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NATURAL RUBBER AND THE STEREO DIENE SYNTHETIC RUBBERS:

CURRENT TECHNOLOGY AND EXPECTED TRENDS [1]

by

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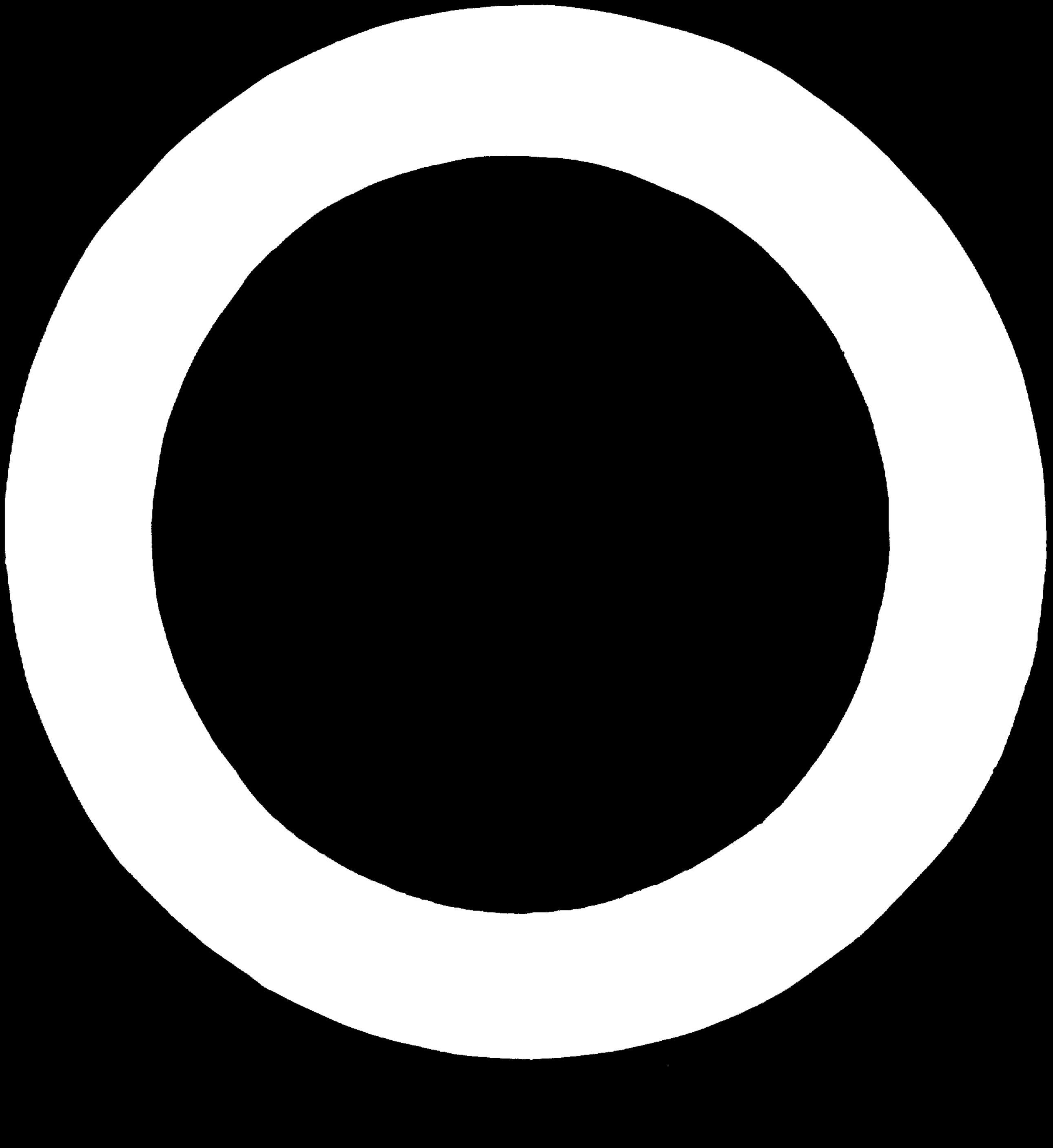

