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Interregional Petrochemical Symposium on the
Development of the Petrochemical Industries in
Developing Countries

PET. SYM 5/4

Taku, USSR, ~~29~~ - 31 October 1969
21

MERITS OF THE NEWER RUBBERS FOR DEVELOPING COUNTRIES^{1/}

by

R.S. Hamer
J.M. Short
L.V. Howenstine

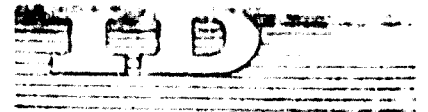
Phillips Petroleum Co.
New York
United States of America

presented by

L.V. Howenstine

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SUMMARY

MERITS OF THE NEWER RUBBERS FOR DEVELOPING COUNTRIES^{1/}

by

R.S. Hamer

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Until the last decade, the synthetic rubber industry was based almost entirely on emulsion butadiene-styrene copolymer which was developed almost thirty years ago. Within the last ten years, several new types of synthetic rubber processes based on solution polymerization have become important commercially. These new solution rubbers frequently have and can replace emulsion SBR and natural rubber with important advantages. The choice of the best rubber to suit the requirements of a developing nation requires a careful consideration of the immediate needs of that nation in the light of the variety of new rubbers available today. The choice can be limited to emulsion SBR, cis-polybutadiene, cis-polyisoprene and solution polymerized polybutadiene and solution SBR

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copolymers.

At first glance, emulsion SBR appears to have much to offer. It is an old, thoroughly established product, made by a process that is highly perfected. There are, however, very serious limitations which can easily be overlooked. Emulsion SBR is not a satisfactory rubber for heavy duty truck tires, and this constitutes the largest requirement for developing nations. Even in less demanding applications, emulsion SBR rubber is generally mixed with some of the new rubbers to overcome cracking and tread wear deficiencies.

Cis-polybutadiene has a number of outstanding properties, particularly low hysteresis, high crack resistance and outstanding abrasion resistance. It is deficient in tear resistance and in skid and traction properties, consequently it is always used in a blend with butadiene-styrene copolymer or natural rubber, generally at less than 50 per cent of the total rubber hydrocarbon, for tire construction.

Cis-polyisoprene can be produced today to virtually duplicate natural rubber performance. Like natural rubber, cis-polyisoprene is poorer than SBR rubber in treadwear, and it is frequently blended with SBR or polybutadiene to offset this deficiency. Moreover, there are only a very few highly industrialized areas in the world which have the necessary feedstocks available to produce isoprene needed for the manufacture of cis-polyisoprene.

The solution SBR rubbers and polybutadiene made with butyllithium catalyst have grown tremendously in importance during the last few years. World capacity for these rubbers exceeds 500,000 annual tons. Indeed, the development of this class of rubbers must surely rank in importance with discovery of emulsion SBR.

The butyllithium solution polymerization process for manufacturing rubber offers many advantages not available in any other single rubber process. It is a new process, one which will provide continuing new developments for many years. It is a highly versatile process, capable of producing butadienestyrene copolymers, polybutadienes, high styrene resins, block copolymers, and thermoplastic elastomers which can be used in some cases without vulcanization. A single plant can supply a variety of rubbers suitable for the tires, electrical and mechanical goods, footwear and plastics. It is economical, particularly when production requirements are relatively small, on the order of 10,000 to 25,000 annual metric tons.

Phillips Petroleum Company and their partners have solution rubber plants in Belgium, Spain, Australia, Japan and the United States with a combined capacity in excess of 150,000 tons per year. These plants produce a variety of butadiene and butadiene-styrene copolymers under the Solprene trademark. Experience in Spain has shown that a single Solprene plant can readily supply the major rubber requirements of a developing economy with a family of high quality rubbers suited to a variety of applications.

Since the beginning of the modern synthetic rubber industry the "work-horse" polymer that has accounted for more than 70% of all synthetic rubber that has been produced to date has been a copolymer of butadiene and styrene. Essentially all of this SBR rubber has been made in an emulsion process, using a free radical catalyst, a mercaptan modifier to control molecular weight, and a shortstop to stop polymerization at about 60 to 75% conversion of the monomers. The resulting latex is stripped to recover the unreacted monomers and the residue is coagulated, washed and dried. The most significant change that has been made in the polymerization process since its commercialization was the shift of most SBR production to the cold rubber process in the late nineteen forties. The development of oil-extended rubber and black masterbatch were also notable variations in the form of the finished product.

Emulsion SBR rubber as produced today is an excellent product, made in a wide range of grades, and adapted to many uses. Oil-extended grades, including those containing up to one-third oil, provide economical products that presently sell on the U.S. market at prices as low as 12¢ per pound.

The technology of the production of emulsion SBR rubber is highly developed, and in much of the world there is now adequate plant capacity to fill all requirements for this rubber even in periods of high demand. It is estimated that the U.S. production of SBR in 1968, a "boom" year, was near 90% of rated plant capacity. Much of this capacity is in fully depreciated plants that have been in production for more than 20 years and are now able to produce at low manufacturing costs. Similarly, the technology of the use of emulsion SBR rubber is now well developed. Rubber users have standardized many of their compounds on some grade of SBR rubber.

