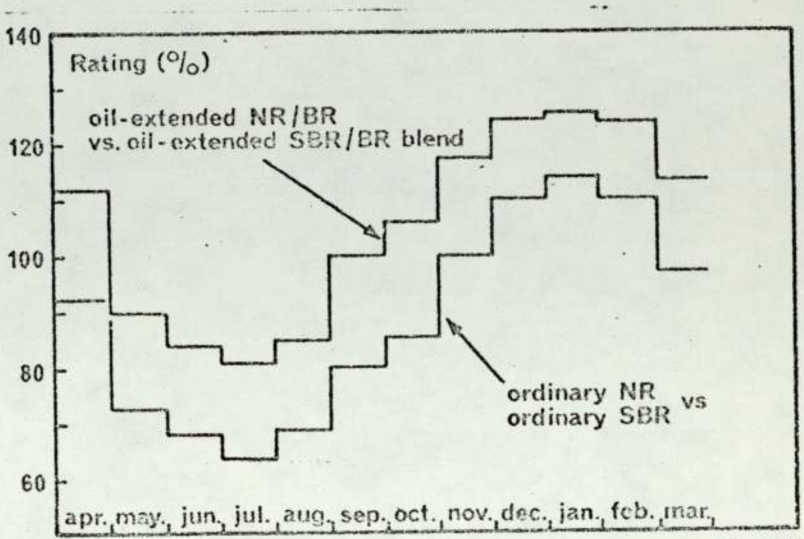
$$\text{and} \quad F = fs$$

where A is the wear per unit distance at small or moderate slip, γ the abradability (abrasion per unit energy dissipation), ρ the resilience of the wheel, F the reaction force (side, accelerating or braking force); f the wheel stiffness and s the slip. The resilience and stiffness in this equation refer to the whole tyre and not to the tread alone.

Plotting the seasonal changes in wear ratings of NR vs SBR, and OENR/BR vs OESBR/BR on a fast car, the graph shown (Figure 3.1) was obtained (34) The average rating of NR vs SBR was 88; for oil extended NR/BR vs oil-extended SBR/BR it was 104.

3.3.3. 4. Resilience

NR was outstanding in its high resilience until cis poly butadiene rubber (BR) and cis polyisoprene (IR) appeared. Its high resilience and low heat build-up gives NR its predominant position in large tyre treads and all tyre carcasses. Though NR has a lower resilience than polybutadiene (BR), its heat build-up is less than that of BR.



(cont.)

Figure 3.1.

Right: Seasonal changes in wear ratings of NR vs *SBR, and OENR/BR* vs *OESBR/BR on a fast car. Average ratings NR* vs *SBR 88; OENR/BR* vs *OESBR/BR 104.*

3.3.3. 5. Fatigue and Cut Growth

Fatigue failure has been described as "the gradual weakening of rubber specimens and eventual failure brought about by repeated deformations much lower than the breaking strain". Gent, Lindley and Thomas (37) postulated that fatigue failure of rubber specimens undergoing repeated extensions is caused by the growth of small flaws which are initially present in the rubber. The flaw or cut growth was attributed to mechanical rupture of chains. Lake and Lindley (38) attributed the growth of cuts or flaws to two mechanisms, namely mechano-oxidative rupture and ozone scission. Beatty (39) discusses fatigue failure and cut growth at length and the factors involved in it. He points out that "the usual manner of failure of a rubber article subjected to dynamic stress cycles is for failure to initiate on the surface from an ozone crack, a nick incurred in service, an inhomogeneity such as a particle of some kind, or voids. The time for initiation to occur depends on the sensitivity to the factors mentioned above. For example SBR and EPT (ethylene-propylene terpolymer) are more resistant to crack initiation than natural rubber, but even so, fail much more quickly with subsequent flexing in the crack growth cycle". It has indeed been seen that cracks appear in NR sidewall compounds before they do in SBR ones but that they remain small while those in the SBR compound grow much larger (Lake and Clapson (40)) These authors also point out the advantages of using NR/BR blends where high fatigue resistance is required. BR has a high mechanical fatigue limit (inhibiting crack initiation), while NR has very good high strain fatigue and tear properties.

Gent, Lindley and Thomas (37) summarise their findings on cut-growth and fatigue failures of the crystallising NR and the non-crystallising SBR as follows:-

1. Static cut growth and fatigue occur in SBR but not in NR except at tearing energies close to the catastrophic tearing energy.

2. For SBR the cut growth and fatigue behaviour changes markedly with temperature; for NR there is very little variation.

3. The cut growth rate of SBR is proportional to the fourth power of the tearing energy, whereas that for NR is proportional to the square. Tread groove cracking (41) is one specific and economically very important type of fatigue failure. The relationship between structure, hardness and groove cracking is often, if not always, reversed when one goes from SBR passenger car tyres to natural rubber truck tyres.

3.3.3. 6. Low Temperature Flexibility

The low temperature flexibility of NR gives it an advantage over the synthetics. NR maintains its flexibility at temperatures as low as -50°C.

3.3.3. 7. Ageing

The high degree of unsaturation in the natural rubber molecule renders it susceptible to attack by atmospheric oxygen and ozone. SBR has a similar tendency to oxidative degradation with the difference that NR softens with oxidation while SBR hardens. Chain scission occurs in NR with oxidation whereas in SBR it is cross-linking. In both materials the resistance to oxidative degradation is improved by compounding with suitable anti-degradants and with other polymers particularly BR.

Unprotected NR stocks fare better than unprotected SBR stocks in resistance to ozone cracking, SBR can be protected to a much greater degree than NR by means of anti-ozonants. (Ossefort) (42)

3.3.3. 8. Rubber to Metal Bonding

NR gives stronger bonds with brass plated steel than does any synthetic. The significance of this is in steel cord carcass and breaker plies and in bead wire attachment.

3.3.3. 9. Reversion (or over-vulcanisation)

NR compounds show a more marked tendency for the vulcanisate properties to fall off with time at higher temperatures than is the case with SBR or BR. Vulcanisation temperatures are therefore lower for NR than for the others. This means that curing times are longer for NR compounds. It also means that NR is at a disadvantage when injection moulding is considered. Injection moulding of tyres has been seen to be probable in the 1980s. Reversion has been shown by NRPRA workers to be due to the S8 cross-links changing over into mono- and di-sulphidic links. (43) (44) It has been pointed out that NR compounds must be injection moulded at temperatures below 300°F while SBR and BR compounds can tolerate 350°F. Steps to improve the reversion properties of NR include the use of efficient and semi-efficient vulcanising systems, (EV and semi-EV systems). (45) (46) A more basic deviation from conventional cure systems to meet the problem has been the urethane cross-linking of NR. Urethane cross-linked NR vulcanisates are said to possess physical properties on par with the best sulphur vulcanisates, while their ageing properties are superior to those of semi-EV systems. (47)

3.3.4. THE GRADING OF NATURAL RUBBER

The grading of Natural Rubber till recently has been done on the basis for this classification and the multiplicity of grades were common complaints against NR itself.

The SMR (Standard Malaysian Rubber) Scheme introduced in 1965 was aimed at producing clean rubber; dirt content was the important parameter and the labelling of the grades was on the basis of dirt content. SMR 5 had a dirt content of less than 0.05 per cent, SMR 20 less than 0.20 per cent and SMR 50 less than 0.50 per cent. Other parameters were ash content, copper content, manganese content, nitrogen content and volatile matter content. This scheme was revised in 1970 to include Plasticity Retention Index (PRI) in place of copper and manganese contents, and Plasticity. The introduction of SMR and similar schemes in the other rubber producing countries has been welcomed by consumers. Evidence is found in the growing volume of SMR production and sales.

Table 3.1

Tonnages of Standard Malaysian Rubber shipped 1966 to 1973

Year	Tonnage shipped
1966	5,981
1967	18,971
1968	81,497
1969	138,713
1970	224,281
1971	319,201
1972	367,179
1973	481,485

The original (1965) specifications and the revised ones of 1970 are given in Tables 3.2 and 3.3. Suggestions for improvements to these specifications have been made by C.J. Heal in a paper read to the International Rubber Conference in Brighton in 1972. He recommends inclusion of acetone extract as a parameter and a reduction in the value of the permissible amount of nitrogen. Heal agrees that the system of technical specification for NR has proceeded towards achieving its objectives of reducing the number of NR grades, achieving uniform quality by means of a technical specification and improving packaging of the rubber without the need for the undesirable bale coating. Pike (48) has reviewed the progress of the SMR scheme and describes the improvements adopted in 1970.

TABLE 3.2

ORIGINAL SMR TECHNICAL SPECIFICATIONS

	SMR 5L	SMR 5	SMR 20	SMR 50
Dirt content, %, less than	as for SMR 5	0.05	0.20	0.50
Ash content, %, less than		0.5	1.0	1.5
Copper content, parts per million, less than		8	8	8
Manganese content, parts per million, less than		10	10	10
Nitrogen content, %, less than		0.7	0.7	0.7
Volatile matter, %, less than		1.0	1.0	1.0
*PRI (Screening level) greater than		65	50	40
*Colour	Good ADS Standard	-	-	-

* Producer level for grading with no consumer guarantee.

TABLE 3.3

REVISED SMR TECHNICAL SPECIFICATIONS

(October 1st, 1970)

	SMR 5L*	SMR 5*	SMR 10	SMR 20	SMR 50
Dirt content, %, less than	0.05	0.05	0.10	0.20	0.50
Ash content, %, less than	0.60	0.60	0.75	1.00	1.50
Nitrogen content, %, less than	0.65	0.65	0.65	0.65	0.65
Volatile matter, %, less than	1.00	1.00	1.00	1.00	1.00
PRI, greater than	60	60	60	60	60
Plasticity (Wallace) greater than	30	30	30	30	30
Colour (Lovibond), less than	6.0	-	-	-	-

* Restricted to Latex Rubber

3.3.5. Constant Viscosity (CV) and Low Viscosity (LV) NR

One of the drawbacks of NR was storage hardening - the increase in viscosity of the rubber with time. This has been traced to the presence of aldehydic groups on the rubber molecule. (24) Constant Viscosity (CV) rubbers are made by the addition to the latex of materials like hydroxylamine which block the aldehyde groups. Up to 30 per cent saving in mastication time is claimed for CV rubbers. The low viscosity rubbers are prepared so as to have Mooney viscosities in the range 45 to 65. These LV rubbers need no mastication. The CV and LV rubbers have now been brought under the SMR scheme and are available in the SMR 5 grade. The viscosity ranges are shown below.

TABLE 3.4

REVISED CV AND LV MOONEY VISCOSITY SPECIFICATION

Marking		Mooney Viscosity Range (ML4, 100°C)
LV 45	---	40 - 50
LV	CV 50	45 - 55
LV 55	CV 55	50 - 60
LV 60	CV	55 - 65
LV 65	CV 65	60 - 70
---	CV 70	65 - 75

3.3.6. Oil-Extended NR (OENR)

The use of oil-extended Natural Rubber (OENR) in tyre treads, particularly winter treads, has been mentioned. OENR is made either by soaking dried rubber crumbs in oil or by the addition of oil to latex. Interest appears to be only in SMR 10 and SMR 20 grades of OENR made from field coagulum. OENR as a market grade of rubber has not proved very popular yet. Part of the problem has been ascribed to "the international nature of the NR polymer market, with accompanying problems of regulation and conflicting tariff laws". The suggested second factor is "the molecular weight and molecular weight distribution necessary for good properties on oil-extended polymers. Typically molecular weight of NR has been controlled in the consumer's plant by breakdown, with the attendant changes in molecular weight distribution. Oil extension takes away this degree of freedom; however, technically specified rubber may make it unnecessary by reducing lot to lot variation."

Basically, it appears that the question is whether it is cheaper to incorporate the oil into rubber in the factory or to ship the oil both ways, say from Europe to S.E. Asia and back.

Morton (49) welcomed the decision to offer CV and LV rubbers and hoped that they would be available in sufficient quantities: At present they were not.

In Morton's view (49) rubber manufacturers object to oil-extended NR because compound mixing costs are not high enough to justify the payment of any premium for oil extended rubber over the cost of rubber plus oil. Rubber manufacturers, in his view, preferred to do the addition of oil themselves. OENR has more promising prospects in the rubber growing regions where the question of freight does not come in. The possibility of tyre manufacture on a large scale there will be discussed later.

3.3.7 NEWER FORMS OF NATURAL RUBBER

3.3.7.1. TYRE RUBBER

Tyre Rubber has been developed by the Rubber Research Institute of Malaya to provide an easily processible form of NR that is not subject to storage hardening. It consists of:

Latex rubber	30 parts by weight
Unsmoked sheets	30 "
Field coagulum	30 "
Oil	10 "

The oil can be added to the latex containing crumbs of field coagulum and of the sheet rubber. These crumbs can also be soaked in formic acid, drained of excess acid, and added to a mixture of oil and latex.

It is claimed that Tyre Rubber does not need mastication, is not subject to storage hardening and crystallisation, and gives products with improved heat build-up properties.

Tyre Rubber will have to face the same objections as those raised against OENR. Morton (49) stated that rubber manufacturers preferred to add the oil in their own factories and did not want it added on the plantations.

3.3.7.2 HIGH DYNAMIC QUALITY NR

It has already been mentioned that removal of some of the nitrogenous non-rubber constituents improves the fatigue properties of NR vulcanisates. Auto-coagulation is also said to improve these properties. Pike (42) reports that NR prepared by rapid coagulation (2 minutes) with a surfactant like sodium sulpho-succinate and a salt like calcium chloride gives compound with higher resilience and reduced heat build-up.

3.3.7.3 FREE-FLOWING NR POWDER

The need for easier processing forms of NR has often been stressed. Powdered rubber, preferably compounded, would permit continuous processing operations. Pike (48) mentions that his firm has been successful in making powdered free-flowing NR both with and without compounding ingredients. The significance of free-flowing rubber powders to tyres is the expectation that in the 1980s tyres will be made by injection moulding techniques.

3.3.7.4 LIQUID RUBBERS

Liquid Rubbers consist of relatively short chains terminated by reactive groups, that cause polymerisation at higher temperatures. Heavy mixing equipment is not needed. Liquid Rubbers allow tyres to be made by casting. Firestone have already announced (21) that they have been successful in making a cast tyre.

MRPRA now announce (Cuneen (50)) that they have succeeded in making liquid rubber from NR. Liquid Rubbers with molecular weights as low as 3000 and terminated with carbonyl groups are said to have been made by photochemically induced cleavage of the double bonds of natural rubber by nitrobenzene". Chain extension in this case is achieved with a bifunctional carbonyl reagent, such as a bis-hydrazide. Vulcanisation is by conventional methods. Much more development work remains to be done before commercial exploitation of these liquid rubbers.

3.3.7.5. THERMOPLASTIC RUBBERS FROM NR

Thermoplastic Rubbers have blocks of polymer segments in the "glassy" state alternating with segments of a rubber nature; in SBS thermoplastic rubber blocks of polystyrene alternate with segments of polybutadiene. The material therefore softens and is processible at higher temperatures, while "setting" at ambient temperatures. The synthetic thermoplastic rubbers are said to cost 1.5 to 7 times as much as the thermoplastic rubbers made at MRPRA from NR. The special vulcanising system is said to give cross-links that are thermo-labile. They are strong at room temperatures, but rupture ('open') at higher temperatures and reform on cooling. The problems encountered include finding an efficient method of modifying the NR molecule to give pendent groups for cross-link attachment, and, the formation of permanent cross-links on remoulding. (50)

The significance of thermoplastic rubbers for tyres is that since they can be re-processed they present no problems of disposal in these days of environment consciousness.

3.4. THE TECHNICAL PROPERTIES OF THE SYNTHETIC TYRE RUBBERS

3.4.1 Introduction

SBR made by emulsion polymerisation of the monomers is the world's largest volume rubber. Depending on whether the polymerisation is carried out at 50°C or 5°C we get hot or cold SBR. Cold polymerisation gives longer polymer chains with less branching than hot SBR. Another form of SBR and indeed of most synthetic rubbers is the oil-extended form, (OEP or OESBR). This material is made by the addition of substantial quantities of aromatic or naphthenic oils to polymer material of very high molecular weight that would not lend itself to normal processing. The addition of these large quantities of oil like 37.5 parts oil to 100 of polymer results in a material that is easy to process, is cheaper and results in no loss of physical properties for certain applications. For instance, OESBR has been the predominant polymeric material used in car tyre treads for about 20 years now. During the past year however not only have SBR prices gone up but it has been in short supply. Until almost last year SBR prices had not only been very low, but discounts were given on the list prices, the exact amount of the discounts not being made known. The present shortages have been triggered off by the diversion of large quantities of benzene precursors into gasoline in the U.S.A. to replace the lead compounds as required by the recent "clean air" legislation. SBR still continues its role as the "workhorse of the rubber industry".

SBR is generally used in combination with polybutadiene which improves the wear and fatigue resistance of the compounds as well as their resilience and ageing characteristics. Synthetic cis polyisoprene is used to replace part of the natural rubber used in tyre compounds. Other polymers which may be useful in tyres are the ethylene propylene rubbers, the high and medium vinyl polybutadienes, 1.5 trans polypentenamer and the Alfin rubbers.

Availability and cost of monomers for manufacture of the synthetic rubbers are serious problems synthetic rubber producers have to face. Competition from natural rubber is another. Natural rubber prices have fallen below SBR prices in 1974 for the first time ever.

3.4.2. STYRENE-BUTADIENE RUBBER SBR

3.4.2.1. Introduction

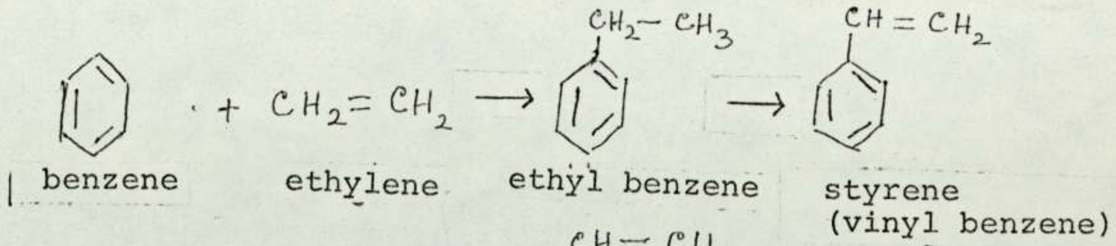
Styrene butadiene rubber (SBR) made by emulsion polymerisation of styrene and butadiene is the world's largest volume rubber. Nearly twice as much SBR as NR is used in tyres in the U.S.A. as seen in Table 3.5 below.

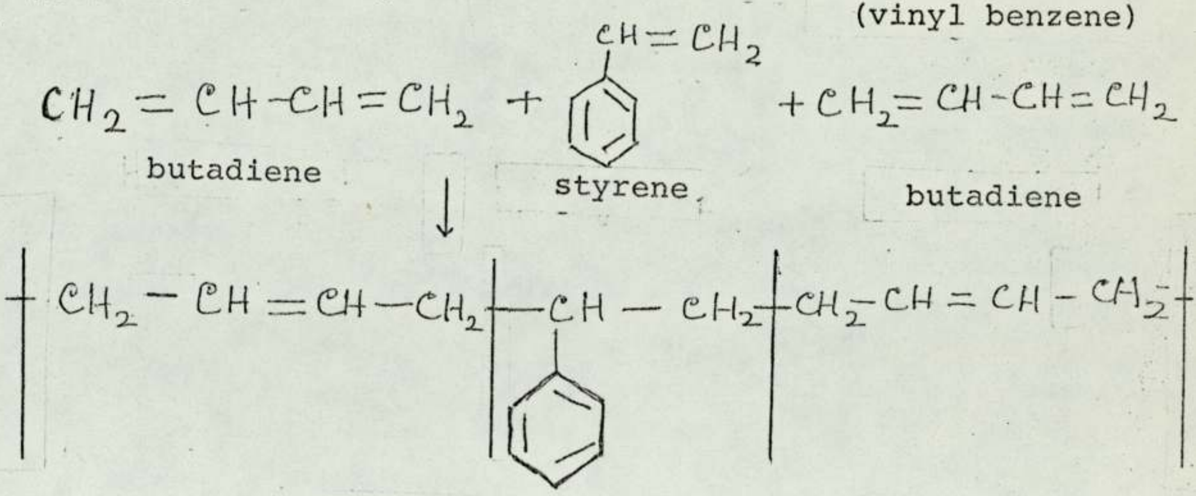
TABLE 3.5

	Tire and Tire Products						
	Natural	S-Type	Butyl	N-Type	Stereo	Other	Total Synthetic
Year 1973	515,209	1,021,834	88,668	421	394,441	4,756	1,507,120
Up to end June 1974	287,291	491,099	45,586	4090	208,617	2,810	752,202

3.4.2.2 Manufacture

SBR is made by the random polymerisation of styrene and butadiene in emulsion or in solution. Emulsion polymerisation is carried out at 50°C to give hot SBR or at 5°C to give cold SBR. Cold polymerisation gives much longer polymer chains with less branching than hot SBR.





styrene butadiene polymer (SBR)

Oil extended SBR is made by adding substantial quantities of aromatic or naphthenic oils to very high molecular weight SBR polymer material that does not lend itself to normal processing. The addition of these large amounts of processing oils, up to as high as 37.5 parts oil to 100 of polymer, results in a material that is cheaper and easy to process. It is found that the physical characteristics of the oil extended product compare favourably with those of the normal material. SBR 1500 with 23.5 per cent bound styrene is the best known grade of cold SBR and SBR 1712 with 23.5 per cent bound styrene and 37.5 parts oil p.h.r. Owing to the difficulty in obtaining styrene supplies manufacturers have reduced styrene levels of SBR to about 16 per cent.

Oil extended SBR has been the preferred polymer for treads of passenger car tyres for about 20 years now. The range of SBR types available is wide. 266 types of emulsion SBR has been described, as shown in the table below. The demand is now being made for the reduction in the number of all grades of rubbers and blacks. Carbon black masterbatches of SBR as well as SBR-carbon black-oil masterbatches are available.

TABLE 3.6

EMULSION SBR AVAILABLE

11SRP* SBR Classification	Types available
Hot	38
Cold	52
Cold + black	32
Cold + oil	67
Cold + oil and black	77
	266
Viscosity Range, ML - 4/212	20 to 130
Bound Styrene Range, %	5 to 43
Oil level (4 types)	25 to 75
Black level (14 types)	35 to 105

The usual level of bound styrene in SBR used in tyres was 23 per cent. The level is reported to have been brought down to 15 or 16 per cent because of the shortage of styrene monomer. (91) The effects of bound styrene on treadwear and roadholding characteristics is shown in Figure 3.2. Higher styrene contents are shown to increase wet traction but to reduce the wear properties.

3.4.2.3 THE TECHNICAL PROPERTIES OF SBR

SBR does not crystallise when stressed as natural rubber does and therefore has poor strength in unvulcanised and vulcanised poor gum compounds. It is the addition of fine reinforcing blacks that give it its strength.

Some of the technical characteristics of SBR have been discussed in the previous section dealing with natural rubber.

3.4.2.3.1 Processing Properties

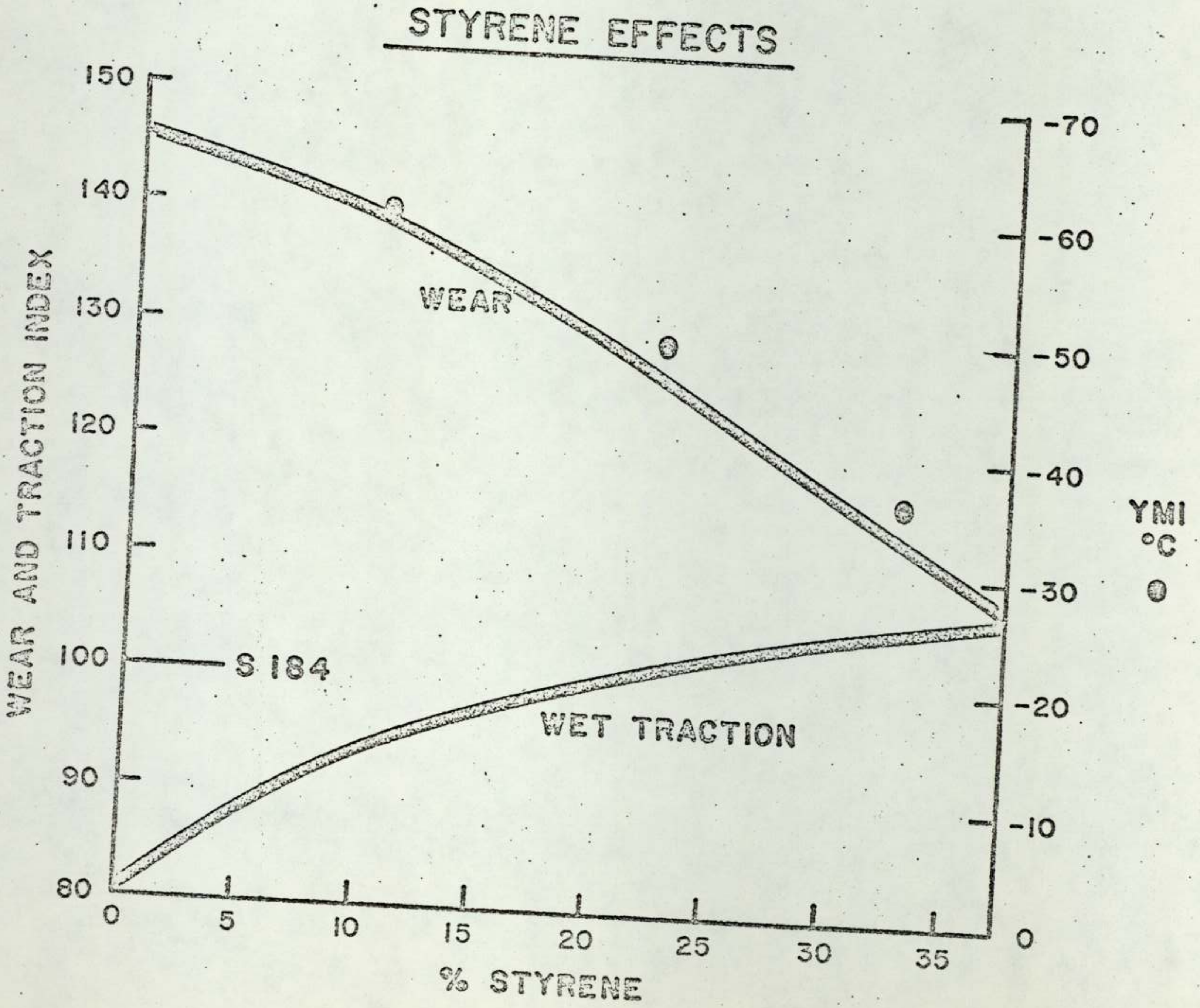
1. Storage hardening and crystallisation

SBR is an amorphous polymer not subject to crystallisation. It is not necessary to warm SBR bales.

2. Plastication

SBR particularly cold SBR breaks down less readily than NR, but plastication is not necessary as it is available in a variety of grades with a wide range of

Figure 3.2


STYRENE EFFECTS
WEAR AND TRACTION INDEX
150
140
130
120
110
100
90
80
S 184
WEAR
WET TRACTION
YMI
°C
-70
-60
-50
-40
-30
-20
-10
0
0
5
10
15
20
25
30
35
% STYRENE

viscosities. SBR is not subject to plasticity changes during processing

3. Dispersion of compounding ingredients

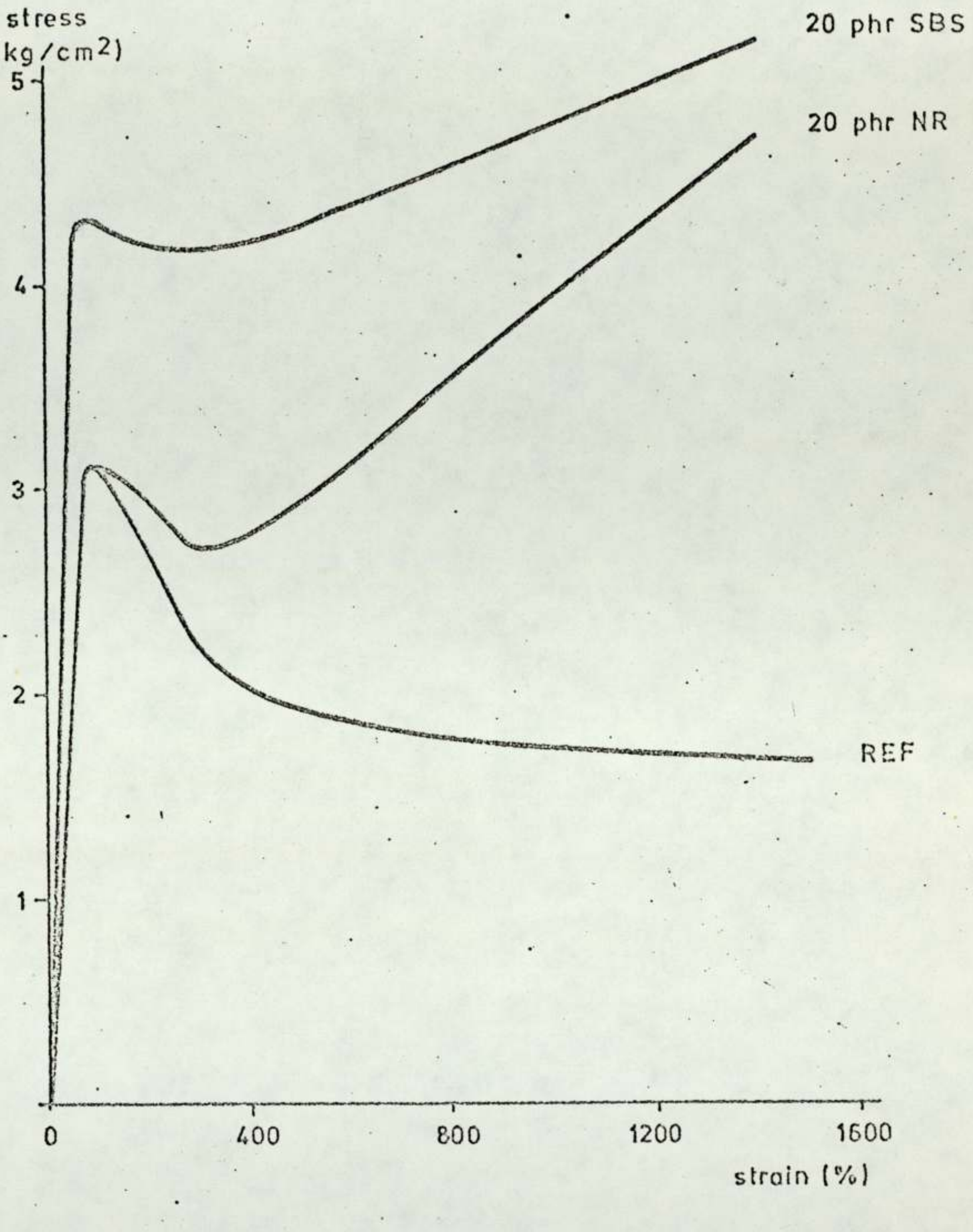
SBR lacks the "nerve" of natural rubber. Dispersion of compounding ingredients is therefore poorer, more so in some types.

4. Tack

The raw SBR polymer has poor tack which is obtained by the addition of tackifiers like pine tar and conmarone resin to compounds.

5. Compound green strength (green strength)

SBR is deficient in green strength. This property can however be improved by the addition of proportions of natural rubber or thermoplastic rubbers (52), (53), as shown in Figure 3.3. It is seen here that partial replacement of SBR (20 per cent) by the block copolymer (SBS) in an SBR based carcass compound the SBS copolymer is more effective than NR in increasing the green strength of the compound. The effect of SBS copolymers on IR is similar. Addition of these materials increase not only the total energy required for rupture but also the yield strength. These results are significant in their application to the building of radial ply tyres, where the uncured compound should be able to resist the forces created by the pneumatic expansion of the assembled "green" tyre. No data is available on how these blends compare with NR, but the high cost of SBS thermoplastic block polymers makes it economically questionable. The lower tack and green strength of SBR compounds present



CASING COMPOUND:
EFFECT OF PARTIAL REPLACEMENT OF SBR BY SBS OR NR ON GREENSTRENGTH

Fig. 3.3.

Recent Application Developments in
Thermoplastic Rubbers

K. van Henten

IISRP 13th annual meeting (66)

problems during tyre assembly operations, particularly with carcass compounds.

6. Scorch

SBR compounds contain higher proportions of accelerator than NR compounds owing to their slow curing nature. The tendency to scorch is much less than in NR compounds. This fact together with the greater resistance to breakdown leading to smaller changes in viscosity permits the re-processing of SBR compounds several times.

7. Extrusion and calendering

SBR compounds can be extruded and calendered to close tolerances with low variability between batches.

Kastein (44) presents the case for SBR as follows:-

"SBR is basically much more tolerant of heat during processing than NR but at the same time can be compounded to cure at a fast rate at the elevated curing temperatures.

SBR may be obtained at almost any desired viscosity range and does not need any pre-plastication to be ready for mixing or subsequent processing. At the same time it is resistant to change in plasticity during factory operations, and extruded treads may be again warmed up and again extruded without significantly changing the extruded tread shape. Tread dimensions are accurately obtained day after day, lot after lot. Mill warm-up, either for calender or for tuber, is an easier process with SBR."

A table prepared by this author comparing the processing properties of SBR, SBR/BR blends solution SBR and NR is reproduced below.

TABLE 4

Factory Processing Comparisons

	SBR	SBR/BR (Diene)	S-SBR (Stereon)	NR
Plastication used	No	No	No	Yes
Reprocess Scrap	Yes	Yes	Yes	Yes?
Scorch Time	OK	OK	OK	OK?
Mixing Cycle	OK	OK	OK	OK
MB max. temp., °F.	360	360	360	340
Tubing	OK	OK	OK	OK
Max. temp., °F.	250	250	250	250
Calendering	OK	OK	OK	OK?
Mill warm-up	OK	OK	OK	OK?
Building - Tack	Poor	Poor	Poor	Good
- Green Strength	Fair	Poor	Poor	Good
Curing -	OK	OK	OK	OK
max. temp., °F.	350	350	350	300

3.4.2.3.2 SBR VULCANISATE PROPERTIES

1. Tensile properties

As already mentioned SBR being an amorphous polymer needs fine carbon black for reinforcement. Even then its tensile properties are poor compared with natural rubber as seen in the Table 3.7 (54) below.

TABLE 3.7

ESTABLISHED GENERAL PURPOSE RUBBERS: TREAD VULCANISATE PROPERTIES

	SBR	BR	IR	NR
Tensile Strength (kg./sq. cm.)	190	130	270	300
Heat build-up °C Goodrich Flexometer	40	33	22	24

2. Tear Strength

The tear strength of SBR is inferior to that of NR, the difference being more pronounced at higher temperatures.

3. Resilience and heat build up

The resilience of SBR is decidely lower than that of NR and the heat build up higher as seen in the Table 3.7 above. This limits the use of SBR to uses where heat build up is not a serious consideration, such as car tyre treads.

4. Abrasion Resistance

The relative abrasion resistance of SBR and NR have already been discussed. SBR tread stocks have superior abrasion at higher temperatures, and NR at lower temperatures, the ratings being reversed at an ambient temperature around 14°C. This corresponds to a tyre surface temperature around 35°C.

Cold SBR has better abrasion resistance than either hot SBR or NR. Passenger car tyre treads are therefore made largely with cold SBR or oil extended SBR.

5. Skid Resistance

The skid resistance of SBR tyre treads, particularly when oil extended, is superior to that of NR treads. This is explained by the lower resilience of SBR, further depressed by oil-extension.

6. Fatigue Resistance

The mechanical fatigue limit is higher for SBR vulcanisates than in NR ones. The cut growth resistance and the fatigue life of SBR compounds are however lower than for NR. Once cracks appear their growth is faster than in NR. Consequently the number of cracks in SBR vulcanisates is smaller, but the cracks themselves are larger and deeper than with NR. With SBR compounds the state of cure has a strong effect on cut growth resistance, high states of cure increasing the modulus and causing a fall in the cut growth resistance.

7. Low-Temperature Properties

SBR has less resistance to exposure to short periods of time than NR. NR however being a crystallisable polymer shows crystallinity increasing with time at low sub-zero temperatures, whereas SBR being amorphous does not crystallise.

8. Ageing

Ageing of SBR is due to atmospheric oxygen and ozone as is the case with NR, but whereas NR vulcanisates are softened by oxidation through chain scission, SBR vulcanisates actually harden, the oxygen causing cross-linking. Atmospheric oxidation is slower with SBR than with NR. SBR can be said to be marginally superior to NR in atmospheric ageing. The deterioration of SBR through ozone action can be more effectively reduced by compounding than that of NR.