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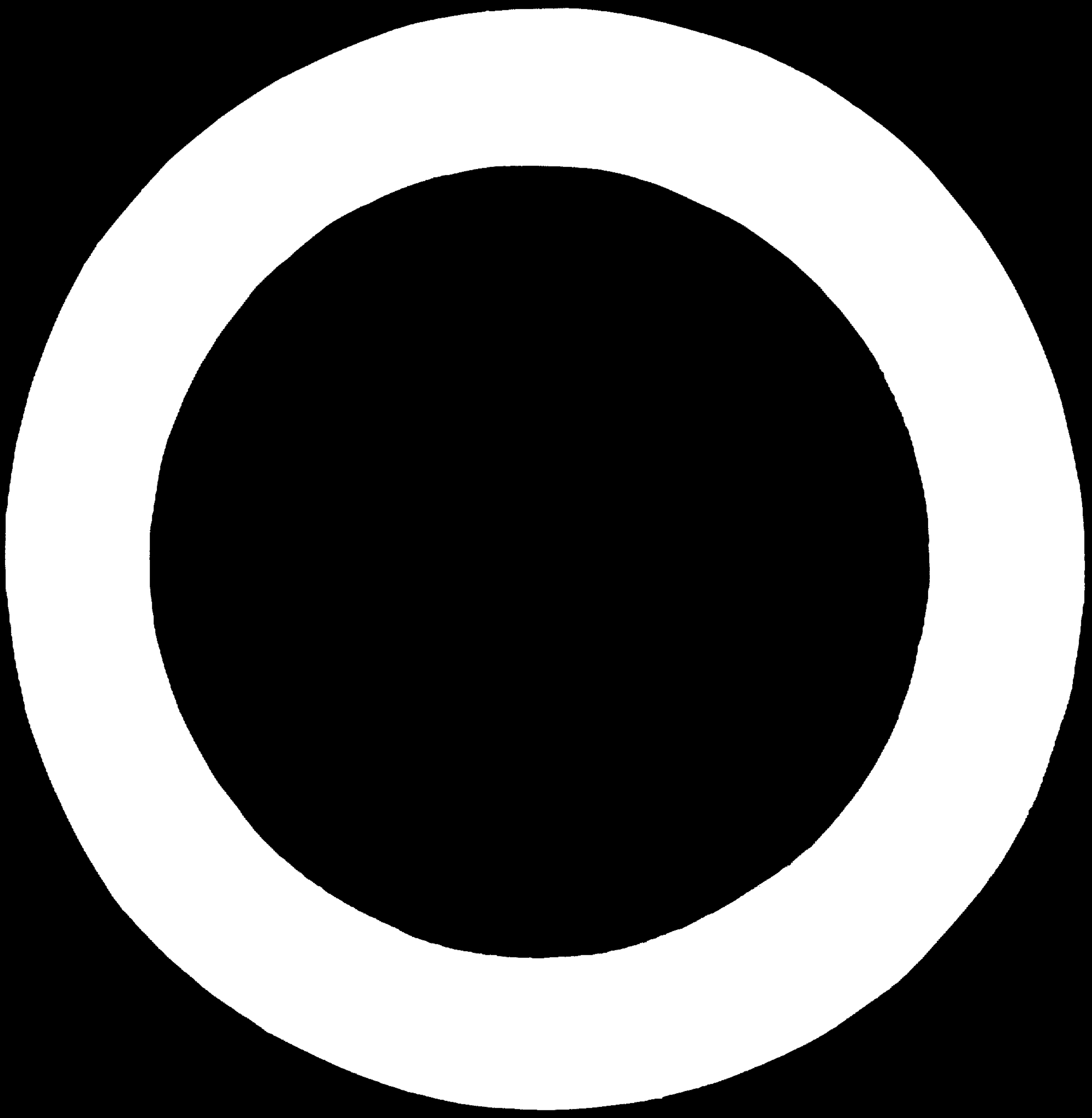


I. INTRODUCTION

1. As an international commodity and a construction material, available from both agricultural and petrochemical sources, rubber is unique as a commercial category of materials, besides being a technologically unique family as well. Its growth and technology are closely intertwined with the growth and technology of motor transport, and the reverse is equally true. Society's motorized mobility is growing faster than its overall standard of living, so that worldwide rubber usage is assured of brisk growth for years to come. Greater technological complexity in both tire and synthetic rubber manufacture is increasing the number of options even faster.

2. Against this background, decisions on what type of rubber capacity in which to invest during the next decade will, if anything, be more difficult than in the past, inasmuch as:

a. The diversity of major tire categories, as well as the ways in which various rubbers are used in them, is increasing rather than decreasing;

b. Major improvements in natural rubber growing technology portend appreciably lower costs at the plantation;

c. The explosive growth in polymer research in the last 15 years is resulting in a greater number of general purpose synthetic rubbers being put into production.

d. Greatly intensified research on lower cost monomer processes by petroleum and chemical companies is making the newer rubbers more commercially competitive;

e. As a result of these expanded R & D efforts on both monomers and polymers, synthetic rubber plants are proliferating throughout the world, and so are the types of rubber made therein;

f. Trade restrictions designed to protect local investments, both in chemicals and chemical end products, seem to be growing more common.

3. Against this background of great flux in both technological and commercial factors, we plan to look at recent and current trends in rubber usage patterns; to relate these to structural features, performance, and cost characteristics of various rubbers; to examine the role of current and near-future shifts in tire technology on rubber usage; and to look briefly at possible future rubbers and their potential role in the overall picture.

II. CURRENT USAGE AND INTERDEPENDENCE OF RUBBERS

4. As the newer synthetic rubbers have emerged in the last decade and been adopted into tires, the usage technology has usually been

characterized by their being used in blends with natural rubber. has generally been found is that such blends outperformed compound based primarily on one rubber -- that is, taking into account proce ing, the tire building steps, and performance on the car. Thus, a symbiotic relationship has evolved wherein the advantages of the va ous synthetics complement those of natural, and vice versa. Natur rubber and the new stereo synthetics have become more mutually bene ficial to each other than was being predicted when the new syntheti were just emerging from the laboratory in the late 50's.