At first glance, emulsion SBR appears to have much to offer. It is an old, thoroughly established product, made by a process that is highly perfected. There are, however, very serious limitations which can easily be overlooked. Emulsion SBR is not a satisfactory rubber for heavy duty truck tires, and this constitutes a large requirement for developing nations. Even in less demanding applications, emulsion SBR rubber is generally mixed with some of the new rubbers to overcome cracking and tread wear deficiencies.

Within the last ten years, several new types of synthetic rubber processes based on solution polymerization have become important commercially. These new solution rubbers frequently can replace emulsion SBR and natural rubber with important advantages. The choice of the best rubber to suit the requirements of a particular market requires a careful consideration of the immediate needs of that market in the light of the variety of new rubbers available today. The choice can be limited to emulsion SBR, cis-polybutadiene, cis-polyisoprene and solution polymerized polybutadiene and solution SBR copolymers.

Cis-polybutadiene has a number of outstanding properties, particularly low hysteresis, high crack resistance and outstanding abrasion resistance. It is deficient in tear resistance and in skid and traction properties, consequently it is always used in a blend with butadiene-styrene copolymer or natural rubber, generally at less than 50 per cent of the total rubber hydrocarbon, for tire construction.

Cis-polyisoprene can be produced today to virtually duplicate natural rubber performance. Like natural rubber, cis-polyisoprene is poorer than SBR rubber in treadwear, and it is frequently blended with SBR or polybutadiene to offset this deficiency. Moreover, there are only a very few highly industrialized areas in the world which have the necessary quantities of feedstocks available to produce isoprene needed for the economical manufacture of cis-polyisoprene.

The solution SBR rubbers and polybutadiene made with butyllithium catalyst have grown tremendously in importance during the last few years. World capacity for these rubbers already exceeds 500,000 annual tons. Among the several reasons for the rapid growth of alkyllithium solution polymerization are the following:

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 color, lower in odor, and is less contaminated with fatty acid, soap, and ash than is emulsion SBR. Non-hydrocarbon contaminants typically run below 1% vs 7% 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 to 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.

Probably the principal advantage for alkyllithium solution polymerization compared to emulsion free-radical polymerization lies in the opportunity to alter fundamental polymer characteristics such as microstructure, molecular weight distribution and branching. Additionally the solution process permits variation in comonomer incorporation to yield block copolymers of several types not possible in emulsion polymerization. A further advantage, perhaps of secondary importance, lies in the colorless, low ash, low odor properties of solution polymers making them ideal as plastics modifiers, for electrical insulation products, light-colored mechanicals and footwear. Solution-polymerized polybutadiene has been long recognized as a most important contributor to improved tire performance in heavy duty tires as well as passenger types. Polybutadiene improves tread wear when used in combination with natural rubber or with SBR, reduces tread cracking, and contributes to carcass durability through improved resistance to heat and reversion. Introduced in the late 1950's polybutadiene was the first of many "solution" type polymers to be commercialized and is an important rubber for any country's library of polymers.

Commercial solution polymerization systems which produce copolymers of butadiene and styrene are presently based on lithium catalysis. Phillips Petroleum Company has developed such a system to produce a complete line of butadiene-styrene copolymers as well as polybutadiene under the tradename of "Solprene" rubbers.

A brief description of these rubbers and their uses follows.

The Solprene family of rubbers comprises polybutadiene, block butadiene-styrene copolymers, random butadiene-styrene copolymers, and oil masterbatches. Typical rubbers in each category are shown in Table I.

TABLE I

Solprene Elastomers

<u>Solprene No.</u>	<u>Butadiene/ Styrene Ratio</u>	<u>Oil, phr</u>	<u>Typical Mooney, MI-4</u>	<u>Uses</u>
<u>Polybutadienes</u>				
245	100/0	0	45	Tires - blended with SBR and natural rubber
201	100/0	0	55	High impact plastics
<u>Block Copolymer</u>				
1205	75/25	0	47	Footwear, flooring, electrical products, processing aid
303	52/48	0	45	Footwear, microcellular sponge
410	52/48	0	47	Footwear
<u>Random Copolymer</u>				
1204	75/25	0	56	General purpose - tires, footwear, mechanical goods
1206	75/25	0	33	Sponge
301	75/25	0	77	Plastics modification, processing aid
306	75/25	0	56	Tires, mechanical goods
<u>Oil Extended</u>				
277	100/0	37.5 ^a	40	Tires - blended with SBR and natural rubber
375	75/25	37.5 ^b	46	Footwear, mechanical goods
377	75/25	37.5 ^a	50	Tires
380	75/25	37.5 ^a	50	Tires

a - Staining - highly aromatic oil

b - Non-staining - naphthenic oil

Two polybutadiene types are shown - one for use in tires blended with natural rubber or SBR (either solution or emulsion type) and the other for the production of high-impact polystyrene. The block copolymers are used in footwear, flooring, electrical products, microcellular sponge, and as processing aids to smooth out mixing, extrusion, and molding operations. The random copolymers include general purpose types for tires, footwear and mechanical goods, and special products for plastics modification and sponge. Several random copolymers as well as polybutadiene are made as oil masterbatches to permit cost reduction in several product lines.