9. Reversion

The tendency to reversion is much less with SBR and BR than with NR. Consequently SBR and SBR/BR tyre treads can be cured at 330 to 350°F or lower. (51)

For use in tyres SBR is superior in four important qualities - wear resistance, resistance to groove cracking, resistance to ageing and speed of cure. Its main drawback is the high heat build up. It therefore finds use chiefly in the treads of passenger car tyres is also used in different proportions in the sidewalls of cross-ply car tyres, car tyre carcasses and in the tread and sidewall of the smaller sizes of truck tyres.

3.4.2.4 SOLUTION-POLYMERIZED SBR

The interest in solution polymerised SBR has been explained as being due to the following factors. (56a)

1. Solution-polymerized SBR, while similar in many respects to the emulsion product, has some molecular structural differences. It is more linear and has a narrower molecular weight distribution. It gives superior performance in many uses.

2. Solution SBR is lighter in colour, lower in odour, and is less contaminated with fatty acid, soap, and ash than is emulsion SBR. Non-hydrocarbon contaminants typically run below 1 per cent. vs 7 per cent. for emulsion SBR.

3. Solution SBR can be made in block, partially block or random structures. Also, long chain branching can be controlled. This provides special grades that cannot be produced at all in an emulsion process.

4. The solution process is a simple process, with few ingredients and easy control. Off-specification product is minimized.

5. A plant designed to produce solution SBR's will also produce various grades of polybutadiene. It is ideally suited to provide a one-plant synthetic rubber industry.

Solution polymerised SBRs show similarities to solution polymerised polybutadiene. They differ from emulsion SBRs in their higher molecular weights, narrower distribution of molecular weight (see Figure 3.4) and different cis-trans ratios. Their products are said to be more resilient and to have better resistance to reversion and to low temperatures. The undermentioned tables show improved abrasion resistance, greater resistance to cracking and cut growth and lower heat build-up. They are however more expensive than emulsion SBRs. The development of improved types of "second generation" solution SBR by modifying the microstructure and molecular configuration by control of polymerisation conditions has been described.

POLYMER CONTRIBUTIONS TO PASSENGER TIRE PERFORMANCE

TREAD	E-SBR	BR AND E-SBR	S-SBR
ABRASION RESISTANCE	100	120	130
WET TRACTION	PAR	EQUAL	EQUAL
LOW NOISE LEVEL	OK	OK	OK
CRACK RESISTANCE	PAR	BETTER	BETTER
CUT GROWTH RESISTANCE	PAR	BETTER	BETTER
BODY			
HEAT REVERSION	GOOD	GOOD	GOOD
HEAT BUILD-UP	PAR	BETTER	BETTER
PROCESSING			
MIXING	OK	OK	OK
TUBING	OK	OK	OK
GREEN STRENGTH/TACK	POOR	POOR	POOR
CURING	GOOD	GOOD	GOOD
PRICE	PAR	HIGHER	HIGHER
AVAILABLE (IN THOUSANDS L.T.)	1,829	300 BR	60

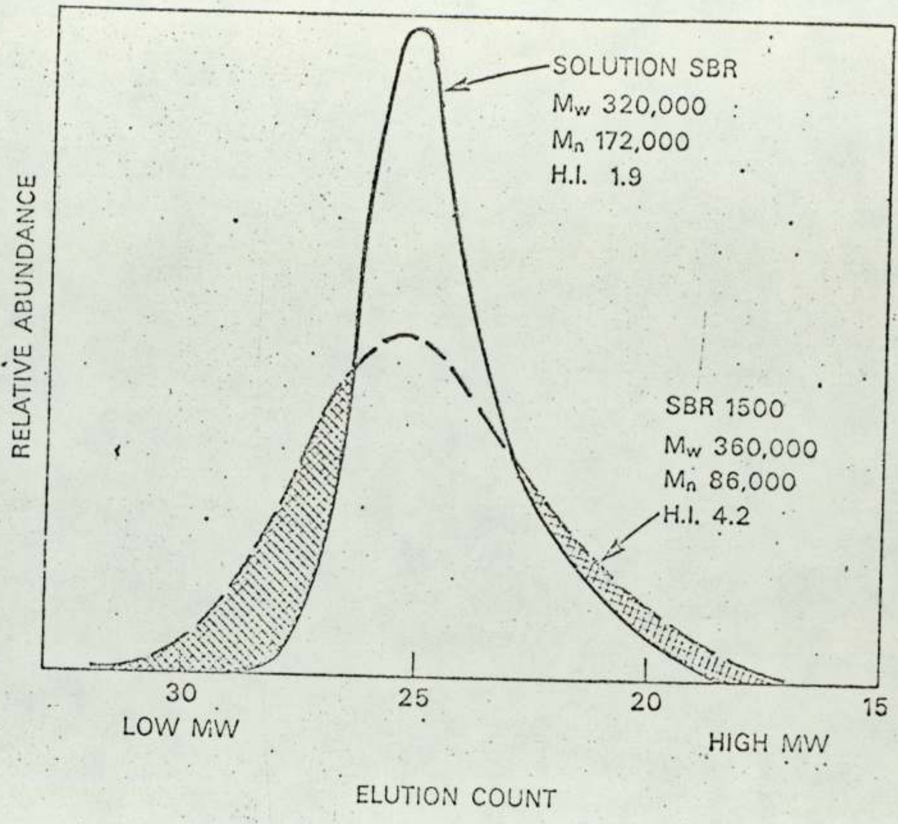


FIGURE 2

COMPARISON OF MOLE. WT. DISTRIBUTION OF EMULSION AND SOLUTION SBR RUBBERS

Fig. 3.4. Molecular weight distribution of emulsion and solution SBR (56a)

Cis 1,4 polybutadiene rubber (BR) made with Ziegler-Natta catalysts was the first rubber to have a resilience comparable with NR. Once thought of as a likely replacement for NR, BR has now found its place is in blends with primary rubbers NR, SBR and IR. The main reason for this is the difficulty in processing BR.

White and Tokita (56) explain that at high temperatures polymers like BR with a narrow molecular weight distribution give smooth, transparent, fluid films on the roll. As the temperature is lowered, these films crumble, and become a bag. Increasing the roll speed or decreasing the nip accelerates this effect. Other factors responsible for BR's poor processing performance are its low green strength, high material stiffness under high rate of deformation and the rapid stress relaxation of uncured material.

The advantages of BR are:-

High Resilience, higher than that of NR.

Very High Abrasion Resistance.

Excellent Ageing Properties.

Excellent Flex Resistance owing to its high mechanical fatigue limit.

Ability to take up large quantities of extender oil and

Does not need plastication.

The disadvantages of BR are:-

Difficulty in milling, extruding and calendering.

Low tack and poor cohesion.

Low green strength.

Low tensile strength,

Low tear strength and high resilience leading to chipping and chunking when used in high proportions in tyre treads.

The heat build up of BR is greater than NR (33°C vs 24°C) but lower than SBR (40°C).

The higher heat build up of BR in spite of its higher resilience is explained on the basis of

BR's higher internal friction. Though resistance to crack initiation is good in BR subsequent crack growth is rapid so that overall flex-life is poor. In NR/BR blends the two polymers reinforce each other, NR with good high strain fatigue and tear properties and BR with a high mechanical fatigue limit.

BR has poor wet skid resistance but BR/NR blends have good traction on ice and snow. BR is blended with NR and SBR to improve ageing and ozone resistance, abrasion resistance, and resistance to fatigue and crack initiation. It is normally used in quantities up to 30 per cent of the weight of the polymer blend.

3.4.3. CIS 1,4 POLY-ISOPRENE RUBBER (IR) AND NATURAL RUBBER A TECHNICAL COMPARISON

Introduction

Cis 1,4 poly-isoprene rubber (IR) is the chemical homologue of natural rubber and except in a few properties comes closer than any other polymer towards duplicating the properties of NR. It was first prepared using the Ziegler-Natta catalysts for stereo-specific polymerisation - a combination of aluminium tri-ethyl and titanium tetrachloride. Extreme high purity of the monomer was a requirement of this catalyst system. The resultant polyisoprene is said to be between 96 and 98 per cent 1,4 cis configuration and 2 to 4 per cent 3,4 configuration. The material had a high molecular weight with a narrow range of distribution. It was considered in terms of a replacement for NR. The two troublesome features of this material were its high gel content and the considerable degree of cross-linking. This material is referred to as high cis poly-cis-isoprene because it has a cis content of 96 to 98 per cent as against the 92 per cent cis content of the "low cis" material which also has 1 to 2 per cent trans 1,4 and 6 to 7 per cent 3,4 material.

The production of the low-cis material was largely pioneered by the Shell Oil Company. This method uses lithium catalysts e.g. butyl lithium and secondary butyl lithium. This catalyst also was developed by Ziegler though it does not bear his name, Duck and Ridgewell have discussed the performance of these two catalyst systems.(57) They list the problems of using the Ziegler-Natta catalysts as follows:-

1. Dry, pure and air-free hydrocarbon solvents were required as a medium in which the catalysts and resulting polymers could be dispersed or dissolved as the organometallic compounds are very sensitive and easily decomposed.
11. Reactor construction problems regarding the thick viscous reaction masses of dissolved or suspended polymer were encountered which

affected adequate heat transfer and control of reaction.

lll. Isolation of the polymer from the solution, removal of catalyst residues and recovery of large volumes of solvent.

lV. Supply of monomers of extremely high purity. Accurate analytical techniques for trace quantities of impurities were needed.

Duck and Ridgewell summarise the advantages of using the lithium catalysts as follows:-

1. Reactions have a fast initiation and a relatively slow propagation step. This means that molecular weight distributions are narrow and that polymer chain lifetimes are infinite under the correct conditions - in other words, the reaction proceeds until stopped, following only one injection of catalyst.

ll. Catalyst efficiencies are very high and products do not contain the harmful transition metal residues.

lll. Only a one -, or at most a two-component catalyst is used compared with the Ziegler catalyst's minimum of two and up to four components.

lV. An even greater versatility is possible than with the Ziegler mixed catalysts as the

polymer chain structure can be changed
easily at any time during the reaction.

Capitani (61) points out that the mechanical characteristics of synthetic cis polyisoprene, particularly tensile strength and tear resistance, depend on molecular weight distribution and on the degree of long chain branching.

Whereas the high cis IR shows some similarity in processing to NR, the low cis material has processing characteristics quite different to those of NR. Its molecular weight distribution is narrower than in the high cis material. The molecular weight distribution of NR is in turn much wider than either of the synthetic polyisoprenes. Low cis isoprene has been promoted as being complementary to NR rather than as a replacement for it.

Technical Properties of IR and NR

Bristow, Cuneen and Mullins (58) report the results of a detailed study of the comparative properties of samples of natural rubber grade SMR5 and five type samples of synthetic polyisoprene rubber (IR. One of these (Polyisoprene A) is a low cis type while the others are all high cis types. They point out that the most important differences in processing behaviour of the natural and synthetic isoprene rubbers result from the higher unvulcanised compound strength (green strength) (see Figure 3.5) and better tack and tack retention of natural rubber. These characteristics and the reduced degradation during processing are said to enable natural rubber to meet more readily the increasing stringent demands in extrusion, calendering and building operations encountered in radial tyre manufacture. Low cis polyisoprene, these authors state could be a useful processing aid for NR in proportions up to 20 per cent on the weight of NR.

Table 3.3.9 is a summarised comparison in vulcanizate properties of natural rubber and the five types of synthetic polyisoprene tested. The broad similarity in properties of the two rubbers is evident. NR however exhibits superior tensile properties at higher temperatures as seen in Table 3.10.

In the view of Bristow, Cuneen and Mullins, the higher tensile and tear strengths of natural rubber are reflected in its better fatigue, cut growth, flex cracking and wear resistance characteristics. NR can also be better protected against ozone. The higher level of set in NR is connected with its residual non-rubber constituents. These authors therefore hold that NR "still remains the better rubber for large truck, earthmover, and aircraft tyres and in engineering applications.

Duck (60) discusses the economic and technical prospects for IR. Capitani (61) quotes figures showing IR giving better adhesion to brass than NR.

Dreyfus and Toullec (59) have summarised the relative advantages of the two materials as follows:-

TABLE 3.8

MAIN ADVANTAGES OF NR OVER HIGH-CIS IR

1. Ability to crystallise.
    - Improved green strength
    - Improved tack and tack retention
    - Helps processing of synthetic polymers
2. Less processing degradation.
3. Better fatigue, flex-cracking and ozone resistance.
    - Better response to antiozonants
    - Network of fine shallow cracks instead
    - Large and deep cracks
4. Easier dispersion of blacks and chemicals
    - Low structure blacks
    - Sulphur and accelerators
5. Higher Strength
    - Tear properties
    - Better rubber to rubber adhesion
6. Freedom from problems connected with shortages in oil supplies

Fig. 3.5.

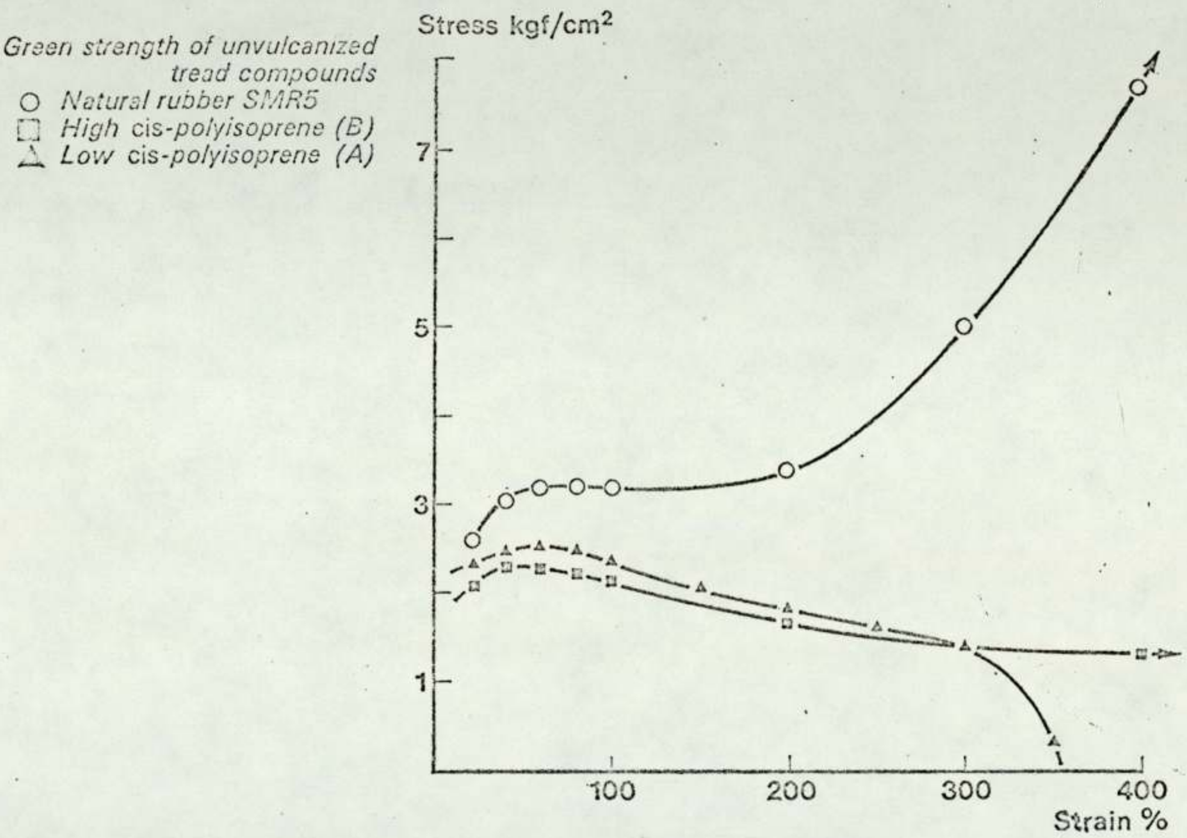

Green strength of unvulcanized tread compounds
○ Natural rubber SMR5
□ High cis-polyisoprene (B)
△ Low cis-polyisoprene (A)
Stress kgf/cm²
7
5
3
1
100
200
300
400
Strain %

TABLE 3.3.9

PROPERTIES OF NATURAL RUBBER AND VARIOUS POLYISOPRENES IN A TREAD COMPOUND

Rubber, 100; N285 black, 45; oil, 4; wax, 1; antiozonant, 2; zinc oxide, 5; stearic acid, 3; sulphur, 2.5; santocure, 0.5
Cure 40 min at 140°C

	Natural rubber SMR5	Polyisoprene				
		A	B	C	D	E
Tensile strength kgf/cm^2	317	258	307	299	290	293
MR50 kgf/cm^2	12.9	11.8	11.6	11.8	12.6	11.9
M300 kgf/cm^2	155	107	127	133	129	127
Elongation at break %	547	572	573	536	551	557
Hardness IRHD	67½	65½	65	64½	65½	66½
Tear strength* 20°C	1.7	1.0	1.4	1.4	1.6	1.6
kg 100°C	2.6	0.6	1.0	1.4	1.0	1.2
120°C	1.4	0.4	0.6	0.7	0.6	0.6
Akron abrasion index	100	64	81	69	74	77
Resilience % 20°C	68.6	69.0	67.5	68.3	66.1	66.1
Resilience % 100°C	80.9	85.2	83.7	84.7	83.3	83.3
Aged 3 days at 100°C:						
Tensile strength kgf/cm^2	169	98	168	114	153	141
Elongation at break %	284	251	338	259	279	332

*Mean maximum for four tests on two test pieces

TABLE 3.3.10

DEPENDENCE UPON TEMPERATURE OF TENSILE STRENGTH OF NATURAL RUBBER AND POLYISOPRENE A STOCKS

Rubber, 100; LS-HAF black, 45; zinc oxide, 5; oil, 4; stearic acid, 2; antioxidant, 1; sulphur, 2.5; sulphenamide, 0.5

	Temperature°C		
	20	60	100
Tensile strength kgf/cm^2			
Natural rubber	300	261	210
Polyisoprene (A)	240	173	101
Elongation at break %			
Natural rubber	585	645	735
Polyisoprene (A)	630	605	510
M300 kgf/cm^2			
Natural rubber	103	77	61
Polyisoprene	76	64	58

Cure: 35 min at 140°C (NR); 40 min at 140°C (IR)

TABLE 3.1

MAIN ADVANTAGES OF HIGH-CIS IR OVER NR

1. Physical form-cleanliness
11. Technical specifications
111. Lower power consumption
1V. Lower processing temperatures
V. Better flow characteristics
V1. Relative price stability
V11. Independence of Hevea plantations (political implications)

Many of these claims made on behalf of IR are no longer tenable. Under the Malaysian SMR and other specification schemes, NR is sold to technical specifications and the tonnage of technically specified rubbers is increasing rapidly. In these technical specifications, dirt content is the most important parameter and the grades are numbered according to the dirt content. The lower power consumption and lower processing temperature, after allowance has been made for mastication, are a reflection of the shear force needed to mix the material. The high shear rates of NR lead to the most thorough dispersion of compounding ingredients in any general purpose polymer. Oil prices are no longer stable or low. Recently it was the prices of oil and of synthetic rubber that went up, taking with them the price of natural rubber.

Gregg and Macy (49) explain the differences in behaviour between NR and IR as follows:-

"The causes of some of the differences in properties between compounded natural rubber and compounded synthetic poly-isoprene have been traced to the insoluble non-rubber material in natural rubber. This material is mostly denatured proteins and is responsible for the higher modulus, faster scorch time, higher heat build up, and higher hot tear strength of natural rubber. These properties may be related to the pigment effect of the denatured protein to act as a reinforcing filler at low concentrations (3-4 per cent by wt.) as well as a curing agent.

The greater green strength of compounded natural rubber has been related to its greater configurational regularity which contributes to faster crystallisation. The crystallite concentration increases with increasing stress and the crystallites act like a reversible reinforcing pigment which disappears when the stress is released."

3.4.4. Ethylene Propylene Rubbers

Rubbers prepared from only ethylene and propylene (EPM) have excellent ageing resistance and low cost but are of little value to industry as conventional vulcanising methods cannot be used with them. Consequently a third monomer, a diene monomer containing two double bonds was introduced to give ethylene propylene terpolymer rubber (EPDM). One of the double bonds is used up in the polymerisation reaction while the other remains to be available for vulcanising using conventional accelerator systems.

Though great expectations were had for EPDM rubbers these have not been realised for two main reasons.

1. These polymers lack tack and are difficult to process.
2. When EPDM is used in blends with the general purpose rubbers the vulcanising agents react preferentially with the large number of double bonds in the latter rubber leaving the EPDM poorly vulcanised (62).

It is still expected that these shortcomings in EPDM can be overcome and that its excellent fatigue ageing and ozone resistance properties can be made use of by the tyre industry. Its uses are mainly in non-tyre products today.

3.4.5 THE NEWER SYNTHETIC RUBBERS

The newer synthetic polymers of special interest to the tyre industry are medium vinyl polybutadiene, trans 1,5 polypentenamer, the Alfin rubbers and the thermoplastic rubbers.

3.4.5.1 Trans 1,5 polypentenamer has had strong claims made on its behalf by its sponsors, Farbenfabriken Bayer A.G. (63) (64). TPP is said to be capable of being made with a high degree of uniformity using the Ziegler-Natta catalysts. It crystallises like NR and has good low temperature properties. Its main characteristics are:

1. Good low temperature properties.
2. Tendency to crystallise in both the stretched and unstretched condition.
3. Resistance to dynamic stresses.
4. High green strength (35 kg/cm^2 as against 20 kg/cm^2 for NR) (54).
5. High tack.
6. Has fewer double bonds in the molecule and is therefore more resistant to oxidation than NR.
7. Lends itself to oil-extension and compounds can be made cheap.

The properties of TPP make it eminently suitable for use in tyre carcass stocks. Duck (60) states that "It would appear to combine the best characteristics of a linear polybutadiene with the best processing characteristics of a high cis synthetic polyisoprene". TPP has however not yet been made available as a commercial polymer. Butcher of International Synthetic Rubber Co. Ltd. (65) points out that "There is continued speculation concerning the commercial viability of polypentenamers, made by the ring opening polymerisation of cyclopentene since though the properties of this new elastomer are superior to polyisoprene in many respects, the cost and supply of monomer continue to cast doubt on earlier claims that it is a new general purpose rubber".

The synthesis of the polypentenamer from the C5 fraction of petroleum refineries is shown in Fig. 3.6. Cyclopentene is derived from cyclopentadiene that is found in the C5 stream from oil refineries.

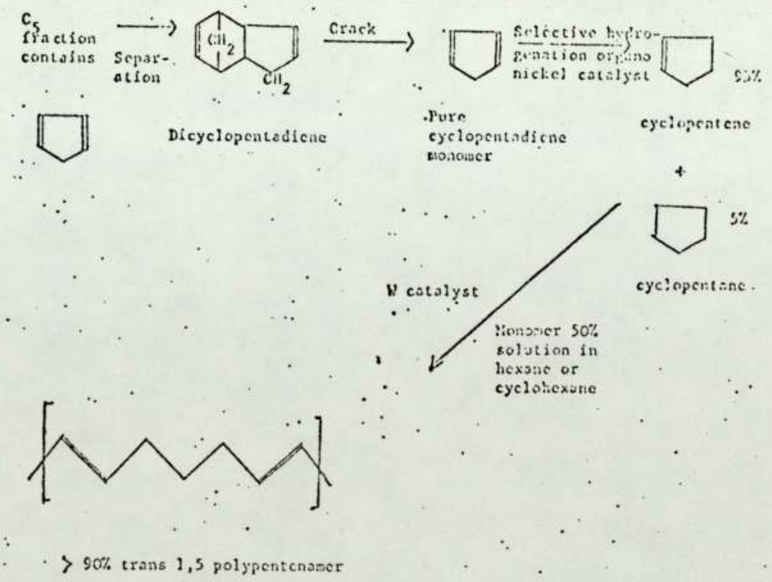


Fig. 3.6 Route from C5 fraction (containing cyclopentadiene) to trans 1,5 polypenamer (66)

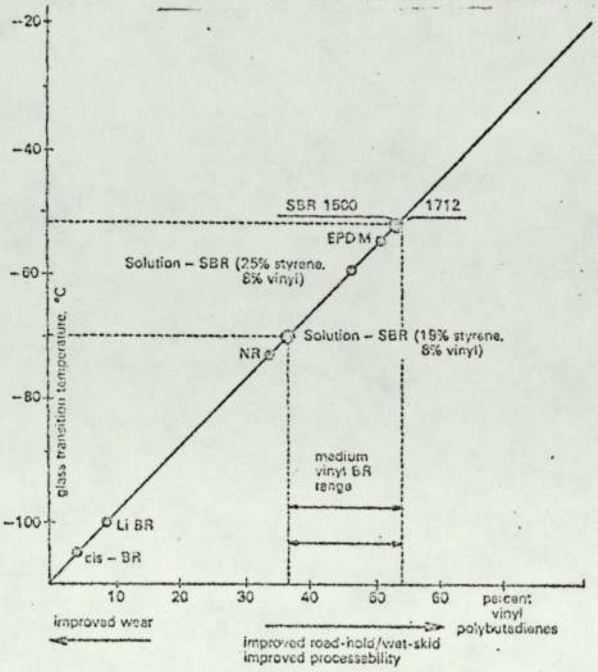
3.4.5.2 HIGH AND MEDIUM VINYL POLYBUTADIENES

By a study of the correlation of the physical properties of a number of elastomers with their glass transition (Tg) values Bayer workers pointed out "that the glass transition temperature, which is a measure of chain flexibility, determines a number of basic properties" (64).

It was reported that "Experiments have shown that the most useful compromise between abrasion resistance and skid resistance is a glass transition temperature of about -70°C, which represents a blend of 60 parts SBR and 40 parts BR." They also showed that two other products also had a Tg value of -70°C. One was a solution SBR with low vinyl content and a styrene content of 19 per cent, the other a homopolymer of butadiene with a vinyl content of 35 per cent. The processibility of this BR could be adjusted by controlling the molecular weight distribution and the long chain branching. This could indeed by called a "tailor-made" rubber.

The current shortage of styrene has led polymer producers to seek a replacement for SBR. High on their lists are these high and medium vinyl polybutadiene. Nordsiek (66) summarises their findings so far on the suitability of these materials for use as replacements for SBR as follows:"......we have found that homopolymers of butadiene with 1,2 (vinyl) contents between 30 and 50

Figure 3.7 Rubber Classification System according to glass transition temperature



Source: E.W. Duck: High Vinyl Polybutadiene Today and Tomorrow Paper presented to fifteenth annual Meeting of the International Institute of Synthetic Rubber Producers Inc.

per cent represent a genuine alternative both to the butadiene- styrene copolymers (S-SBR) with the same Tg values and the now common SBR/BR blends. Besides their greater ease of handling compared with blends, the special homopolybutadienes afford a number of economic advantages over equivalent modern solution SBR grades.Polymerisation processes with only one monomer component are principally easier to handle...... In Western Europe a surplus of butadiene is forecast for the coming decade, whereas the trend for styrene is the opposite".

Dr. E.W.Duck in his plenary lecture to the 1973 International Rubber Conference in Prague (66) predicted the replacement of SBR as the world's leading elastomer in the next few years, owing to the growing shortage of aromatics. He stated "These new medium vinyl polybutadienes, when prepared to 90 Mooney or higher and suitably oil extended, give more than adequate replacements for the tyre grade sbrs." Their properties are tabulated in Duck's paper Table 3.11 and show the properties of the medium vinyl polybutadienes to be comparable in tread stock recipes to the emulsion and solution SBRs. Duck (69) claims that when SBR is replaced by medium vinyl polybutadiene in tyre compounds the tyre runs a degree or two cooler and shows no tread cracking.

TABLE 3 - Comparison of the properties of Medium Vinyl Polybutadienes and Conventional SBRS.

	Medium Vinyl Polybutadienes				Conventional SBRs	
Vinyl Content - %	42	48	53.5	63	-	-
SBR (23.5% Bound Styrene)	-	-	-	-	Emulsion	Solution
Vulcanisation (Monsanto t_{90} at 145°C) - minutes	20	24	24	30	30	20
300% Modulus - Kg/cm^2	83.7	109.3	102.8	87.8	133.3	114.0
Tensile Strength - Kg/cm^2	161.3	165.1	147.3	153.4	211.0	206.1
Elongation at Break - %	480	410	410	460	450	520
Hardness - IRHD	59	59	59	60	64	62
Compression Set - %	33.6	27.3	25.0	22.7	36.9	38.1
Resilience at 20°C	45.8	47.0	44.2	42.9	38.6	42.9
Resilience at 50°C Dunlop	51.0	53.2	45.8	50.4	48.2	48.8
Resilience at 70°C Tripsometer	55.2	55.2	51.6	53.9	54.4	53.2
Skid Resistance (wet asphalt)	65	69	68	72	70	64
Goodrich heat build up °C	45	45	45	44	44	44
DIN abrasion loss (mls)	0.1589	0.1666	0.1713	0.2486	0.1990	0.1465
Compound 2nd order transition temperature (Dunlop tripsometer) °C	-48	-48	-39	-32	-32	-44

The International Synthetic Rubber Company Ltd., announced late in 1973 the availability of trial quantities of medium vinyl solution polybutadiene rubber Intolene 50 for evaluation as a replacement for SBR in tyre applications. This product is thought to have a vinyl content of 48 per cent. Oil extended to the same level as the popular SBR1712 tyre tread polymer. Intolene 50 is offered at £20 more per ton than SBR 1712 (161). No reports are available yet of the progress of this material since. It is felt that there are difficulties in producing batches of consistent quality. Besides, the ageing qualities of this material are said to be poorer than those of SBR. The tendency of polybutadiene to cross link oxidatively has been documented. Loan (69a) states that polybutadienes with 10 per cent vinyl side groups showed a cross-linking efficiency of about two and that the value was much higher for a 98% vinyl compound, one result suggesting a value of over 100. Hergenrother (69b) reports that cross-link densities obtained with peroxide cures are highest with polybutadienes with the highest 1,2 contents. The work of Grassie and Heaney (69c) show that vinyl polybutadienes react at much lower temperatures than do the cis and trans materials.

3.4.5.4 ALFIN RUBBERS

The Alfin Rubbers are copolymers of butadiene with styrene or isoprene prepared by using the Alfin catalysts. An Alfin catalyst has been described as "an insoluble heterogeneous system composed essentially of equimolecular quantities of a sodium alkyl, usually sodium allyl, a sodium alkoxide, usually sodium isopropoxide and by-product sodium chloride, all prepared in the presence of each other in an inert hydrocarbon medium" (69d). These catalysts were known many years ago but interest in Alfin Rubbers was lost as their very high molecular weights made processing difficult. Interest was aroused again by the discovery of "control agents" to limit molecular weights. A 25,000 ton-per-year capacity Alfin Rubber plant was installed in Japan a few years ago. Alfin Rubbers were thought to have a promising future until the oil and feedstock shortage caused problems. Neither the isoprene nor styrene monomers are likely to be available at prices to enable Alfin Rubbers to compete on equal terms with the medium vinyl polybutadienes.

3.4.5.4 THERMOPLASTIC RUBBERS

SBR is formed by the random copolymerisation of styrene and butadiene. If blocks of polystyrene were formed alternating with segments of polybutadiene chains we would get a three-block polystyrene-polybutadiene-polystyrene (SBS) polymer (Fig. 3.8) (54). It is possible to make SIS block polymers from styrene and isoprene in a similar manner. These polymers are thermoplastic in nature. Their advantage lies in their ability to be moulded like other thermoplastics by heating and then cooled (without

Fig. 3.8 **Model of SBS or SIS block copolymer**

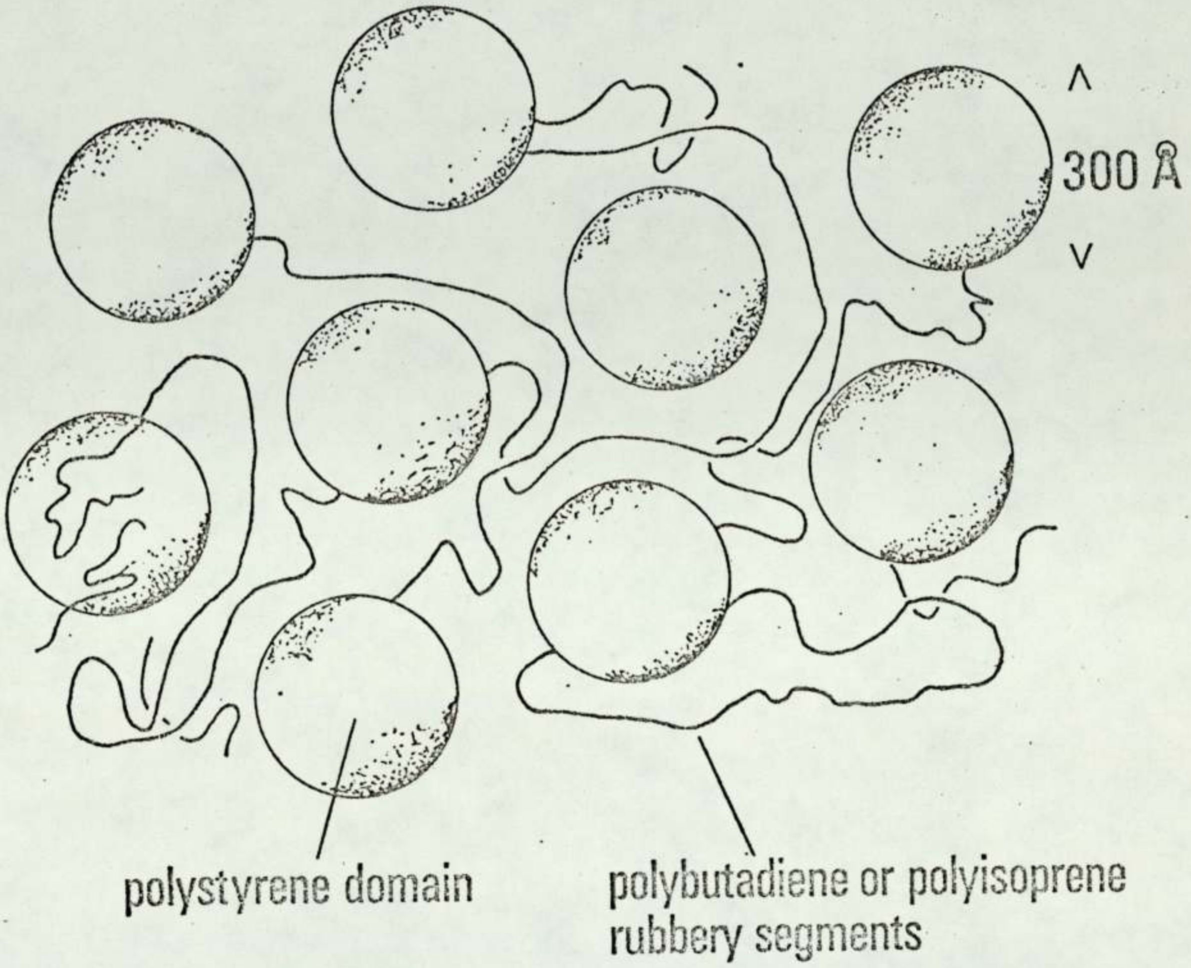


Fig. 3.8 Model of Styrene-butadiene-styrene (SBS) or Styrene-isoprene styrene (SIS) block copolymer.

the need for a vulcanisation reaction). Their possible use in increasing the green strength of rubbers like SBR and IR in tyre carcass stocks has already been mentioned. They cannot be used as the major polymer in components of today's tyres as they generate heat in service and soften. Their use in tyres for slow speed vehicles is possible in the future. An added advantage is that the polymer can be reprocessed. There will be less of a disposal problem with thermoplastic polymers.

4. THE CHOICE OF RUBBERS FOR THE DIFFERENT COMPONENTS OF TYRES

4.1. Passenger Car Tyres

The relative importance of each of the components of a passenger car tyre from the point of view of rubber usage can be gauged from the figures given by Grosch (70) and quoted in Table 4.1 for the percentage of rubber used in the tyre which goes into each of the components of a radial and cross-ply tyre.

TABLE 4.1

DISTRIBUTION OF RUBBER USED IN A PASSENGER CAR TYRE BETWEEN ITS DIFFERENT COMPONENTS

	Cross-ply	Radial
Tread	35	33
Breaker belt	-	14
Carcass	37	21
Inner Liner	14	14
Sidewall	14	18

4.1.1. Tread

Diamond (71) gives the following percentages of natural and synthetic rubber in the composition of a typical cross-ply and radial car tyre.

TABLE 4.2

PASSENGER TYRE COMPOSITIONS, U.K, %

	Natural rubber	Synthetic rubber
5.60-13 Cross-ply	10.5	89.5
1.55-13 Radial ply	36.0	64.0

Corish (72) had tabulated the typical tread stock properties of the main polymers.

TABLE 4.3

TYPICAL TREAD STOCK PROPERTIES OF THE MAIN POLYMERS

Property	NR	Emulsion SBR	Cis BR
1. Resilience	High	Medium	Very high
2. Tensile Strength	Very high	High	Medium
3. Tear Strength	Very high	Medium	Medium
4. Abrasion Resist	High	High	Very high
5. Wet Skid Resistance	Low	High	Very low
6. Oxidation Resistance	Medium	Medium	Medium
7. Permeability	High	Medium	Very high

The behaviour of IR parallels that of NR generally.