5. Prior to 1940, natural rubber was, of course, the sole elastome in tires. After the war, the combination of vastly increased overa demand and the fortunate appearance of the war-born SBR decreased natural rubber's share in the U.S. to 60% by 1950 and to 35% by 196 See Figures 1 and 2. Following the early sixties, when the stereo synthetics came into production, the pattern evolved to a present o all use in tires of about 50% SBR, 25% natural rubber, 20% stereos, and 5% other types. On a total tonnage basis, however, all categor have increased in the last decade.

6. The expansion of rubber usage becomes far more dramatic when th worldwide figures are considered. Here we see natural rubber usage climbing nearly 50% in the last decade. A continuation of this tre would place 1980 usage near 5 million long tons.

7. Demand for rubbers of all types will continue to remain so stro that no single elastomer can take a dominant position in the immedi future. This situation supports even further the likelihood that co pounds used within specific tires will tend to be based even more or blends, so that compounders will be able to shift compositions sligh without performance loss as rubber prices and short term availabili fluctuate.

8. Since tires themselves will continue as the major outlet for rubber, the increasing mobility of society will account for most of the projected rubber growth. The qualities that are blended into today's tires are illustrated in Table I.

TABLE I

TIRE POLYMER COMPARISON*

	POLYISOPRENE (Natural rubber or synthetic PI)	SBR	Cis PBD	EPDM
Treadwear	100	115	150	115
Resilience	100	75	95	85
Heat Durability	100	150	150	150+
Cold Flexibility	100	90	120	100
Weather Resistance	100	115	100	150

* When tested as only rubber in the compound.

9. On the basis of a 100 rating for natural rubber or synthetic polyisoprene, the physical properties of synthetics might be rated about as shown above.

10. Once compounded and cured, differences between synthetic and natural polyisoprene are marginal. Principal differences are in raw polymer handling, and the two polymers -- so alike in chemical and physical properties -- compete primarily on the basis of the all-in costs of a finished tire. The green strength advantage of natural rubber continues as an important factor in fabrication of many tire categories, and dictates use of a significant fraction of natural rubber in the carcasses of such tires.

11. The other rubbers show some differences from the polyisoprenes. SBR is recognized for improved treadwear and aging stability it imparts, but its use is limited to smaller tires where its relatively low resilience will not cause overheating.

12. Polybutadiene, of course, outperforms SBR as a tread rubber, and its high resilience and superior aging make it an important carcass component as well. Its primary limitation, low tensile and low traction on wet roads, restricts its use to relatively moderate contents in blends -- less than 50%.

13. EPDM is most outstanding for weather and age resistance. Its problems are processability and compatibility -- that is, limitations on how much can be used in blends with the much more highly unsaturated diene rubbers because of the great differences in cure systems used. Nevertheless EPDM has found a place in sidewall blends to improve weatherability.

14. Thus, we see that with each of these rubbers -- as well as with several others under development for tires -- there are specific strengths and weaknesses that the tire manufacturer can balance in order to realize the optimum potential of each tire component. In the blend, each component rubber offsets certain weaknesses of its partners, and in turn, its weaknesses are covered by them. Table II illustrates in broad terms the blending practices of the U.S. tire industry for the principal parts of a tire.

TABLE II

TIRE COMPONENTS

(Approximate U.S. Industry Averages)

	Carcass	Tread	Liner	Sidewall
Polyisoprene	50		40	
SBR	25			
OE-SBR		75		
Hot SBR				80
PBD	25	25		
Chlorobutyl			60	
EPDM				20

15. The carcass rubber, in a composite with cords, provides the tire's sinews. It must adhere well to cords, must not overheat on severe flexing, and must retain its properties under prolonged exposure to elevated temperatures.

16. Current practice calls on natural rubber or synthetic polyisoprene for building tack and overall processing, and for resilience and hot strength in the finished tire. SBR improves aging characteristics, while cis-polybutadiene combines key advantages of both of these -- resilience, good aging

17. The tread rubber must provide traction, abrasion resistance, and crack resistance. For this, the compounder employs a higher black level and high molecular weight SBR diluted with petroleum oils to make it processible. But a key ingredient for the past ten or so years is cis-polybutadiene for increased abrasion resistance. Compounds have been tried with up to 50 percent PBD, but such treads do not have acceptable traction on wet roads. A level near 25% represents the best balance between the increased treadwear and decreased wet traction.

18. The liner material in tubeless tires has severe requirements, having to prevent air diffusion, not only when new, but after years of exposure to hot air under two atmospheres of pressure. A normal blend for this usage would be 60% chlorobutyl and 40% polyisoprene, although there are wide variations in usage--all the way to SBR/polyisoprene/reclaim blends.

19. The tire sidewall also has severe aging and cut resistance requirements. It must resist ozone, salts, and oils under conditions of severe flexing and elevated temperatures and retain protection for the carcass and good appearance. In black tires, this is accomplished with heavy doses of antiozonants and waxes in SBR, with or without some polyisoprene and reclaim. For white or colored sidewalls, however, EPDM and waxes provide the protection. Hot SBR, with its good over-

all aging, adhesion, and scuff resistance, is the main component.