As Solprene rubbers differ from emulsion rubbers in varying degrees, so processing properties are also somewhat different. For example, the structure of some Solprene rubbers gives rise to low shrinkage which may lead to a mill handling problem but it is these same characteristics which give fast extrusions with a smooth, glossy surface. Likewise, several of the Solprene elastomers have a narrow molecular weight distribution which may make them tougher and more difficult to process but which also contributes to improved hysteresis properties and allows the compounder to use increased amounts of oil and filler.

Advantages in physical properties which can be gained through the use of various types of Solprenes are listed below.

<u>Property</u>	<u>Solprene Rubbers</u>
Excellent color	245, 201, 1205, 1204, 301, 1206, 303, 375
Improved abrasion resistance	245, 277, 1205, 1204, 380
Improved cracking resistance	245, 277, 1204, 1205, 375, 377, 380
High resilience, low heat generation	245, 277, 1204, 375, 377
High hardness	1205, 303, 410
Excellent extrusion properties, low shrinkage	1205, 303, 377
Low brittle point	245, 277, 1205
High oil capacity	245, 1204, 375, 377, 380
Good flow during cure	1204, 1205, 1206, 303

POLYBUTADIENE

Solprene 245 polybutadiene provides low heat generation in dynamic applications and excellent abrasion resistance. Stress-strain and processing characteristics are marginal when this polymer is used alone indicating the desirability of blending this product with other polymers. In such blends, Solprene 245 rubber imparts improved resistance to abrasion and cracking. When blended with natural rubber it provides greater thermal stability and greater resistance to adverse effects of reversion and overcure. In blends containing relatively large amounts of Solprene 245 polybutadiene, high filler and plasticizer levels improve processing properties without sacrificing abrasion resistance. The rubber is beneficial in tire treads, carcasses, and in mechanical goods requiring outstanding abrasion resistance and high resilience. Typical tire tread compounds are shown in Table II.

TABLE II

Tire treads containing Solprene 245 polybutadiene

	<u>Formulation</u>					
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
Solprene 245	40	-	-	30	-	-
Cis-Polybutadiene	-	40	-	-	30	-
Natural rubber	60	60	100	-	-	-
SBR	-	-	-	70	70	100
ISAF Black	60	60	60	70	70	70
Oil	18	18	18	40	40	40
	<u>Properties</u>					
300% Modulus, psi	1200	1270	1600	1000	1000	1100
Tensile, psi	3400	3400	3700	3000	3000	3500
Δ T, F	60	58	53	66	64	67
Resilience, %	64	64	64	60	60	54
	<u>Performance</u>					
Groove cracking, % of control	5	5	100	40	40	100
Skid resistance	-	-	-	95	95	100
Abrasion resistance	110	110	100	112	118	100

Both cis-polybutadiene and Solprene 245 (medium cis content) confer the desirable properties of solution polybutadiene to their respective compounds. Cis-polybutadiene is slightly better in its influence on abrasion resistance when mixed with SBR but is not as good in processing characteristics as Solprene 245 in this application.

BLOCK COPOLYMERS

Solprene 1205 is a simple block copolymer, having linear molecules that consist of polystyrene segments on one end and polybutadiene segments on the other. A product of this type displays unusual properties. Because of its block configuration, it is considerably more thermoplastic than conventional rubbers and softens in the raw state above about 150 F. This characteristic imparts outstanding molding and extrusion properties to compounds stock based on this rubber. Vulcanizates display high glass and hardness and good abrasion resistance. Unlike many rubbers that exhibit high hardness, Solprene 1205 displays excellent low temperature flexibility. The over-all balance of properties cannot be matched by any of the emulsion SBR rubbers. A comparison of the properties of Solprene 1205 and SBR 1503 is shown in Table III.

Block copolymers can be used advantageously either alone or in blends with conventional rubbers in many applications where easy moldability, fast extrusion, surface appearance, hardness, or low temperature flexibility are important. Frequently, a compound based on a block copolymer will give a better result at lower compound cost than possible with emulsion SBR rubbers. For example, some sole stocks from Solprene 1205, which display high hardness without addition of high-styrene resins, offer quality advantages in appearance, color, flex-life, and abrasion resistance as well. Block copolymers are also of interest for the manufacture of high quality floor tile in attractive new pastel shades, or in some cases translucent patterns. High glass and easy extrusion are important benefits in the manufacture of extruded pipe base. The balance of fast extrusion, good electrical properties and low temperature flexibility have resulted in applications in the wire and cable field.

Solprene 410 copolymer is similar in composition to Solprene 303 having a styrene content of 48%. It contains approximately 30% of the styrene as block styrene compared to only 11% in Solprene 303 and is therefore considerably harder. In fact, Solprene 410 copolymer finds its principal application in shoe products where it replaces conventional blends of high-styrene resins and natural rubber or SBR.

RANDOM COPOLYMERS

A typical random copolymer made in a solution process is characterized by the properties shown below:

TABLE IV

Typical properties of random butadiene-styrene copolymers

	<u>Solution-polymerized (Solprene 1204)</u>	<u>Emulsion-polymerized (Philprene 1500)</u>
Butadiene-styrene ratio	75/25	77/23
Color	White	Brown
Raw Mooney ML-4	58	50
Ash, %	0.13	1.0
Acid, %	0.02	6.0
Soap, %	0.02	0.30
Antioxidant, %	0.50	1.20
<u>Vulcanized properties*</u>		
Tensile, psi	3450	3650
300% Modulus, psi	1350	1300
Elongation, %	600	620
△ T, F	60	67
Resilience, %	66	60

* In a tread recipe containing 50 phr HAF black and 10 parts highly aromatic oil.