4.1.1.1 Wear properties of passenger car tyre treads

It has been widely reported that car tyre treads are made of a blend of SBR (mainly oil-extended) and BR. Only very small quantities of NR if any were said to be used. The proportion of BR in the treads or radial tyres are said to be less than that in the 25/75 SBR/BR blend used in cross-ply tyres. Kastein (51) summarises the technical grounds for preferring SBR to NR for car tyre treads as follows:-

> "SBR has been the preferred polymer for passenger tyre treads because of better abrasion resistance, wet traction, crack resistance and quieter running than treads made with natural rubber."

Even if technical considerations allowed the use of NR for this use sufficient quantities of NR are just not available to use in all car tyre treads - Bateman (45).

Grosch and Schallamach (31) (32) have shown that tyre wear is determined by the tyre surface temperature (TST). Grosch (31) showed that the TST for comparative equal wear of NR and SBR treads was raised by 5 to 10°C when the NR is blended with BR. Though NR has been generally dismissed in the technical publications as a car tyre tread polymer on grounds of poor wear and skid resistance, it has been observed that some manufacturers in Europe do use NR in car tyre treads. The tyre factory in Sri Lanka has used NR in all parts of the car tyre including the tread. In the only controlled comparative road test of NR and SBR tyre treads carried out in Sri

Lanka the NR treads wore off at about 20,000 miles compared with 24,000 miles for the SBR treads.

4.1.1.2 Skid Resistance of passenger car tyre treads

Grosch and Maycock demonstrated that skid resistance varied inversely with the resilience of the rubber compound.(73)NR which has a high resilience therefore has a lower skid resistance than SBR. Oil extension further lowers the resilience of SBR and so improves the skid resistance of oil extended SBR compounds. Oil-extended SBR is the polymer material in the high μ tread compound.

In NR, oil extension affects primarily the resilience of the compound unlike in SBR where several other properties including wear resistance are affected. Grosch and Maycock determined the skid resistance of NR and oil extended NR (OENR) compounds in road tests under different conditions. Their findings shown in Table 4.4 give normal unextended NR compounds a rating of only 84 to the 100 skid rating of a commercial high Mu compound. μ is the symbol denoted to express the hysteresis loss. High Mu (μ) compounds therefore have a low resilience. Oil extension increases the skid resistance of NR compounds and a 55/45 OENR gives better skid properties than the SBR high μ compound but the 55/45 blend is difficult to handle in the factory because of its high oil content and low viscosity.

TABLE 4.4

SKID RATINGS OF NR AND OENR COMPOUNDS IN RELATION TO A HIGH μ COMMERCIAL OESBR COMPOUND

Polymer	Skid Rating
Commercial high μ compound	100
NR plus 50 HAF	84
OENR 67/33 plus 50 HAF	95
OENR 55/45 plus HAF	108

On ice NR has greater skid resistance than SBR.

TABLE 4.5

SKID RATINGS OF OIL-EXTENDED TREADS ON SNOW-PACKED ROADS

	16 km./h		40 Km./h	
	Studded	Not Studded	Studded	Not Studded
OENR vs OESBR	131	112	110	120
OENR/BR (80/20) v. OESBR/BR (80/20)	138	115	118	111

One other point that must be made in regard to tyre tread properties is that a great deal of emphasis has been placed on polymer properties as affecting tread behaviour. The importance of road texture and of tyre construction has not been adequately appreciated. Until recently the radial tyre for instance has been shown to have greater traction than the cross-ply. Lees and Williams point out that "while the broad concepts (of the roadhold problem) are known and reported it is a measure of the complexity of the subject that the complete theoretical solution is still awaited and the practical application of what is known lags far behind its publication". It must be realised that tyre tread studies must be done in relation to road surfaces and not on the existing roads alone.

4.1.2. Tyre Carcass

In the U.S.A. where the proportion of NR used in a car is no more than 25 per cent of its total polymer, content, most of this goes into carcass compounds. D'Ianni (75) explains: "The carcass of a tyre is the main strength member - it is the mass of cord plies and rubber that must flex and twist to transform engine energy into vehicle motion and to absorb the shocks and vibrations of that motion. The carcass compound must provide an excellent bond to the fabric, and, because of the rise in temperature, heat durability is a prime consideration." Low heat generation, good heat resistance, tack and high green strength are demanded of tyre carcass polymers. This is a field where natural rubber is outstanding. In cross-ply tyres, Grosch (70) points out, 60/40 blends of NR/SR are used: in radials the proportion of NR is higher - 70 per cent. This is because the carcass compound must have sufficient tack and green strength to maintain the tyre cords in position during calendering, cutting and assembly of the carcass plies. In radial tyre building not only is greater precision needed but the unvulcanised tyre carcass must resist distortion when it is expanded pneumatically. SBR was used in tyre carcasses mainly on grounds of cost. Its better heat resistance also improves the reversion characteristics of the compound. (51) Small proportions of BR are also added to improve ageing. Gardner (61) maintains that the addition of BR is done on the basis of known good ageing characteristics, but that experiments carried out on tyres do not bear this out. Another important feature of NR useful in carcass compounds is its excellent bonding to tyre cord fabric. It bonds particularly well to steel cord fabric.

Tyre carcasses must be one of the tyre market sectors. Bateman has referred to, that NR had held "in the face of tremendous commercial and technical pressures". He points out that for NR to have done so "its advantages there must be of substance and hence to enhance them to a relatively minor degree would consolidate its market hold quite disproportionately". It is therefore logical to study possible improvements in NR technology as applicable to tyre carcasses.

a) "In-rubber" degradation of poly-ester cord

Polyester is a major carcass material of car tyres in the U.S.A. NR has excellent adhesion to steel cord and good systems have been worked out for bonding it to polyester. IR and TPP (trans-polypentenamer) also bond well to polyester and steel. When polyester cord is stressed in service while embedded in rubber in the absence of air the cord material disintegrates. This deterioration is more severe when the rubber is NR. The explanation offered is that the nitrogenous products resulting from protein breakdown in NR catalyse the in-rubber degradation of polyester. The relative inaction of IR in promoting this in-rubber degradation is probably due to the absence of non-rubber protein material in it. Deproteinised NR of "high dynamic quality" is now being offered with fatigue resistance particularly in mind. This material would presumably serve polyester cord better than RSS. ICI have developed a substituted triazine derivative that protects polyester against this anaerobic heat degradation.(77) The question of in-rubber degradation with particular reference to natural rubber needs detailed study; polyester is the popular tyre cord material in the U.S.A. presently for car tyres, the annual consumption of NR used in car tyre carcass compounds being of the order of 150,000 tons. Polyester is also being considered for use in truck tyres. The layers of material are thicker in truck tyres and the heat developed much greater so that the problem of in-rubber degradation will be much more severe. The importance of the problem can be gauged when we realise that tyre carcasses are one of the largest sectors of the industry that NR has continued to hold.

The main requirements of tyre carcass compounds are good fatigue resistance, low heat build-up and good resistance to heat ageing.

4.1.2.1 Heat Build-up

Schallamach explains the heat build up in a tyre as follows (34): "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. The losses manifest themselves as rolling resistance and heat build up. The latter is the more serious effect as it can lead to catastrophic failure... 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 strength, makes its use in carcasses indispensible. The proportion used rises from about 50 per cent in the carcasses of passenger tyres to some 75 per cent in those of truck tyres".

Heat build-up is due to the frictional viscosity of rubber. Rubber is formed of a continuous elastic phase with embedded frictional viscous elements. When a rubber is deformed part of the energy is consumed by the viscous elements and appears as heat. Similarly energy is dissipated when the elastic phase retracts during strain recovery and releases its stored energy. Resilience is a function of the configuration of the rubber molecule and is connected with elasticity. The dynamic properties of rubber are dependent on compound viscosity and modulus.

The heat build-up characteristics of NR are found to be improved by the following methods. (45)

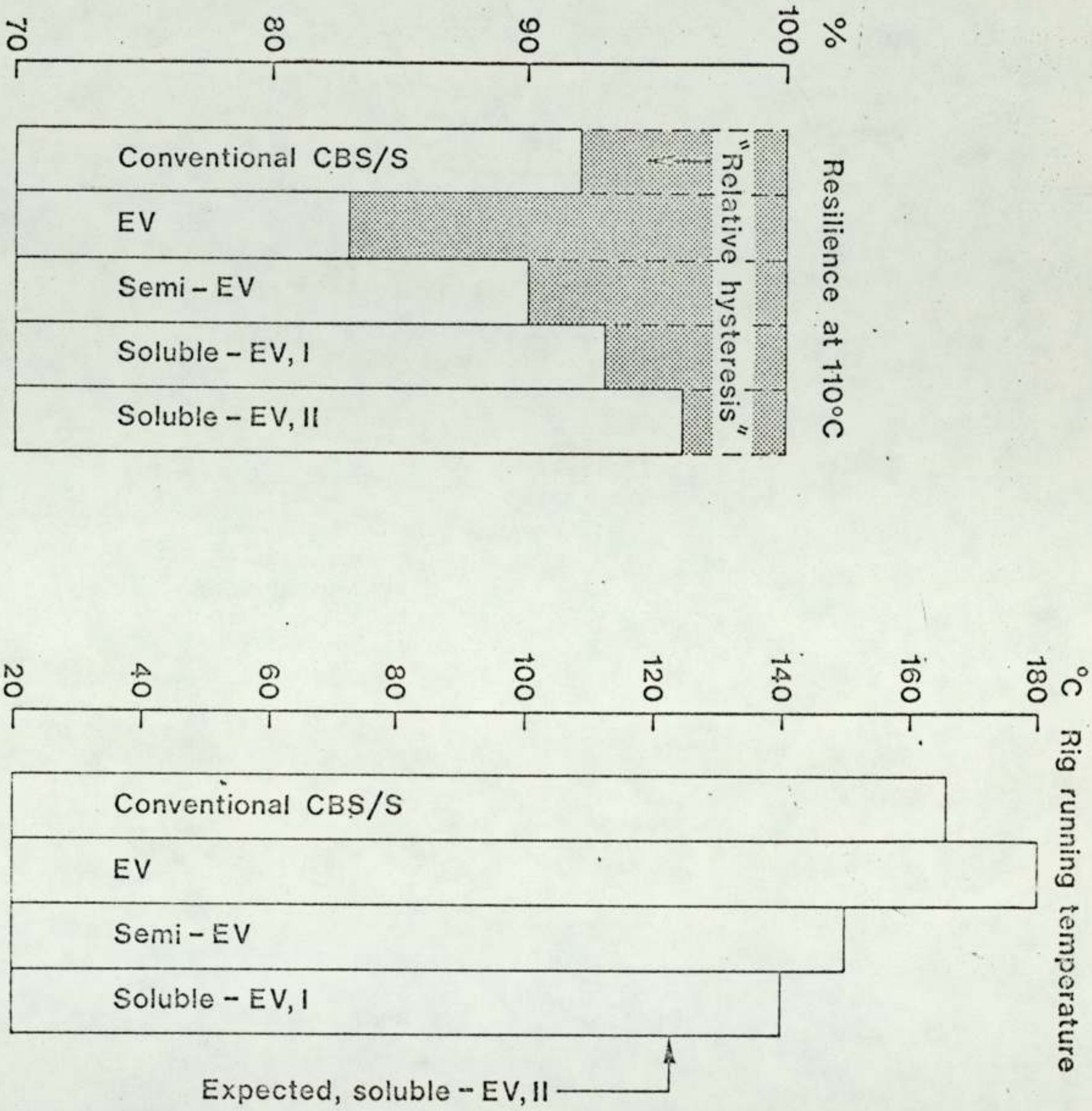
1. Auto coagulation of the latex
2. Removal of nitrogenous components of the rubber
3. Use of soluble EV (efficient vulcanising) systems (Figure 4.1)
4. Vulcanisation with urethane cross-linking agents.

4.1.2.2 Fatigue Resistance

NR's fatigue resistance at high rates of strain is superior to that of SBR and BR. It has also been shown that the removal of nitrogenous non-rubber material from NR improves its fatigue resistance. Improved performance was shown in a punch fatigue test by carcass compounds prepared from natural rubber from which the nitrogenous constituents had been selectively rmoved. Fatigue life of NR compounds have shown improvement when urethane vulcanising systems were employed. Good tensile and tear properties at high temperatures is characteristic of NR vulcanisates. Figure 4.3 shows this clearly.

Figure 4.1

Resilience and Rig Running Temperatures of NR Carcass Mixes Vulcanized by Different Methods

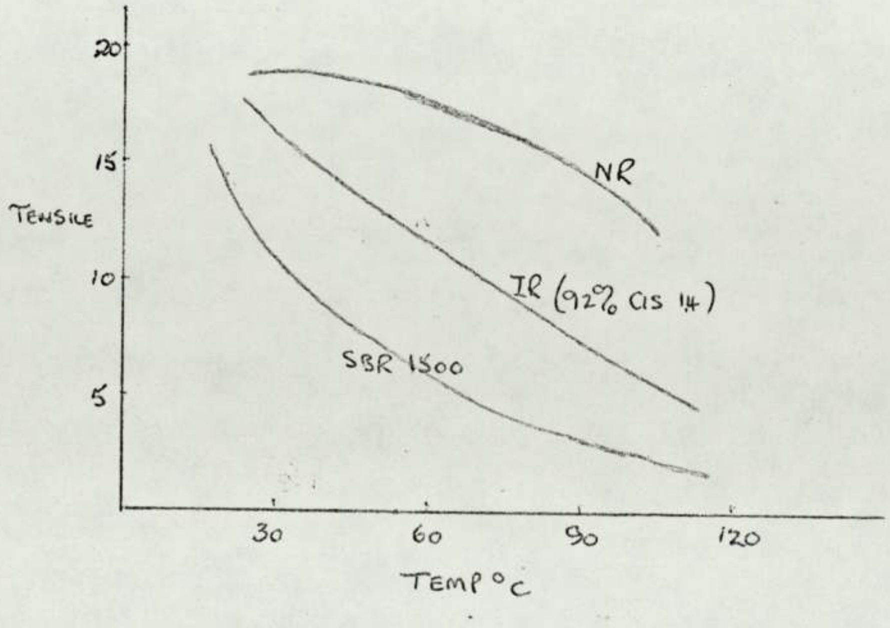


4.1.2.3 Reversion in NR carcass compounds

NR vulcanisates show a tendency for a fall of in physical properties when maintained for a period of time at high temperatures - the phenomenon of reversion. This has been shown to be due to the S8 linkages progressively breaking down to di- and mono-sulphidic ones. (43), (44) It has now been shown that the use of vulcanising ingredients soluble in the rubber not only achieve the desired stability of properties but actually improve the dynamic properties of the vulcanisates. These are named the "Soluble EV" formulations. (45), (78) The soluble EV systems give improved vulcanisates presumably because being more evenly dispersed, they give more homogeneous vulcanizates. Reversion is also suppressed by the use of urethane cross-linking systems. Reversion is however much less of a problem with car tyres than with large tyres.

FIGURE 4.2

Initial Strengths of Conventional Tyre Tread Compounds at different temperatures.



With these many improvements in technical characteristics and the economics now running in its favour NR should be able to more than hold its own in this sector of tyre carcasses where its properties have long been recognised.

4.1.3 Breaker Belts

Breaker belts of radial and belted bias tyres are made of rayon, steel, fibreglass and du Pont's aramid fibre Kevlar. The preferred polymer here is NR. It is reported that at present, "most steel belt skims are made from natural rubber blended with an apparent maximum of 30 per cent synthetics"; this also seems to apply to glass cords where OCF (Owens Corning manufacture the fibreglass in the U.S.A.), has recommended "a medium modulus stock based on 80/20 NR/SR)".

4.1.4 Inner Liners of Tubeless Tyres

The properties needed here are:-

1. Good bonding to the adjacent layers
2. Low air permeability
3. Low heat generation on flexing, and
4. Good ageing.

In Europe NR/SBR/Reclaim blends seem popular while in the U.S.A. chloro- or bromo-butyl in admixture with equal proportions of NR is popular; butyl rubber (IIR) is also widely used in inner tyre liners. (63)

The halo-butyls have the advantage of being compatible with unsaturated polymers like NR and SBR so that the liner bonds well to the adjacent layers. Chlorobutyl also has low air permeability and improves ageing.

4.1.5 Sidewall

The sidewalls of a radial tyre are subjected to more severe flexing than those of a cross-ply tyre. Fatigue resistance is therefore important for the polymer used here. Flex cracking begins earlier in NR sidewalls but the growth of the cracks is slower than in SBR. Sidewall cracks developed in the all-NR tyres made in Sri Lanka but the problem was overcome by adjusting the modulus of the rubber compound. The ones in SBR compounds are fewer but longer and deeper, leading to earlier failure of the tyre. Therefore, whereas an SBR/BR blend or hot SBR is used in cross-ply tyres (with EPDM at time for improved ageing and flex resistance) the preferred polymer for radial ply tyres is NR, 60 to 70 parts of NR could be used but sometimes part of it is replaced by IR. The remainder consists of SBR and BR. It has been stated that on technical considerations about 90 per cent of NR can be replaced in tyre sidewalls. Table 4.6 prepared by Dreyfus and Toullec (59) compares the suitability of the main polymers for use in tyre sidewalls.

TABLE 4.6

POLYMERS FOR RADIAL CAR TYRE SIDEWALL COMPOUNDS

Polymer	Factory Processing	Mechanical Properties	Fatigue Resistance (Protected)	Resistance to Ozone (Protected
NR	E	E	F to E	F to E
IR	F to E	E	F to E	F to E
Emulsion SBR	F to E	E	F	E
Solution SBR	F to E	E	F to E	E
Solution BR	F to E	E	E	E

E - Excellent; F - Fair; P - Poor; L - Low; M - Medium; H - High

The column on cost has been omitted as it is not applicable today.)

Schallamach (34) has pointed out that the sidewalls of cross-ply tyres can be made of SBR, (except white sidewalls because of staining) because SBR is better than NR at low strains. However, since NR is better at large strains, the sidewalls of radials contain relatively large proportions of NR - about 60 per cent on the average. Grosch (70) has pointed out that the sidewalls of radials are more prone to chafing and other gross damage because of the larger bulge produced in the contact area and that here the high tensile strength of NR compounds is also advantageous.

In the U.S.A. most tire manufacturers are said to be using 20 to 30 per cent of EPDM amounting to about 0.2 lb per tyre in their white sidewalls to get ozone protection without staining. Anderson (79) states that EPDM is also used in black tyre sidewalls.

4.2. TRUCK TYRES (COMMERCIAL VEHICLE TYRES)

Truck tyres can be divided roughly into two groups:-

(a) Light truck tyres up to size 8.25-20, and

(b) Heavy truck tyres size 9.00-20 and above

Light truck tyres

Polymer usage in light truck and van sizes follows the pattern of passenger car tyres; the quantity of NR used increases with the size of the tyre. Size 8.25-20 would have about the same proportion of NR as size 9.00-20 which is classified as a medium or heavy truck tyre.

The characteristics demanded of truck tyres are low cost per mile, safety and comfort, in that order.

Shearer (6) summarises the lines that truck tyre development will take as follows:-

1. Greater standardisation of tyre sizes and load ratings.

11. Lower profiles

111. Tubeless construction on 15° Drop Centre Wheels

1V. Radial ply tyres with high remould potential and tread patterns suited to particular axle positions.

It has been estimated that "by 1975 82 per cent of the 19 million-odd cv tyres sold in Europe at that time will be radial". The switch will be much slower in the U.S.A.

Steel is likely to dominate the field of tyre cord used in carcass and breaker plies. Nylon will also hold some portion of the carcass material.

The most popular truck tyre size in Britain today is the 10.00-20; in Europe where axle loadings are heavier it is 11.00-20 and 12.00-20. The relative proportions of NR and SR in present day British 10.00-20 radial and cross-ply tyres is given in Table 4.7. (71)

TABLE 4.7

TRUCK TYRE (10.00-20) COMPOSITION U.K. PER CENT

	Radial	Cross-ply
Natural rubber	95	65
Synthetic rubber	5	35

Since truck tyre sections are thick and rubber has poor heat conductivity, heat build up is of paramount importance in truck tyre compounds. Assessments have been made of the contributions made by each of the tyre components to total heat build-up in a truck tyre. (Collins, Jackson and Oubridge (80), Kainradl and Kauffmann (81). It has been shown that "heat is generated in tyre compounds by two methods:-

a) Under constant bending which is proportional to the loss modulus, and

b) Under constant compression which is proportional to the loss modulus divided by the square of the complex modulus.

Energy is lost in the tread area by both methods and in the casing by bending alone. By measurement of the complex and loss moduli using a Dunlop Rotary Power Loss machine it has been possible to determine the energy lost by each tyre component as a percentage of the total energy loss of the tyre. These percentages are shown below in Table 4.8. (80)

TABLE 4.8

TYRE ENERGY LOSSES (PER CENT)

	9.00-20 Tyre	2.25-g Tyre
Tread Compressive Component	32	22
Tread Bending Component	27	29
Ply Rubber Component	12	4
Sidewall Component	-	5
Cord System Component	29	40

4.2.1. Tread

From the preceding table it is clear that the greater part of the heat generated in a truck tyre originates in the tread. Low heat generation is therefore of the utmost importance particularly in the tread base. High heat build-up would lead to reversion of the carcass rubber compound and ultimately separation of the plies.(80),(81),(82) The other properties required of a truck tyre tread compound are:- good resistance to fatigue, abrasion and ageing, particularly heat ageing. An all-NR truck tread shows groove cracking - a manifestation of fatigue and ozone degradation. Groove cracking occurs particularly in tyres with a nylon carcass. The high permanent set of the nylon carcass produces strain in the tread rubber making it susceptible to groove cracking. The replacement of about 20 to 30 per cent of the NR with BR greatly reduces the tendency to groove cracking, at the same time increasing the resistance to abrasion and ageing. Kainradl and Kauffmann have determined that the major portion of the heat generated in the tread comes from the tread base, the tread cap contributing less than 10 per cent of the total heat build-up. The question of extruding the tread cap and base separately has been studied, the tread cap compounded for wear resistance and the base for low heat build-up. The two parts, cap and base were to be then combined. Difficulties however arise in the factory. It would mean for instance that tread extrudate rejected for dimensional variations cannot be reprocessed. Factory costs also rise if the two parts of the tread are extruded separately and then combined.

The introduction of BR into truck treads to combat groove cracking has been studied by MRPRA and the Avon Rubber Company. The improvement in abrasion resistance and ageing have already been mentioned. Lake and Clapson (40) attribute the successful performance of NR/BR blends in combating groove cracking in truck tyres to the high mechanical fatigue limit of BR and the good high strain fatigue and tear properties of NR. It is pointed out that though proportions of BR as low as 15 per cent of BR considerably reduce groove cracking, proportions as high as 30 parts are used. More than this is not used as processing difficulties arise and the tendency to rib tearing becomes pronounced at higher proportions. The tendency to rib tearing becomes pronounced at higher proportions. The tendency to groove cracking is less pronounced in radials and a smaller proportion of BR is used in the tread. Another approach to the problem of tread groove cracking would be the use of anti-flex cracking agents. The two methods cannot be compared directly in the absence of a quantitative estimate of the relative effectiveness of each method.

The statement that IR can replace NR up to 20 per cent in large truck treads, 40 per cent in truck carcasses and up to 90 per cent in truck sidewalls has been repeated. (81) This is rarely achieved in practice, if ever. Price, processing and final properties of the finished product are against it. Papers delivered at the International Symposium on Isoprene Rubbers held in Moscow in November 1972 claimed that NR could be completely replaced by IR in truck tyres. (82)

It has also been claimed that IR compounds give lower heat build-up in truck treads. At equal black loadings IR does indeed give lower heat generation. But at equal black loadings the IR compounds have only 85 per cent of the abrasion resistance of equivalent NR compounds. When more black is added to bring the abrasion resistance of the IR compounds to the level of the NR compounds the resilience suffers. In tests carried out at equal Levels of abrasion resistance at MRPRA the NR treads ran 7°C cooler than the IR treads. (84)

It appears that NR/BR blends will continue to be the favoured combination in truck treads, with the proportion of BR being reduced in radials. The good tensile and tear properties of NR particularly at high temperatures, the low heat build-up and resistance to crack growth if combined with the high fatigue limit of BR and its good abrasion and ageing properties make a strong combination in this application. (85)

4.2.2. Carcass

The tyre sectors that Bateman has (45) were being retained by NR "in the face of tremendous commercial and technical pressures" include mainly truck tyre treads and carcasses. He explains NR's superiority here as follows:-

"The outstandingly good high temperature strength properties of NR plus dynamic properties giving rise to comparatively low heat build-up are identifiable key factors in determining its continuing essential value in carcass and breaker stocks and in heavy duty treads."

This position of NR in carcass stocks is being consolidated by further improvement in heat build-up, fatigue and reversion properties. Recent work has shown that a carcass stock prepared from auto-coagulated NR runs cooler than one made from acid coagulated NR. It has also been shown that selective removal of nitrogenous material from NR improves its fatigue properties.

Barnard and co-workers at MRPRA have found that urethane cross-linking of NR improves its reversion and ageing characteristics while maintaining the good physical properties of NR. Of particular interest in carcass compounds is the fact that urethane-crosslinked NR adheres even better to metal and textile materials.

The use of mixed sulphur/urethane vulcanising systems allows the retention of the "excellent reversion and ageing characteristics of urethane vulcanisates at considerably reduced cost" as well as the higher resilience and low running temperatures of conventionally vulcanised NR systems.

The switch to radials and the use of metal cords in carcasses also favour NR, which gives excellent adhesion to brass-coated steel cord. Small quantities of BR are added to carcass compounds particularly in the outer plies. Gardner (76) thinks that this is done on theoretical grounds to improve the heat resistance of the compounds, but finds no justification for it in the results of road tests. The reason he finds in the possibility that the improved heat resistance is offset by the poor tear properties of BR when the tyre is new. Gardner continues that for tyre carcasses "quite low grades of NR, with large particles of foreign matter removed by straining, are adequate; the use of polyisoprene here will probably depend on its price relative to the lower grades of Natural". It has been claimed that 40 per cent of NR in truck tyre carcasses can be replaced with IR. With present high prices of feedstock, together with its processing drawbacks that are discussed in the next chapter, IR is unable to offer any worthwhile competition to NR in truck tyre carcasses.

A polymer that could compete with NR in tyre carcasses on technical grounds is trans 1,5 polypentenamer (TPP). TPP is said to have high tack, high green strength and good fatigue properties. Though solution SBR with its low hysteresis has been mentioned as a possible replacement for NR here (Kastein) the escalating price of SBR due to the styrene shortage rules out this possibility.

Breaker compounds are similar to carcass compounds in composition.

4.2.3. Sidewall

Truck tyre sidewall compounds contain NR and SBR with a small proportion of BR added to improve flex life. Some reclaim is also added to improve moulding and reduce cost. It has been repeated that on technical grounds it is possible to replace 90 per cent of the NR in sidewalls with IR. Higher cost and processing problems have contained IR's penetration of this field. Radial truck tyre sidewalls use more NR than do cross-ply ones, because of the higher strains that radial sidewalls are subjected to. (86) The addition of some BR increases the resistance to crack initiation, NR providing the resistance to crack growth. Schallamach (34) observes that "sidewalls of truck tyres are made in a wide range of blends, 100 per cent natural rubber not being uncommon. It appears that at least 15 per cent natural rubber is necessary for building tack".

Other possible competitors to NR in this field in the future are trans polypentenamer and EPDM rubbers. TPP has excellent fatigue resistance and EPDM excellent oxone resistance. EPDM is expensive, TPP has yet to be available in commercial quantities. The sidewalls of the truck tyres produced wholly of NR in Sri Lanka have performed well, in spite of severe overloading.

4.2.4. Inner Liner

The needs of inner liner compounds for truck tyres have been summarised by Dreyfus and Toullec (59) thus:-

"The high inflation pressures (more than often above 7 bars) together with the internal heat generation, impose a choice of inner liner providing better air impermeability than that used for car tyres. This inner liner must also give good resistance to oxidation, flex-cracking, good adhesion to the underlying compounds, be easy to process under normal conditions and, of course, be at a reasonable cost. These requirements are fulfilled through the use of halogenated butyl or of SBR with high styrene contents".

Chloro-butyl and bromo-butyl are used in admixture with NR in about equal proportions. The halo-butyl has about equal resistance to air permeation as butyl but has the added advantage of being compatible with other common polymers so that the liner can be made to give good anchorage to the adjoining layers of the tyre. NR/halobutyl blends are said to be less likely to result in ply- and tread-separation than the NR/SBR/reclaim blends used with car tyres.

It has also been claimed (Fawcett and McDonel) (63) that "A blend of poly-epichlorhydrin and butyl rubber is also finding use in heavy duty truck and off-the-road tire liners, where operating conditions of 250°F are common and liners must have excellent ageing properties as well as extremely low permeability".

4.3. Earthmover Tyres

Shearer (6) divides earthmover tyres into two categories - the working machines which load the earth and the haulage machines which move it away. Both types operate on rough terrain and carry heavy loads. Working machines carry heavier loads and operate at speeds around 5 m.p.h. They have the added problem of vehicle stability. The loads for haulage machines are heavy though not so heavy as for working machines. These vehicles usually weight about 300 tons and travel distances like 20 miles at speeds around 50 m.p.h. Development is towards heavier machines of both types. (87)

Heat generation is therefore a serious problem. The thick rubber sections of the tyre and the arduous nature of the terrain and heavy loads dictate the use of natural rubber for earthmover tyres. Laverty (26) points out that the average tyre of this type (18.00-25) contains 600 lb. of elastomers, and that this sector in 1967 consumed 31,600 long tons of elastomers representing 2.3 per cent of the total rubber consumed that year in the U.S.A. He reports that of this, 26,800 long tons were NR, i.e. 85 per cent of the rubber used in an earthmover tyre is NR. Laverty states that Goodyear switches "rather indiscriminately" between NR and IR (its own Natsyn) here. The price of natural rubber is said to be the determining factor of how much IR is used. The other polymers used are SBR and BR.

4.4. Aircraft Tyres

Aircraft tyres are required to be able to absorb very severe stresses and very high temperatures for short periods of time. Natural Rubber is almost exclusively used here. Kovac (88) states "Aircraft tyre loads can go as high as 75,000 pounds. Speeds can reach 320 m.p.h. Deflections can go as high as 35 per cent. Aircraft tyres carry several hundred times their weight". NR can best bear these stresses.

The suitability of each of the rubbers considered in this chapter for the manufacture of the different components of the main types of tyres is summarised in

Tables 4.9 and 4.10 Their prospects will be discussed after the economic aspects of polymer usage in tyres are considered in the next chapter.

TABLE 4.9

BEHAVIOUR DURING PROCESSING OF SOME ELASTOMERS WHICH ARE USED ALONE

Elastomers	*Advantages*	*Drawbacks*
Natural rubber	Excellent dispersion of ingredients. Excellent building tack and green strength. Dimensional stability in semi-finished parts.	Lack of uniformity. Use of machinery and consumption of electricity for plastification. In winter in some countries it must be heated before use since it crystallises at low temperature.
Polyisoprene	Constant properties. Does not require plastification.	Building tack inferior to that of natural rubber Lack of green strength. Difficulties in calendering, extrusion and tyre building.
Emulsion or Solution S B R	Constant properties. Does not require plastification.	For some types, difficulty in dispersing ingredients. Difficulties in tyre building due to poor building and green strength.
Polybutadiene	Constant properties. Does not require plastification.	Has no cohesion, must be used together with other elastomers. Even in a blend it is difficult to work. Difficulty in extruding. Insufficient green strength and building tack.
Butyl	Constant properties. Does not require plastification.	Difficulty in dispersion of ingredients. Dangerously contaminates other elastomers and vice versa. Difficulties in extrusion and splicing.

BEHAVIOUR OF SOME ELASTOMERS IN TYRES

Elastomers	*Advantages*	*Drawbacks*
Natural rubber	Has excellent mechanical properties without any need for reinforcing fillers. Excellent tensile strength and tear resistance, even at high temperature. Exceptional elasticity, low heat build-up. Resistance to chipping and chunking.	Poor performance as regards reversion and ageing. Cracks easily in tread grooves and sidewalls. Poor wear and unsatisfactory grip as compared to certain synthetic elastomers.
Polyisoprene	Has good mechanical properties without reinforcing fillers. Low heat build-up.	Moduli, tensile strength and tear resistance sometimes inferior to natural rubber.
Emulsion or Solution S B R	Is not subject to reversion, ages well. Satisfactory resistance to wear and cracking in passenger car tyres. Acceptable grip.	Requires reinforcing filler. Poor tear resistance. Excessive heat build-up.
Polybutadiene	Improves resistance to heat build-up, wear, flexing and cracking. Reduces heat build-up. Improves grip on snow and ice. Stands up well to low temperatures.	Requires reinforcing filler. Low static modulus; tensile strength and tear resistance poor. Bad resistance to chipping and chunking. Unsatisfactory wet grip.
Butyl	Ages well. Retains the air in inner tubes better than other elastomers.	Requires expensive curing systems.

TABLE 4.10

USES OF SOME ELASTOMERS

Elastomers	*Tread*	*Sidewalls*	*Breaker Belt*	*Carcass*	*Liner*	*Inner Tubes*	*Curing Bladders*	*Miscellaneous*
Natural Rubber	Radial and cross-ply Truck Tyres	Radial car Tyres Radial and cross-ply Truck Tyres	Radial car Tyres Radial Truck Tyres	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres	Car and Truck Tyres	Car and Truck Tyres	—	Complementary Compounds
Polyisoprene (With Natural Rubber)	Radial and cross-ply Truck Tyres	Radial car Tyres Radial and cross-ply Truck Tyres	Radial car Tyres Radial Truck Tyres	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres	—	—	—	Complementary Compound
Emulsion or Solution SBR	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres	—	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres	Radial and cross-ply car Tyres	—	—	Complementary Compounds
Polybutadiene (With other elastomers)	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres	Radial car Tyres Radial Truck Tyres	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres	—	—	—	Complementary Compounds
Butyl	—	—	—	—	—	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres	—
Chlorobutyl	—	—	—	—	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres With other elastomers	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres	—
Poly-chloroprene	—	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres With other elastomers	—	—	—	—	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres with other elastomers	—
E P D M	—	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres With other elastomers	—	—	—	—	Radial and cross-ply car Tyres Radial and cross-ply Truck Tyres With other elastomers	—

5. ECONOMIC ASPECTS

5.1 The Tyre Industry

5.1.1 Introduction

5.1.1.1 Organisation

The world's tyre industry can be divided into the following groups.

1. The large multinational companies like Goodyear, Firestone, Dunlop-Pirelli and Michelin.

2. The tyre manufacturing organisations in the Socialist countries.

and 3. The national tyre manufacturing companies which usually have overseas affiliations for basic technical know-how. It is interesting to note that all the tyre companies in Japan have arrangements with U.S.Companies for technical information. The Sri Lanka Tyre Corporation obtains information on technical developments from the U.S.S.R.

The U.S.A. has the largest tyre industry in the world and used 3135.8 metric tons of rubber in 1973 compared with 1045.0 metric tons by Japan and 455.9 metric tons by the United Kingdom.

5.1.1.2 Original equipment and replacement tyre markets

The tyre companies supply their products to motor manufacturers for use as original equipment (OE) on new vehicles and also to the replacement market. The replacement tyre market in the USA represents about 70 per cent of total tyre sales (15). It is a stabilising factor for the tyre industry in times of recession when motor vehicle manufacture is cut down.

5.1.1.3 Range of activities

Most tyre companies engage in the manufacture of a wide range of other rubber products which could include hose, belting, industrial rubber goods, footwear and sports goods. Michelin, it would appear, is probably the only company which does not manufacture other rubber goods besides tyres. They generally have substantial interests in a synthetic rubber manufacturing organisation. Goodyear and Firestone have their own synthetic rubber plants. The U.K. Dunlop group of tyre companies own the International Synthetic Rubber Company. It may be recalled that it was the Goodyear Tire Company who, rearing a serious shortage of natural rubber in the 1960s ventured out to manufacture synthetic cis polyisoprene. They achieved their aim. A few of the tyre companies, including Dunlop, Goodyear and Firestone own extensive rubber plantations.

5.1.2 Dependence of the tyre industry on the motor industry

The tyre being used on motor vehicles, the tyre industry is largely dependent on the motor industry. The motor industry itself thrives when economic conditions are bright. Recession conditions in the country affect the motor and the tyre industries more than they do some other industries.

The motor industry is beginning to regard the tyre more and more as a component of the motor vehicle and a very important one too. The requirements they lay for tires are becoming more stringent and General Motors have even laid down a total specification for tyres to be used on their vehicles. Some of the requirements being sought by motor manufacturers will affect the tyre industry quite adversely. For instance, the development of a run-flat tyre will mean that each motor car will use four instead of five tyres. To the motor manufacturer however it will mean more space in the car or a more compact car at a lower cost.