20. Thus the whole tire has evolved into a highly complex assemblage of several types of rubbers, each carefully selected to perform its function on the "team", so that the whole complex may have the balance of properties best suited for the tire's overall performance.

III. RELATION OF SOME STRUCTURAL FEATURES TO PERFORMANCE

21. Every performance feature of a rubber -- processibility, ease of fabrication, durability it imparts to the finished article -- can ultimately be traced back to the various structural parameters of the molecule itself, taken in sum. It is very difficult indeed to isolate the role of individual structural parameters in determining their specific contribution to performance, desirable though this may be from the standpoint of designing new synthetic rubbers. Fortunately, the proportion of science to art is on the increase in this area, and certain generally accepted principles of molecular architecture have emerged over the years. Some of the principal ones are enumerated in Table III.

TABLE III

Molecular Structure Parameters of Significance to Tire Performance

Structural Feature	Preferred Range
Tg	Preferably below -50°C
Mn	Between 40,000-300,000
Gel content (masticated)	Less than 20%, preferably below 5%
Ratio Mw/Mn	2 to 4
Readiness to crystallize*	Moderate
Content of highly polar groups	Below 5 mol %
Proportion of non-chain alkyl groups	Preferably less than 40%

* On cooling or on elongation.

22. The foregoing generalizations are based on performance measurements taken on rubbers having known molecular structures, where such rubbers were evaluated as the only rubber. Actual practice in tire technology -- as pointed out in the preceding section -- has been to develop compounds based on blends that exploit the advantages of the individual component rubbers to achieve overall performance superior to that achievable with only one rubber predominant. Thus, we find blending practices developing along the lines of Table IV.

TABLE IV

Structural Aspects of Differing Rubbers Combined in Blends

Structural Feature	To Achieve
High and low Tg rubbers	Better traction, while retaining adequate low temperature performance
Readily crystallising rubbers with slow crystallising or amorphous rubbers	Green strength during fabrication; hot tensile and tear in cured products
Low Mn with high Mn rubbers	Easier processing
Low Mw/Mn ratio rubbers with high Mw/Mn ratio rubbers	Better dynamic properties

23. The family of polyisoprene rubbers itself offers a good illustration of how certain of these findings can be applied:

TABLE V

Structural Parameters of Polyisoprenes and Their Effect on Certain Performance Features

		Microstructure					
Polymer	Mn	1,4	Trans 1,4	1,2 and 3,4	Tg (°C)	Cryst'n Tendency	Used to Impart*
Natural rubber	High	98		2	-72	High	Green strength, hot tensile, and hot tear.
Synthetic polyisoprene (Al/Ti type)	High	97	-	3	-27	Moderately high	Hot tensile and hot tear.
Synthetic polyisoprene (Li type	Very high	90	3	7	-70	Low	Dynamic properties (however, deficient in green strength, hot tensile and tear).
Balata (and synthetic equivalents)	Medium	-	98	2	-72	Very high	Green strength, when used in small amounts.
High 3,4 polyisoprene	Medium	(Under 50)		(Over 50)	>-37	Nil	Traction.

* In blends in which non-polyisoprene rubbers are also used.

24. Thus, even within one "homologous" category, the range of physical and chemical properties is quite wide. This is reflected in the range of individual properties that are exploited to warrant the use of an individual species: ease of crystallization for natural rubber and the trans polyisoprenes; high Mn in the case of synthetic polyisoprene made with lithium catalyst; and high Tg in the case of the high 3,4 polyisoprenes.

25. We can see, then, that the world usage pattern which has evolved derives from a combination of so-called "pragmatic" factors -- prices and individual national policies, including protective subsidies -- and technological factors. The technological factors are related to molecular structure (and associated performance) of the individual rubbers. Each category of factors -- the "pragmatic" and technological -- will continue playing a major role in determining the overall usage pattern for the foreseeable future. Both categories have so many imponderable aspects as to defy logical approaches to forecasting, but let us nevertheless examine certain areas where reasonably predictable developments should play a major role in both the shorter range (pre-1980) and longer range (post-1980) future.

IV. NEW DEVELOPMENTS AFFECTING THE 70'S

26. The tempo of technological change is quickening in both the preparation of new rubber and in tire manufacture, and it is therefore appropriate to examine those changes deemed likeliest to be manifest within the next few years:

A. The tire "mix": In passenger cars two concurrent trends are having quite different effects on tire usage. On the one hand, larger, heavier tires are being put onto the large size and standard size cars in the U.S. (1500 kg and larger), due to the more stringent safety requirements and the greater performance levels demanded by the customer. On the other, the surging popularity of mini cars, occurring at the expense of heavier cars, has meant that the average tire size has actually decreased. Thus, there is emerging a greater spread in the rubber usage pattern between the larger and smaller passenger tires, with the latter demanding less of the high resilience and high abrasion resistant rubbers to meet customer requirements.