The data of Table IV illustrate the principal differences in physical properties between emulsion- and solution-polymerized random copolymer. The solution-polymerized product is lighter in color, and freer from non-rubber residues. Vulcanizates of the solution polymer are lower in tensile and elongation, but are higher in resilience and have lower heat build-up than the emulsion product.

Since these two products, both random polymers of about the same Mooney viscosity and butadiene/styrene ratio, behave differently, there must be other structural differences between them.

One of these is molecular weight distribution. Solution polymers nearly always have a narrower molecular weight distribution than corresponding emulsion polymers. Figure 1 shows comparison of gel permeation chromatographs of Solprene 1204 and SBR 1500, both random butadiene styrene copolymers. It is apparent that emulsion SBR contains a much larger low molecular weight fraction (shaded area on the left side of the figure) and a somewhat larger high molecular weight fraction (shaded area on the right side of the figure) than its solution polymer counterpart. A second difference is in branching. Emulsion polymers are known to be highly branched while solution polymers tend to be more linear in structure. Differences in branching affect the rheological properties of polymers and in this case probably account for most of the difference in processing properties between the two products. The lower heat build-up of solution SBR can be accounted for by its higher linearity and narrower molecular weight distribution.

Random solution SBR can be used successfully to replace emulsion SBR in many commercial uses, often with improved product performance. Since the two are not identical, it can be expected that the new rubber will not process exactly as its predecessor, and some adjustment of mixing and extrusion procedures must be made. For example, solution SBR has lower shrinkage than emulsion SBR, and die sizes must be changed to accommodate the new rubber. With lower tensiles and elongation and higher resilience, compounds based on solution SBR do not always duplicate factory specifications set up for emulsion polymer.

In 10 tire tests Solprene 1204 has shown treadwear averaging 8% superior to the controls made with SBR 1500. Results from some of these tests are shown in Table V, showing treadwear ratings of high and low modulus compounds tested at moderate and high severities. The solution SBR compounds gave best performance at moderate wear rates; that is, highway driving. Other tests have shown that the Solprene polymers give better treadwear under severe conditions when compounded with high structure blacks.

TABLE V

Passenger car treadwear on solution SBR

	<u>50 HAMMILL - 1000</u>		<u>1300 PSI Modulus - 2000</u>	
	<u>Solprene 1204 (Solution)</u>	<u>SBR 1500 (Emulsion)</u>	<u>Solprene 1204 (Solution)</u>	<u>SBR 1500 (Emulsion)</u>
	<u>Moderate Severity (15 Miles/hour)</u>			
1300 PSI Modulus	107	100	105	100
1800 PSI Modulus	96	100	115	100
	<u>High Severity (35 Miles/hour)</u>			
1300 PSI Modulus	102	100	100	100
1800 PSI Modulus	98	100	101	100

Similarly, oil-extended solution copolymers are satisfactory replacements for conventional oil extended SBR rubbers such as SBR 1712, either alone or in a mixture with polybutadiene. Here again, the blends using solution SBR do not process the same and do not have identical physical properties to established emulsion SBR-polybutadiene blends. After adjusting processing steps to accommodate the new rubbers, however, performance of the end products are generally quite satisfactory.

Table VI shows results of tests to compare performance of solution with emulsion low tire grades in skid and traction. Both oil-extended and inextended rubbers were used. Tires of identical size and tread pattern were tested on the same surface of a 12' test track surfaced with compact Portland cement concrete and with aggregate cements. The first test rated dynamic traction, the maximum draw-bar pull exerted by a vehicle capable to spin the wheels. The second test rated skid resistance as the percentage of the skid friction with locked wheels at 100 ft. Reproducibility in such tests is not very low, and, within that limitation it does not appear that there is any significant difference between the emulsion and solution rubber in skid resistance. In dynamic traction, the solution polymer gave results averaging 4% below the emulsion polymers. These differences were overshadowed by the effect of oil extension, which gave an over-all average improvement of over 10% in both skid and traction. Solution polymers, both polybutadienes and solution SBR, are nearly always used in high-oil compounds.

TABLE VI

Skid and traction-rubber oil extenders

	<u>W. 11 - 20 Black</u>		<u>W. 61 - 70 Black</u>	
	<u>Solprene 1204 (solution)</u>	<u>Solprene (emulsion)</u>	<u>Solprene 177 (solution)</u>	<u>SBR 177 (Emulsion)</u>
	<u>Dynamic Traction</u>			
Asphaltic concrete	100	104	100	105
Portland concrete	96	100	116	120
	<u>Skid Resistance</u>			
Asphaltic concrete	95	100	109	100
Portland concrete	106	100	109	114

THE SOLUTION POLYMERIZATION PROCESS

A solution process is one in which the polymerization reaction is run in a reaction vessel containing an hydrocarbon or other inert solvent in which both the initial monomers and the resulting polymer are soluble. Thus, we start with a solution of butadiene and styrene, add a catalyst, allow the reaction to proceed, and end up with a solution of rubber with perhaps more than 90% of the initial monomers reacted. As the polymerization proceeds, the solution becomes more and more viscous, and the final product is a thick cement. The remainder of the process consists in recovering the rubber from the cement. The essential steps in the process are shown in Figure 2.