5.1.3 Features of the tyre industry

5.1.3.1 Fierce competition is evident in the tyre industry. Each tyre company pays a great deal of attention to its "image" in its marketing campaigns. The multinational companies have factories in one another's countries.

5.1.3.2 This competition is reflected in the dynamism of the industry. New tyre constructions and new designs are constantly forthcoming, and newer materials of construction and improved compounding ingredients like carbon blacks used. No tyre company can afford to lag behind in the face of this intense competitive - hence the large sums of money being spent on research and development.

5.1.3.3 Research and development costs are high for tyres. This is explained in the chapter on tyre testing because testing of tyres is expensive. The tyre being a composite of several components where not only the materials used but the design of the tyre and the manufacturing precision is important, the performance of a tyre can only be gauged by road tests. Since the performance of a tyre is determined by so many factors, some internal others external, evaluating the performance of a tyre in road tests is expensive.

5.1.3.4 A result of the sharp competition among tyre manufacturers is the low profit margins on which tyre companies operate. This is shown in Table 5.1 where the profits made by U.K. tyre companies in 1971 and 1972 are shown as a percentage of the capital employed. (89)

Table 5.1 Post tax profits of U.K.Tyre Companies as percentage of capital employed (89).

	Profits as percentage of capital employed	
	1971	1972
Dunlop Holdings	4.3	4.7
Michelin	13.1	11.8
Goodyear	5.9	2.4
Avon	6.1	5.9
Firestone	7.3	1.2
Pirelli	0.8	4.0
Uniroyal	4.9	3.0

5.1.3.5 The low profits leave little for investment in the new equipment needed for the industry. At the second IRI National Rubber Conference - Rubber Processing 1974 held in Blackpool in May 1974 the point was made that processing equipment in tyre plants could not be modernised because of the low profit margins these plants are operating on. Adequate profit margins are required to finance the expensive equipment required for producing improved tyre versions like the steel cord tyres towards which the industry is now oriented. The high amortisation rate of equipment due to rapidly changing tyre design and construction adds further to the problems of the industry. The US tyre industry was reluctant to change from crossply to radial ply construction and decided on the compromise belted-bias construction because the belted bias tyres could be made with the existing equipment, while the radials could not.

5.1.4 Rubber usage in tyres

5.1.4.1 The factors which influence polymer usage in tyres have been listed in section 1 of this dissertation. The economic factors are availability and cost. Shortages in the supply of natural rubber and fluctuations in price have damaged the case for natural rubber while regular supplies and steady prices have favoured the use of synthetic rubber. Sharp fluctuations in price of the basic raw material make the pricing of the manufactured product a difficult problem. The cost to the user includes not only the price of the raw material but also the cost of processing it so that any additional processes like warming of the bales and premasticiation involve added costs.

5.1.4.2 Distribution of rubber used in tyres

The quantity of rubber used in a tyre depends on the size of the tyre. An earthmover tyre will use more raw rubber than a truck tyre and a truck tyre would use more rubber than a car tyre. A large car tyre would use more raw rubber than a small car tyre. Commercial vehicle tyres made in the UK in 1971 used 82,700 tons of raw rubber as against 101,600 by car tyres (90) although the number of commercial vehicle tyres was 7 times less than that of car tyres. It can be assumed that one truck tyre equals four car tyres (91). Laverty (26) point out than an average earthmover tyre (size 18.00-25) contains 600 lb of rubber.

The distribution of the rubber used in a tyre between its components as given by Grosch (70) was shown earlier in Table 4.1.

.1.4.3 Factors affecting rubber demand for tyres

The condition of the motor industry is the deciding factor in tyre demand and hence of rubber demand. The present situation in the world illustrates this point clearly. Serious cutbacks in the production of motor cars particularly the larger models has led to a drop in tyre demand. Consequently the demand for rubber has dropped and natural rubber is selling at prices below that of general purpose synthetics.

The switch from large to compact motor car models in the face of increasing fuel costs will lead to the use of smaller tyres containing less rubber.

Increased fuel costs are also resulting in less running of motor cars so that tyres last longer and tyre demand falls.

Radial tyres wear less than conventional crossply tyres giving about twice as many miles. This will adversely affect the replacement market for tyres.

Greater use of retreaded tyres and the use of improved techniques for retreading radial tyres will lead to fall in new tyre demand.

The use of ground vulcanised rubber waste in tyre compounds especially in tyre retreading is reported by Ruebensaal (93).

The energy situation is expected to remain difficult at least for another 3 or 4 years during which the demand for motor car tyres will be low. Britain is one of the few countries expected to show a steady increase in the number of cars.

Though passenger car tyre demand may be restricted the growth in the demand for commercial vehicle (bus and truck) tyres, agricultural and industrial tractor tyres and earthmover tyres is expected to continue. These tyres use much larger amounts of rubber than car tyresand are the types which need greater amounts of natural rubber.

5.1.5 The cost of manufacturing a tyre

The break-down of the cost of tyre manufacture will vary according to country. In rubber growing countries like Sri Lanka where natural rubber is produced locally the rubber is cheaper but the other raw materials are more expensive than in Western Countries. Table 5.2 shows the relative costs of tyre manufacture in Sri Lanka during 1973 and 1974 (before audit) while Table 5.3 gives a breakdown of tyre manufacturing costs for 1968 (based on the census of production that year). in U.K.

Table 5.2: Percentage Breakdown of the cost of tyre manufacture in Sri Lanka 1973 and 1974 (before audit)

	1973	1974
Rubber	11.2	8.8
Other raw materials	34.7	44.8
Electricity and steam	5.7	6.4
Machinery depreciation	8.8	5.6
Upkeep and Insurance	4.0	4.0
Wages and Salaries	33.0	25.4
Administration & other expenses	2.6	5.0

Table 5.3: Percentage breakdown of the cost of tyre production (1968) - U.K.

	Per cent
Rubbers	13.6
Other raw materials	28.5
Fuel and electricity	3.3
Transport	2.6
Wages and salaries	28.9
Other costs and profit	23.1

Wages and salaries are said to account for around 31 per cent for the UK tyre group today.

From these figures it is seen that the rubber accounts for about 8 to 15 per cent of the cost of a tyre, and for one third to one fourth of all raw materials used. Raw materials represent 40 to 50 per cent of the cost of a tyre. It is also evident that tyre manufacture is labour intensive.

5.1.6 Tyre manufacture in rubber growing countries

Malaysia, Indonesia, Thailand and Sri Lanka all have tyre factories but they operate only on a modest scale, as can be seen from the rubber consumption figures during 1972 in each country; Indonesia 40,000 tonnes. Malaysia 23,000 tonnes, the Phillippines 20,000 tonnes and Sri Lanka 6,200 tonnes (95).

The large international tyre companies appear to be willing to start tyre production in the rubber growing countries on a much larger scale. Four of these companies

Goodyear, Firestone, Uniroyal and Toyo are reported to be negotiating with the Malaysian Rubber Development Corporation to establish joint ventures with the M.R.D.C. (95). Each of these companies is said to be interested in opening up estates of up to 100,000 acres. The reasons for this interest are the ready source of rubber the low wages and the absence of some constraints found in Western Countries.

5.1.7. Effects of the energy crisis on the tyre industry

The most serious impact of the energy crisis on the rubber industry is on the supply of raw materials. Raw materials it has been pointed out account for over 40 per cent of the cost of a tyre. Synthetic rubber prices have more than doubled since January 1973 - SBR1500 ex-works price then was £187.50 per metric ton. Today it stands at £385.00 per metric ton. Other petroleum based tyre materials including nylon and polyester tyre cord, carbon black, processing oil and chemical ingredients have gone up in price in similar fashion.

John R. Hall (91) discusses the impact of the energy crisis on the tyre industry particularly its effect on the supply and prices of synthetic rubbers.

Costs of the rubber industry in Britain are expected to increase by about 20 per cent between 1973 and 1977 as a result of direct and indirect energy price increases (92).

5.1.8 The future of the world tyre industry

The picture is rather confused and no definite forecasts can be made. Some general treads are however discernible. In the short-term, up to about the end of this decade, tyre production in car sizes will show little or no growth. The reaons have already been discussed. The demand for truck and other large tyres will continue to grow.

Technical innovations will continue because of the sharp competition within the industry and because of outside pressures like government tyre legislation (to be discussed in the next chapter) and the more stringent requirements of the motor industry. A run-flat tyre at a moderate price will probably be developed within the next five years while a tyre without a reinforcing cord body is a distinct possibility within the next 10 years. This will have serious repercussions for the industry as some of the expensive equipment installed will become redundant. Work will proceed on a cast tyre but it does not seem likely to become a reality within the next 10 years.

Motor industry developments will continue to decide tyre development. A motor car for town running offers prospects for use of thermoplastic rubbers. The economics have however changed away from these materials as will appear from the next section and conventional type rubber will continue to be the basic raw material of tyre ten years hence, as Shearer has predicted. This must surely be the reasoning for the interest shown by the four international tyre companies wishing to establish large rubber plantations of their own in Malaysia.

5.2. The Synthetic Rubber Industry

5.2.1. Introduction

The manufacture of synthetic rubber had its beginnings during World War I in Germany, but the material produced was far inferior to natural rubber. The loss of over 90 per cent of the world's sources of natural rubber to the Allies spurred the United States government into a massive programme to make synthetic rubber suitable for use in tyres. Output of synthetic rubber was raised from a mere 5,400 long tons in 1941 to over a million long tons in 1944. The development of the synthetic rubber industry in the U.S.A. is well described by Charles F. Phillips, Jr., in his book "Competition in the Synthetic Rubber Industry". (96) At the end of the war only four countries, the U.S.A. the Soviet Union, Germany and Canada had facilities for producing synthetic rubber. Today 23 countries manufacture these materials. Total world output of synthetic rubber in 1973 was 7,307,500 metric tons representing 67.66 per cent of total world output of all rubbers. (1)

5.2.2. Classification of rubbers

Allen (97) divides rubbers into 3 categories on the basis of their usage volume: the large; medium - and small tonnage rubbers. The large tonnage rubbers are used in substantial amounts in tyre manufacture and account for over 90 per cent of the total rubber used; the medium tonnage rubbers which account for around 10 per cent of total rubber and the small tonnage rubbers which account for around 1 per cent of total rubber used. On this basis natural rubber (NR), SBR, polybutadiene (BR) and polyisoprene rubbers (IR) are large tonnage rubbers; nitrile rubber (NBR), polychloroprene rubber (CR), isobutylene (butyl) rubber (IIR) and ethylene propylene terpolymers are medium tonnage rubbers. A list of the Allen's small tonnage rubbers is given by Ruebensal (93) who calls them small-volume speciality rubbers. In this classification system all of Allen's large tonnage rubbers are called general purpose rubbers and all the others special purpose or speciality rubbers. Allen's medium tonnage rubbers become large-volume special purpose rubbers.

The synthetic rubbers can also be classified on the basis of their chemical structure which is determined by their building blocks, the monomers; where more than one monomer is used the resulting rubber is called a copolymer. For example, SBR (styrene butadiene rubber) is a copolymer of styrene and butadiene monomers.

Synthetic rubbers are generally offered in the following forms:-

Dry rubber bales, e.g. SBR 1500

Latex

Oil extended rubbers, e.g. SBR 1712

Carbon black masterbatches
(rubber + black), e.g. SBR 1601
Carbon black - oil masterbatches
(rubber + oil + carbon black) -
e.g. SBR 1801

Newer forms are powdered rubber and liquid polymers.

As shown earlier in Table 3.6 SBR alone has 266 types. The demand now is for reduction in the number of grades so that plant operation efficiencies can be improved and the cost to the user reduced.

5.2.3. The structure of the synthetic rubber industry

Synthetic rubber plants can be wholly government owned as in the socialist countries and Canada. They were government owned in the United States from 1942 to 1955 when they were sold to private industry. The buyers were ten producers, of whom four are large tyre companies (Firestone, Goodrich, Goodyear, and United States Rubber), three petroleum companies (Gulf, Phillips and Shell), two chemical companies (Texaco and United Carbon) and two representing co-operative producers' associations (American Synthetic and Copolymer). (96) The International Synthetic Rubber Company of Britain is owned by the British tyre group of companies, with Dunlop the major shareholder. Two of the French companies are owned jointly by French tyre and chemical manufacturing interests and by Goodyear and B.P. chemicals. In India Synthetic and Chemicals Ltd., as owned by Indian interests and Firestone, Japan has a well developed synthetic rubber industry. A number of plants are operated with imported technology under licence and foreign collaboration. Synthetic rubber manufacture is soon to begin in the Middle East countries' petrochemical complexes to be set up with U.S., Western Europe and Japanese assistance. Japan is moving ahead with her plans for setting up these petrochemical complexes in Saudi Arabia, Kuwait and Iran in exchange for guarantees of oil supplies from these countries to Japan. Japanese projects for setting up synthetic rubber plants in Singapore and Indonesia in the heart of the rubber growing region of South East Asia are also being pushed ahead in spite of protests from Malaysia. The Soviet Union is helping Iran set up a polyisoprene rubber plant. The future appears to show the oil producing nations of the Middle East and of the socialist bloc replacing the western nations and Japan as the world's major synthetic rubber producers. (106)

The International Institute of Synthetic Rubber Inc. (IISRP) whose members are synthetic rubber producers in countries outside the socialist group of countries has been established in 1960 to promote international trade in synthetic rubber and to foster technological advances in the industry. It has its headquarters in New York.

5.2.4. Synthetic Rubber capacity

Table 5.4. gives the synthetic production capacities of the different countries (93). World production capacity for all types at the end of 1974 was 9,215,000 metric tonnes. The U.S.A. had a capacity of 2,977,000 metric tonnes at the end of 1974, Western Europe 2,432,000 metric tonnes, Japan 1,311,000 metric tonnes, and the Socialist countries 1,738,000 metric tonnes. SBR's share was 62.3 per cent of total world synthetic rubber capacity. The capacity for polybutadiene rubber was 1,242,000 metric tonnes (13.5 per cent of total world capacity) and for polyisoprene rubber 633,000 metric tonnes representing 6.9 per cent of total world synthetic rubber capacity.

5.2.5. Synthetic Rubber Production

It is estimated that world synthetic rubber production in 1974 will be about 4.3 per cent lower than that for 1973 which was 12.7 per cent higher than 1972. Total production of all synthetic rubbers during 1973 is estimated at 7,354,000 metric tonnes of which more than a third, 2,627,000 metric tonnes, were made in the U.S.A., 980,000 metric tonnes in Japan, 965,000 metric tonnes in the Soviet Union and 1,829,000 metric tonnes in Western

Table 5.4.

WORLD SYNTHETIC RUBBER PRODUCTION
(000's MT)

	1965	1966	1967	1968	1969	1970	1971	1972	Estimated 1973	Forecast 1974
U.S.A.	1,842	2,002	1,943	2,165	2,286	2,232	2,277	2,455	(A) 2,627	2,500
JAPAN	161	233	281	381	527	698	780	819	980	870
FRANCE	148	164	189	223	275	316	323	368	(A) 458	425
UNITED KINGDOM	175	194	204	237	273	306	277	307	(A) 356	315
FED. REP. OF GERMANY	164	196	190	238	292	302	306	300	(A) 350	330
ITALY	120	122	118	125	135	155	160	200	(A) 270	250
NETHERLANDS	100	110	125	163	214	200	191	186	265	235
CANADA	206	203	200	197	199	205	197	195	(A) 230	220
BRAZIL	39	54	52	59	62	75	78	95	120	125
SPAIN	--	1	11	27	35	39	45	70	(A) 75	70
BELGIUM	20	20	20	25	35	50	60	60	(A) 65	60
ARGENTINA	3	10	17	23	38	39	38	44	(A) 53	58
AUSTRALIA	21	20	26	30	33	33	43	42	45	48
MEXICO	--	1	20	34	36	40	45	40	45	40
INDIA	16	16	22	25	25	30	33	28	22	25
REP. OF SO. AFRICA	16	19	24	25	24	29	30	30	30	30
TOTAL NON-CENTRALLY CONTROLLED	3,031	3,365	3,442	3,977	4,489	4,749	4,883	5,239	5,991	5,601
% INC. NON-CENTRALLY CONTROLLED	7.3	11.0	2.3	15.5	12.9	5.8	2.8	7.3	14.4	-6.5
U.S.S.R.*	540	615	635	680	725	790	850	910	(A) 965	1,025
GERMAN DEMOCRATIC REP.	95	101	110	102	114	118	129	133	(A) 135	138
POLAND	39	37	40	41	48	62	66	78	95	100
RUMANIA	31	35	51	54	55	61	71	73	(A) 75	78
CZECHOSLOVAKIA	30	30	33	35	40	50	52	52	(A) 53	55
CHINA*	25	25	25	25	25	25	25	25	(A) 25	25
BULGARIA	--	--	--	--	--	--	5	15	15	25
TOTAL CENTRALLY CONTROLLED	760	843	894	937	1,007	1,106	1,198	1,286	1,363	1,436
% INC. CENTRALLY CONTROLLED	8.9	10.9	6.0	4.8	7.5	9.8	8.3	7.3	6.0	5.4
TOTAL WORLD	3,791	4,208	4,336	4,914	5,496	5,855	6,081	6,525	7,354	7,037
% INC. OVER PRIOR YR.	7.6	11.0	3.0	13.3	11.8	6.5	3.9	7.3	12.7	-4.3

* Provisional Estimates
(A) - Actuals

	TOTAL FREE WORLD	FREE WORLD MINUS U.S.A.	U.S.A.	COMMUNIST BLOC
1968 vs. 1967	15.5	20.9	11.4	4.8
1969 vs. 1968	12.9	21.6	5.6	7.5
1970 vs. 1969	5.8	14.3	-(2.4)*	9.8
1971 vs. 1970	2.8	3.5	2.0	8.3
1972 vs. 1971	7.3	6.8	7.8	7.3
Estimated 1973 vs. 1972	14.4	20.9	7.0	6.0
Forecast 1974 vs. 1973	-6.5	-(7.8)	-(4.8)	5.4

* This actual loss in % growth of rubber production (1970 vs. 1969) resulted from the rubber and automotive strikes in the U.S.A.

Reflecting the shortages of crude oil in 1974, Free World Production of synthetic rubber is expected to drop 6.5% from the levels attained in '73. Centrally Controlled Countries are forecasted to increase their production 5.4% which results in a total world drop of only 4.3% but still the second largest production year (7,037M MT) in history exceeded only by the record breaking year of 1973 in which 7,353 M MT were produced.

TABLE 5.5.

WORLD SYNTHETIC RUBBER CAPACITIES
REPORTED AND ESTIMATED CAPACITY BY TYPE AND COUNTRY - THOUSAND METRIC TONS NET RUBBER

COUNTRY LOCATION	SBR END 1974	SBR END 1977	BR END 1974	BR END 1977	IR END 1974	IR END 1977	EPM/EPDM END 1974	EPM/EPDM END 1977	IIR END 1974	IIR END 1977	CR END 1974	CR END 1977	NBR END 1974	NBR END 1977	TOTAL ALL TYPES END 1974	TOTAL ALL TYPES END 1977
U.S.A.	1824	1826	397	397	123	123	169	217	163	163	186	186	115	118	2977	3030
CANADA	150	150	30	30	-	-	-	-	42	42	-	-	30	30	252	252
TOTAL NORTH AMERICA	1974	1976	427	427	123	123	169	217	205	205	186	186	145	148	3229	3282
ARGENTINA	58	61	-	20	-	-	-	-	-	-	-	-	2	2	60	83
BOLIVIA	-	35	-	-	-	-	-	-	-	-	-	-	-	-	-	35
BRAZIL	119	174	18	24	-	30	-	-	-	-	-	-	4	4	141	232
MEXICO	84	94	-	-	-	20	-	-	-	-	-	-	3	3	87	117
PUERTO RICO	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
VENEZUELA	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
TOTAL LATIN AMERICA	261	364	18	44	-	50	-	-	-	-	-	-	9	9	288	467
BELGIUM	45	45	10	10	-	-	-	-	60	60	-	-	-	-	115	115
FINLAND	5	5	-	-	-	-	-	-	-	-	-	-	-	-	5	5
FRANCE	263	263	137	137	45	45	30	45	40	40	30	30	37	37	582	597
GERMANY	263	297	60	70	-	-	20	20	-	-	50	60	25	25	418	472
ITALY	286	396	45	65	30	60	50	50	-	30	-	-	22	22	433	623
NETHERLANDS	169	229	-	-	70	70	40	40	-	-	-	-	10	10	289	349
PORTUGAL	-	50	-	-	-	-	-	-	-	-	-	-	-	-	-	50
SPAIN	75	94	6	20	-	-	-	-	-	-	-	-	5	5	85	119
SWEDEN	-	7	-	-	-	-	-	-	-	-	-	-	-	-	-	7
UNITED KINGDOM	350	358	40	40	-	-	20	20	44	44	30	60	20	22	504	544
TOTAL WESTERN EUROPE	1456	1744	298	342	145	175	160	175	144	174	110	150	119	121	2432	2881
EGYPT	-	15	-	-	-	-	-	-	-	-	-	-	-	-	-	15
AUSTRALIA	50	50	22	27	-	-	-	-	-	-	-	-	-	-	72	77
IRAN	-	40	-	-	-	60	-	-	-	-	-	-	-	-	-	100
INDIA	30	50	-	20	-	-	-	-	-	-	-	-	2	2	32	72
JAPAN	766	906	280	356	85	115	30	50	47	80	77	77	26	26	1311	1610
SOUTH AFRICA	41	45	-	-	-	-	-	-	-	-	-	-	1	1	42	46
SOUTH KOREA	25	50	-	-	-	-	-	-	-	-	-	-	-	-	25	50
TAIWAN	-	99	-	-	-	-	-	-	-	-	-	-	-	-	-	99
TURKEY	32	32	14	14	-	-	-	-	-	-	-	-	-	-	46	46
TOTAL ASIA, AFRICA, AUSTRALIA	944	1287	316	417	85	175	30	50	47	80	77	77	29	29	1528	2115
TOTAL NON CENTRALLY CONTROLLED COUNTRIES (EX (EX. USA)	2811	3545	662	833	230	400	190	225	233	296	187	227	187	189	4500	5715
TOTAL NON CENTRALLY CONTROLLED COUNTRIES WORLD	4635	5371	1059	1230	353	523	359	442	396	459	373	413	302	307	7477	8745
CENTRALLY CONTROLLED COUNTRIES	1108	1378	183	273	280	445	30	115	30	50	75	129	32	52	1738	2442
WORLD GRAND TOTAL	5743	6749	1242	1503	633	968	389	557	426	509	448	542	334	359	9215	11187

Europe. Ruebensaal (93) forecasts a 5.4 per cent increase of synthetic rubber production in 1974 over 1973 and a drop of 6.5 per cent in the rest of the world, reflecting the effects of the energy crisis and the world economic situation. Table 5.5. shows world synthetic rubber production.

5.2.6. Synthetic Rubber Consumption

The consumption of synthetic rubber by tonnage in different countries is shown in Table 5.6.

Ruebensaal (93) forecasts a drop in the percentage of synthetic rubber consumed in 1974 over that in 1974 in the countries of highest SR consumption, the U.S.A., West Germany, France, Japan, U.K., Italy and the Netherlands as shown in Table 5.7.

TABLE 5.7

PERCENTAGE CONSUMPTION OF SYNTHETIC RUBBER IN 1973 (ESTIMATED) AND 1974 (FORECAST)

CONSUMPTION OF SYNTHETIC RUBBER AS % OF TOTAL RUBBER CONSUMED

	% SYNTHETIC			
	1970	1972	Est. 1973	Forcst. 1974
U.S.A.	77.4	78.1	(A)77.8	77.1-
Canada	72.6	74.2	(A)75.3	75.3
West Germany	64.0	65.2	(A)65.3	64.0-
France	62.3	64.4	(A)64.6	63.8-
Japan	63.7	65.3	67.0	65.0-
United Kingdom	59.3	61.1	61.5	60.7-
Australia	54.7	55.8	55.8	56.3
Italy	63.5	65.1	68.1	67.1-
Russia*	71.0	78.8	79.0	79.2
Netherlands	67.6	71.3	71.6	69.7-
Argentina	58.7	61.6	61.9	62.1
Brazil	69.7	72.2	74.5	75.2
India	27.1	26.8	15.9	16.7

Figure 5.5 shows the growth of world consumption of synthetic, natural and total rubber consumption in the world since 1965.

SBR leads all other rubbers in volume of consumption.

5.2.7. Marketing of synthetic rubber

The marketing of synthetic rubber has been discussed by Phillips (96). Synthetic rubber is mostly marketed direct by the producers to consumers. There are no commodity exchanges. Since tyre companies own substantial interests in synthetic rubber manufacturing plants a large portion of the market is captive. In the U.S.A. it is legally obligatory for synthetic rubber producers to "be designed best to afford small business enterprises and users, other than the purchaser of a facility, the opportunity to obtain a fair share of the end products of the facilities sold and at fair prices".

The market for spot sales is not formally organised. Information on prices is desseminated directly by producers or through the medium of trade journals.

Consumption of rubber, both natural and synthetic, is determined by general economic factors outside the control of the rubber producers.

Synthetic rubber prices are administered and do not change to equate short-run supply and demand, as seen in Figure 5. and Figure 5. Fluctuations in monthly consumption are absorbed by inventory adjustments. Effects of changes in demand affect production schedules only 3 or 4 months later. Emphasis appears to be on short-term price stability than on short-term profit maximisation.

Innovations have been continually made and has led to intensified competition not only with natural rubber but also within the synthetic rubber industry.

Phillips (96) points out that SBR producers were earning a net return of 6 to 9 per cent on their investment. That was up to 1960. The energy crisis has changed the situation and in Britain the International Synthetic Rubber Company netted a loss of just over one million pounds in 1973.

The price structure

As seen in Figure SBR prices showed a downward trend till 1967 and remained reasonably steady until 1972. Since then the price increases forced on it by the energy crisis have forced it sharply upwards and today it stands at around £385 per metric ton - about £100 more than that for natural rubber RSS 1 grade.

Average Annual Prices of NR and of SBR during years 1960 — 1973

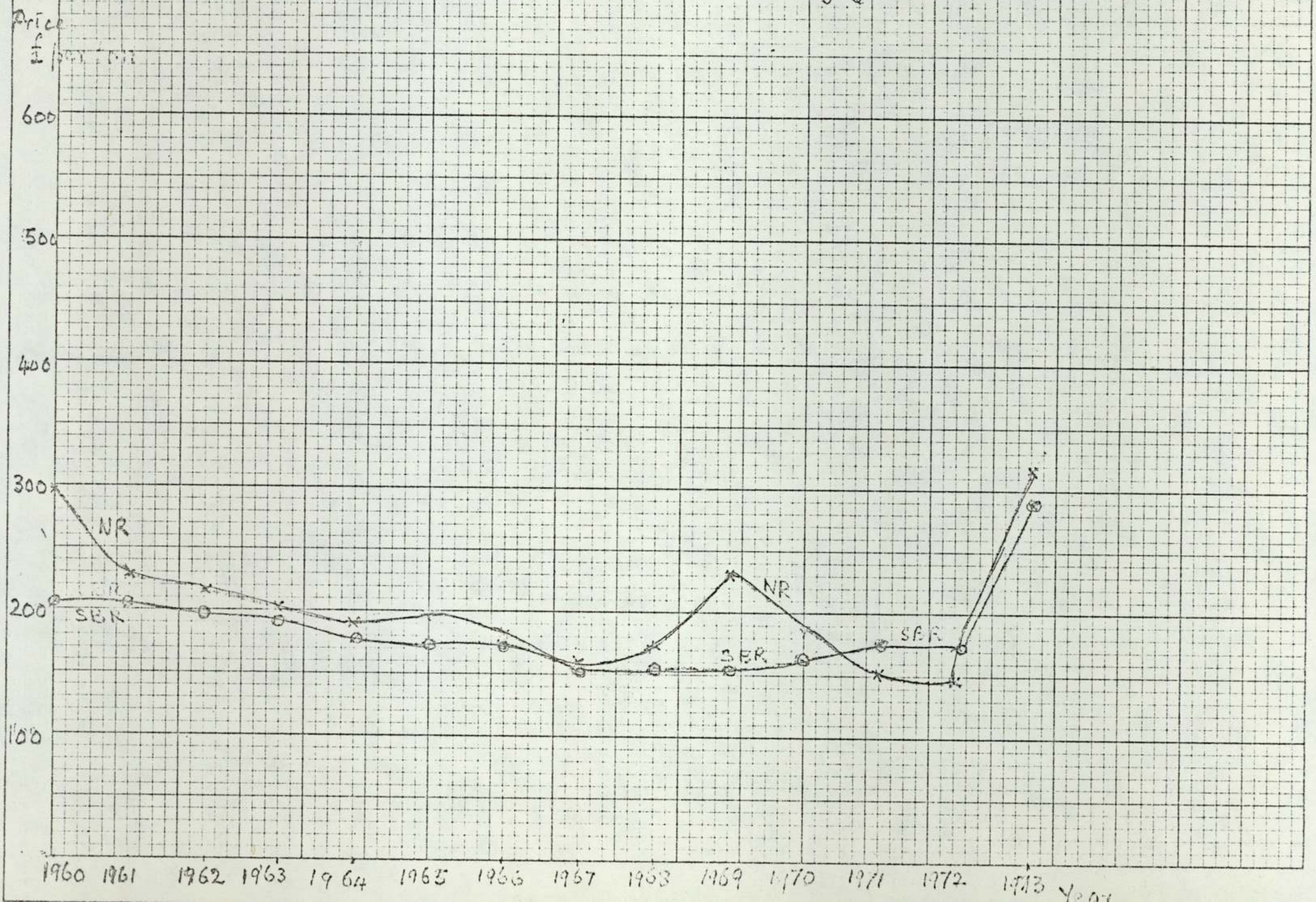
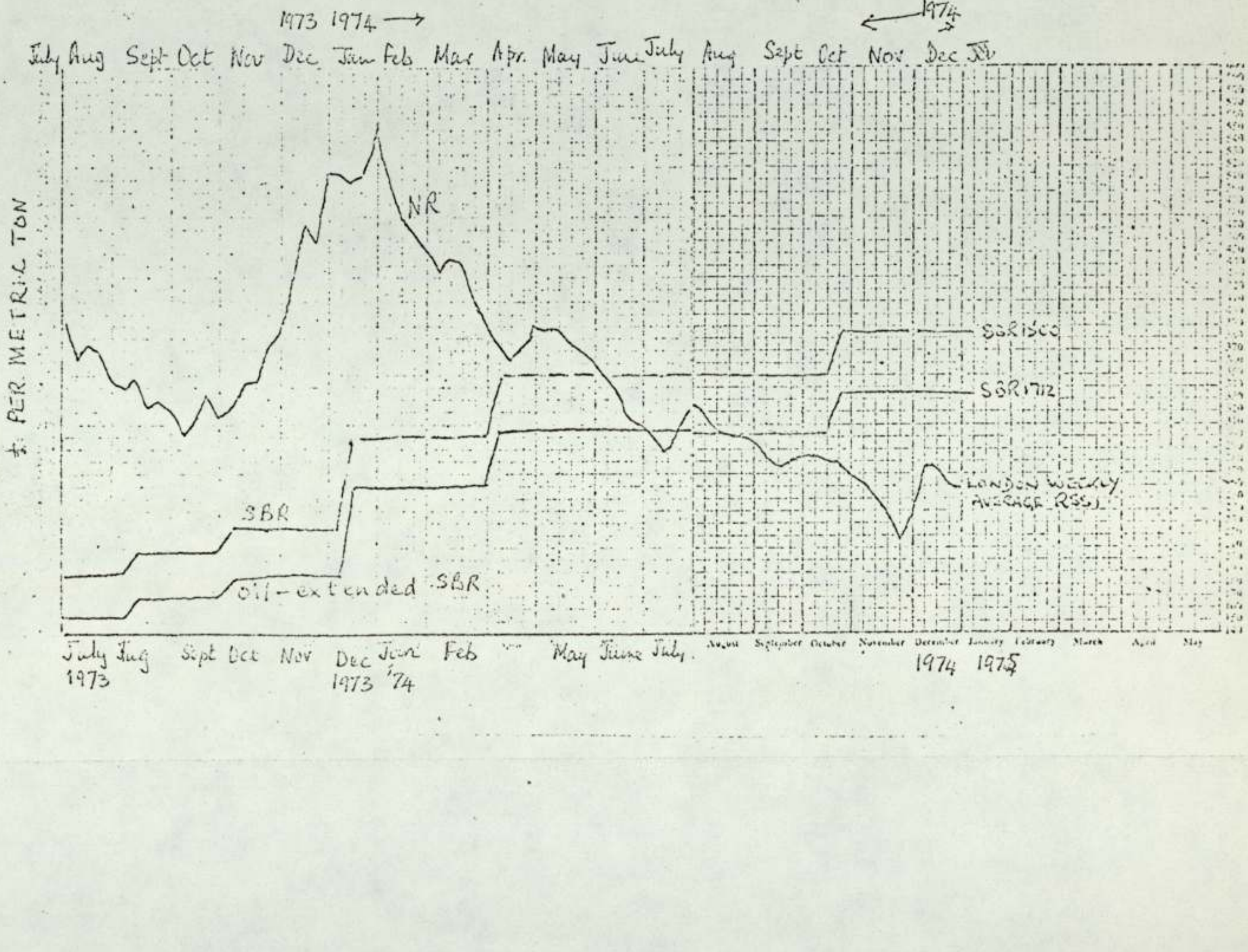


Fig. 5.1b Variation in price of Natural Rubber (RSS·1), cold SBR (SBR 1500) and oil extended SBR (SBR 1712) during, July 1973 — December 1974.



5.2.8. Synthetic rubber demand

The tyre industry is the largest consumer of both natural and synthetic rubbers as has been shown in Section 1. Tyre demand in turn depends on motor vehicle demand. The present drop in demand for all rubbers reflects recession conditions in the world motor industry. The resulting drop in synthetic rubber production has been mentioned in the previous paragraph. The demand for both natural and synthetic rubber therefore reflects general economic conditions.

5.2.9. Raw materials for synthetic rubber manufacture

The economics of SR production can only be studied against the background of the whole petrochemical industry of which synthetic rubber production is only a part. Other segments of the petrochemical industry include plastics, fibres, fertilisers and detergents. Table 5.8 and Table 5.9 show the main routes for making these varied materials from natural gas and from petroleum.