B. Changing tire constructions: Two major improvements in tire construction over the standard bias tire are being reflected in rubber usage:

The radial tire, long established in Western Europe, is making a bid to become a significant factor in North America and elsewhere, despite its high fabrication cost. Estimates vary as to its ultimate level of usage; cost-to-manufacture is likely to be the determining factor. Widespread efforts to lower this cost -- and especially to automate some phases of manufacture -- are going on worldwide. The role of the rubber compound, especially green strength and shape holding ability prior to cure, plays a relatively greater role in fabrication of the radial tire than it does in other types. This is one reason why somewhat higher levels of natural rubber are required in radial tires, and will help support demand for natural rubber worldwide as long as none of the synthetics yet quite equal natural in this vital fabrication characteristic. Once low cost synthetics are developed that equal or exceed natural rubber in green strength, and particularly if they outperform natural in other respects, natural rubber's role in radial tires will be less essential technologically; and its usage will then be determined by whether its price is lower than the new synthetic. It goes without saying that there is considerable research and development effort on low cost synthetics with high green strength by the large rubber companies.

The bias belted tire -- wherein a steel, fabric, or fiber glass belt is applied to a low aspect ratio, standard bias ply carcass -- is considerably lower in cost to manufacture than the radial ply tire, and performance is intermediate between the standard bias ply and the radial tire. Its ease of fabrication is much less critically dependent on green strength of the uncured components, and therefore the rubber compound options are much wider. Comparisons of the three types is shown in Table VI.

TABLE VI

Performance of Several Tire Constructions

(Polyester carcass in all tires)

Construction	Bias	Bias belted	Radial
Type of belt	--	Fiberglass	Rayon
Treadwear rating	100	140	200
High speed (mph)	110	115	120
Wet skid rating	100	110	112
Ride (low speed) rating	100	98	96
Relative fuel consumption	100	99	104

The relative penetration of the radial tire and the bias belted tire into each other's domain by, say, 1975, will be difficult to forecast, being dependent in a complex way upon labor costs, rubber prices, and trends in automotive development. Just what this balance turns out to be will be in part related to progress in tire technology in minimizing dependence on an appreciable content of natural rubber as an aid in fabrication; and in part to progress in developing new synthetics of high green strength; and on economic factors.

C. Safety requirements. Government involvement in testing and setting performance standards for tires -- already well along in the U.S. and expected in due course to become a major factor worldwide -- is beginning to affect the choice of rubbers used in tread compounds, and will ultimately play a major role. This will in large part be because traction and treadwear requirements are likely to become a subject of government regulation in the not-too-distant future. Called "traction rubbers," such polymers are characterized by relatively high brittle temperatures and high hysteresis losses. Examples are: emulsion SBR having much higher styrene contents than the usual 16 to 23%; and high 1,2 content solution polybutadiene. Because of their high brittle temperatures, poor dynamic characteristics, and low treadwear ratings, such rubbers are used only in moderate amounts in blends along with major amounts of high treadwear, high resilience rubbers. Usage at present is small worldwide, but will inevitably increase once the government regulation of traction and treadwear becomes a factor in overall performance.

D. Rubber Prices: While price trends for most products involved in international commerce have been upward in the last decade, rubber prices have, in general, tended downward. We believe that -- except for occasional short-term upward surges -- this downward trend might well continue for the 70s, even in the face of rapidly rising production. Factors contributing to this belief are:

a. Lower monomer prices, resulting from (a) increasing availability of by product of olefins -- deleterious to the petrochemical streams from which they are removed; (b) competition between monomers -- especially between well established monomers and those trying to gain a foothold in the elastomer market, such as propylene oxide; (c) increased R & D programs by petroleum and chemical companies to achieve low price monomers (under 10¢/lb).

b. Lower plantation costs. The combined effects of introducing Ethrel, the new latex flow-stimulant, and greater mechanization on the plantation augur for lower natural rubber production costs, even though labor rates and freight costs are rising.

c. Regional overcapacity from too many synthetic plants. The sprouting of new tire plants in developing countries tends to be followed by a desire to have one's own synthetic rubber plant. Since polymer plants have to be quite large in order to be competitive, the accompanying excess capacity is a virtual guarantor of low overall prices -- regardless of what category of rubber has the excess capacity.

27. Taken together, the foregoing considerations render the process of deciding on new rubber capacity -- type, when, where, and how much -- a very difficult one indeed, far more so than, say, 10 or 15 years ago. This is especially the case when viewed from the

standpoint of organizations involved only in producing rubber--i.e. who do not, like the tire companies, also consume it. The tumbling prices of many petrochemical products on the world market--especially plastics--further contribute to caution on the part of potential investors in new capacity. Finally, there is the additional shadow cast by the prospect of really major technological changes coming out of still-undisclosed research projects that may obsolesce--slowly, but inevitably--a significant proportion of the rubbers now being produced.

28. Let us look into these possibilities.

V. A LOOK AT THE LONGER RANGE FUTURE

29. What developments in the longer term have both a reasonable prospect of being commercialized if adopted, and the likelihood of affecting the rubber usage pattern in a very substantial way?

30. One might first raise that always-asked question: Could there arise a new synthetic rubber which would challenge the well established rubbers--even though natural and the current synthetics are looked upon as serving quite adequately at present? For, despite "adequate" service from present rubbers, there still remains much room for improvement in several key areas of performance.