In a butyllithium-catalyzed polymerization, one needs only to have a dry solution of the monomers in a stirred, temperature-controlled autoclave, add a predetermined amount of the catalyst, and continue stirring for a few hours during which the rubber is produced. The Mooney viscosity of the final product is determined by the amount of catalyst used - more catalyst produces a lower Mooney polymer.

It is not to be inferred, however, that there is not a great deal of art and know-how in operating a process of this type. Referring to Figure 2, the first problem is that of purifying the ingredients for the reaction process. This, incidentally, was the step that blocked large-scale introduction of solution polymerization until about 1950 - no one was able to remove impurities from the monomers and solvents adequately by commercially practical means so as not to 'kill' the small charge of catalyst employed. This means streams containing less than 5 ppm water, and similarly purified to avoid alcohols, sulfur compounds, acetylene and many other possible contaminants. Much has been learned in the past 15 years about purifying these ingredients and monitoring their purity so as to avoid a costly plant shutdown and these steps are performed routinely on very large scale today.

Although simple alkyl lithium compounds are useful catalysts, more sophisticated catalysts may be necessary for some special grades of polymers. Also, it is sometimes desirable to employ additives in the polymerization or recovery system to control structure or introduce branching.

When the polymerization process is completed, there is still the problem of recovering the polymer from the cement, while also recovering the solvent for reuse. Here, again, a great deal of art and know-how are involved; however, the processes have been worked out to the point that it is done in reasonably trouble-free operations in many plants around the world.

A critical question at this point is the investment and manufacturing cost of producing rubber by the solution process compared to the conventional emulsion process. When considering only new plants of less than 25,000 MTY, our estimates show that a Solprene plant requires less investment than emulsion SBR. At all levels of production, up to 25,000 MTY, the estimated manufacturing costs of solution rubber were below that of emulsion SBR.

PRESENT AND FUTURE ASPECTS OF SOLUTION POLYMERS

Solution polymerization production capacity in the world today exceeds one million metric tons per year with alkylithium processes accounting for more than 900,000 metric tons. This latter capacity is divided principally among twelve world-wide plants as shown in Table VII. It should be recognized that most of the plant capacity shown in Table VII was built to provide medium cis-polybutadiene for use in passenger and truck tires in a mixture with SBR and/or natural rubber as well as for butadiene-styrene copolymer. It is difficult to estimate present world-wide production capacity for solution SBR since this rubber is produced as a coproduct in several plants that also produce polybutadiene. Table VII lists 12 plants that are reported to be of this type. Six of these are plants built by Phillips Petroleum Company and its partners, using technology developed by Phillips. All are presently in operation. All these plants produce polybutadienes as well as SBR, with the product mix depending on markets. Thus, a plant having a capacity to produce 20,000 MTY of solution SBR may actually produce one-half or less of that amount, the balance or part of its production being polybutadiene. The Firestone plant at Orange, Texas, is believed to produce mostly polybutadiene, however, this company also markets solution SBR under the name "Styron". In the same way, the Asahi plant in Japan and the International Synthetic Rubber plant in Scotland have introduced solution SBR's under the names "Tufrene" and "Indiene", respectively.

Projections have appeared from time to time on future requirements for SBR world-wide. The curves in Figure 3 represent a compilation of these data. In the years ahead continued growth is forecast for SBR as the principal synthetic rubber for tires and also because of important non-tire uses. On the other hand we expect the consumption of emulsion SBR to level off at a figure comfortably close to present production capacity and for future growth in SBR to be in solution types. The curves in Figure 3 show consumption of about 400,000 metric tons of solution SBR in 1975. If polybutadiene is included, the total may well be twice this figure.

TABLE VII

Alkyl lithium solution polymerization plants

<u>Company</u>	<u>Location</u>	<u>Capacity, MT/Yr.</u>
Phillips Petroleum Company	Wenger, Texas	20,000
Firestone Tire & Rubber Co.	Lake Charles, La.	70,000
Firestone Tire & Rubber Co.	Orange, Texas	80,000
International Synthetic Rubber Company, Ltd.	Grangemouth, Scotland	50,000
Calatrava S.A.	Santander, Spain	40,000
Phillips Imperial Chemicals, Ltd.	Kurnell, Australia	20,000
Firestone-France S.A.	Port Jerome, France	22,500
Asahi Chemical Industry Co.	Kawasaki, Japan	40,000
Negromex, S.A.	Salamanca, Mexico	30,000
Petrochim N.V.	Antwerp, Belgium	55,000
COPERBO	Recife, Brazil	27,500
AA Chemical Company	Oita Kyushuu, Japan	<u>20,000</u>
		475,000

The butyllithium solution polymerization process for manufacturing rubber offers many advantages not available in any other single rubber process. It is a new process, from which new high-quality rubbers will evolve for many years. It is a highly versatile process, capable of producing butadiene-styrene copolymers, polybutadienes, high styrene resins, block copolymers, and thermoplastic elastomers which can be used in some cases without vulcanization. A single plant can supply a variety of rubbers suitable for tires, electrical and mechanical goods, footwear and plastics. It is economical, particularly when production requirements are relatively small, on the order of 10,000 to 25,000 annual metric tons. It will continue to grow in importance.