It must be borne in mind that petrochemical products represent no more than 5 per cent of total world oil consumption. Dix (99) doubts if they will account for 10 per cent of oil consumption even in 1985. The major products of the oil industry are the fuels -

TABLE 5.8 PETROCHEMICALS MANUFACTURED FROM NATURAL GAS - MAIN PETROCHEMICAL ROUTES

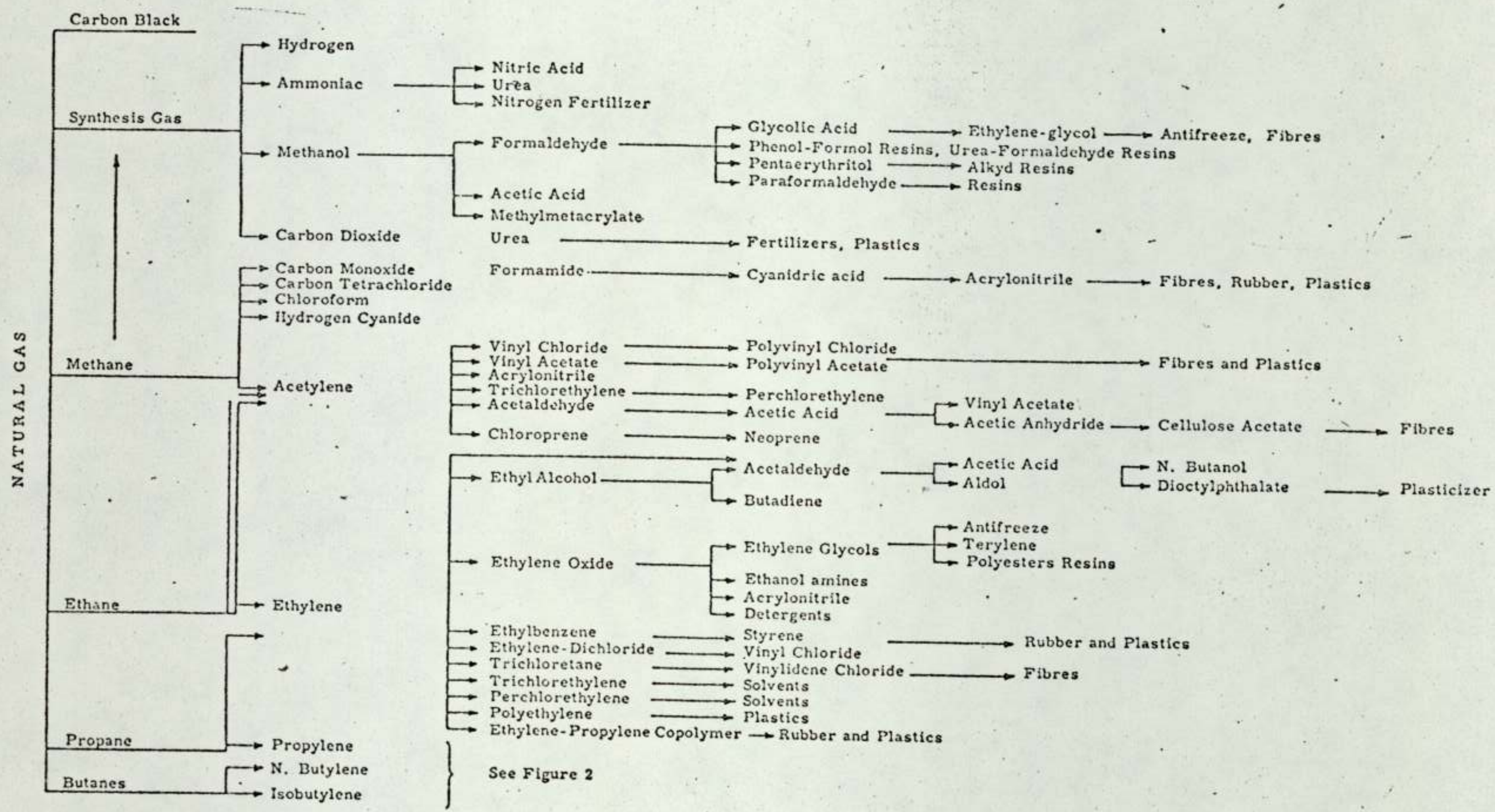
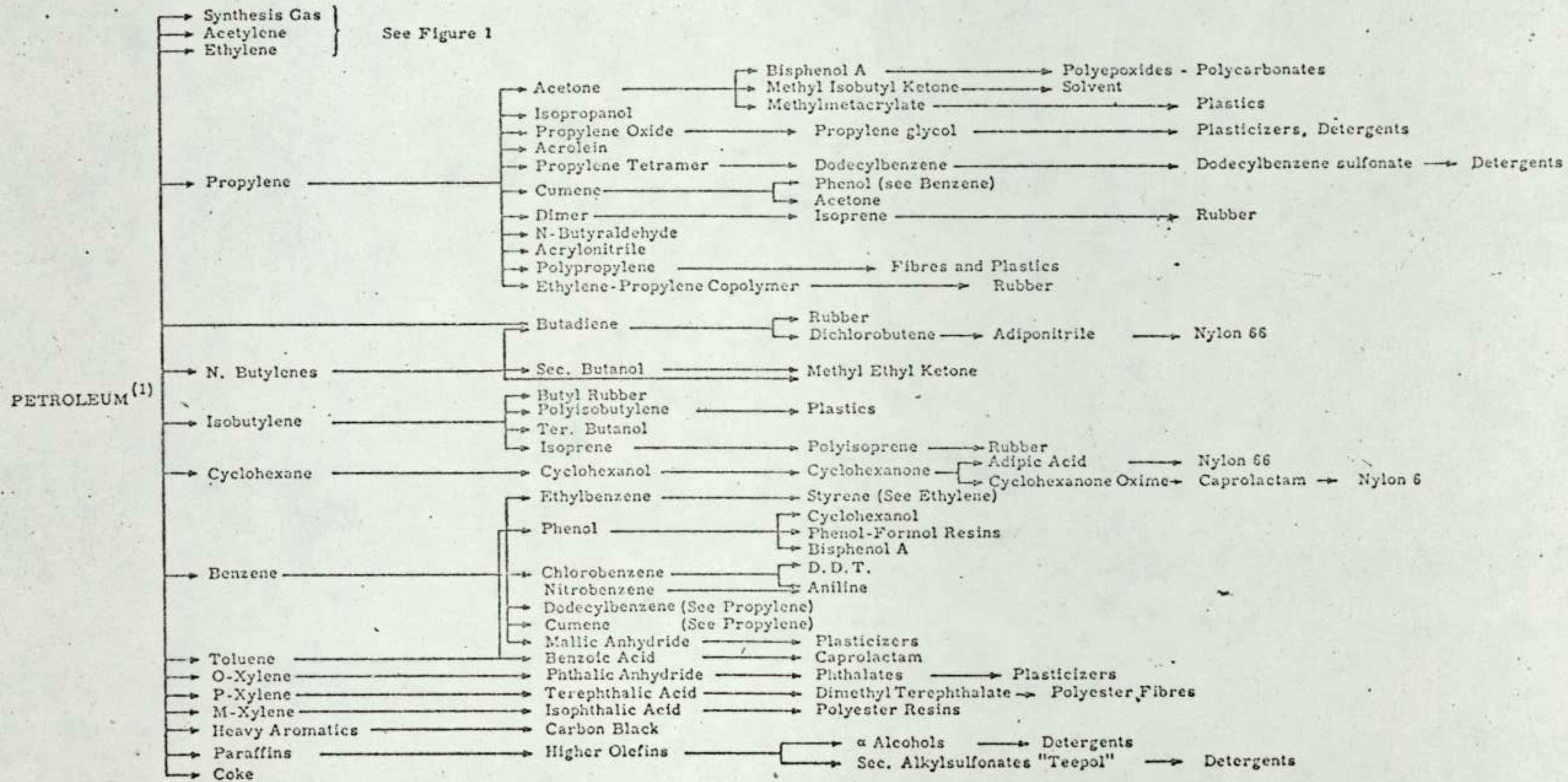


TABLE 5.9

PETROCHEMICALS MANUFACTURED FROM PETROLEUM - MAIN PETROCHEMICAL ROUTES



(1) Condensate included.

gasoline, the middle distillates (kerosene and diesel fuel) and fuel oil.

Two processes are basis to the petroleum industry - refining and cracking -

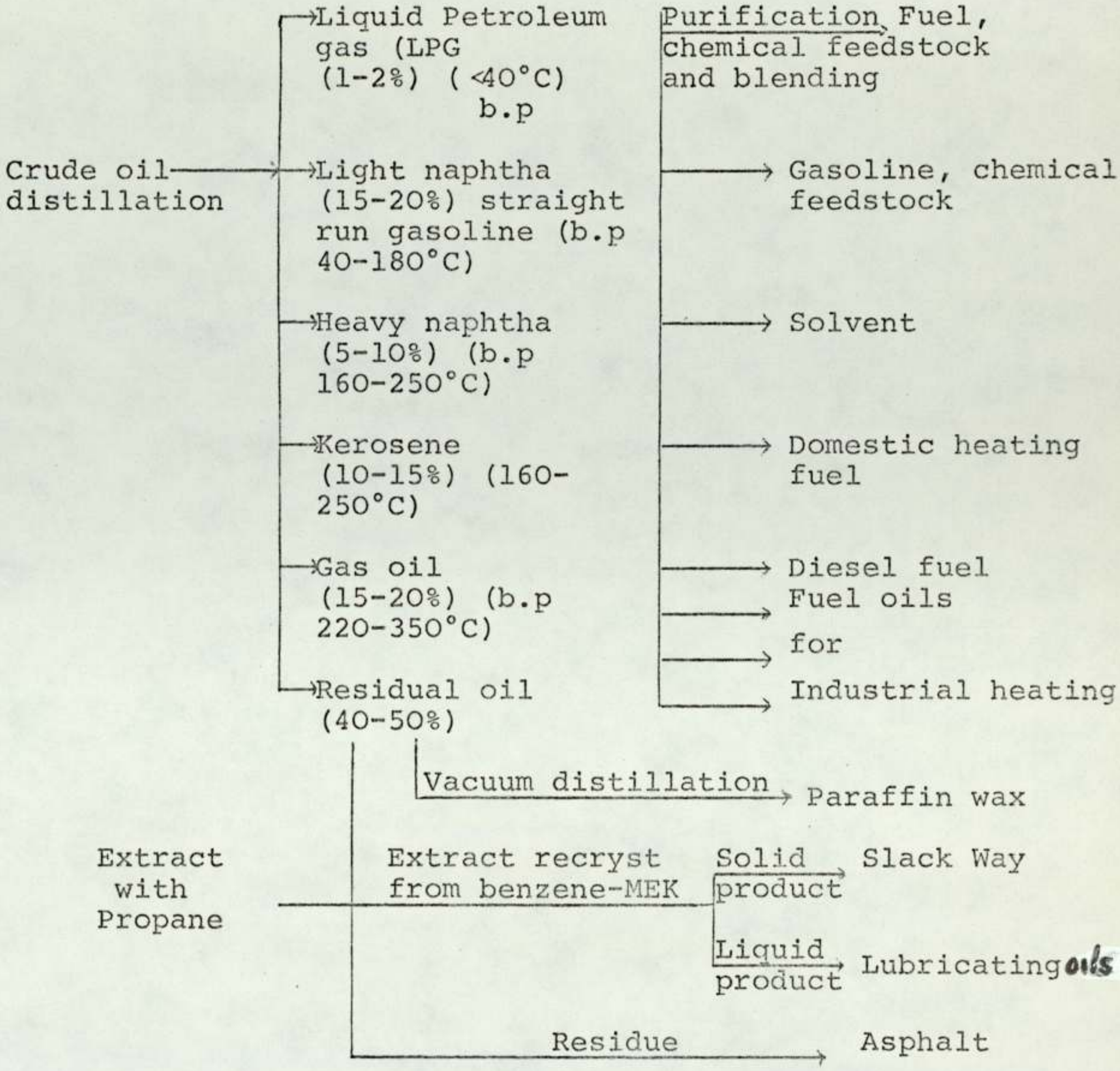
1. Refining

The crude oil is first distilled at atmospheric pressure to yield fractions boiling at temperatures up to 350°C. Figure 5.1 (99) shows the products of this distillation and their end uses.

2. Cracking

The high boiling distillate fractions naphtha and gas oil as well as the natural gas liquids are then heated during thermal cracking to temperatures of about 600°C to decompose them into simpler more volatile products such as ethylene, propylene, butylene and butadiene. Some of these products are also present in the refinery gases, from which they are isolated. In catalytic cracking which is more popular temperatures around 450 - 550°C are used with an acidic silica alumina catalyst. Reforming processes upgrade gasoline by increasing their aromatic content. Benzene and its homologues are extracted during cracking. These materials are the starting points for the manufacture of the chief synthetic rubbers.

Operations in a simple "hydrostripping" oil refinery (99)



In the U.S.A. the light olefins like propylene and butylene which are used in monomer production have so far been obtained mainly from thermal and catalytic crackers. But now they are following Europe in obtaining these olefins from naphtha and gas oil.

Oil refineries are also faced with the problems of environment pollution. The added cost of anti-pollution measures has greatly reduced the optimal size of refinery units.

The following trends have been noted in oil refining in Europe (Manuel Santa-Olalla). (100)

i. Lead additive levels in gasoline will decrease to a minimum by 1980. This will mean higher severity cracking.

ii. Demand for desulphurised fuel oil will increase rapidly.

iii. The demand for liquid cracking feedstocks like naphtha and gas oil will increase further.

iv. There will be little upgrading of heavy fractions into lighter ones.

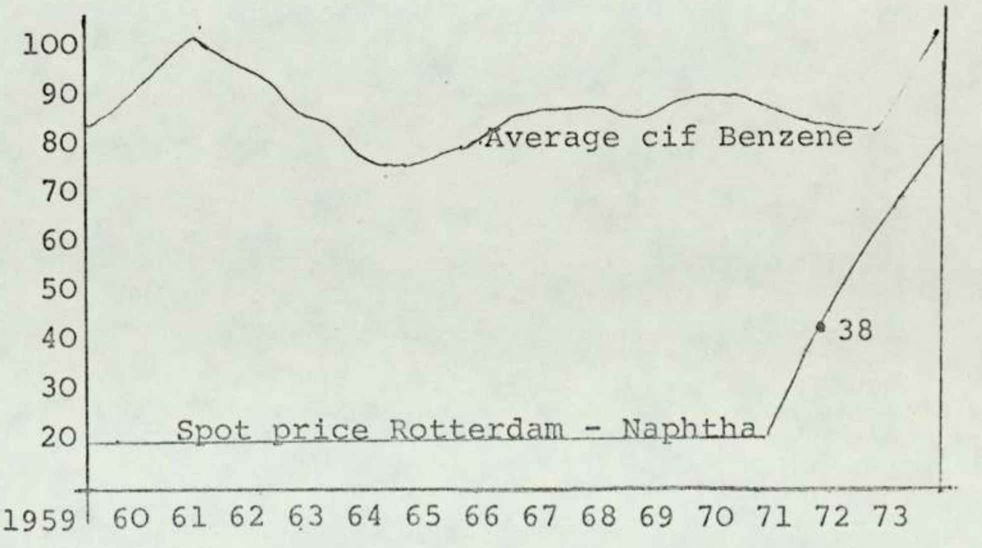
5.2.9.1. Feedstock problems

The rise in feedstock prices can be gauged from Figure 5.2 (102) showing the price variations of benzene and naphtha during 1959-1973. Naphtha prices remained at 20 dollars/ton from 1959 to 1971, rose to 38 dollars in 1972 and are now standing at 70 dollars. Benzene prices show a steep climb from the end of 1972.

Two main reasons have been attributed to the rise in feedstock prices. The first is the rise in crude oil prices. The second reason is the inability of the industry to cope with the sharply increased demand for aromatics for gasoline motor fuel. The reduction in the levels of lead derivatives allowed in gasoline to reduce atmospheric pollution resulted in benzene being used in place of lead compounds. The industry did not have the required type of secondary oil processing equipment to meet this demand. Competition with the motor industry put up the price the petrochemical industry pays for benzene and hence for naphtha.

FIGURE 5.2

PRICE VARIATION OF NAPHTHA FEEDSTOCK AND BENZENE 1959-73



Dix (98) points out that there will be adequate hydrocarbon feedstocks for chemicals .... at a price. He adduces two reasons for this. Firstly, feedstock and energy required for manufacture of chemicals (including synthetic rubber) account for less than 5 per cent of total world oil consumption. Secondly, chemicals represent a premium use of hydrocarbons. One reason for placing chemicals in the premium category is the value and importance of petroleum based products to the consumer. The other is their use to the economy as they are required by so many other industries. Dix argues that chemicals can therefore afford to pay premium prices for primary hydrocarbons to attract them away from other uses. The hydrocarbon raw materials for feedstock manufacture will be available, though at a price.

What is inadequate now is "the physical capacity to convert crude hydrocarbons to intermediate chemical feedstocks such as ethylene, benzene, butadiene etc". Dix points out that the construction of the needed capacity for making the feedstocks is delayed uncertainty about a number of factors. He lists these factors as -

1. Supply of feed and energy
2. Cost of feed and energy
3. Demand level for chemicals

and 4. Cost of constructing new capacity

Dix, admitting the difficulties of predicting chemical demand with the present uncertainties of the future of the world economy, ventures that a reasonable conclusion is that chemicals would continue to grow faster than the economy as a whole. He states that once the present over-reaction and runaway construction cost trends subside, construction costs will settle at much more reasonable levels which will however be a great deal higher than in the past.

An FAO team of experts are reported (95) to have made the following observations after studying the effects of the energy crisis on the costs of the base chemicals used as feedstocks for synthetic rubber manufacture. At the end of 1972, the cost of the raw materials used to manufacture these base chemicals accounted for 55 5o 60 per cent of the cost of these chemicals while energy costs were 15 to 20 per cent. It was therefore concluded that naphtha based feedstock prices would show a more than three fold increase between the end of 1972 and 1974 and prices of feedstock from natural gas a 100 per cent increase. They forecast that between 1974 and 1980 naphtha based feedstock prices would increase by one third and natural gas based feedstock prices by one half.

Feedstock prices have indeed gone up, judging by the increase in the prices of synthetic rubber during the past year. General purpose synthetic rubbers are no longer sold in the 15-20 U.S. dollar cents per lb. Prices have more than doubled.

5.2.10 Economics of the production of polybutadiene and styrene butadiene rubbers (SBR)

Butadiene is co-polymerised with styrene to give SBR. Polymerised alone it gives two types of polybutadiene of interest to the tyre industry. The cis 1,4 polybutadiene has been used in tyres since the early 1960s in admixture with natural rubber, SBR and synthetic polyisoprene rubber. Medium and high vinyl polybutadiene are comparative newcomes to the field and the prominence they have gained is greatly due to the difficulties in obtaining supplies of styrene needed to make SBR. These medium and high vinyl polybutadienes are not proved materials and will take time to establish themselves if their technical shortcomings can be overcome.

5.2.10.1 Availability and cost of Monomers

Butadiene

Butadiene is present in the refinery gases from crude oil distillation, and is also produced in the cracking of natural gas liquid and gas oil. It is also prepared from the n-butane and n-butylene present in the C4 stream from oil refining. Figure 5.3 below shows the routes to butadiene. (97)

FIGURE 5.3

ROUTES TO BUTADIENE

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow CH_2\text{=}CH\text{-}CH_2\text{-}CH_3 \longrightarrow CH_2\text{=}CH\text{-}CH\text{=}CH_2$$

n - butane n - butylene butadiene

Table 5.8 below shows that sufficient quantities of butadiene are available in Western Europe for the next 4 years. (73)

TABLE 5.8

BUTADIENE - EFFECTIVE CAPACITY, PRODUCTION & CONSUMPTION

	Million tons		
Year	Effective Capacity	Production	Consumption
1973	1,420	1,208	1,047
1974	1,607	1,410	1,137
1975	1,783	1,553	1,259
1976	1,953	1,621	1,336
1977	2,102	1,770	1,502

The possibility of medium vinyl polybutadiene replacing SBR as the major elastomer has already been mentioned. This is however not likely to greatly alter the demand pattern for butadiene before 1977. Not only have the most suitable polymers in the series to be identified and their production conditions worked out and the plants themselves constructed, replacement of one polymer in tyres by another is always carried out in stages with a sharp look-out for any shortcomings that show up.

It has been pointed out that even if all SBR was replaced by medium vinyl polybutadiene in 1977 it would only mean an additional demand of 8.5 per cent per annum for butadiene ~~raising the demand of 8.5 per cent per annum for butadiene~~ raising the demand in 1977 to 1.631 m. tons as against a projected availability of 1.770 m. tons. Quant (101) sees an excess of supply over demand for butadiene in 1978 in Europe (150/1.75 million tons) and in Japan (0.98 vs.0.88 million tons).

An FAO report is quoted (95) as giving the price rises for butadiene monomer as: end 1972, 19.8 U.S. dollar cents per kilogram; end 1974, 63.9 U.S. dollar cents per kg.; end 1980, 80.0 to 86.0 U.S. dollar cents per kg.

5.2.10.2 Styrene

The shortage of styrene was felt well before last year's Middle East war. It arose from shortages of both benzene and ethylene which are reacted to give Ethylbenzene, from which Styrene is obtained by dehydrogenation. Styrene and butadiene are polymerised to give SBR-Styrene-Butadiene Rubber. Ethylene and benzene feedstock costs are stated to account for 16 and 56 per cent respectively of the cost of styrene monomer. Plant capacity is available; the problem is one of feedstock shortage.

5.2.10.2.1 Benzene

To begin with, the light hydrocarbon fractions which provided the feedstocks for the petro-chemical industry found demand in motor and airplane fuels. The most serious problem was caused by the reduction of the lead content permitted in the U.S.A. in gasoline in order to limit air pollution by lead compounds. Lead compounds are used to raise octane ratings of gasoline. The addition of aromatics was found to be a simple and effective way of maintaining the octane level of the gasoline once the lead compounds were reduced. The hydro-dealkylation of toluene provides an alternative method of producing benzene, but even these plants are now used to desulphurise fuel oil to meet the tightened environmental laws. It is stated that "during 1973 the price of aromatics used in the production of chemicals has doubled because of the increasing tightness of crude oil supplies, the increasing demand for gasoline and a shortage of alternative octane boosters". (102)

5.2.10.2.2 Ethylene

Ethyl benzene, the pre-cursor of styrene monomer has to compete for ethylene with polyethylene and with glycols the other major outlets for ethylene. The tight position with regard to ethylene supplies can be gauged from Table 5.9 giving the forecast of production and consumption from 1973 to '77.

TABLE 5.9

ETHYLENE - CAPACITY, PRODUCTION AND CONSUMPTION 1973-'77

Source: CEFIC forecast. Nov. 1973. EEC production/consumption of ethylene, propylene, butadiene and requirements for naphtha feedstock 1967-1977 (102)

Million tons

Year	Effective Capacity	Production	Consumption
1973	9,859	8,701	8,561
1974	10,973	10,153	9,749
1975	11,399	11,003	10,710
1976	12,530	11,787	11,795
1977	13,689	12,736	12,736

SBR which uses only about 17 per cent of styrene production in the U.S.A. has to compete for styrene with polystyrene, the demand for which has risen sharply in the last two years. Table 5.10 below shows an excess of world demand for styrene monomer over production amounting to 974,000 tons. (103)

TABLE 5.10

1974 PRODUCTION FORECAST VS. DEMAND FOR STYRENE MONOMER (In Thousand Metric Tons/Yr.

	Nameplate Capacity	Production (p)	Demand (D)	Balance P Vs. D.
U.S.	2,975	2,380	2,679	-299
Europe/Africa	2,911	2,212	2,647	-435
Canada	171	137	186	- 49
Latin America	120	96	216	-120
Pacific/ Australasia	1,252	1,073	1,073	- 71
Total world	7,429	5,827	6,801	-974

(World production is assumed as 78.4% of nameplate capacity.)

Styrene monomer prices (in U.S. dollar cents per kilogram) are quoted (95) as follows from an FAO report:-

end 1972 - 15.2; end 1974 - 36.0; 1980 - 44.0 to 47.5

5.2.10.3 SBR and polybutadiene monomer and polymer prices

The following table has been reproduced (95) from the report of the FAO team of experts who studied the effects of the energy crisis on the raw materials used in synthetic rubber manufacture.

TABLE 5.11

COSTS OF GENERAL PURPOSE SYNTHETIC RUBBER AT END-1972 AND ESTIMATES FOR END-1974 and 1980
(U.S. cents per kg.)

	end-1972	end-1974	1980
a) Styrene	15.2	36.0	44.0- 47.5
Butadiene	19.8	63.9	80.0- 86.0
SBR 1500	37.0	81.5	97.5-104.0
b) Butadiene	19.8	63.9	80.0- 86.0
BR	40.9	99.6	120.5-129.0

Source: F.A.O.

Prices of SBR published by the International Synthetic Rubber Company are as follows:-

5.2.10.4 Future prospects for SBR and polybutadiene

The styrene shortage is expected to continue and SBR prices show no signs of dropping. However emulsion SBR is expected to continue for some more years as the largest volume synthetic rubber because there is no established competitor for it. Solution SBR production is limited by the capacity for manufacturing solution polymers. Medium and high vinyl polybutadienes suffer from the additional problems of consistency in manufactured quality and being as yet unproved in tyre usage. Ruebensaal (93) sees the economic position of EPDMs vis-a-vis SBR changing in favour of EPDMs for the following reasons.

1. The changing monomer cost situation favours EPDMs.

Ruebensaal points out that though ethylene, propylene, butadiene and styrene have all roughly "doubled their late 1973 selling prices" by May 1974 the ethylene and propylene prices in late 1973 were only 4 U.S. dollar cents per lb. compared with dollar cents per lb. for butadiene and dollar cents per lb. for styrene then.

2. EPDMs can be extended with as much as 700 parts of oil and fillers.
3. They have a specific gravity of 0.86 compared with 0.94 for SBR, the effects being reflected in their relative volume costs.

5.2.11 Economics of the production of Cis polyisoprene rubber (IR)

Cis 1,4 Polyisoprene is considered in some detail here as it is the chemical homologue of natural rubber and comes closer to duplicating its properties than any other polymer.

Duck (60) emphasises the following points as important in considering the future prospects of IR:-

(a) Cost and availability of isoprene monomer and the monomer purity.

(b) Utilisation of the other components of the C5 stream from naphtha crackers and the importance of these components (e.g. cyclopentene, cyclopentadiene and piperylene) in relation to isoprene. (Duck and Capitani consider the C5 stream as the most economic source of isoprene monomer).

(c) Long-term availability and cost fluctuations of natural rubber.

(d) Optimum catalyst and polymerisation systems available for the preparation of synthetic polyisoprene and the effect of such systems of the structure of the polyisoprene and the significance of the latter in relation to natural rubber.

(e) The potential competition from other synthetic rubbers.

(a) Isoprene monomer-availability and cost.

Duck (60) points out that the most economic source of isoprene monomer is the C5 stream from naphtha crackers. For the process to be economic it is necessary that a sufficient quantity of the C5 fraction must be available in one location. This should pose no problem with the increasing size of crackers and the greater co-ordination between the refining and petrochemical arms of the oil industry.

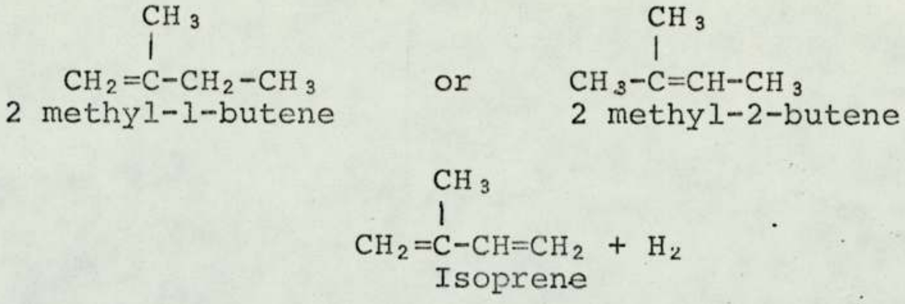
Ruebensaal (93) was reported in July 1973 (before the Middle East conflict) as stating that "the breakeven point for natural rubber averages about 13 cents per pound at the plantation. In contrast, rising feed-stock costs could push isoprene costs up to 12 to 15 cents per pound by the late 1970s".

Processes for Isoprene Monomer Production

The following processes are used for commercial production of Isoprene monomer. (Rhoad, Capitani)

1. Isoamylene dehydrogenation
2. Propylene dimerisation, isomerisation and pyrolysis
3. Isobutylene - formaldehyde condensation and cracking
4. Isopentane dehydrogenation
5. Acetone/acetylene condensation and cracking
6. Extraction from C5 stream from cracker plants.

1. Isoamylene dehydrogenation.

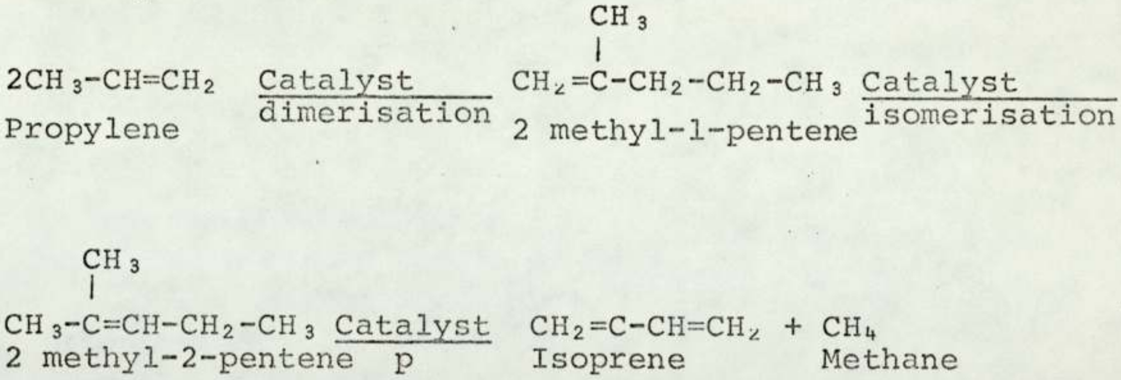


$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2{-}CH_3$ 2 methyl-1-butene or $CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_3$ 2 methyl-2-butene

$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 + H_2$ Isoprene

Isoamylene is obtained by catalytic cracking of light gasoline and is catalytically dehydrogenated to isoprene. The isoprene is then purified by extractive distillation using acetonitrile.

2. Propylene dimerisation, isomerisation and pyrolysis.



$2CH_3{-}CH{=}CH_2 \xrightarrow[\text{dimerisation}]{\text{Catalyst}} CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2{-}CH_2{-}CH_3 \xrightarrow[\text{isomerisation}]{\text{Catalyst}}$

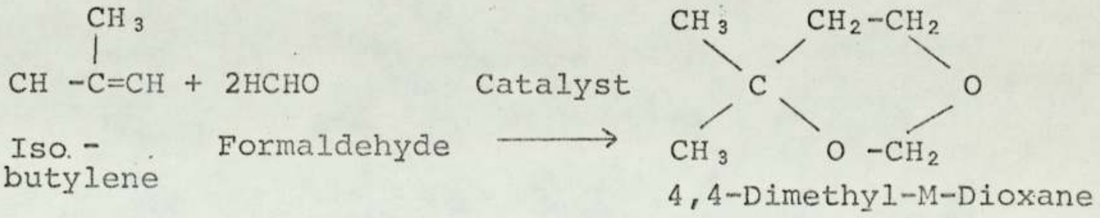
Propylene, 2 methyl-1-pentene

$CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_2{-}CH_3 \xrightarrow[p]{\text{Catalyst}} CH_2{=}C{-}CH{=}CH_2 + CH_4$

2 methyl-2-pentene, Isoprene, Methane

Goodyear Tire and Rubber Company use this process.

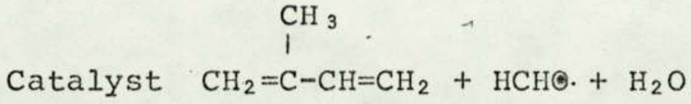
3. Isobutylene-formaldehyde condensation and cracking.



$CH\ {-}\overset{CH_3}{\overset{|}{C}}{=}CH + 2HCHO \xrightarrow{\text{Catalyst}}$

Iso-butylene, Formaldehyde

4,4-Dimethyl-M-Dioxane



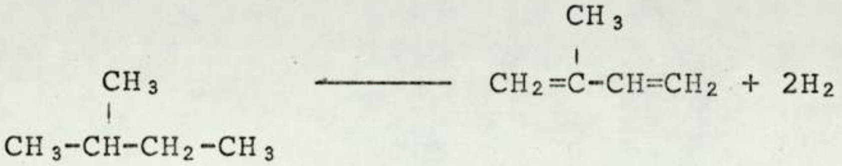
Catalyst $CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 + HCHO + H_2O$

Isoprene Formaldehyde

This process is used in Japan, France and Germany.

A process has recently been developed in Japan to make isoprene from isobutylene in a one-step gas-phase reaction.

4. Isopentane dehydrogenation

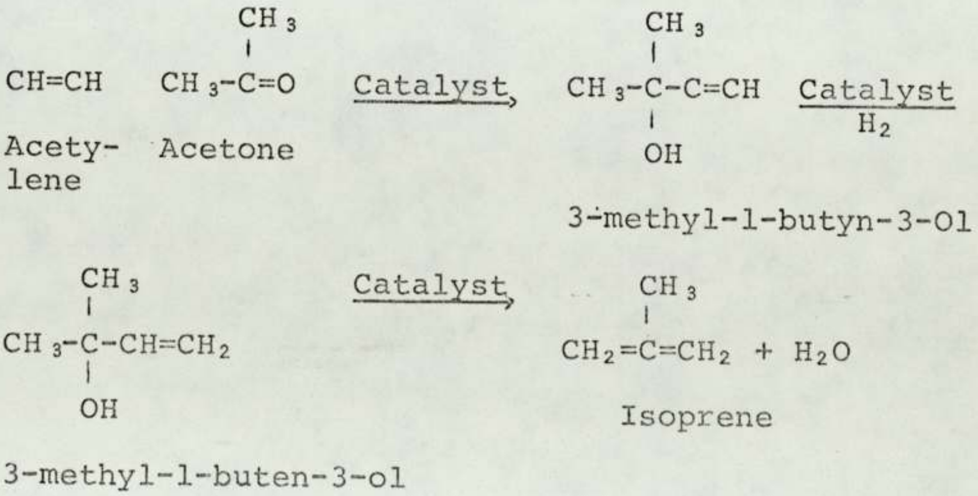


$$CH_3{-}\overset{CH_3}{\overset{|}{CH}}{-}CH_2{-}CH_3 \longleftarrow CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 + 2H_2$$

Isopentane Isoprene

This process is reported to be used to produce 180,000 metric tons of isoprene in the U.S.S.R.; the quantity is expected to rise to 300,000 tons in 2 or 3 years.

5. Acetone-Acetylene condensation and cracking.



$$CH{=}CH \quad CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}O \xrightarrow{\text{Catalyst}} CH_3{-}\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}C{=}CH \xrightarrow[H_2]{\text{Catalyst}}$$

Acetylene Acetone

3-methyl-1-butyn-3-Ol

$$CH_3{-}\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}CH{=}CH_2 \xrightarrow{\text{Catalyst}} CH_2{=}\overset{CH_3}{\overset{|}{C}}{=}CH_2 + H_2O$$

Isoprene

3-methyl-1-buten-3-ol

This process is used in Italy.

6. Extraction from C_5 stream from cracker units.

The C_5 stream from steam crackers using heavy oils contain 12 to 20 per cent isoprene. An isoprene extraction unit therefore needs to collect the C_5 streams from several cracker units. Complex extraction systems are needed to extract and purify the isoprene. Solvents used include acetonitrile, dimethyl formamide, N-methyl pyrollidone and formyl morpholine.

Rhoad (104) lists the following factors as determining which of these processes is the most economic.

1. The cost of the raw materials and their alternative use values. These values are fast changing.
2. The energy demand of the process.
3. The value of the by-products.

Capitani (105) points out that C_5 fractions containing Isoprene are being used by refineries to raise the octane levels in gasoline. He goes on to calculate the difference in the value of the C_5 fractions before and after extraction of the isoprene.

Rhoad estimates the percentage demand for isoprene monomer by end use as follows:-

World Isoprene demand ('000 Metric tons)

End-use	1975	1980	1985
Polyisoprene	660	1040	1305
Butyl rubber	20	25	31
Copolymers and other	5	25	40
	685	1090	1376

With crude oil price increases of over 200 per cent on those of the time Ruebensaal made his statement isoprene monomer prices have made IR prices much higher.

(b) Utilisation of the other components in the C_5 stream.

Duck points out that cyclopentadiene can be utilised for making either EPDM or trans poly pentenamer, while the piperylene can be used for making EPDM.

The composition of the C_5 fraction has been given as:-

Isoprene		15 per cent
C_2 - C_4 hydro carbons		10
C_5 hydrocarbons		25.9
C_5 mono-olefins		15
C_5 acetylenes		0.1
Pentadienes		12.0
(cis 1,3	4	
trans 1,3	6	
trans 1,4	2	
Cyclopentadiene		15
C_6 and higher compounds		7

(c) The long term availability and cost of natural rubber are dealt with at length later in this paper.

(d) Polymerisation systems.

This question has been dealt with at length under the technical properties of IR.

(e) Competition from other synthetic rubbers.

Of the polymers known trans 1,5 poly-pentenamer seems to be able to offer the stiffest competition to both NR and IR. It has however failed as yet to materialise as a commercial proposition. Its properties make it highly suitable for use in tyre carcass compounds.

The competition for natural rubber from polyisoprene rubber appear to have been felt mostly in the socialist countries. Two main reasons are discernible. The availability of oil deposits in these countries and the shortage of foreign exchange. Equally important must be the question of availability of NR to these nations especially in times of international crises. They have no voice in questions affecting the supply of NR. It may be recalled that a United Nations resolution prohibited the sale of strategic war materials including rubber to China. It was at this time that China concluded her rubber-rice pact with Ceylon who was then not a member nation of the U.N.

Polyisoprene capacity

Estimated growth of world IR capacity is shown below in Table 5.12 presented by Ruebensaal to the annual meeting of the IISRP in May 1974.

TABLE 5.12

PRESENT AND PROJECTED WORLD IR CAPACITY
(in thousands of long tons)

	end-1974	end-1977
U.S.A.	123	123
Western Europe	145	175
Japan	85	115
Iran	-	60
Latin America	-	50
	353	523
Socialist countries	280	445
World Total	633	968

It is interesting to note that the U.S.A. is not planning any new IR capacity. By the end of 1977 the Socialist countries will have more than half the world's IR capacity.

Polyisoprene production

TABLE 5.13 ESTIMATED WORLD PRODUCTION OF SYNTHETIC POLYISOPRENE BY COUNTRY, 1969-74
('000 Metric tons)

	1969	1974
U.S.A.	110[a]	119[a]
U.S.S.R.	70	200
Netherlands	60	60
Italy	-	20
Japan	-	35
France	-	6
Total of above	240	440

a. RSB reported figures (rounded)

It has been pointed out (95) that synthetic polyisoprene has little or no advantage over natural rubber in presentation or consistency of quality and that synthetic rubber manufacturers now concentrate their marketing efforts on the technical merit of their product. Capitani (105) promises more sophisticated grades of IR in the future - polyisoprenes of diversified Mooney viscosity, high green strength, oil extended, oil-black masterbatch polyisoprene latex and blends of polyisoprene with other synthetic rubbers.