31. For example, is there a realistic prospect of a new synthetic that might have cis-polyisoprene's strength, tack, and resilience properties but also have both superior aging and abrasion resistance, so that it could do the job now being done by the blendsof rubbers now commonly used throughout tires, and perhaps find a niche?

32. A current example being raised of this possibility is the recent announcement concerning polypentenamer by a Bayer subsidiary Stereokautschukwerke, GmbH. By 1973 they will have on stream a 50,000 metric ton per year plant for this rubber. Polypentenamer could become a classic example of a long-sought new synthetic rubber which possesses three desirable traits for a rubber to a high degree: its high abrasion resistance gives polypentenamer good potential for treadwear; its high green strength would be a major factor in tire carcass fabrication (particularly radial tires), and its monomer cost should make the rubber competitive with polybutadiene and polyisoprene. Moreover, it is reported to age at least as well as SBR, perhaps better.

33. Another example is OPR--oxypropylene rubber--a nonhydrocarbon rubber which has flirted with the specialty rubber field, and whose more recent monomer price reductions (to well below 10¢/lb) and good all-around properties--particularly flex life--could bring it into contention as a tire rubber. There has been progress in overcoming its permanent set problems.

34. While such new synthetic rubbers would initially influence the natural rubber-synthetic rubber usage ratio primarily in proportion to the ease of their being blended with natural rubber and present synthetics for optimum utility, this compatibility aspect would not necessarily be the case for the longer term picture, if high performance tires based on one or the other of these as the primary rubber were developed.

35. In the area of tire technology, there is considerable room for improving longevity of present types of tires, (therefore using substantially less rubber per vehicle mile.) By extending technology already well known, longer wearing tires might well be developed that would not require substantial changes in the rubbers used, e.g. from:

a. Tire design. Just as the radial and bias-belted tire have, in a relatively short time, produced very sizable performance increments over ordinary bias tires at substantial (though acceptable) premiums to the consumer, so might we look for further performance improvements and/or lowering of fabrication cost in the next several years from both these approaches.

b. Tire fabrication techniques. Modifications of present fabrication processes are under constant development, and one area always attracting the tire technologist is to achieve the capability of processing and molding rubbers at much higher molecular weights (Mooneys) than can be handled at present. Treadwear improvements of 20-30% are known to be achievable--an effect which would be equivalent to the earlier introduction of cis-polybutadiene.

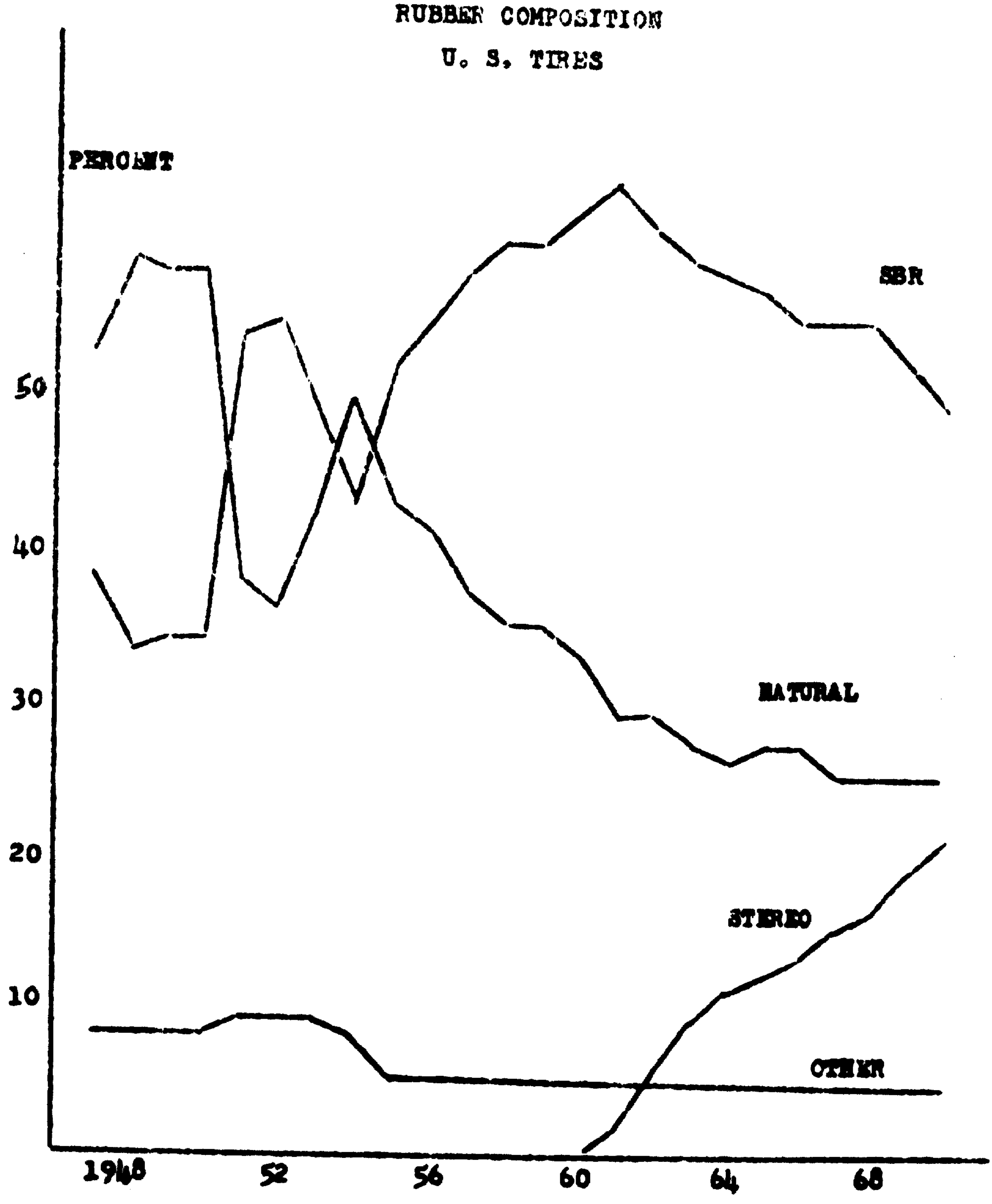
36. Major programs in both these areas are going on and are certain to produce inevitable, though unpredictable, effects on the amount of rubber needed for tires and on the use pattern of the various types.