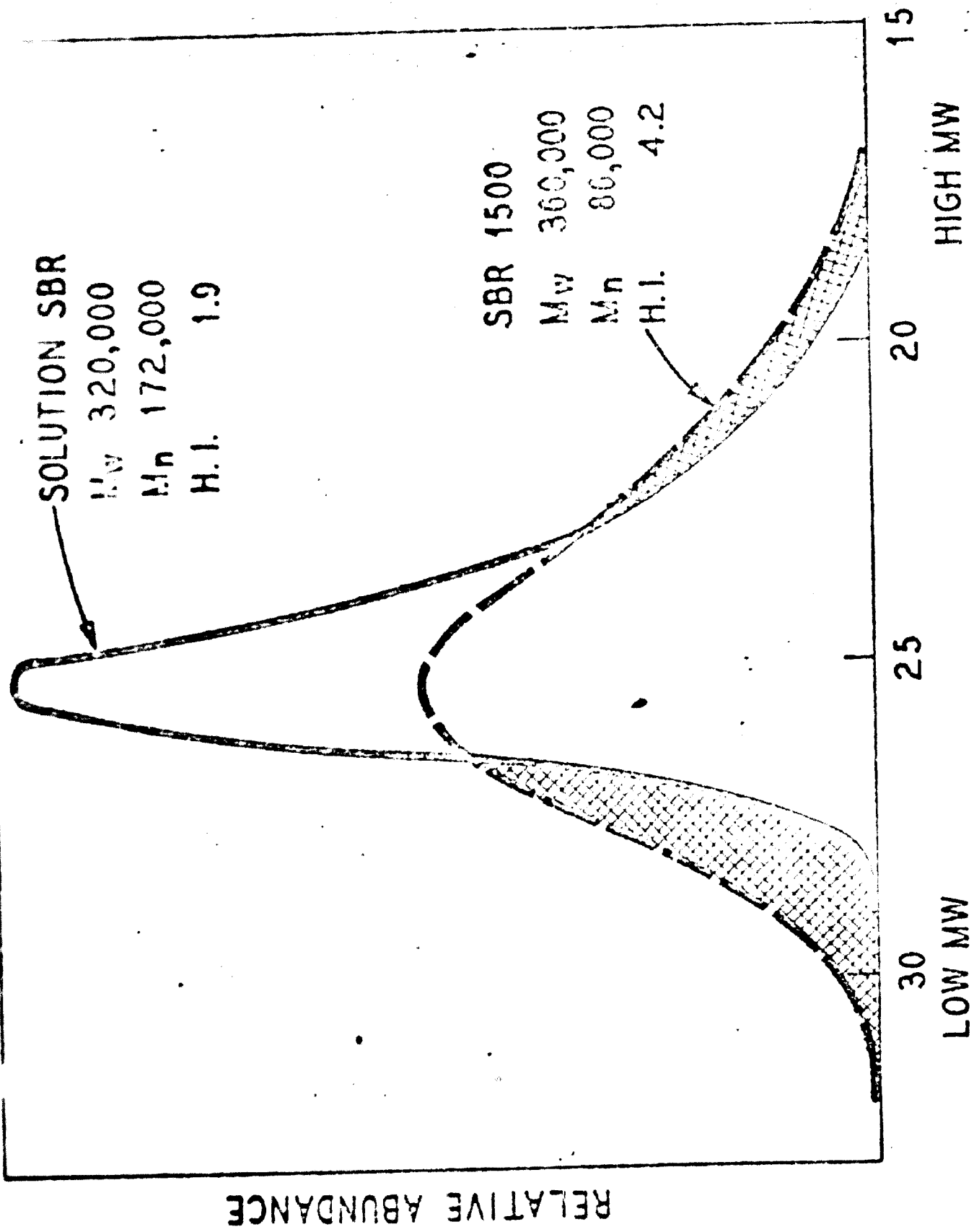


FIGURE 1
 ELUTION COUNT

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

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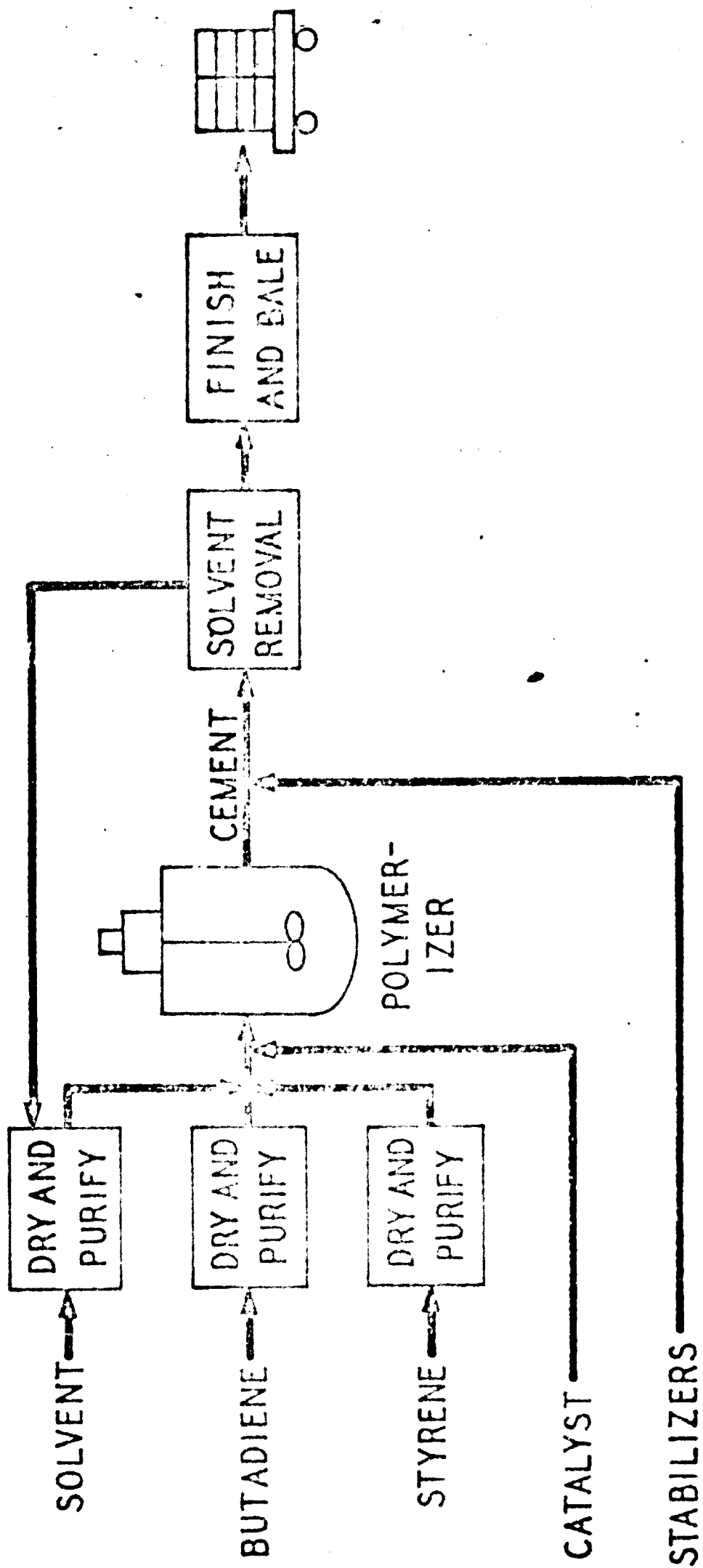