With natural rubber selling at prices about £100 per metric ton below SBR which is much cheaper than polyisoprene, the latter will be hard put to resist competition from the natural product. It will however continue to be fostered to some extent because each country wishes to be independent at least to some degree in respect of a vital raw material like rubber. Besides, once the investment in plant is made, it has to be operated if any return on the investment is to be gained.

5.3 The Natural Rubber Industry

5.3.1 The structure of the natural rubber industry

The synthetic rubber industry is composed of a few manufacturing plants with large capacities and ownership is restricted to a few tyre companies, oil companies, chemical companies and users' cooperative organisations or to government. The number of large rubber plantations on the other hand is few, but their output is in no way comparable to that of a synthetic rubber plant. The natural rubber industry is characterised by its large number of smallholders. Of the total production of 1,489,474 metric tonnes of natural rubber produced by West Malaysia in 1973 791,517 tonnes came from smallholdings. This represents 53.1 per cent of total production. The figure for Indonesia is over 70 per cent. Of the total world production of natural rubber amounting to 3,492,500 tonnes 63.3 per cent represented by 2,210,000 tonnes came from smallholdings.

Malaysia is the world's largest producer of natural rubber and has spearheaded the fight back by natural rubber against competition from the synthetics. Indonesia has great potential but as seen from Table 5.14 (1) has been dropping behind Malaysia in the quantities of rubber produced. Together they produced 70 per cent of total output of natural rubber in 1973. Sri Lanka's annual production of natural rubber has increased by roughly 50 per cent over the 10 year period 1963-1973.

Table 5 shows the percentage of world natural rubber production produced by each of the main rubber producing countries.

Table 5.14 Percentage of total world NR production in 1973 produced by each of the major producing countries.

	Percent
Malaysia	44.8
Indonesia	25.4
Thailand	10.9
Sri Lanka	4.4
India	3.5
Africa (mainly Liberia)	6.3

The structure of the natural rubber industry and the manner of its operation are well described in P.W.Allen's book "Natural Rubber and the Synthetics" (97).

5.3.2 Importance of the natural rubber industry to rubber growing countries.

Sekhar (110) estimates that natural rubber represents the direct livelihood of no less than 25 million people in Southeast Asia. Malaysia's 500,000 smallholders own 67 per cent of the planted rubber land of over 4-6 million acres. The contribution of the smallholders of Malaysia and Indonesia to the nation's output of rubber has already been stated. Rubber plantations in Thailand are all smallholdings while in Indonesia smallholdings account for over 70 per cent of the acreage under rubber.

Rubber brings in 40 per cent of Malaysia's export earnings, 30 per cent of Indonesia's, 14 per cent of Thailand's and 15 to 20 per cent of Sri Lanka's.

The recognition of the importance of the rubber growing industry to the country's welfare is reflected in government action to support natural rubber producers particularly in difficult times.

5.3.3 Production

Over the 30 year period since the end of World War II the increase in natural rubber production has been a little over 2 per cent per year. Over this period total rubber demand has grown at the rate of about 7 per cent annually. As seen in Table 5.15 the annual rate of growth of world NR production has quickened during the last 10 years, mainly due to replanting with higher yielding strains of Hevea.

Table 5.15 Yearly increase of annual NR production

Year	Total world rubber production (1000 metric tons)	Annual rate of increase (%)
1963	2,170.0	Start print
1964	2,352.5	8.4
1965	2,352.5	0
1966	2,392.5	1.7
1967	2,522.5	5.4
1968	2,685.0	6.4
1969	2,695.0	0.4
1970	3,102.5	15.1
1971	3,077.5	negative -0.8
1972	3,112.5	+1.1
1973	3,492.5	12.2
		mean = 6.1%

Mullins (46) has shown in Table 5.16 and Fig. 5.4 how natural rubber has lagged behind total world demand for all rubbers. The gap was filled by synthetics.

TABLE 5.16 World consumption of rubber (million tons)

	1960	1970	1980
Total rubber requirement	3.9	7.8	13 to 14
NR production	2.0	3.0	in excess 5.0

The growth of synthetic rubbers has been attributed to a large extent to the inability of the natural rubber industry to supply the rising demand for rubber.

.3.3.1 The cost of production

Every plantation is conscious of its own cost of production and of those in the area. The production figures

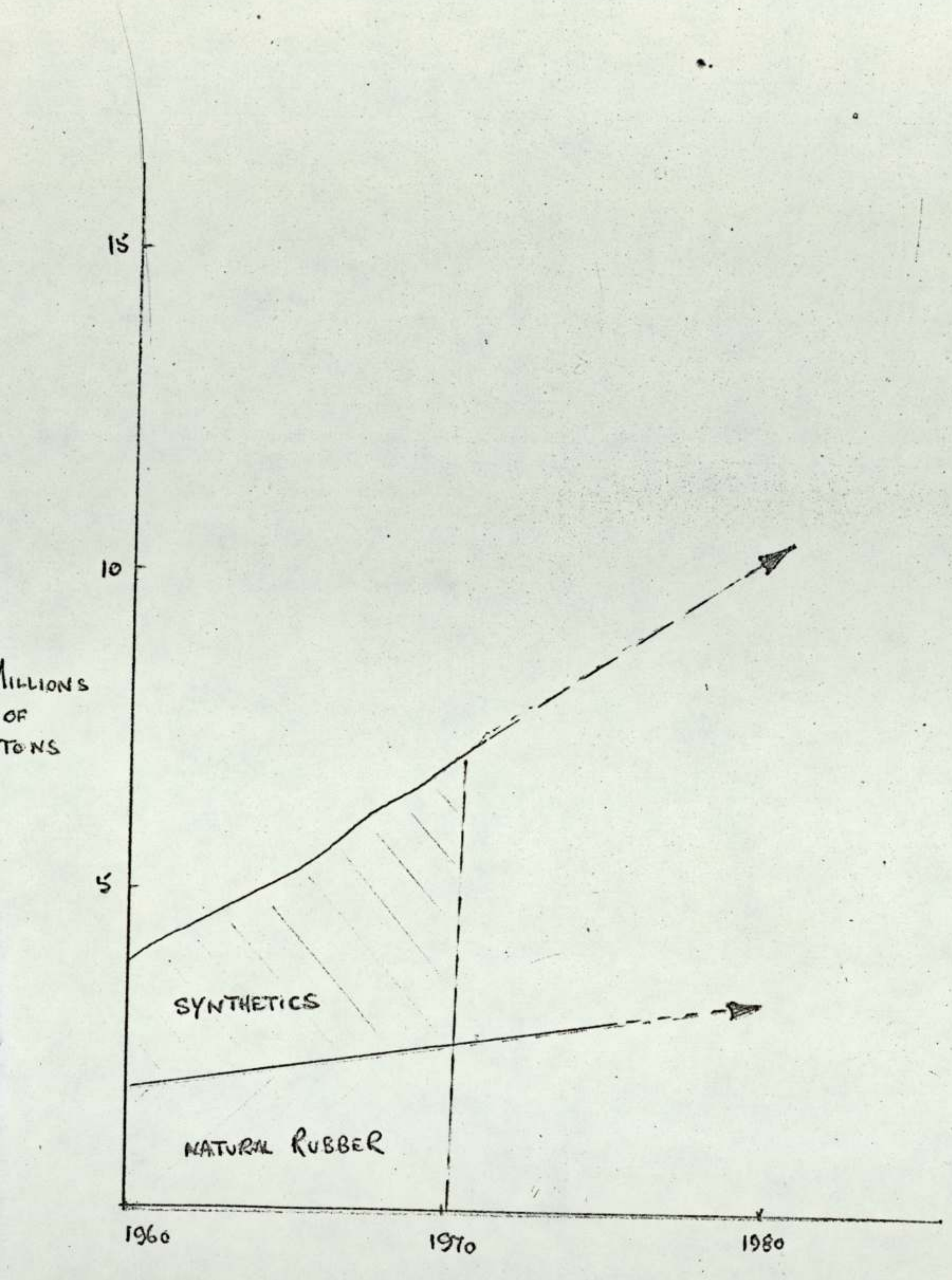


Fig. 5.4 WORLD PRODUCTION OF RUBBER

and the cost of production are what an estate manager is judged upon by his visiting agent who is generally a senior planter in the country. A good "VA's report" is the pride of an estate manager.

The following breakdown of the cost components of NR production have been given by Barlow and Lim Sow Sing. (107).

TABLE 5.17 Components of (NR) Estate operating costs

	Cost as per cent of total operating costs
Tapping & Collection	52
Processing	13
Management	11
Fertilizer & Application	10
Other Costs	14
Total	100

From this breakdown it will be seen that economies can be most effectively made in the expenditure on tapping and collection. The cultivation of high yielding strains of Hevea will lead to significant reductions in the cost of tapping and collection. The development of dwarf rubber plants said to be now proceeding and the use of yield stimulants like Ethrel will also increase the yield of rubber per acre and bring down the costs of tapping and collection. Another cost saver, if adopted, will be poly-bag collection. This procedure involves the weekly or fortnightly collection of the polythene bags used for collecting the latex.

5.3.4 NR consumption

Total NR consumption by country since 1963 is shown in Table 5.18) NR consumption in different countries in relation to total world NR consumption has been shown in Table 1.3 and the usage of NR in tyres in relation to total NR consumption in each of the major NR consuming countries has been shown in Table 1.4. In 1973 the USA used 20.4 of the world consumption of natural rubber. 70.4 per cent went into tyres and tyre products.

Future demand for NR

Bateman and Allen (109) have predicted that both isoprene rubbers, natural rubber (NR) and synthetic polyisoprene rubber (IR) can at best win no more than 42 per cent of the total demand for rubber. This projection has been made on the basis of the present pattern of NR usage. Rhoad's figures for isoprene rubber (NR + IR) are around 38-40 per cent of total world demand. His distribution of the share of the isoprenic rubber consumption is shown in Table 5.19.

TABLE 5.18 World Elastomer Consumption

(Including U.S.S.R. China and Eastern Europe)

Year	Total rubber consumption ('000 metric tonnes)	NR and IR consumption as % of total rubber	NR as % of total rubber
1965	6154	40.4	39.4
1970	8581	37.8	35.0
1975	11,117	38.7	32.8
1980	13,787	39.6	32.1
1985	17,170	39.2	31.6

On the basis of a study made by the Malaysian Rubber Research and Development Board Sekhar (110) concludes that if adequate supplies of NR could be made available at stable prices NR's potential share of the rubber market would be about 60 per cent. When allowance is made for available and committed supply of synthetic isoprene rubber, NR's normal share could be around 50 per cent. Conceding ground further for "marginal processing advantages of certain synthetics, Sekhar arrives at a more conservative estimate of 42 to 43 per cent.

Sekhar insists that this increased demand can be met if rubber producers were willing to replant on an organised basis because high yielding planting material giving 3360 kilograms per hectane per year are available.

5.3.5 The marketing of natural rubber

Natural rubber could not be sold direct by the producer to the consumer in the manner of synthetic rubber for the following reasons:

1. The output of each rubber growing unit is small compared to the output of a synthetic rubber plant. Besides, it has a large number of smallholders. Most of the rubber estates in the proudcing countries are not large enough to make arrangements with individual buyers.

2. Whereas the tyre companies have large interests in synthetic rubber manufacturing facilities, less than 10 per cent of the rubber plantations are owned by tyre companies These include the plantations owned by Dunlops in Malaysia, Firestone in Liberia and Goodyear in Indonesia. The plans of four large tyre companies to open up plantations up to 100,000 acres in extent has already been mentioned.

3. The physical distances between the plantations and the users necessitates a buffer stock of rubber being maintained in the consuming country. Individual rubber producers cannot afford to maintain such a buffer stock.

Between the producer and consumer are the producer's agent, the dealer and broker. The Singapore market has been the largest commodity market. The London market handles rubber for the UK and the continent while the New York market supplies America. Allen explains this subject in his book "Natural rubber and the Synthetics" (97).

The smallholder sells his rubber to small dealers or to his cooperative. In Sri Lanka the smoked sheet rubber is purchased by government depots to enable the government to obtain adequate suppliers to meet its obligations to other countries it has contracted to supply. The smallholder also receives a fair price for his rubber.

The natural rubber market is well known for speculative buying and selling. The rubber is not physically transferred but there are paper transactions, whence the term "paper rubber". Speculative buying was responsible for natural rubber prices going beyond the £500 a ton level at the beginning of 1974. These fluctuating prices have done untold harm to the natural rubber industry. It makes it very difficult for the rubber manufacturer to price his products or to contract to supply rubber goods. The harm fluctuating prices do to the rubber growing industry is recognised by rubber growing interests but no concrete steps have been taken to remedy the situation. The Malaysian government has set up the Malaysian Rubber Exchange and Licensing Board (MRELB) to control the activities of the market with powers to punish offending rubber traders. The natural rubber producers voice their loudest protests when rubber prices are down. The time for them to protest and act is when rubber prices are peaking. It would help to establish their bona fides with the consumers on the question of stable prices Figs. 5 and 5 show how NR prices have varied over the last years and during the past year. The MRELB is also considering the advisability of setting up sales centres on the continent, equipping the foreign exchange market to provide spot and forward quotations and improving finance, banking and insurance facilities (111).

Malaysia is taking action in the correct direction. It is hoped that it will be possible for the Organisation of Natural Rubber Producing Countries to act jointly in the setting up of bodies to help in the development of the natural rubber trade just as the synthetic rubber producers set up the International Institute of Synthetic Rubber Producers (IISRP),

5.3.6 Improvements made in the natural rubber industry

Credit must be given to Malaysia for the lead she has given the other rubber producing in re-organising and re-vitalising her natural rubber industry. Most of the innovations made in the industry during the past 20 years have been introduced by Malaysia.

5.3.6.1 Improved planting material

The improvement in yield with the newer planting material is seen from the following figures for popular planting material given in kilograms/hectane/yield:
1940s - 1120; 1950s - 1460; 1960s - 2350; 1970s - 3360.

New varieties of Hevea have been bred which can be tapped in 3 to 4 years instead of the usual 6 to 7 years. These varieties have been described as precocious varieties.

Dwarf varieties of Hevea have been bred that will give more rubber per acre of land.

5.3.6.2 Novel exploitation methods

The application of ethylene releasing hormone type stimulants to the tapping cut has been found to prevent the formation of plugs of rubber in the latex vessels which stop further latex flow. The rubber yield per tree is found to be sometimes even doubled by the use of these yield stimulants.

5.3.6.3 Polybag collection

This topic has already been discussed.

5.3.6.4 Grading of rubber according to technical specifications

The SMR classification of rubbers was discussed in section 3.3.4.

5.3.6.5 Newer forms of NR have been made available. Consumer reaction has been most favourable to the Constant Viscosity (CV) and Low Viscosity (LV) forms of rubber described in section 3.3.5.

5.3.6.6 Improvements in the production and marketing of smallholders rubber

The Malaysian Rubber Development Corporation Berhad has helped to organise group processing centres to process smallholders' rubber. These centres are popular and have helped the smallholder obtain a fair price for his rubber.

5.3.6.7 The Malaysian Rubber Exchange and Licensing Board controls the marketing aspects of natural rubber. Its activities have been described in section 5.3.4.

5.3.6.8 The Rubber Research Institute is diversifying its activities to serve the varying needs the rubber planting industry. A new Techno-Economic Unit was set up to evaluate the effects of techno-economic forces on the natural rubber industry. Recently a professional unit was set up for post-graduate training of chemists, engineers and physicists.(113)

5.3.7 Future prospects for natural rubber

The demand for rubber is a derived demand, and depends to a large extent on the growth of the motor industry. In Western countries the motor industry developed with the increase of private motoring. In terms of energy consumption however private motoring is wasteful. The pattern of growth of private motoring is bound to change. The use of large cars and the use of three or four cars by one family will be restricted. Private motoring will also be reduced by world recession conditions which are an indirect result of the energy crisis. The demand for all rubbers will not be in line with the pattern of growing demand that existed before 1973. Natural rubber must therefore compete with the synthetics for available demand. The competitiveness of natural rubber with the general purpose synthetics will now be discussed.

Competition of natural rubber with the synthetics

In all assessments of the future prospects of natural rubber it is stressed that if natural rubber is to remain competitive with the synthetics it must be available in adequate quantities at a stable price. Availability and price are of the greatest importance.

5.3.7.1 Availability

Future demands for natural rubber has been estimated at between about 30 to 43 per cent of total rubber demand. Sekhar is confident that NR production can be stepped up to meet his projected demand of 43 per cent of total rubber, provided organised replanting is done with the improved Hevea strains mentioned earlier.

In recent months owing to the drop in natural rubber prices and demand it is reported that production has been reduced by discontinuing the use of yield stimulants. It is understandable that when prices are as low as £220 per metric ton of RSSI that it is no longer profitable for plantations to use yield stimulants, but the suggestion that the Malaysian government thereby aims at exerting pressure on consumers by restricting supplies of natural rubber is probably quite unfounded. The Malaysian Rubber Research and Development Board has always stressed the need for rubber producers to ensure adequate supplies at a stable price. Restriction of production for any short-term benefits will vitiate all the effort that has gone into staging the great come-back by natural rubber.

5.3.7.2 Price

Price-wise natural rubber can compete most effectively with the synthetics. The prices issued by the International Synthetic Rubber Co.Ltd. (115) for natural rubber, SBR, oil extended SBR, and polybutadiene are given below

TABLE 5.10 ISR list price of R.S.S. No.1 and Synthetic rubbers

	Prices in £ per metric ton ex-works or ex-store			
	July 1973	Jan 1974	July 1974	Jan 1975
R.S.S.I. (Spot)	320.00	535.00	290.00	252.00
SBR 1500 (cold-SBR)	187.50	300.00	350.00	385
SBR 1712 (oil-extended)	153.00	259.00	305.00	335.50
Polybutadiene (BR)	203.00	319.00	375.00	412.50
EPDMs	280.00 to 325.00	382.00 to 432.00	420.00 to 470.00	460.00 to 515.00

Polycisisoprene prices are much higher than SBR or BR prices but details are not published.

There is no likelihood of reduction in synthetic rubber prices, as neither the price of crude oil, nor plant or plant operation costs show any signs of coming down.

The problem of sharp fluctuations in the price of natural rubber has been the bane of the natural rubber producers and consumers alike. The Malaysian Rubber Exchange and Licensing Board (MRELB) has been set up to control the thereafter. For us in the NR industry the price level we legitimately can expect in the future could be of the order of U.S. 5 ¢ more than general purpose synthetics is 40 ¢ a pound will make sense in the competitive area at present and in the future".

5.3.7.3 . Technical quality

In technical quality in the major segments of the tyre industry NR must concede only the passenger car tread area to SBR. In most other fields it is able to stake a stronger claim for use alone or together with BR up to proportions of 30 parts BR to 70 of NR.

Of the present polymers natural rubber is best equipped to meet the requirements of the newer types of tyre like the Dunlop Denovo and the Pirelli DIP tyre. The technical suitability of a mixture of EPDM and trans-polypentenamer synthetic rubbers has been mentioned for these applications, but the latter has not even reached the stage of commercial production. Speaking specially of synthetic polyisoprene rubber Sekhar (110) states that it has no advantages to offer in respect of price or quality.

Ethylene propylene terpolymers could well be the materials natural rubber will have to contend with.

5.3.7.4 Captive markets

The ownership of synthetic rubber plants by tyre marketing activities involving natural rubber. The plans for expansion of its activities have been mentioned earlier. Cooperation between the natural rubber producing countries in the field of marketing with an organisation equivalent to the International Institute of Synthetic Rubber Producers Inc. (IISRP) should help both producer and consumer. Measures to control speculation in "paper rubber" will not be far away with the governments of NR producing countries becoming aware the extent of the damage done to the economies of these countries by speculation on the rubber market.

Stable and fair prices for natural rubber is the desire not only of the consumers but also of the producers. A stable price over a period of time would enable the rubber grower to plan his replanting over a period of time. It should be remembered that about six years elapses between planting and tapping and that during this period the grower receives no return on his investment. What in the view of the natural rubber producer represents a fair price for him can be gauged by the following remarks made by B.C.Sekhar at the Malaysian Rubber-in-Engineering Conference (114). "The assessment we have made recently on the basis of information available in the developed countries, is that general purpose synthetic rubber will not any more be available in the U.S. 16 to 20 ¢ per lb. range, but rather in the U.S. 30 to 35 ¢ per lb. range. This calculation is based on the conservative estimate of U.S. $9.00 a barrel of oil. On the basis of present value of money, we could expect this situation to be effective into the 1980s and firms has been mentioned earlier. This provides a captive market for synthetic rubbers. It is correct that tyre manufacturers favour using synthetic rubber from their own plants than imported natural rubber. How far they can push this depends on the relative costs of using natural and their syntbetics. Costs here would include not only price and processing cost but also the value of the performance of the tyre to the image of the company. No tyre company can afford to go on subsidising an unprofitable synthetic rubber plant for very long except under exceptional circumstances. The tyre industry is too competitive to afford such a luxury.

5.3.7.5 National self sufficiency in rubber

The special circumstances mentioned above include above all government or industry policy for rubber supplies. The Rubber Act of 1948 (Public Law 469 of 31 March 1948) declared U.S. policy to be "that the security of the United States can and will best be served by the development within the United States of a free, competitive, synthetic rubber industry". This could be said of the other countries too, whether it be U.S.S.R. Japan, China or Britain. Synthetic rubber can be pushed that far but no further.

5.3.7.6 The Materials shortage

Natural rubber falls into the category of cyclical or replaceable materials while synthetic rubber is non-cyclic being made from non-replaceable oil. This is an important fact in the context of today's material shortage.

5.3.7.7 The energy crisis

Much less energy is consumed in the production of natural rubber than in that of synthetic rubber. The materials used in synthetic rubber manufacture also represent a significant though small amount of energy.

8. The environment

The processes involved in the manufacture of synthetic rubber cause atmospheric air pollution. Natural rubber manufacture causes no air pollution.

.3.8 Suggestions for further improvements in the natural rubber industry

5.3.8.1. The research and development work being carried out on natural rubber is landable. More could however be done on the aspects of actual technical usage of natural. Sri Lanka for instance research on usage of natural rubber in tyres could be sponsored at the state owned tyre factory. It would be only fair that the larger part of this research should be financed by the rubber plantation industry.

5.3.8.2 Much could be learnt at such factories to establish rubber plantation factories as industrial waits rather than as parts of an agricultural set-up. Most of these factories use equipment and methods which are inefficient. There is much room for the development of the equipment and methods used at these factories.

A study is merited into the aspects of drying rubber in estate factories. Some factories air dry their crepe laces which others use forced drying consuming oil or electricity. The economics of air drying rubber is worth studying in the light of today's high energy costs.

5.3.8.3. A second look could be had at some of the accepted ideas in the rubber industry. The design of the tapping knife is one such example. Different kinds of tapping knives are used in different countries but the humble tapping knife though a vital piece of equipment has not been thought of as a fit subject for study. In Malaysia the tapping knife is designed to be pulled towards the tapper. The Sri Lanka version (the Mickey-Goolidge) is a pushing type with two sharp points in front.

5.3.8.4 Though rubber plantations are labour intensive and labour represents more than half the costs of production of natural rubber no in-depth study of the subject of labour in rubber plantations has been attempted. The same attitudes are adopted by some management to labour as cheap labour in days gone by. The studies and action based on these studies are necessary if the rubber plantations are to be spared the industrial unrest that can be seen in some of the other industries.

Rubber goods manufacture in rubber growing countries

5.3.8.5. It is seen that the total quantity of rubber consumed in the rubber growing countries was only 150,000 tons in 1973. These countries have certain advantages to offer besides a ready supply of rubber. Wages are low and abundant labour is available. Their skill is on par with labour anywhere in the world, when competing on equal terms. All efforts should be made to establish rubber based industries if possible indigenously, otherwise in collaboration with foreign capital. Malaysia has four large tyre companies coming in. Plans have also been made to establish a plant for manufacturing latex threads - It is not so much the lack of technological know-how that is hindering the development of industry in these countries. It is the lack of capital and managerial expertise.

SUMMARY

The use of natural rubber in tyres

Natural rubber has an assured market for all components of earthmover, airplane and large truck tyres. In car tyres its use in the carcass will continue.

The proportion of natural rubber used in the different tyre components will depend on its competitive position with the synthetics. This aspect has been dealt with in the last section. Total rubber demand (natural plus synthetic) will depend on the world economic climate. Should the world go into recession the motor industry will be one of the worst affected. These effects will be transmitted through the tyre industry to the rubber producing industry.

Economic considerations and technical developments predicted for the next ten years favour natural rubber over the synthetics, provided that adequate supplies can be made available at a reasonable price. Natural rubber producers should therefore make every endeavour in the area of marketing to maintain a stable price for their product, at the same time fighting all efforts to resist measures that could even be interpreted as being directed towards the restriction of supplies.

6 TESTING OF TYRES, TYRE COMPONENTS AND TYRE COMPOUNDS

6.1 Introduction

Tyre testing is carried out for purposes of tyre development, establishing standards for tyres and process control. Tyre development includes working out new designs for tyres, testing the use of new or improved materials in tyre manufacture and estimating new techniques in tyre technology.

Tyre testing represents the largest item of expenditure in tyre development. The sums of money can be gauged from the fact that, apart from the largest American tyre companies and a very few in Europe, all the other tyre factories in the world have technical agreements with one of the "giants" for basic technological development know-how.

The decision of the U.S. Government to enforce safety performance standards for motor vehicle systems including tyres and a Uniform Quality Grading System for tyres has aroused widespread interest and close scrutiny of tyre testing methods.

The only reliable method of evaluating the total performance characteristics of a tyre is road testing. Road testing of tyres is however a very expensive operation and is used only as the final test of tyre quality. In development work laboratory and test track methods are used to identify the most promising types of tyres which are then road tested.

The problem of tyre testing is complex. It has been pointed out that "A tire has so many different functions which it must simultaneously perform that it is probably the most complex one-piece component of the vehicle. The degree to which the tire can perform any one function properly is, therefore, the result of the compromises which have been made in its design". (116).

An overall view of tyre testing is available from two reviews of rubber testing by Brown and Scott in 1972 (117) and by Thomson and Gurney. (118).

6.1.1 ROAD-TESTING OF TYRES

The difficulty of predicting service performance of tyres from laboratory tests arises from the difficulty of reproducing road conditions in the laboratory. Road conditions are so varied that it is indeed impossible to duplicate them in the laboratory. Road conditions which affect tyre performance include macro- and micro-surface structure, road surface temperature, surface moisture, gradient of slopes and road camber. For this reason tyres must finally be road-tested under conditions of usage. Road tests help evaluation of tread wear, flexing of cord body, bead chafing, etc.

Road testing of tyres is done under controlled and uncontrolled conditions. In the latter case, the testing is carried out under actual conditions of usage. They can be fitted on a fleet of taxis or, in the case of truck tryes, on a fleet of buses or lorries. The tires are moderately overloaded and run continuously. The test conditions are therefore more severe than the average conditions under which the tyres will be used, but are basically similar to them. The data so obtained correlates better with service performance, but takes more time and requires the use of a larger number of vehicles to compensate for the larger number of variable factors.

Controlled road tests generally are carried out under conditions of accelerated wear and therefore take a shorter time to yield results. A smaller number of vehicles is involved. The results however do not correlate as closely with service performance as do those from uncontrolled tests.

It is however possible to vary the factors under study with greater accuracy. Veith (119), for example, describes a sophisticated system consisting of "an instrumented two wheeled trailer, a towing vehicle with appropriate control and recording instrumentation and various supplementary measurement devices". This system allows variation and control of tyre slip angle and resulting cornering force, camber angle, load and speed. Such systems allow more precise monitoring and recording of test data.

6.1.2 TRACK TESTING OF TYRES

The large tyre companies maintain very expensive testing grounds for proving of tyres. Some of the facilities described are those of Goodyear and Pirelli (119, 120). The test tracks contain different types of surface to measure wear and cut resistance. Sharp corners and steep banking as well as slippery patches are included. Both Goodyear and Dunlop have provided a stretch of transparent glass through which photographs of tyre prints are taken.

Modern tyre testing grounds are described by Brown and Scott as "huge and complicated facilities to provide controlled conditions and sophisticated instrumentation. The instrumentation has reached the stage where test parameters are transmitted from the vehicle, recorded and processed by computer, and special track surfaces used to allow photographic recording of the tyre contact area".

The pitfalls of road and track testing include the effects of the driver's characteristics. Beatty and Studebaker (121) report the case of a group of test tyres they personally made but the mileage (to smoothness) figures obtained from 3 private cars were 7,000 miles, 20,000 miles and 30,000 miles. They comment that "....it is obvious that the fellow who wore out the identical tires in 7,000 miles ...." imposed quite a bit more severe wear condition on his tires... This means it is almost impossible to set up et of conditions for tests".

6.1.3 Indoor (Rig) Testing of Tyres

Rig testing of tyres is carried out for process control work or to determine particular characteristics of tyres like carcass strength. In spite of a great deal of effort no rig test has been devised which correlates with the road performance of tyres.

6.1.4 Laboratory testing of tyre components and tyre compounds

Laboratory testing of tyre components and tyre components is carried out for development and process control work. Laboratory tests evaluate the properties of the individual components or compounds by themselves. In a tyre, however, their value lies in how well they perform together with the other components of the tyre.

6.2.1 Road testing for Wear Resistance of Tyres

Comparison between wear resistance of different tyre tread compositions can be made by having the tread of each tyre made with only compound or more than one, usually two. The advantages of testing more than one compound on the same tyre include economy and reducing the number of variable factors. Amon and Dannenberg (122) have shown by analysing the various factors operating in two road tests that 12,000 miles of testing with "half and half" ("two-way") tyres was equivalent to 48,000 miles with whole tyres. On the other hand, unless the tread compounds are finely balanced in composition the tyre and the vehicle balance could be upset. This is a serious consideration especially in high speed testing, and may affect the rate of wear of the tyre tread.

Southern (123) is of the view that whole tyre testing is necessary for reaching definite conclusions on tread wear. Derringer (124) however, argues statistically that up to 10 tread compositions can be tested on a single tyre, provided the proper analysis is made.

Treadwear is assessed by measuring the depth of the tread grooves or by weighing the tyres. There appears to be no linear relation between these two methods and the rate of wear is not uniform. Treadwear is found to slow down with time. It is now generally expressed as "miles to smoothness".

As already stated road tests can be controlled or uncontrolled. Veith (119) has described a system using an instrumented trailer and a towing vehicle to monitor and record the different parameters of the tyre. The use of a trailer permits closer control of the operating conditions and has been used by Schallamach (32), Southern (123) and Bulgin and Walters (125). It was used by MRPRA in their experiments on the evaluation of oil extended natural rubber in winter treads. Rellage (126) has described the testing of tyres by Shell Company to investigate the performance of their polymers in tread compounds.

Veith divides the gross factors affecting tire wear into two categories (1) those external to the tire or environment and use factors and (2) intrinsic or internal factors that are particular to the tyre itself. They are listed below.

External

1. Pavement; texture, type.
2. Environmental conditions: Temperature, rain, wind, dust, snow.
3. Tire forces: lateral or cornering forces and longitudinal forces of driving or braking.

Internal

1. Tread composition.
2. Tread design.
3. Carcass and other tire construction features.

Gough (127) had earlier proved that cornering is the major source of tyre wear.

It is being realised now that treadwear is not solely a property of the tyre alone since it is the result of interaction between the tyre and various road surfaces under widely varying environmental conditions. Treadwear itself has been shown to be caused by cutting and tearing by sharp asperities on road surfaces, by fatigue failure due to repeated deformation of the rubber at the tyre surface by smooth projections from the road surface and by roll formation on the tyre rubber surface. The extent to which each mechanism predominants depends on the texture of the road surface.

Ambelang (128) is of the opinion that the "treadwear rating of a tyre cannot be adequately or unequivocally expressed by a single figure; but an array of numbers would be required to include, for example, the two types of abrasion and the dimensions of temperature and side force".

Road testing of tyres is therefore planned to obtain data on the performance of tyres under the conditions of usage. Snyder (129) has discussed the effects of different environments on treadwear.

In actual road testing of tyres on vehicles, the experiment needs to be statistically planned. Such planned road experiments have been described by Dannenberg (130) and by Stiehler and co-workers (131).

6.2.2 In track testing of tyre treadwear different road surfaces are laid, the track is banked at sharp slopes and the vehicles driven at speeds well above the legal limits on highways. On the Goodyear test track at San Angelo, Texas, it is reported (119), the usual tests for wear, durability and cracking are carried out at speeds between 85 to 140 mph and the five mile track is banked accordingly. Special roads have been constructed to increase the rate of treadwear.

6.2.3 Indoor (Rig) Testing of Tyres

6.3.1. Wear testing.

Abrasion tests have received a great deal of attention over the years as the wear resistance of tyre treads is one of the most important characterisitcs of a tyre. The National Bureau of Standards constructed a giant facility to test the wear resistance of whole tyres, but correlation with service performance was claimed to be no more than 70 per cent. In this apparatus the roadway is the inner surface of a steel cylinder 28 feet in diameter and 3½ feet high lined with 3 inch concrete (132).

McIntosh (133) describes a tilting drum abrader where the tyre is abraded by tungsten carbide gritter bars. He claims these results correlate well only with the slow wearing of tyres.

The basic problems of wear testing are summed up thus by Ambelang (128): "Treadwear cannot be expressed solely as a property of the tyre since it is the resultant of the interaction of the tire with multivariant environmental conditions".

6.3.2 Durability testing of tyres

A routine test carried out to test the durability of tyres is the dynamometer test where the tyre rotates loaded against a large rotating steel drum. These drums have a smooth surface and transverse ridges of semi-circular cross section. This test gives information on the following parameters:

1. bead durability
2. heat generation
3. general durability of casing and tread

Diameter of the drum is 67.23 inches so that one revolition is equal to 1/300th of a mile.

The drum should be as large as possible so that the outer surface is as near to being flat as possible. Radial ply tyre treads make a flat footprint with the road surface owing to the action of the rigid breaker belt. Larger than usual drums are therefore necessary for testing radial ply tyres.

2. High speed testing is carried out on sophisticated equipment where speeds, loads, braking force, etc. can be accurately varied.

.3.3 Skid testing (hydroplaning)

These tests are done on the surface of an indoor drum, straight ahead on a track or on a curved path on a track. Drum testing allows the depth of the water layer to be controlled, but hydroplaning speeds are not achieved.

6.3.4 Tests for cornering force, self-aligning torque and slip angle. These tests are carried out for development work.

Cornering force is defined as the sum of the forces exerted by the tyre on the car when the steering wheel is turned. Self-aligning torque is a measure of the extent the tyres (and the steering wheel) tend to return to their original inclination when the controlling hand of the dirver is removed. Slip angle is the angle between the direction the tyre is included to travel and the direction it is made to travel.

6.3.5 Tests for rolling resistance, Testing of tyres for rolling described by Glemming and Bowers (159).

Rolling resistance is the resistance offered by the tyre to start it rolling and keep it rolling. It is related to the fuel consumption caused by the tyre.

6.3.6 Fatigue Testing of Tyres

Examples of fatigue failure of rubber compounds in tyres are groove cracking and rib tearing of treads, chipper edge failures and chunking of solid tyres. NRPRA workers have explained fatigue failure in rubber on the basis of the rate of growth of cracks in the rubber. The initial cracks are formed by inhomogeneities in the rubber compound or caused by external forces like stones on the road surface or by ozone. The rate of crack growth has been related to a parameter called the tearing energy. This has been defined as the energy released by a unit increase in crack area with the external forces doing no work.

Kovac and O'Neil (134) describe a laboratory test the Goodyear Tire Fatigue Test to test the fatigue performance of tyres. The equipment consists of two 45 in. steel dynamometers driven by a 30 h.p. motor. The maximum load on each tyre is 7500 lb and the maximum speed 100 m.p.h. Non-fatigue failures due to heat are minimised by the on-off cycle (automatic intermittent operation) and the buffing of the tread rubber down to the level of the grooves. In correlation of the laboratory test results with service performance 1.00, 0.99 and 0.95 values were obtained for probability of complementary events. Nevertheless, these authors stress that "Although valuable lab. tests should only supplement the millions of road miles necessary to assure satisfactory tire performance".

Lake and Clapson (40) have described an empirical method which enables the available elastic energy to be estimated for a tyre groove by measuring the amount by which a crack made in a sample of the compound opens under stress. Predictions for groove cracking made on the basis of values so obtained for available elastic energy were proved correct by regular tests as well as road tests with buses.

6.3.7 Testing of Tyres to meet legislative requirements

The U.S. National Traffic and Motor Vehicle Safety Act of 1966 required the establishment of motor vehicle safety standards and a uniform quality grading system. Accordingly Federal Motor Vehicle Safety Standard 109 for passenger car tyres was made obligatory from September 1968. It required compliance with the following laboratory tests (136).