37. Turning to more revolutionary possibilities, can we foresee rubbers processible in liquid or semi-liquid form that might permit totally automated plants? The gain in quality control and savings in labor costs could well permit paying a premium for the base polymer. What is more, none of the synthetics produced today would appear to have a significant role in this development.

38. Such a dramatic change in molecular architecture of the cured network most likely will require a rubber quite different from those we have discussed so far, one designed specifically for use in the new process. One U.S. manufacturer has recently accelerated the ever-present latent interest in this area by a series of announcements and publications on the results of its program to mold cordless tires from liquid rubbers. If such a revolutionary technology were to become successful, it would usher in a demand for a whole series of new rubbers to match up with the demands placed on various types of tires.

39. Summing up, then, we are looking at a current rubber usage pattern that is considerably more complex than it was five years ago, and seems likely to become appreciably more complex five and ten years hence. Though the unquestioned stronger demand will assure even wider markets for rubber, the question of which rubbers to place the greatest emphasis on for new investment is getting more and more complicated, because of ever-more-rapid shifts in tire manufacturing technology, in polymer technology, and in pricing practices. Taken longer range, prices are being pushed lower, and investment planning based on expectations of higher prices in the future would seem to be quite imprudent.

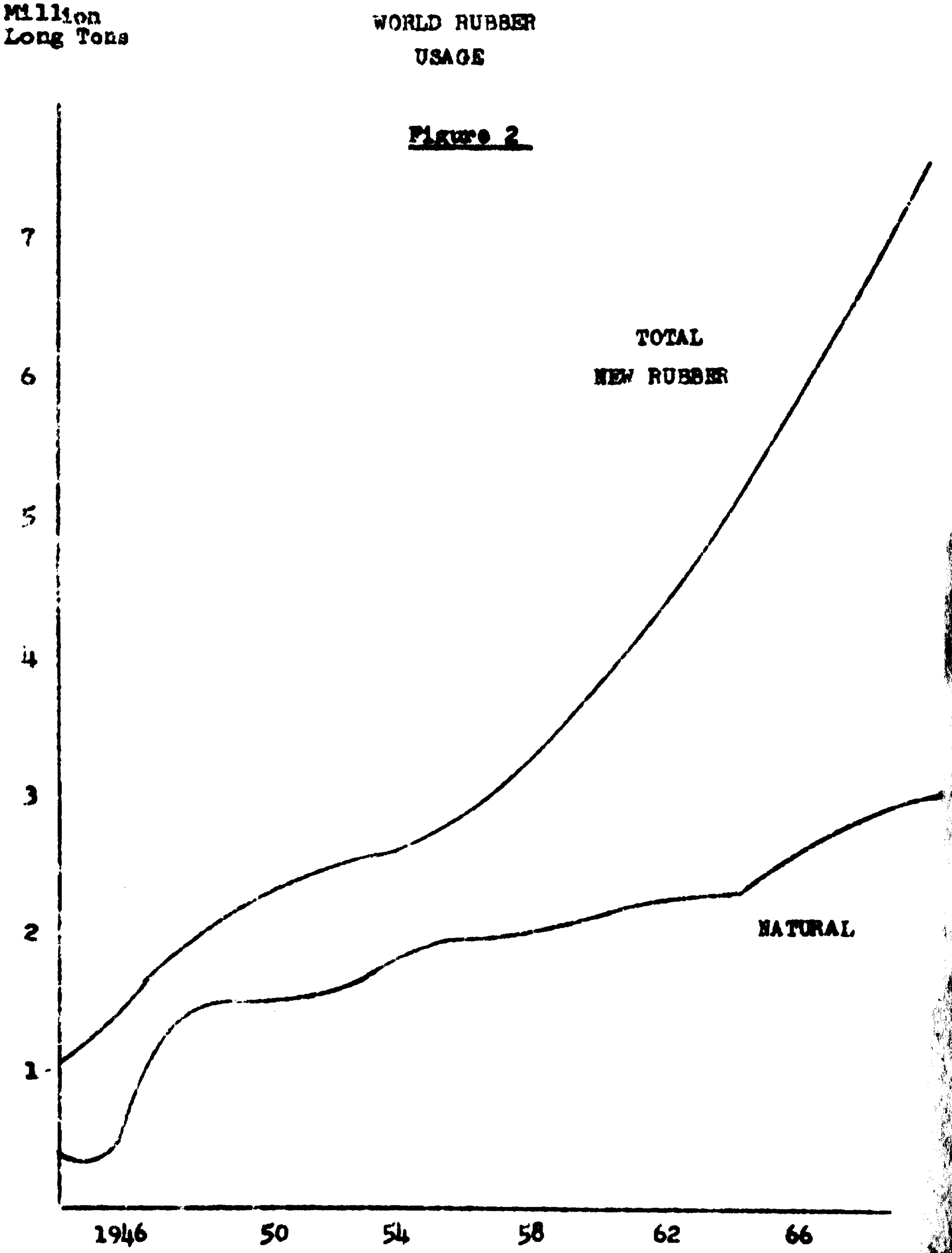
Figure 1

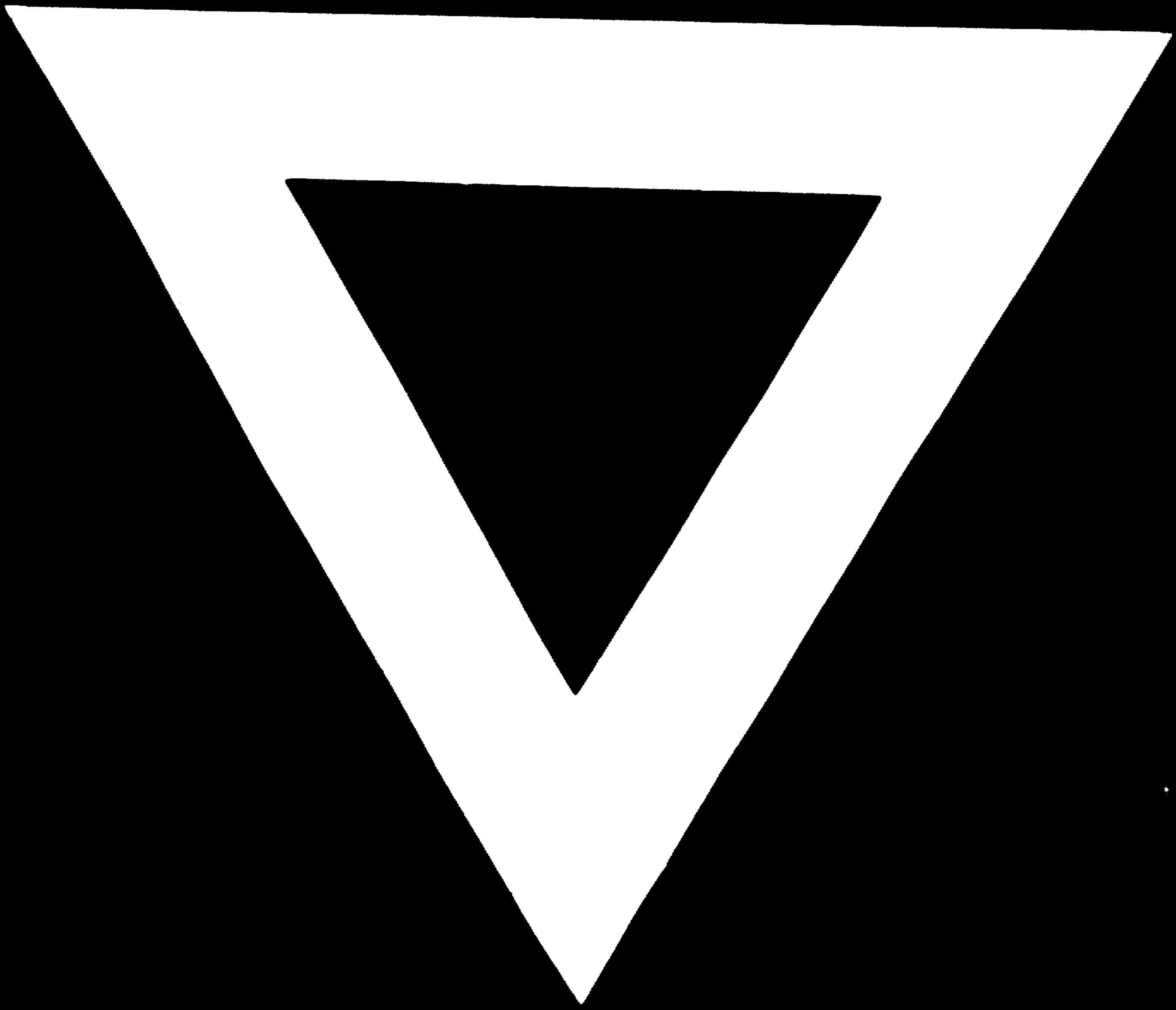


RUBBER COMPOSITION
U. S. TIRES

WORLD RUBBER
USAGE

Figure 2





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