FIGURE 2
SIMPLIFIED FLOW DIAGRAM FOR
SOLUTION SBR MANUFACTURE

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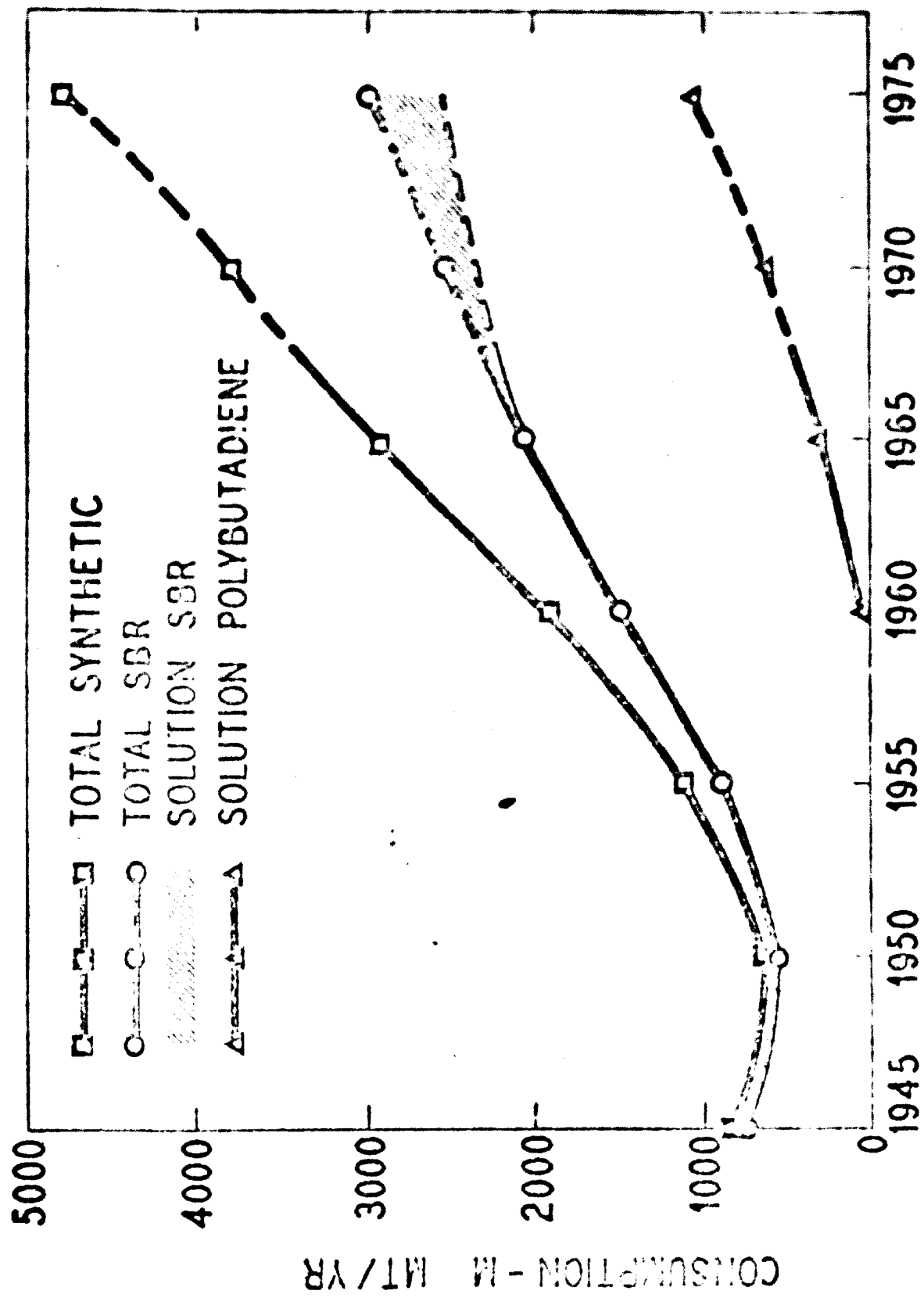