1. Bead unseating or push-off test.
2. Breaking energy or plunger (strength) test.
3. Stepped-overload endurance test in a controlled high-ambient atmosphere.
4. Stepped-speed high speed test in a controlled high ambient temperature.

U.S.Motor Vehicle Safety Standard 119 covers tyres for trucks, buses, motorcycles, and all other types of motor vehicles (except cars) using public highways.

The uniform tyre quality grading system is intended "to assist the consumer to make an informed choice in the choice of motor vehicle tires.." The U.S.Department of Transportation (DOT) has listed the following three characteristics of the tyre in determining its quality level.

treadwear
traction (or wet grip)
high speed performance

The dispute between DOT and the tyre manufacturers represented by the Rubber Manufacturers' Association RMA over acceptable test methods has dragged on during the past few years. It hinged on the definition of the standard tyre. DOT has now proposed that representative tyres of the particular type made by the industry may be used as standards. The RMA has counter suggested the use of an "intermediate" tyre as standard.

European countries have decided to use only one laboratory test, the high speed capability test, in grading tyres.

Brenner (135) discusses the problems involved in developing performance tests related to consumer needs.

.4 Non-destructive Testing of Tyres

The non-destructive testing of tyres permits the use of these methods in routine tyre sorting and grading.

An X-ray fluoroscopic technique with an electronic and optical magnification procedure known as the image intensification system has been used for some time mainly for detection of flaws in tyres. X-ray inspection is stated to have been particularly important in the manufacture of radial ply tyres.

Ultrasonic studies on tyres have shown that tyre trea separation occurs through additional heat history. The use of ultrasonic techniques in detecting faulty tyre carcass fabric splices, porosity, incipient separation of tread-carcass interface and variations in tread thickness are described by Halsey (136a).

Split laser beams are used in the holography technique for detecting flaws and deformities in tyres. This technique depends on the fact that any flaw or deformity in a tyre causes surface irregularities which though imperceptible to the naked eye can be detected by the use of laser beams. Holography has been described as an optical technique for producing three-dimensional images by using split laser beams to produce, after reflection from the observed object and a reference mirror, an interference pattern.

.5 Laboratory Testing of Rubber Compounds

.5.1 Laboratory Testing of processing characteristics of rubber compounds.

.5.1.1 The instrument most widely used for the characterisation of processing and curing qualities of rubber compounds is the Monsanto Oscillating Disc Rheometer. (ASTM specification D2705-68). A biconical disc oscillates in a small arc of about 1^{o} within the rubber compound, and the resistance of the rubber compound to this oscillation is recorded. The rotor in the Mooney viscometer rotates fully. The Mooney instrument while useful for measuring scorch characteristics does not provide information on the characteristics of the rubber compound once vulcanisation begins. The Rheometer helps to predict optimum cure times and reversion characteristics.

6.5.1.2 The Brabender Plasticorder has received attention recently as an instrument for evaluating the processing characteristics of rubbers, particularly natural rubber (137, 138, 139) Basically it consists of a small mixing chamber equipped with mixing blades and a sensitive torque recorder. The instrumental therefore performs the dual role of mixer and viscometer. Jacket temperatures and rotor speeds are adjustable. The torque and temperature are recorded. A typical plasticorder chart is shown in Fig. 6.1. The degree of dispersion and the power consumption can be assessed from this chart.

Studebaker and Beatty were able to correlate points on the plasticorder chart with progress of the rubber mixing operation in a Banbury mixer. Averill (138) describes a method to determine the curing characteristics of natural rubber using the Brabender Plasticorder and an oscillating disc rheometer. He claims that the test is more reproducible and more sensitive to differences in properties than stress-strain methods. Dove, Howard and Thrall (137) describe

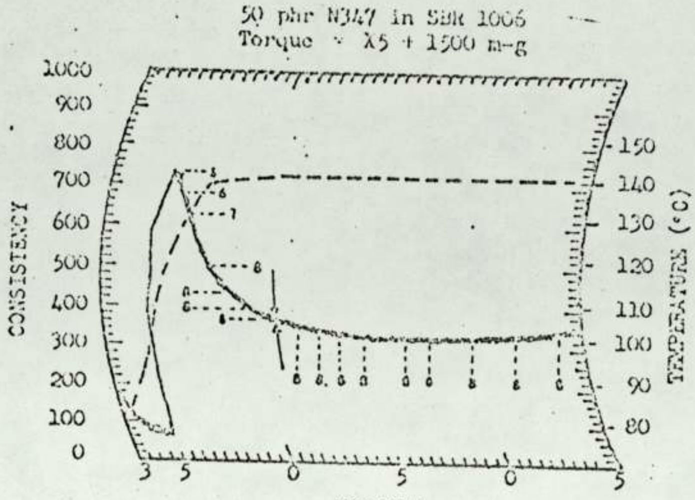


Fig. 6.1 Brabender Plasticorder:
Variation of Consistency and Temperature of rubber compound with time of mixing.

the development of a test where the behaviour of sample of unmasticated natural rubber in a Brabender Plasticorder is used to predict its processing characteristics.

6.5.1.3 The Garvey Die Extrusion Test (ASTM D2230-68) is used to determine the extrudability of unvulcanised elastomeric compounds. The extrusion behaviour of the test compound is compared with that of a standard compound given. The rate of extrusion through a standard die and the characteristics of the extrudate including die swell are measured by this method.

6.5.2. Laboratory testing of vulcanised tyre compounds

6.5.2.1. Tensile properties

The tensile properties of tyre compounds are evaluated for quality control and development work. Three properties are generally determined, the tensile strength (or tensile stress), the elongation at break and the modulus at 300 per cent elongation (more accurately the stress at 300 per cent elongation). Harris (140) has pointed out that the comparison of (static) tensile properties becomes less misleading if the following limitations are borne in mind.

1. First of all, it has already been stated that no known relationship exists between the tensile properties as they are commonly run under standard conditions and the end use performance of a part made from that polymer. In some rather rare instances, the time, temperature and environment of the application are similar enough to the conditions of testing to allow the data to be used for engineering purposes. These cases are rare indeed.
2. Secondly, the standard tensile properties with the exception, perhaps, of the modulus of elasticity, are most useful only for identification, specification and quality control purposes. This is particularly true of

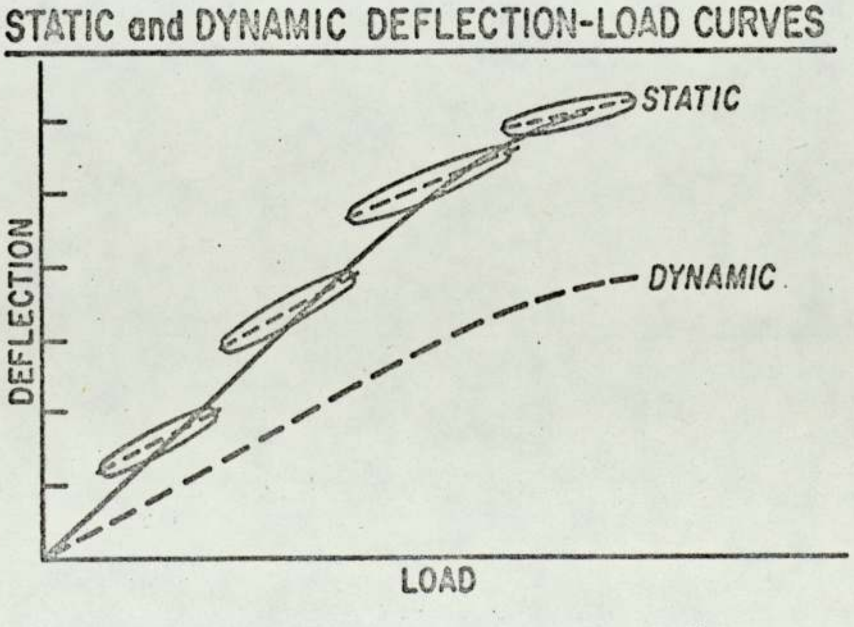
the ultimate stress and strain which reflect most accurately the quality of the polymer.

3. Finally, the modulus of elasticity is a reliable means of measuring the stiffness of a material. It is not as sensitive to changes in testing speed in many instances, particularly in the range of speeds used in standard tensile testing.

(The modulus of elasticity may be used with more freedom when comparing materials than can other tensile properties due to its relative insensitivity to speed and small temperature changes.

Beatty and Studebaker (141)point out that the dynamic stiffness of a rubber compound is more important than the static stiffness in many applications. They describe the use of the Roelig machine and the Goodrich flexometer to measure this property. Their figure showing what is happenging when dynamic stiffness measurements are being made is reproduced. Figure 5.2.

FIGURE 5.2



6.5.2.2. Hysteresis

Hysteresis has been described as the energy loss per cycle or $\frac{\Delta W}{W}$. Beatty and Studebaker point out (141)that tyre components are a compromise to give the lowest hysteresis with the other desirable properties of carcass durability and treadwear. Hysteresis is responsible for the temperature rise in a rubber compound on flexing. Two methods are available for testing hysteresis characteristics of a rubber compound. The Roelig dynamic tester is a non-resonance tester where the frequency and amplitude of vibration as well as the test temperature can be varied. Hysteresis is expressed as the tangent of δ, the angle the restoring force is out of phase with the impressed force. In the Goodrich Flexometer which was used in our tests the static load and the angle of vibration can be varied. Frequency is 30 cycles/ second. Hysteresis is measured as the temperature rise, measured at the base of a 0.7 in. diameter x 1 in. high cylinder. The temperature rise is a function of the amplitude of vibration, the static load and the dynamic modulus of the rubber compound being tested.

6.5.2.3. Laboratory methods for determining abrasion resistance of tyre tread compounds

All laboratory abrasion tests consist of wearing the test sample against a sharp abrasive surface and expressing the results as an index indicating the wear of the test compound relative to the wear of a standard tyre tread compound. One of the persistent problems has been the variation in the samples of the standard compound prepared in different laboratories, as shown in round-robin studies.

Bulgin and Walters identify two types of laboratory abrasion tests for rubbers as (a) those in which the rubber sample is pressed against carborundum paper of defined grade and (b) those in which the rubber test piece is a moulded circular disc that rotates in contact with a rotating abrasive disc.(125)

(a)(i) In the du Pont abrasion tester two rubber samples are pressed against a rotating disc of silicon carbide paper. The abrasive surface of the paper is easily clogged by abraded particles and the narrow circular area of usage wears off easily. The results from this test correlate poorly with service performance and are easily affected by the presence of waxy blooms. It is still used for process control work purposes in some laboratories.

(a)(ii) The German DIN Abrasion Tester has the test piece moving along a carborundum paper wrapped round a large rotating drum. This arrangement reduces the clogging and wear of the abrasive paper.

(b) The most commonly used laboratory abrasion machine for tyre tread compounds is the Akron Angle Abrader. The test piece is a moulded rubber disc and runs against a carborundum wheel. The angle at which the test piece is held can be adjusted but is usually 15°. The discernibility of the test results is low and the correlation with service performance doubtful.

Cotten and Dannenberg (142) report that the sensitivity and accuracy of the Akron Angle Abrasion Test was appreciably improved when SBR with 30 p.h.r. black loading was used and that the results correlated better with road test results than the ASTM NR formulation, when evaluating the reinforcing effects of carbon black. The Lambourn machine works on the same principle as the Akron.

All these tests examine only the resistance of tyre tread compounds to cutting and tearing by sharp asperities. Fatigue wear is low.

Beatty and Studebaker (141) state that the Pico Abrasion Test (ASTM D2228-63T) gives results that correlate closest to service performance. This method uses the scraping action of tungsten carbide blades in the form of truncated 60° prisms with a flat edge rotating upon the rubber test piece under load. A special dust is used to coat the abraded dust and make it non-sticky. The results of this test are shown to correlate well with service performance under conditions of high severity. (Cotten and Dannenberg. (142) Tyre Science and Technology Vol.2 No.3 August 1974 p.211.) Under conditions of low and medium severity, the latter being the most commonly encountered in actual service, however, the correlation is poor. Abrasion in this test is attributed mainly to the frictional forces developed between the flat surface of the blades and the rubber.

The advantages claimed for the PICO abrasion test are that the severity of the test conditions can be adjusted. The severity of the test at ambient temperatures is controlled by (1) the type of dusting powder (2) the sharpness of the blades (3) the speed of rotation of the knives and (4) the weight on the knives.

It was realised early that the lack of correlation between laboratory abrasion results and service performance was due to the inability to reproduce the range of road and other service conditions. The limitation of laboratory abrasion results have been discussed by Bulgin and Walters (125). They point out that in order to limit the time of testing the wear process is accelerated to obtain measurable loss in a limited time. This is done by having sharp carborundum surfaces, high loads and high slip velocities. Such conditions are hardly ever encountered in service. Another problem of laboratory abrasion tests is that the abraded debris tend to readhere to the test piece or to clog the abrasive wheel. Tackiness of the test sample or a wax bloom will also clog the abrasive wheel. Use of a dusting powder to prevent readherence of abraded material will affect the abrasive process, thus introducing another variable into the experiment.

the heat ageing characteristics of the rubber compound.

Martin and Biddison (143) are doubtful if the same wear mechanism prevails for different polymers, even for the same road surfaces and driving conditions.

6.5.2.4. Laboratory tear testing of rubber compounds

1. The usual laboratory method of testing the resistance of rubber compounds to tearing is the crescent tear test. A crescent shaped test piece is punched out from a tensile slab and a nick of 0.02 in. made accurately by moving the test piece held in a sample holder mounted on rails over a mounted blade. The nicked specimen is then stretched to rupture on a tensile testing machine.

The results depend on stress concentration in the sample and are greatly influenced by the dimensions of the nick.

This test however shows poor correlation with performance of products made with the compound. It also fails to show any marked differences between rubber or vulcanisates thought to differ in intrinsic tear strength. It has been point out (144) that the main reason for this confusion and lack of discrimination in this tear test is the direct influence of compound modulus on measured tear strength.

The reasons for poor correlation between laboratory abrasion tests and service wear have become clearer with the greater understanding of the process of tyre abrasion. Three mechanisms have been postulated to account for tyre abrasion: (1) Cutting and tearing of the tyre tread rubber (micro-cutting) by sharp asperities on the road surface. This is a purely mechanical process. Abrasion on rough surfaces is therefore thought to be a cutting or catastrophic tear process. (2) Fatigue failure of the tread rubber by local frictional forces generated by repeated deformation of the rubber at the surface by smooth projections on the abrading surface. Bulgin and Walters explain that these frictional forces can cause small tears in the rubber similar to the incremental tears of rubber in fatigue processes. (3) "Roll formation" on the surface rubber with rough abradant surfaces. This has been termed "frictional wear". Here rubber sliding over a smooth surface with a high coefficient of friction is peeled back into rolls.

It is their considered opinion that abrasion is caused by the operation of all three mechanisms working in relative proportions dependent on the nature of the abradant surface. Evstratov and others (160), for instance state that when lorry tyres are tested under relatively mild conditions fatigue wear predominates. They also point out that the abrasion resistance of tyres operating on relatively smooth surfaces at high speeds and high temperatures is considerably affected by

2. <u>The trousers test piece test</u>

NRPRA workers (145), (146) have shown that the resistance to tearing is determined by a parameter called the tearing energy. It has been defined as the energy released by a unit increase in crack area with the external forces doing no work. It has been defined as the energy released by a unit increase in crack area with the external forces doing no work. It has been shown to be independent of the sample shape.

For the trousers tear specimen (see figure 6.1) the tearing energy or tear strength is shown to be

$T = 2\lambda F t^{-1} - wW$ - Equation 1.

where T = tear strength in lb. per inch thickness (per unit torn)

λ = extension ratio in the "legs" of the test specimen

F = force applied to ends of test piece (in pounds)

W = total width of test piece

t = thickness

W = strain density in legs of test piece.

It has been shown that for certain vulcanisates if w is chosen large enough the elongation of the legs is minimal ($\lambda \simeq 1$) and W is essentially zero. Then

$$T = 2\ F/t \qquad \text{Equation (2)}$$

Equation 2 has been used to calculate the tear strength. Veith (144) however points out two serious deficiencies in determining the tear strength by this method. Firstly there is appreciable leg extension (λ 1) even if w is chosen quite large. Secondly, knotty tears can develop and tearing could occur in a lateral direction down one leg of the test specimen. Equations (1) and (2) are based on the tear progressing down the central axis of the test piece. Veith therefore suggests the use of a test specimen with a longitudinal groove of specified dimensions and the reinforcement of the legs of the test piece to ensure tear occurring down the groove.

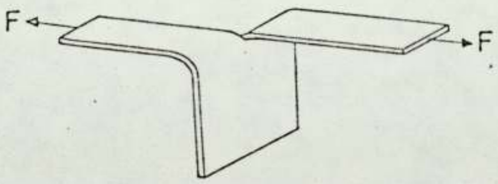


Fig. 6.1. The trouser tear test piece

6.5.2.5. Laboratory flex tests for rubber compounds

6.5.2.5.1. The most commonly used laboratory method of fatigue testing is the de Mattia flexion test. The test pieces are rectangular slabs with a semi-circular groove across their middle. As the samples are repeatedly flexed cracks appear in the grooves and grow as flexing proceeds. The degree of cracking is estimated visually against photographs given in the standard.

Derringer (147) has described a statistical method of analysing flex cracking results with the aid of a computer.

Crack growth is estimated on the basis of the number of flexing cycles required to increase the length of a standard cut, made with a piercing tool of specified dimensions, by 2 mm. and 6 mm.

The limitations of the de Mattia flex-fatigue method have been stated as follows:-

a) The strain acting on a sample of rubber cannot be measured readily and varies in the sample.

b) Reproduction of the same strain condition in each sample is difficult.

c) If the samples have different moduli, it is not possible to produce the same stress in each for comparative purposes.

d) The results depend on the judgement of the operator and are therefore subjective. Besides, the operator has to be in constant attendance.

For these reasons reproducibility can be low.

de Mattia results are not satisfactory probably because the strain produced in the samples is difficult to adjust and almost impossible to measure.

6.5.2.5.2. The Wallace-NRPRA Flexing Machine has four horizontal rows each of six 'grips' on either side. Each grip consists of a pair of pulleys, side by side, free to rotate. Ring specimens are used as test pieces,each ring passing over 4 pulleys to reduce friction problems. The lower sample clamps rise approximately 4 mm. when a vertical stress is applied to the sample and in doing so operate microswitches which trigger individual electrical impulse counters. Failure of the sample by rupture automatically stops the appropriate counter. (149)

For the Wallace NRPRA tester are claimed speed and quietness of operation, objectivity of results, the ability to directly compare the fatigue properties of rubbers of different kinds under specified strain deformations, deformations, or at constant strain energy, ease of operation and lack of need for surveillance.

6.5.2.5.3. Monsanto Fatigue Machine

The Monsanto Fatigue Tester operates on the same principle as the NRPRA Fatigue Tester. (148)

Dumbell samples are subjected to repeated cyclic extension at 100 r.p.m. The sample is strained for half a cycle using a cam designed to give constant acceleration and deceleration. The strain is altered by changing cams. Fatigue resistance can be estimated on this machine either at constant strain or constant strain energy. Strain energy is the work done in extending the sampel and is taken as the area in the graph under the stress-strain curve. The use of strain energy enables absolute comparisons to be made on samples of different moduli.

Data has been quoted to show that while the de Mattia method discriminates well between unprotected and stocks protected with antidegradants but not between stocks protected with antidegradants, the Monsanto Fatigue test discriminates between different antidegradants as well.

For the Wallace NRPRA tester are claimed speed and quietness of operation, objectivity of results, the ability to directly compare the fatigue properties of rubbers of different kinds under specified strain deformations, or at constant strain energy, ease of operation and lack of need for surveillance.

6.5.2.5.4. In the Avon fatigue tester the dumb-bell test peices are held between the perimeters of two linked plates, one horizontal and are inclined. "As the plates rotate together the samples are subjected to a sinusoidal strain cycle with a frequency of 97 cycles/min. whose amplitude and minimum strain can be set by adjusting the tilt and separation of the plates.

NRPRA Method for cut-growth testing

Lindley and Lake (38) identify the two basic mechanisms of cut growth as

(1) Mechanico-oxidative cut growth, due to mechanical rupture at the tip of a flow, which is considerably enhanced by the presence of oxygen.

and

(2) Ozone cut growth, due to primarily chemical scission.

They use a tensile strip test piece with a cut on its edge for determination of crack growth. The tearing energy T for this test piece is given by

$$T = 2kWc$$

where W is the strain energy per unit volume and c is the length of the cut in the unstrained state. k varies slightly with strain but may be taken as 2, so that

$$T = 4Wc$$

The strain energy W is the area under a tensile stress-strain curve or a load-deflection curve.

The advantage of using this method ties in the crack growth resistance is expressed in terms of the tearing energy which is independent of the form of the test piece used and is therefore a basic property of the material.

In this method tensile strips are punched from moulded tensile slabs and their load-deflection characteristics noted. A razor cut about ½ mm. long is made in the middle of one edge and set up at the required maximum extensio and cycled on the test machine. The length of the cut is measured with a travelling microscope during the test. The rate of growth of the crack de/dn is determined from the difference in cut length divided by the number of cycles between two readings. This rate is referred to the tearing energy T, calculated from the average of the two cut lengths and the strain energy density at the maximum strain of the cycle using equation (1).

Andrews (150) questions the value of these "surface fatigue" tests on the grounds that in such tests "the conditions of stress and strain in the region of interest (i.e. at the surface) must be derived from bulk deformations and bending stresses on the assumption of a Hookeau elasticity and are therefore only known approximately".

7. AN EXERCISE ON COMPUTER - ASSISTED COMPOUNDING OF TRUCK TYRE TREADS BASED ON NATURAL RUBBER

7.1 Introduction

The classical method of studying the effects of varying the amounts of different ingredients in a rubber compound consisted of varying each of them in turn while holding the others constant. The summation of the individual effects was thought to give the total effect of varying the levels of the several compounding ingredients investigated. This method suffers from the drawback of the expense of carrying out a large number of experiments or the lack of information provided on the interactions of the different factors varied. The number of experiments needed to find these interactions is several times larger than the number of initial experiments. For example to find the effect of varying 4 ingredients at 3 levels without allowing for interaction effects 12 experimental compounds would have to be evaluated. To allow for the possibility that the effect of a given change in amount of one ingredient may depend on the amount of another ingredient present (second order interactions) the number of experimental compounds needed would be 81.

Computer aided compounding using the technique of regression analysis is more economical and more informative. For example it is possible by evaluating 27 formulations where 4 ingredients are varied at 3 levels to predict within the limits of the experimental region the properties of any selected levels and combinations of the compounding ingredients investigated. Derringer (151) has explained that computer compounding is merely the statistical analysis of data collected to meet the specifications of a statical experimental design. He points out that "the computer merely does the necessary computations and nothing else". The value of the results of a computer compounding exercise therefore depends on the statistical design of the experiment and on the figures fed into the computer.

Derringer lists the important considerations involved in computer compounding as follows:-

1) Selection of an experimental design.
2) Evaluation of the results of the statistical analysis.

and 3) Intelligent use of the results.

.2 Previous Use of the Computer in Rubber Compounding

Reported examples of the use of the computer to assist in the formulation of rubber compounds include the work of

(1) Bertsch on Viton A-HC compounding (152)

(2) Weissert and Cundiff on BR/NR blends for Truck Tyres (153)

(3) Buckler and Kristensen on polybutadiene compounds (154)

(4) Hartmann and Beaumont on passenger car tyre tread compounds (155)

(5) Pyne and Kristensen on medium quality mechanicals compounds for automobile compounds (156),

and (6) Bentley, Gee and Thomson on heat resistant nitrile rubber compositions, non-black fillers in EPDM compounds and reversion resistant natural rubber compounds. (157)

The technique used in computer aided compounding is regression analysis. The relationship between any one property or other attribute, like cost, of a rubber compound and its composition or processing conditions is expressed by means of a mathematical equation, the regression equation. This mathematical equation (or model) is derived from experimental data and is therefore empirical. Its usefulness will depend on the accuracy of the experimental results from which it is calculated. Derringer stresses this point and warns against expecting the computer to do more than mere calculations. The regression equation is then used to calculate the value of any property for any combination of levels of composition (or processing conditions as the case may be) within the limits used in the experiment.

The functions performed by the regression equation have been listed as follows by Bertsch (152):

1. It allows for an efficient and economical method for gathering data.
2. It permits interpolation of all possible combinations of the variable levels.
3. It allows, through the use of this economic interpolation, a very complete graphical analysis of a system.

4. It allows a simultaneous study of several properties either mathematically or graphically.

5. It provides through this simultaneous study of properties an efficient method of arriving at some balance of properties necessary for a particular set of service conditions.

The regression equation is derived from experimental data and is therefore empirical. It has no fundamental theoretical basis. Pyne and Kristensen (156) describe the regression equation as "a practically useful predictor rather than the expression of a basic causal relationship".

7.3 An exercise on Computer-assisted Compounding to modify formulations of Truck Tyre Treads based on Natural Rubber

7.3.1 Context of exercise

7.3.1.1 Control Sample

For this exercise a natural rubber based truck tyre compound of a type some knowledge of whose performance is available to the author was selected. The control sample used N-oxydiethylene benzthiazyl sulphenamide (Santo-cure MOR) as accelerator and ISAF black as reinforcing agent. Features of the control formulation relevant to this exercise are listed below, amounts being expressed in parts by weight.

Smoked Sheet RSS 1	100.0
Antioxidant PBN	0.5
N-Nitroso-diphenyl amine	0.7
ISAF black	45.0
Dutrex R	10.0
Santo cure MOR	1.3
Sulphur	1.8

7.3.1.2 Experimental Compounds

7.3.1.2.1 Accelerator.

It has been found that Santo-cure MOR [N(OXYDIETHYLENE)- benzthiazyl sulphenamide) decomposes rapidly under the prevailing conditions of temperature and humidity in Sri Lauka. The delayed action effect of the material is progressively reduced as decomposition proceeds. 6 months is a fair estimate of the maximum safe period of storage at the factory. Santo-cure NS (N-tert. butyl-benzthiazyl sulphenamide) which is a much more stable material and whose processing safety lies between those of Santo-cure (cyclo hexyl benzthiazyl sulphenamide) and Santo-cure MOR was selected as accelerator for these experiments. Its other characteristics are similar to those of the other two sulphenamides mentioned.

.3.1.2.2 Carbon black. The use of certain shipments of ISAF black at the Sri Lanka tyre factory has in the past contributed to the considerable problem of scorching experienced there. Besides, supplies of ISAF black have sometimes been difficult to get and recourse has had to be made to importing HAF black from India, where ISAF is not made yet. HAF black has posed no processing problems.

ISAF black is stated to give 3 to 7 per cent improvement in treadwear over HAF and slightly better resistance to tread cracking (Drogin) (158). It is hoped that the use of different loadings of HAF black (with suitable adjustment of oil content to maintain hardness at the same level) may avoid this loss of treadwear resistance.

HAF black was therefore used in these trials.

7.3.1.2.3 Retarder.

N-Nitroso-diphenylamine is known to cause porosity in rubber compounds and also to affect the cure rate. PVI (N-cyclohexyl-thiophthalimide) a more effective retarder which does not suffer from these drawbacks was therefore selected as retarder for the experimental compounds.

7.3.2 Selection of variables

The following factors were considered as possible variables for study in this exercise.

1. the grade of natural rubber
2. the amount of HAF black
3. the amount of processing oil
4. the amount of accelerator
5. the amount of sulphur
6. the amount of retarder

7.3.2.1 Grade of rubber

Smoked sheet is normally used alone or blended with crepe rubber, usually brown crepe, in truck tyre tread compounds. There are differences in price between smoked sheet and crepe rubber and also between the grades of each of these two types. The prices and price differences fluctuate. The grading of smoked sheet and crepe rubber is done visually, and has no technological basis. The lower grades of smoked sheet and crepe have been reported to be suitable for use in tyre tread compounds. The price differential between RSS 5 and RSS 1 can be as much as 15 per cent and represents a possible means of saving on material costs, and therefore a fit subject for study here.

However, the grade of natural rubber is a qualitative factor and there is no parameter that can be estimated quantitatively in deciding the grade of rubber. The design of this experiment allows quantitative variations but not qualitative ones in the factors under study. Besides, the variations in technological properties of the rubber can be greather within grades than between grades.

The cost of raw materials, it may be pointed out, represents the largest single factor in the cost of manufacturing a tyre and generally outweighs all the other cost factors combined.

.3.2.2 Carbon Black

HAF black having lower reinforcing properties than ISAF black may have to be used at higher loadings or with less oil than ISAF black in tyre tread compounds. For the Sri Lanka tyre factory it would be useful to have formulations with HAF black as it is used when supplies of ISAF black are not available. As already stated, the use of HAF black obviates the troublesome scorching problems associated with ISAF black.

7.3.2.3 Processing Oil

The use of varying amounts of black affects the properties of the tread compound. It therefore becomes necessary to change the quantity of processing oil used. The advisability of using fixed amounts of oil with each level of black loading was considered so that all mixes should be of essentially the same hardness. This idea was not accepted as the optimum quantity of oil corresponding to each level of black loading in natural rubber is not known for certain. The use of different amounts of oil for each black loading in this exercise enables us to try to find the optimum levels of oil to be used.

It is necessary to point out that the cost relation between processing oil and natural rubber and between carbon black and natural rubber applicable to countries in Europe does not apply in rubber growing countries like Sri Lanka. To such countries oil and carbon black are imports and rubber an export commodity. The relationship is not a static one with oil and black prices rising and natural rubber prices fluctuating.

7.3.2.4 Accelerator

The control compound has a relatively high proportion of accelerator (1.3 phr) and a low proportion of sulphur (1.8 phr). Monsanto Chemical Company the manufacturers of this accelerator (Santo-cure MOR) recommend only 0.6 parts of accelerator with 2.0 parts of sulphur.

Owing to the tendency of Santo-cure MOR to decompose rapidly under tropical conditions liberating MBTS which promotes scorching in the tread compounds, an alternative accelerator was sought. Santo-cure NS (N-tert. butyl-benzthiazyl-sulphen-amide) was selected for this experiment because of its greater storage stability. Its delayed action effect is intermediate between Santo-cure and Santo-cure MOR, but the speed of vulcanisation and the vulcanisate properties are similar to those of Santo-cure MOR. The use of Santo-cure NS with a sufficient amount of retarder to suppress scorching tendencies therefore appears to be an attractive alternative to Santo-cure MOR.

7.3.2.5 Sulphur

The advisability of having the amount of sulphur tied to the amount of accelerator as shown below was considered.

Santo-cure NS	0.8	1.3	1.8
Sulphur	2.3	1.8	1.3

These would have been arbitrary relative proportions of the two materials. Besides, as already pointed out, the combination of accelerator and sulphur in the control compounds is different from those generally used in tyre tread compounds. It was therefore thought preferable to have the amounts of accelerator and of sulphur as two independent variables.

7.3.2.6 Retarder

The retarder used in the control samples is N-Nitroso-diphenyl amine (NDPA). This material decomposes at processing temperatures tending to cause porosity and influences the vulcanisation reaction. These tendencies would be more pronounced with Santo-cure NS which would need more retarder since it has less delayed action than Santo-cure MOR.

Santo-gard PV1 (n-cyclohexyl-thiophthalimide) is a much more effective retarder; 0.25 parts of PV I are claimed to increase the scorch time considerably more than 1.0 part of NDPA. It does not cause porosity and does not affect the vulcanisation reaction.

Being so effective, the level of PVI required in these compounds will be small and very unlikely to affect the levels of cured properties. It is therefore considered unnecessary to vary the amount of PVI. If necessary, small adjustments to the level of PVI to obtain variations in processing safety can fairly confidently be made in subsequent single variable experiments.

For reasons explained above the following 4 factors were varied in this exercise.

1. The amount of the HAF black used.
2. The amount of processing oil.
3. The amount of accelerator (Santo cure NS)
4. The amount of sulphur.

Compounds

As already mentioned, it was decided to use ISAF black and Santo-cure MOR in the control samples; and HAF black and Santo-cure NS in the experimental ones. Since N-nitroso-diphenyl amine the retarder used in the control is replaced by Santo gard PVI in the experimental compounds an additional compound No. 2 was introduced identical to the control compound except that it has PVI as retarder. The behaviour of this compound relative to the control would indicate what effects the use of PVI in place of N-nitroso-diphenyl amine has on the experimental compounds. Another difference between the control and experimental compounds is that the PBN in the former is replaced by Flectol H in the latter because of the general move in the rubber industry away from PBN.

3.3 Design of Experiment

In our experiment, the amounts of 4 compounding ingredients in a truck tyre tread formulation based solely on natural rubber, are varied at 3 levels. Weissert and Cundiff (153) ~~(2)~~ had studied the effects of varying 3 compounding ingredients at 5 different levels in a truck tyre tread formulation based on a 50/50 blend of natural rubber and polybutadiene. Using a centre composite design of experiment, they studied the effects of varying the 5 ingredients at the 5 levels by testing only 27 experimental compounds.

As will be seen later, this is the same number of experiments carried out in the present exercise to study the effects of varying 4 compounding ingredients at only 3 levels.

The stages in our experiment were:-

1. Deciding the range of variation for each of the variable factors, i.e. of the 4 compounding ingredients selected.
2. Statistically designing the experiment and selecting 27 experimental formulations from a possible 81.
3. Mixing, vulcanizing and testing of the experimental controls and 3 repeat batches of the control compound. Stated in statistical terms, determining properties (Y values) of mixes with the variables $X_1 - X_4$ at extreme and mid-range values.
4. Deriving quadratic response equations (using the test results with a regression analysis computer program) relating the tested properties to the variations in compound composition. The general quadratic equation shown below is used as the model.

$$
\begin{aligned}
y = {} & A_o + A_1x + A_2x_2 + A_3x_3 + A_4x_4 + A_{11}x_1^2 + A_{22}x_2^2 \\
& + A_{33}x_3^2 + A_{44}x_4^2 + A_{12}x_1x_1 + A_{13}x_1x_3 + A_{14}x_1x_4 \\
& + A_{23}x_2x_3 + A_{24}x_2x_4 + A_{34}x_3x_4
\end{aligned}
$$

5. Testing the fit of the results to the response equations and examining significance levels of coefficients introduced at each step.

6. Calculation of results predicted for the experimental compounds by equations in which the introduction of coefficients is stopped at the step giving the F value (variance ratio) with the highest level of significance.

7. Utilisation of this data to determine the best value of one property e.g. minimum compound cost, compatible with specified levels of other properties.

This exercise was planned to use the step wise regression method using a full quadratic model on 4 variables.

The range of levels was selected to include all levels that appeared likely to be useful. The levels of the variables used in the experimental mixes are shown below:-

Table 7.1

Levels of Variables used in Experimental Mixes

	Variable	Levels used (Experimental units		
Symbol	Nature	-1	0	+1
X1	Parts of HAF black	35	45	55
X2	Parts of Dutrex R processing oil	1	8	15
X3	Parts of accelerator Santo cure NS	0.4	1.0	1.6
X4	Parts of sulphur	1.5	2.1	2.7

3^4 i.e. 81 combinations are involved in a factorial design with 4 factors being varied at 3 levels. A factorial design is considered to give equal levels of confidence in the results over the whole range of compositions covered by the experiments. A bare minimum of 16 experimental mixes have to be tested to statistically predict the properties the remaining 65 compounds and of any other compound within the boundaries of the experimental region. The degree of confidence in such a prediction would be low. Pyne and Kristensen and Beaumont and Fletcher found that 27 suitably selected experimental compounds are typically required to sample the experimental region adequately. A design for such selection is called a one-third fractional factorial design.

A one-third fractional factorial design was chosen for this exercise, with each of the four variables being examined at three levels. The 27 combinations of the levels of the 4 variables under investigation that were studied in this exercise are those represented by the shaded squares in the diagram below.

investigation that were studied in this exercise are those represented by the shaded squares in the diagram below.

		Parts of Accelerator-Santocure NS								
Parts of HAF Carbon Black p.h.r.	Parts of Oil (Dutrex R) p.h.r.	0.4			1.0			1.6		
		Parts of Sulphur-phr								
		2.7	2.1	1.5	2.7	2.1	1.5	2.7	2.1	1.5
35	1	▨					▨		▨	
	8		▨		▨					▨
	15			▨		▨		▨		
45	1			▨		▨		▨		
	8	▨					▨		▨	
	15		▨		▨					▨
55	1		▨		▨					▨
	8			▨		▨		▨		
	15	▨					▨		▨	

The differences in the compositions of the compounds used in the experiment are shown in Table 7.2

TABLE 7.2 Composition differences between compounds used in the experiment

Sample No.	1* CJ DD	2^x Y	3 H	4 B	5 HH	6 AA	7 EE	8 N	9 S	10 U	11 G	12 D	13 K	14 F	15 JJ
Black	ISAF 45	ISAF 45	35	35	35	35	35	35	35	35	35	45	45	45	45
Oil	10	10	1	1	1	8	8	8	15	15	15	1	1	1	8
Accelerator	MOR 1.3	MOR 1.3	0.4	1.0	1.6	0.4	1.0	1.6	0.4	1.0	1.6	0.4	1.0	1.6	0.4
S	1.8	1.8	2.7	1.5	2.1	2.1	2.7	1.5	1.5	2.1	2.7	1.5	2.1	2.7	2.7

*(1) Control ISAF 45 MOR 1.3 Oil 10.0 S1.8 NDPA 0.7

x(2) ISAF 45 MOR 1.3 Oil 10.0 S1.8 PVI 0.2

Sample No.	16 A	17 T	18 P	19 CC	20 FF	21 BB	22 GG	23 W	24 E	25 L	26 V	27 Z	28 M	29 R
Black	45	45	45	45	45	55	55	55	55	55	55	55	55	55
Oil	8	8	15	15	15	1	1	1	8	8	8	15	15	15
Accelerator	1.0	1.6	0.4	1.0	1.6	0.4	1.0	1.6	0.4	1.0	1.6	0.4	1.0	1.6
S	1.5	2.1	2.1	2.7	1.5	2.1	2.7	1.5	1.5	2.1	2.7	2.7	1.5	2.1

7.3.4 Characteristics of Compounds for Evaluation

The following characteristics of the experimental and control samples were selected for evaluation.

1. Relative volume cost
2. Rheometer scorch time at 140°C
3. Minimum Rheometer torque value
4. Maximum Rheometer torque value
5. Time to reach 90 per cent of maximum Rheometer torque
6. Relative density
7. Tensile strength
8. Percentage elongation at break
9. Modulus at 300 per cent elongation
10. Crescent tear strength
11. Unaged hardness (micro hardness tester)
12. Aged hardness
13. Wallace Multi range hardness (unaged)
14. Garvey die extrudate - Total rating
15. Garvey die swell
16. Akron abrasion resistance
17. Goodrich heat build-up
18. Lupke Resilience
19. Compression set
20. Flexing
21. Crack growth resistance.

Compound costs were calculated from determined specific gravity values and the ingredient values listed in the table below - Prices are quoted in rupees Sri Lanka tyre factory store, October 1974.

TABLE 7.3

Ingredient prices in (Sri Lanka) rupees ex tyre factory store, October 1974.

Ingredient	Rupees per lb.
Rubber, R.S.S. 1	1.63
PBN	12.24
Flectol H	11.87
N-Nitrosodiphenyl amine	12.04
Santogard PVI	31.31
ISAF black	3.19
HAF black	2.75
Dutrex R	1.75
Santocure MOR	18.44
Santocure NS	12.65
Sulphur	1.12

7.3.4. EXPERIMENTAL

Batches of each of the experimental compounds and three batches of the control compound were mixed to the same 5 minutes schedule in a size B laboratory Banbury internal mixer, capacity about 1130 ml. Accelerator, retarder and sulphur were added on the mill.

From the Monsanto Rheographs of these samples at 141°C) were obtained their scorch times, minimum and maximum torque values and the time to reach 90 per cent of the maximum torque. This last item of information was used to decide on the cure times of the test pieces. The cure times are shown below:-

Samples	Time of cure at 143°C (in minutes)
1(a), 1(b), 1(c), 2, 4, 5, 8, 10, 11, 13, 14, 16, 17, 19, 20, 22, 23, 25, 26, 28 and 29	20 minutes
7 and 9	25 minutes
3, 6, 12, 18, 21 and 24	30 minutes
15 and 27	35 minutes

The following samples were vulcanised:-

Slabs for punching tensile and tear test pieces

Akron Abrasion discs

Cylinders for heat build-up test (Goodrich Flexometer) de Mattia flexion test pieces

Discs for determination of Lupke resilience

Discs for determination of Wallace multi range hardness

.3.4.1 Testing

The following tests were carried out and the following determination made:

1. Monsanto Rheometer tests. Samples were tested on the Monsanto Rheometer Model MPV at 141°C 100 cycles per minute anc 3 arc of oscillation of rotor to obtain the following information:

   a. Minimum torque before vulcanisation (M_L)

   b. Maximum torque of vulcanised specimen (M_H)

   c. Scorch time taken as time for a 2 unit (inch lb) rise above minimum torque value

   d. Time to reach 90 per cent of cure, calculated as

$$(0.9(M_H - M_L) + M_L$$

A sample of the control compound and samples of experimental compounds with limiting combinations of accelerator and sulphur were run for 5 hours each to test their reversion characteristics.

2. Garvey die extrusion test.

The extrusion experiments were carried out using a Francis Shaw 1" warm-feed extruder and a No. 1 Garvey die according to ASTM D2230-68 under the following conditions:

barrel temperature	70 ± 10°C
head temperature	110 ± 15°C
die temperature	110 ± 15°C
screw speed	80 r.p.m.

The compounds were pre-heated for 4 min. at 50°C on a two-roll mill. The length of extrudates were measured after standing overnight. Extrudate characteristics of swelling and porosity, sharpness and continuity of the 30 degree edge, surface smoothness, and sharpness and continuity of the corners, were determined according to Method A of the standard.

The quantity of compound available for the experiment was however only about 550 g. compared with the 1000 g. stated in the standard. It was at times therefore difficult to adjust the speed of the conveyor to ensure uniform take-off without stretching the extrudate. As several of the sample had been stretched this way, 3 lengths of 20 cm each were cut off accurately and weighed. It was hoped that these weights would provide some indication of the degree of die swell.

3. The density of the samples was determined according to British Standard 903: Part I.

4. Tensile properties according to British Standard 903:Part A2 using Type 2'E' dumb-bells of width 3.83.

5. Crescent Tear Strength according to B.S. 903: Part A3.

6. Compression Set at constant strain according to B.S. 903: Part A6. Temperature of test was 70°C.

7. Lupke Resilience according to B.S. 903: Part A8

8. Akron Abrasion according to B.S. 903: Part A9

9. De Mattia Flex - cracking according to B.S. 903: Part A10

10. Resistance to cut-growth according to BS 903: Part All.

11. Wallace Dead load and Micro hardness according to BS 903: Part A 26.

12. Heat build up determination using Goodrich Flexometer according to ASTM D623.

Use of the MRPRA Tearing Energy Method of estimating fatigue life and cut growth resistance of the compounds was thought desirable because good correlation is reported between tearing energies determined by this method and groove cracking of truck tyre treads in service. The equipment for determination of tearing energy was however not available at RAPRA and the time available was inadequate for assembling one. The volume of work involved in testing 4 test pieces of each compound ruled out asking an organisation with this equipment to carry out the determinations for us.

Similarly, although it was thought desirable to use the PICO method to test abrasion resistance, it was not possibl to do so because a PICO test machine was not available and lack of time prevented assembling one.

7.3.4.2. Experimental Results

1. Monsanto Oscillating Disc Rheometer

The Rheographs were of the general type shown in Fig. . The values obtained for minimum torque, maximum torque, scorch time and time to reach 90 per cent of the maximum torque are shown in Table

Neither the control sample tested for reversion nor the experimental samples with varying combinations of accelerator and sulphur showed any marked tendency to reversion even after 5 hours in the rheometer.

2. Garvey die extrusion

The recommended volume of batches of compound for the mixing in the laboratory internal mixer at RAPRA is about 1130 ml. and the batch weight therefore about 1290 g. Other tests required about half this quantity so that only about 550 g. of compound were available for the Garvey test. The test specification recommends 1000 g. Two lengths of compound extruded over a one-minute period were marked off and allowed to cool overnight. The time taken to extrude the 550 g. of compound is about 4 minutes. Before extrusion becomes regular and even if it takes about one minute running. The problem was to adjust the speed of the take off conveyor to match the speed of extrusion quick enough to leave sufficient time to get two lengths of extrudate each having been extruded within the space of one minute.

It was found that the cross-sectional areas of the extrudate at different places were dissimilar. This could have been due to stretching by the conveyor belt moving too fast or to the sample being taken before a steady state of extrusion was reached. Some samples were soft and tacky. Owing to non-uniformity of cross section a considerable number of the extrudates the lengths of extrudate issuing through the die in one minute and its weight could not be used in the experiment.

Therefore 20 cm. lengths were accurately cut off from regions of uniform cross-section and weighed. Their volumes are shown in Table 7.5 in the column headed "Extrudate volume-20 cm".

The ratings of the extrudate characteristics of swelling and porosity, sharpness and continuity of the 30 degree edge, surface smoothness, and sharpness and continuity of the corners made according to Method A of the standard are shown in Table The maximum rating was 4 for each characteristic.

3. The relative densities of the different compounds determined according to BS903: Part 1 are shown in Table 1.

4 and 5. Values obtained for tensile strength, elongation at break, modulus at elongations of 100,300 and 500 per cent, and tear strength are shown in Table

8. The Akron Abrasion Test could not be completed as the control compounds smeared the abrasive wheel.

9. The test pieces of the compounds marked with an asterisk in Table 7.9 showed tearing from the side. These results were rejected.

The following tabulated results are shown:

Table 7.4	Data from Rheometer test
7.5	Garvey die extrusion data
7.6	Tensile and tear data
7.7	Data on relative volume cost, relative density, Lupke resilience and heat build-up.
7.8	Data on hardness and compression set.
7.9	Data on flex-cracking and crack growth.

7.3.4.3 Analysis of Results

The experimental results were analysed by the step wise regression method, using a full quadratic model on 4 variables. In stage 1 of the analysis all the variables were introduced in order of importance.

In stage 11 the number of terms to insert to 'optimise' fit were selected. The selection was done on the basis of obtaining the most highly significant level of the F ratio in an analysis of variance.

In stage 111 the stepwise regression was re-run inserting only the number of terms derived in stage 11.

In stage 1V a display table of the values of each property corresponding to all possible 81 (i.e. 34) combinations of levels of each of the 4 variable compounding ingredients for a full factorial design was printed out. This display table was studied.

In stage V one property was optimised under property and variable range constraints.

7.3.4.3.1 Response equations

A response equation was derived with the aid of the computer relating each property to composition using the following general quadratic equation.

$$y = a_o + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_{11}x_1^2 + a_{22}x_2^2 + a_{33}x_3^2 + a_{44}x_4^2 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{14}x_1x_4 + a_{23}x_2x_3 + a_{24}x_2x_4 + a_{34}x_3x_4$$

Table 7.12 shows the values obtained for the coefficients in each of the response equations.

Column I of Table 7.4 shows the estimates of variation predicted in the computer analysis of the results of this exercise. Column II gives the standard deviation values calculated from 3 repeat batches of the control compound.

Pyne and Kristensen (156) point out that the square of the correlation coefficient (R^2) indicates the fraction of the variance of results for a property (a measure of their divergence from their overall mean) which can be attributed to altering the levels of the variables. The values for R^2 and the values of F for analysis of variance are given in Table 7·11

If the balance of physical properties of the control mix could be duplicated or bettered within the experimental region investigated it was intended to optimise with respect of cost i.e. to obtain the cheapest combination of levels of the variables consistent with duplicating the property balance of the control. In practice it was not possible with the HAF black compounding systems examined to duplicate the property balance obtained with ISAF black (the control mixes) in all respects. Hence, optimisation was concerned mainly with obtaining the closest approach to the properties of the control mixes. It is possible to use a desirability function for such optimisation, in which several properties are included with appropriate weighting of each. The necessary computer program was not available and time limitation precluded the writing of one. The optimisation program available allowed only one property to be maximised or minimised at one time whilst constraint levels (more than one stated level and/or less than another stated value) were applied to other properties.

It is worth pointing out that predicted volume cost values (prediction standard error 0.008 unit) for all 81 points of the full factorial design which was fractionated for this exercise were all lower than the volume cost of the control (2.6203-2.9566 units cf. 2.9827 as the control mean).

TABLE 7.4 DATA FROM RHEOMETER TEST

Sample	Composition				Minimum Torque (M_L)	Maximum Torque (M_H)	Scorch	Time of 90% of Optimum Cure
	Black ISAF	Oil	Accelerator (MOR)	Sulphur				
Controls	45	10	1.3	1.8				
1(a)					11.0	72.0	8.5	19.0
(b)					14.0	67.0	9.0	18.3
(c)					9.5	57.5	10.0	20.3
(d)					12.3	66.0	9.0	18.2
	ISAF		(MOR)					
2*	45	10	1.3	1.8	14.5	76.0	7.5	17.7
Experimental								
3	35	1	0.4	2.7	14.5	75.5	7.0	29.5
4		1	1.0	1.5	12.0	63.5	7.2	17.0
5		1	1.6	2.1	14.0	90.0	5.8	17.0
6		8	0.4	2.1	11.5	59.5	8.0	26.0
7		8	1.0	2.7	10.0	72.5	6.5	20.5
8		8	1.6	1.5	9.5	70.0	6.8	16.0
9		15	0.4	1.5	12.0	52.0	8.0	24.0
10		15	1.0	2.1	7.0	59.5	7.7	18.0
11		15	1.6	2.7	10.0	75.0	6.7	15.2
12	45	1	0.4	1.5	15.0	61.5	7.0	25.0
13		1	1.0	2.1	14.0	86.0	6.0	16.3
14		1	1.6	2.7	15.0	102.0	7.0	16.0
15		8	0.4	2.7	13.0	75.0	6.2	30.5
16		8	1.0	1.5	9.0	63.0	7.0	19.5
17		8	1.6	2.1	9.5	80.0	6.3	15.0
18		15	0.4	2.1	12.0	54.0	7.0	26.0
19		15	1.0	2.7	9.7	76.0	7.0	19.5
20		15	1.6	1.5	10.0	64.5	7.0	17.0
21	55	1	0.4	2.1	17.5	79.5	6.5	28.5
22		1	1.0	2.7	17.5	106.0	5.2	17.2
23		1	1.6	1.5	15.5	91.5	5.5	17.0
24		8	0.4	1.5	15.0	58.0	7.5	25.5
25		8	1.0	2.1	13.5	81.5	6.2	16.0
26		8	1.6	2.7	10.0	100.5	5.7	16.0
27		15	0.4	2.7	10.5	66.0	7.0	31.0
28		15	1.0	1.5	10.5	62.0	7.4	17.3
29		15	1.6	2.1	10.5	83.0	5.7	14.8

TABLE 7.5 GARVEY DIE EXTRUSION DATA

Sample	Composition				Extrudate	
	Black	Oil	Accel-erator	Sulphur	Volume (20 cm)	Total Rating
	ISAF		MOR			
Controls	45	10	1.3	1.8		
1 (a)					18.4	15
(b)					17.2	15
(c)					18.8	15
(d)					18.5	15
	ISAF		MOR			
2*	45	10	1.3	1.8	19.2	15
Experimental						
	HAF		NS			
3	35	1	0.4	2.7	19.0	15
4		1	1.0	1.5	19.0	15
5		1	1.6	2.1	19.7	14
6		8	0.4	2.1	22.4	11
7		8	1.0	2.7	17.2	14
8		8	1.6	1.5	17.3	15
9		15	0.4	1.5	20.4	14
10		15	1.0	2.1	18.6	13
11		15	1.6	2.7	20.1	15
12	45	1	0.4	1.5	17.3	15
13		1	1.0	2.1	17.9	15
14		1	1.6	2.7	18.3	14
15		8	0.4	2.7	17.8	15
16		8	1.0	1.5	18.8	14
17		8	1.6	2.1	17.8	15
18		15	0.4	2.1	19.2	14
19		15	1.0	2.7	17.3	16
20		15	1.6	1.5	18.4	15
21	55	1	0.4	2.1	16.6	14
22		1	1.0	2.7	18.2	14
23		1	1.6	1.5	16.3	15
24		8	0.4	1.5	17.9	15
25		8	1.0	2.1	16.8	15
26		8	1.6	2.7	15.8	13
27		15	0.4	2.7	17.5	15
28		15	1.0	1.5	17.7	15
29		15	1.6	2.1	17.8	14

TABLE 7.6 TENSILE AND TEAR DATA

Sample	Composition				Tensile Strength MN/m^2	% Elongation at break	Modulus at elongation of			Crescent Tear Strength
	Black	Oil	Accelerator	Sulphur			100%	300%	500%	
	ISAF		MOR							
Controls	45	10	1.3	1.8						
1(a)					26.32	590	1.93	8.99	20.22	299.60
(b)					25.82	610	1.37	8.04	18.93	280.70
(c)					24.27	590	1.48	7.97	18.95	267.83
	ISAF		MOR							
2*	45	10	1.3	1.8	25.68	530	2.19	10.25	23.68	324.11
Experimental										
	HAF		NS							
3	35	1	0.4	2.7	29.53	630	1.83	8.45	20.41	283.26
4		1	1.0	1.5	28.56	620	1.31	7.70	20.18	292.04
5		1	1.6	2.1	28.90	530	2.15	11.07	25.93	254.72
6		8	0.4	2.1	27.17	630	1.07	6.47	17.18	267.81
7		8	1.0	2.7	26.99	610	1.61	7.67	19.80	277.45
8		8	1.6	1.5	28.16	640	1.54	7.77	19.07	275.80
9		15	0.4	1.5	23.56	670	0.85	4.66	12.88	270.22
10		15	1.0	2.1	23.79	570	1.09	5.91	16.42	272.25
11		15	1.6	2.7	25.20	570	1.18	7.38	18.97	183.54
12	45	1	0.4	1.5	27.39	640	1.16	7.99	18.83	254.17
13		1	1.0	2.1	27.19	540	2.12	11.40	24.33	308.65
14		1	1.6	2.7	25.89	480	3.05	15.26	-	260.98
15		8	0.4	2.7	25.55	550	2.10	10.06	21.81	260.76
16		8	1.0	1.5	27.79	630	1.03	7.50	19.26	268.52
17		8	1.6	2.1	25.77	540	1.37	10.28	23.13	261.06
18		15	0.4	2.1	24.68	650	1.10	6.50	15.53	255.51
19		15	1.0	2.7	24.65	540	2.19	9.66	21.74	247.06
20		15	1.6	1.5	25.99	610	1.59	7.72	18.96	246.09
21	55	1	0.4	2.1	25.89	500	2.79	14.09	25.24	262.76
22		1	1.0	2.7	26.64	460	3.64	16.48	-	283.47
23		1	1.6	1.5	25.49	450	3.02	15.88	-	268.70
24		8	0.4	1.5	24.02	590	1.76	9.22	20.0	251.03
25		8	1.0	2.1	25.88	520	2.31	11.87	23.27	314.89
26		8	1.6	2.7	25.20	450	3.16	15.89	-	254.39
27		15	0.4	2.7	22.69	540	2.11	9.96	20.84	266.37
28		15	1.0	1.5	24.43	560	1.44	8.14	18.92	243.17
29		15	1.6	2.1	21.95	450	2.22	12.21	-	287.18

TABLE 7.7 DATA ON RELATIVE VOLUME COST, RELATIVE DENSITY, LÜPPE RESILIENCE AND HEAT BUILD-UP

Sample	Composition				Relative Volume Cost	Relative Density	Lüpke Resilience	Heat Build up
	Black	Oil	Accelerator	Sulphur				
	ISAF		MOR					
Controls	45	10	1.3	1.8				
1 (a)					2.982	1.109	56	57
(b)					2.984	1.110	52	59
(c)					2.982	1.109	55	58
	ISAF		MOR					
2*	45	10	1.3	1.8	2.974	1.108	55	58
Experimental								
	HAF		NS					
3	35	1	0.4	2.7	2.712	1.089	64	50
4		1	1.0	1.5	2.765	1.088	66	52
5		1	1.6	2.1	2.804	1.089	70	50
6		8	0.4	2.1	2.663	1.082	64	50
7		8	1.0	2.7	2.704	1.085	69	48
8		8	1.6	1.5	2.783	1.095	64	49
9		15	0.4	1.5	2.618	1.075	66	49
10		15	1.0	2.1	2.662	1.079	64	48
11		15	1.6	2.7	2.690	1.077	68	45
12	45	1	0.4	1.5	2.794	1.111	58	62
13		1	1.0	2.1	2.840	1.115	60	53
14		1	1.6	2.7	2.878	1.116	63	54
15		8	0.4	2.7	2.752	1.113	57	56
16		8	1.0	1.5	2.768	1.099	61	54
17		8	1.6	2.1	2.829	1.110	61	54
18		15	0.4	2.1	2.702	1.104	55	56
19		15	1.0	2.7	2.750	1.110	60	53
20		15	1.6	1.5	2.793	1.105	58	55
21	55	1	0.4	2.1	2.875	1.139	52	70
22		1	1.0	2.7	2.912	1.140	57	70
23		1	1.6	1.5	2.956	1.138	54	64
24		8	0.4	1.5	2.824	1.131	49	73
25		8	1.0	2.1	2.867	1.135	51	61
26		8	1.6	2.7	2.900	1.135	53	62
27		15	0.4	2.7	2.785	1.132	48	60
28		15	1.0	1.5	2.803	1.121	50	62
29		15	1.6	2.1	2.863	1.132	55	61

TABLE 7.8 DATA ON HARDNESS AND COMPRESSION SET

Sample	Composition				Micro Hardness Unaged	Micro Hardness aged	Wallace Multi-range Hardness	Compression Set
	Black	Oil	Accelerator	Sulphur				
	ISAF		MOR					
Controls	45	10	1.3	1.8				
1 (a)					68	74	64	33.15
(b)					67	74	63	37.38
(c)					66	71	62	38.40
	ISAF		MOR					
2*	45	10	1.3	1.8	71	75	66	38.02
Experimental								
	HAF		NS					
3	35	1	0.4	2.7	65	67	62	36.48
4		1	1.0	1.5	60	67	58	31.64
5		1	1.6	2.1	69	73	65	33.59
6		8	0.4	2.1	59	63	55	38.39
7		8	1.0	2.7	60	65	60	43.69
8		8	1.6	1.5	62	68	61	34.31
9		15	0.4	1.5	51	56	49	41.91
10		15	1.0	2.1	57	63	54	36.52
11		15	1.6	2.7	60	65	58	34.52
12	45	1	0.4	1.5	65	70	63	36.17
13		1	1.0	2.1	71	76	67	36.68
14		1	1.6	2.7	75	79	71	35.47
15		8	0.4	2.7	69	72	65	38.41
16		8	1.0	1.5	61	68	58	32.87
17		8	1.6	2.1	69	74	64	36.49
18		15	0.4	2.1	59	65	61	38.98
19		15	1.0	2.7	69	74	63	38.39
20		15	1.6	1.5	65	71	60	35.86
21	55	1	0.4	2.1	75	79	73	39.28
22		1	1.0	2.7	82	83	76	38.23
23		1	1.6	1.5	77	81	73	37.48
24		8	0.4	1.5	66	72	56	37.91
25		8	1.0	2.1	71	76	69	37.10
26		8	1.6	2.7	76	80	73	39.92
27		15	0.4	2.7	66	74	66	46.64
28		15	1.0	1.5	64	70	59	37.18
29		15	1.6	2.1	73	78	69	36.77

TABLE 7.9 DATA ON FLEX-CRACKING AND CRACK GROWTH

Sample	Composition				Flex cracking to Grade D No. of cycles	CRACK GROWTH No. of kilocycles	
	Black	Oil	Accelerator	Sulphur		L→L+2	L+2→L+6
	ISAF		MOR				
Controls	45	10	1.3	1.8			
1(a)					159,304	4.62	36.50
(b)					146,100	4.12	45.37
(c)					82,172	2.50	25.9
	ISAF		MOR				
2*	45	10	1.3	1.8	185,591	2.22	6.20
Experimental							
	HAF		NS				
3	35	1	0.4	2.7	200,000	7.6	13.90
4		1	1.0	1.5	92,232	10.25	68.70
5		1	1.6	2.1	30,300*	1.60	4.47
6		8	0.4	2.1	366,186	15.50	26.50
7		8	1.0	2.7	98,150*	3.30	10.50
8		8	1.6	1.5	430,107	4.62	48.50
9		15	0.4	1.5	482,128	28.25	144.20
10		15	1.0	2.1	261,773*	6.00	14.75
11		15	1.6	2.7	84,566*	3.95	10.10
12	45	1	0.4	1.5	84,566	10.25	72.25
13		1	1.0	2.1	92,257*	2.42	7.20
14		1	1.6	2.7	28,244*	1.26	3.19
15		8	0.4	2.7	118,518*	2.47	8.07
16		8	1.0	1.5	52,674	7.85	30.35
17		8	1.6	2.1	118,087*	2.42	7.69
18		15	0.4	2.1	36,525	11.0	149.0
19		15	1.0	2.7	279,500	2.27	6.00
20		15	1.6	1.5	98,150	8.75	50.12
21	55	1	0.4	2.1	116,256*	1.55	11.90
22		1	1.0	2.7	16,256*	1.25	2.96
23		1	1.6	1.5	118.087	8.62	94.25
24		8	0.4	1.5	104,231	16.12	69.0
25		8	1.0	2.1	223,431	7.50	105.0
26		8	1.6	2.7	45,000*	1.82	5.20
27		15	0.4	2.7	179,932	2.20	6.77
28		15	1.0	1.5	266,691	13.50	68.75
29		15	1.6	2.1	28,100	2.25	4.75

TABLE 7.10 VALUES OF COEFFICIENTS IN RESPONSE EQUATIONS

	Relative Volume Cost	Monsanto Oscillating Disc Rheometer Test			
		Scorch Time	Minimum Torque	Maximum Torque	Time to 90% Maximum Torque
a_0	2.78859	6.70	10.53330	74.35190	17.23705
a_1	0.07689	-0.38889	1.11111	6.13890	0
a_2	-0.04833	0.35000	-2.37778	-9.08333	0
a_3	0.04283	-0.42778	-0.94444	9.75000	-5.66667
a_4	0	-0.28333	0	9.02778	0.95000
a_{11}	0	0	0	0	0
a_{12}	0	0	0	-1.95834	0
a_{13}	0	0	0	0	0
a_{14}	0.00617	0	0	1.95834	0
a_{22}	0	0	1.40000	0	0
a_{23}	0	0	0	0	0
a_{24}	0	0	0	-2.37501	0
a_{33}	0	0	1.03333	0	3.74445
a_{34}	0.00642	0	0	0	-1.60833
a_{44}	0	0	0	0	1.02778

	Relative density	Tensile Strength	Modulus at 300% Elongation	Elongation at break	Tear Strength
a_0	1.10919	25.88700	9.89593	561.48200	289.0790
a_1	0.02467	-1.09278	2.59222	-52.77780	0
a_2	-0.00483	-1.58556	-2.01000	17.22220	-10.9644
a_3	0	0	1.44778	-37.77780	0
a_4	0	0	1.34611	-32.22220	0
a_{11}	0	0	0	-20.55560	0
a_{12}	0	0	-0.57250	0	0
a_{13}	0	0	0	0	11.4450
a_{14}	0	0	0.47667	0	11.2617
a_{22}	0	0	0	0	0
a_{23}	0	0	0	0	0
a_{24}	0	0	0	0	0
a_{33}	0	0	0	0	-19.4806
a_{34}	0	0	0	0	-10.5542
a_{44}	0	0	0	21.11100	-15.7022

TABLE 7.10 VALUES OF COEFFICIENTS IN RESPONSE EQUATIONS (CONT.)

	Microhardness (Unaged)	Microhardness (Aged)	Wallace Multirange Hardness (Unaged)
a_0	66.51850	71.44450	63.25930
a_1	5.94444	5.88890	5.11111
a_2	-4.16667	-3.27778	-3.83333
a_3	2.83333	2.83333	2.44444
a_4	2.83333	2.00000	3.16667
a_{11}	0	0	0
a_{12}	0	0	0
a_{13}	0	0	0
a_{14}	0	0	0
a_{22}	0	0	0
a_{23}	0	0	0
a_{24}	0	0	0
a_{33}	0	0	0
a_{34}	0	-0.91667	-1.41667
a_{44}	0	0	

	Lüpke Resilience	Heat build-up	Compression Set	Crack growth L → L+2
a_0	59.14820	56.33330	37.44000	4.15629
a_1	-6.99999	7.88887	1.08111	-1.45889
a_2	-1.11111	-2.00000	1.20833	1.85389
a_3	1.83333	-1.77778	-1.65333	-3.31389
a_4	0	-1.22222	1.46778	-4.56055
a_{11}	0	0	0	2.13889
a_{12}	0	0	0	0
a_{13}	0	0	0	2.50956
a_{14}	0	0	0	0
a_{22}	0	0	0	0
a_{23}	0	0	-1.24917	-1.54833
a_{24}	0	0	0	-1.29511
a_{33}	0	0	0	0
a_{34}	0	0	0	2.28250
a_{44}	0	0	0	1.88056

TABLE 7.11 VALUES OF THE SQUARE OF THE CORRELATION COEFFICIENT (R^2) AND VALUES OF F FOR ANALYSIS OF VARIANCE

	R^2	F
1. Relative volume cost oscillating disc rheometer	0.993	551.651
2. Scorch time	0.680	11.674
3. Minimum torque	0.826	20.031
4. Maximum torque	0.967	79.400
5. Time to 90% of maximum torque	0.967	119.431
6. Relative density	0.965	323.734
7. Tensile strength	0.733	32.974
8. Modulus at 300% elongation	0.962	83.273
9. Elongation at break	0.893	27.484
10. Tear strength	0.684	7.210
11. Microhardness (unaged)	0.933	76.323
12. Microhardness (aged)	0.955	90.481
13. Wallace multirange hardness (unaged)	0.931	44.639
14. Lüpke resilience	0.924	93.995
15. Heat build-up	0.900	49.421
16. Compression set	0.595	6.179
17. Crack growth L → L+2	0.924	19.249

TABLE 7.12 STANDARD ERROR VALUES ASSOCIATED WITH RESPONSE EQUATIONS AND REPEAT MIXES

		Standard error values associated with	
		response equations	repeat mixes
		I	II
1.	Relative volume cost	0.008	0.0016
	oscillating disc rheometer		
2.	Scorch time	0.455	0.237
3.	Minimum torque	1.257	1.228
4.	Maximum torque	3.146	0.356
5.	Time to 90% of maximum torque	1.095	0.356
6.	Relative density	0.004	0.002
7.	Tensile strength	1.006	0.872
8.	Modulus at 300% elongation	0.736	0.465
9.	Elongation at break	25.241	9.429
10.	Tear strength	15.468	13.044
11.	Microhardness (unaged)	2.013	0.816
12.	Microhardness (aged)	1.519	0.447
13.	Wallace multirange hardness (unaged)	1.995	0.816
14.	Lupke resilience	1.850	1.700
15.	Heat build-up	2.541	0.816
16.	Compression set	2.233	2.276
17.	Crack growth L → L+2	2.195	0.905

7.3.5 Optimisation

The computer was programmed to calculate property values from the regression equations using a large number of values of $Y_1 \ldots Y_4$, and to select the combination of giving a minimum or maximum value to one property whilst the other properties were within specified limits.

7.3.5.1. Limits imposed on properties

Since the aim of the experiment was to obtain a balance of properties similar to or better than that given by the control min, the limits imposed were derived from property levels obtained on the batches of the the control mix. Two types of situation existed:-

(a) Where the numerical value of a property was required to be as high as or higher than that of the control a minimum limit was set at:-

Mean of control batches - 2 standard deviations of control batches + 2 standard errors of estimate associated with the regression equation.

Examples are tensile strength, elongation at break, tear strength and crack growth resistance.

(b) Where the numerical value of a property was required to be as low as or lower than that of the control a maximum limit was set at:-

Mean of control batches + 2 standard deviations of control batches - 2 standard errors of estimate associated with the regression equation.

Examples are heat build-up and compression set.

This basis of setting limits (constraints) was used because the distribution of property value for individual batches of a mix about the predicted value is assumed to be substantially a normal (Gaussian) one, so that over 90% of batches would give results within ± 2 standard errors of the predicted value.

A third type of situation, where the numerical value of a property should be as close as possible to that of the control, would desirably have arisen with respect to hardness and 300% modulus for example. However, in all sections of the experimental region where most other property requirements were feasible, hardness and 300% modulus values were lower than those of the control composition. Hence, these properties were made to subjects of optimisation runs to determine the maximum values compatible with the limits imposed on the other properties detailed overleaf. Other optimisation runs determined minimum cure time or minimum compound cost compatible with these limits.

Property	Control Mix		Estimate SE	Limit use
	Mean	SD		
Tensile strength	25,47	0.8718	1.006	25.739 mi
Elongation at break	596.7	9.4287	25.241	628.30 '
Tear strength	282.71	13.044	15.468	287.55 '
Crack growth resistance	3.75	0.9049	2.175	6.23 '
Resilience	54.3	1.6997	1.850	54.60 '
Heat build-up	58	0.8165	2.541	54.55 ma
Compression set	36.31	2.276	2.233	36.22 '

Limits were not imposed on other properties either because they were substantially 'neutral' properties over the ranges involved (e.g. density) or because experimental difficulties had precluded obtaining reliable results (extrusion characteristics and abrasion).

7.3.5.2 Optimisation procedure

Inspection of the predicted property values for the 81 points of the full factorial experimental design enabled the region of search to be restricted to:- X_1 from -1 to 0 experimental unit (EU)

X_2 " -1 to + 0.6 EU

X_3 " -1 to + 1 EU

X_4 " -1 to + 1 EU

Initial solutions were obtained by computerised searching of results predicted from the regression equations for all combinations of levels of $X_1 \ldots X_4$ over these ranges in steps of 0.2 EU, i.e. 6 x 9 x 11 x 11 combinations.

This procedure gave solutions accurate to 2 parts of black (X_1) 1.4 parts of oil (X_2) and 0.12 part of accelerator (X_3) and sulphur (X_4). Search was then made over more restricted areas of composition about these solution points, in which the step lengths were 0.1, 0.143, 0.083, 0.083 EU for $X_1 \ldots X_4$ respectively and there were 4 x 10 x 7 x 7 combinations examined. These step lengths gave final solutions accurate to 1 part black, 1 part oil, and 0.05 part of accelerator and sulphur.

7.3.5.3 Results

(i) Maximum hardness (Wallace Multirange) 60.582

X_1 :- 0.7 EU (38 parts HAF black)
X_2 - 1 (1 part oil)
X_3 - 0.166 (0.90 part Santocure NS)
X_4 - 1 (1.5 part sulphur)

Predicted values of constrained properties:-

Tensile strength (TS)	28.237
Elongation at break (EB)	630.74
Tear strength (T)	291.26
Crack-growth resistance (CG)	10.481
Resilience (R)	64.855
Heat build-up (HBU)	54.328
Compression set (CS)	34.074

Predicted values of unconstrained properties:-

300% modulus (M300)	8.4379	Control mean 8.33
90% cure time (CT)	18.082	18.5
Compound volume cost (VC)	2.7806	2.98
Hardness change on ageing (ΔH)	4.758	6
Minimum torque (MINT)	13.719	12.4
Maximum torque (MAXT)	66.117	68.3
Scorch time (ST)	6.8345	8.83

(ii) <u>Maximum M300</u> 8.4379

X_1 ...X_4 values same as for (i)

(iii) <u>Minimum 90% cure time</u> 16.638

X_1 - 1 EU (35 parts HAF black)
X_2 - 0.286 (6 " oil)
X_3 + 0.166 (1.10 " Santocure NS)
X_4 - 0.917 (1.55 " sulphur)

Predicted values of constrained properties:-

TS	27.432
EB	629.82
T	288.50
CG	11.410
R	66.769
HBU	49.840
CS	34.453

Predicted values of unconstrained properties:-

Hardness (H)	57.914	Control mean	63
M300	7.1579		8.33
VC	2.7392		2.9827
ΔH	5.632		6
MINT	10.085		12.4
MAXT	64.759		68.3
ST	7.1779		8.83

(iv) <u>Minimum compound cost</u> (volume) 2.6967

X_1 - 1 EU (35 parts HAF black)
X_2 + 0.143 (9 " oil)
X_3 - 0.249 (0.85 part Santocure NS)
X_4 - 0.585 (1.75 parts sulphur)

Predicted values of constrained properties:-

TS	26.751
EB	631.66
T	288.82
CG	13.28
R	65.532
HBU	49.314
CS	36.131

Predicted values of unconstrained properties:-

H	55.663	Control mean	63
M3OO	6.2273		8.33
CT	19.632		18.5
ΔH	5.465		6
MINT	9.4081		12.4
MAXT	60.824		68.3
ST	7.4115		8.83

Assessed against the standard deviation of repeat batches of control mix, the range over the different optimum solutions of all constrained properties except heat build-up is too small to indicate that any one of compositions (i) to (iv) is definitely preferable to any other. In this situation, it is reasonable to prefer a solution yielding maximum hardness or modulus; as was pointed out by Scott(162), all other things being equal, a high modulus or hard tyre tread generally has good abrasion resistance.

The range of hardness and modulus values over the different optimum solutions is large enough to suggest real differences amongst the compositions, with (i) giving the highest values. Composition (i) thus seems the most suitable for truck tyre treads containing HAF black which will be as close as possible in performance to those currently made with ISAF black.

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