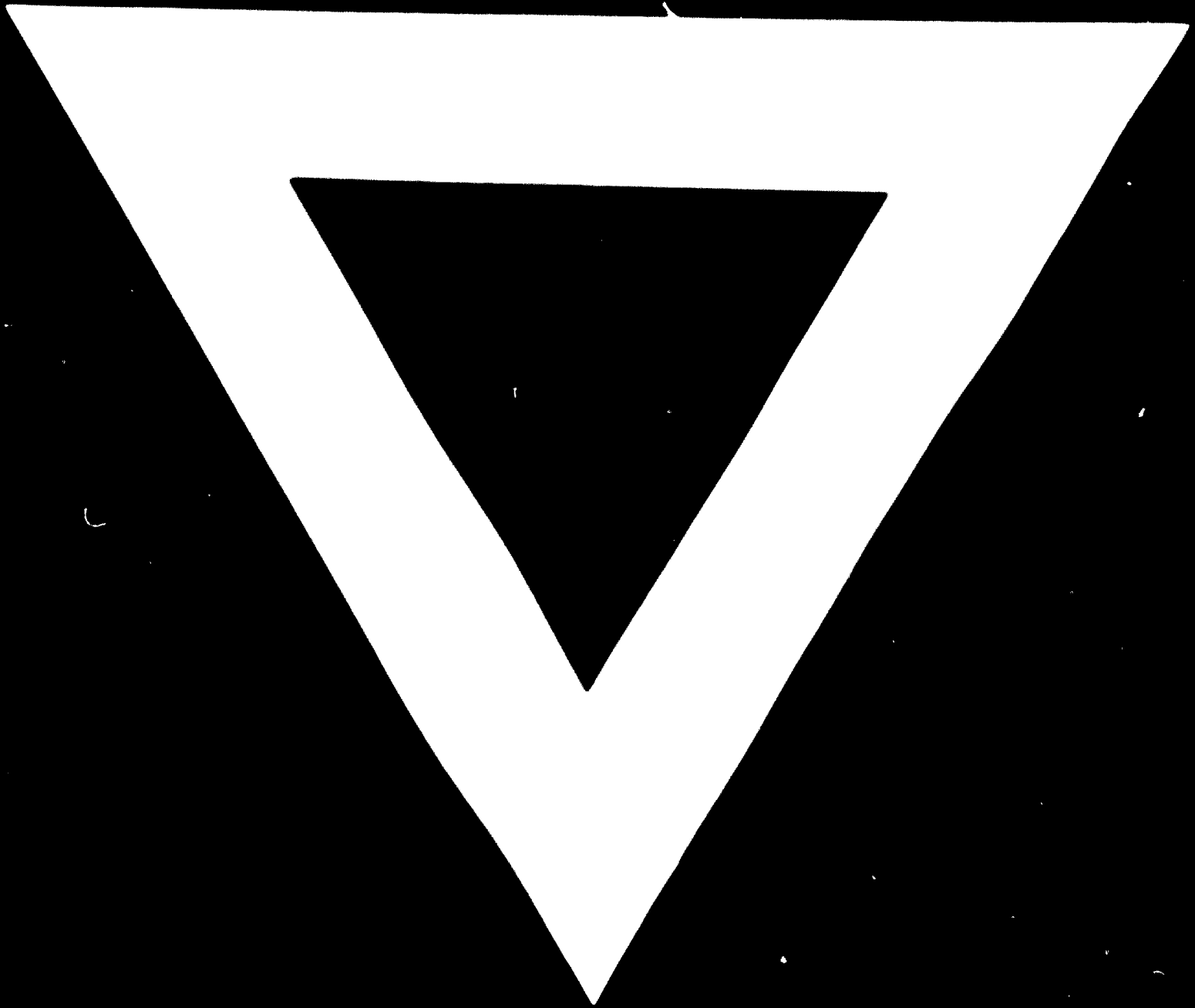


FIGURE 3

SYNTHETIC RUBBER CONSUMPTION OUTSIDE COMECON COUNTRIES



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