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GENERAL PURPOSE RUBBERS BY SOLUTION POLYMERIZATION WITH ANIONIC CATALYSTS[1]

by

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I. INTRODUCTION

Prior to 1960 the world's production of general purpose* synthetic rubbers consisted almost entirely of butadiene-styrene copolymers made in emulsion processes. Large-scale production of this rubber began in the early forties and by 1960 it represented about 40% of the world's consumption of rubber. Most of the remainder was natural rubber. In these early years much experimental work was done with rubbers made in solution systems; however, it appeared that such processes had little chance of competing economically with the emulsion route.

Between 1940 and 1960 several breakthroughs occurred that changed this situation and shifted interest toward solution systems. They include the following:

(1) "Stereospecific" catalysts (polymerization initiators) were discovered that are capable of polymerizing dienes selectively into high-cis, high-trans or high-vinyl polymers. Also with copolymers the monomer sequences could be controlled to produce random, block or alternating copolymers.

*By "general purpose" we mean sulfur-vulcanizable rubbers designed for use in tire treads and carcasses, footwear, mechanical goods, etc. Oil-resistant rubbers and other special rubbers are not included.

(2) Analytical methods were developed to determine the geometrical configurations, monomer sequences and molecular weight distributions of polymers.

(3) Practical industrial methods were developed to dry and purify the solvents used in polymerizations. Instruments were also developed to monitor the water content of such streams.

(4) Practical methods were developed to handle the viscous rubber solutions made in solution processes and to recover the rubber from them.

Meanwhile in the late fifties, U. S. tire manufacturers were in trouble. With increasing highway speeds and the use of automobiles of greater weight, higher horsepower and more efficient brakes, better performance was being demanded of tires. Oil-extended SBR rubber, the preferred product for auto treads, no longer gave the treadwear and carcass durability demanded by customers. The time was ripe for the introduction of new and improved synthetic rubbers.

The first of the new solution polymers to be marketed was cis-polybutadiene, which was commercialized by Phillips Petroleum Company at its Borger, Texas, plant in 1960. This rubber was quickly accepted by the tire industry for use in blends with SBR rubber in tire treads, giving sharply increased treadwear and avoiding the severe tread cracking problem with which the tire industry had been plagued. Within three years the Phillips process for cis-polybutadiene rubber was licensed to three U. S. rubber producers and to one each in France, Germany, Italy and Japan. Other companies developed their own solution polybutadiene processes, and by 1965 blends of SBR and polybutadiene became the standard compound for tire treads.

Meanwhile in [illegible] EPT (ethylene-propylene-diene) rubber was introduced, followed in [illegible] by commercial production of cis-polyisoprene (synthetic natural rubber). Production of these products has grown rapidly as shown in Figure 1, and by 1972 world production of solution rubbers outside the Communist countries exceeded 2.0 million tons.

With more than 2½ million tons of emulsion SBR capacity already existing, and with many of these plants operating below capacity, there was no great incentive to develop solution processes for butadiene-styrene copolymers. However, with continued research it soon became apparent (1) that by the use of certain anionic catalysts (metal alkyls) in solution systems, butadiene-styrene copolymers having unusual molecular structures and properties greatly superior in some applications to emulsion SBR could be produced; and (2) the cost of building a plant and producing such copolymers was not materially greater than that of a similarly sized plant employing an emulsion SBR process. Thus in 1962 solution SBR rubbers began to be produced, and in recent years this family of rubbers has been commercialized world-wide by Phillips Petroleum Company and its licensees. The Firestone Tire and Rubber Company also produces solution SBR and has licensed the process to several other producers. Exact capacity for solution SBR is hard to estimate since the same plants produce both SBR and polybutadiene; however, our best estimate at present is that non-Communist world capacity for these products exceeds 400,000 tons.

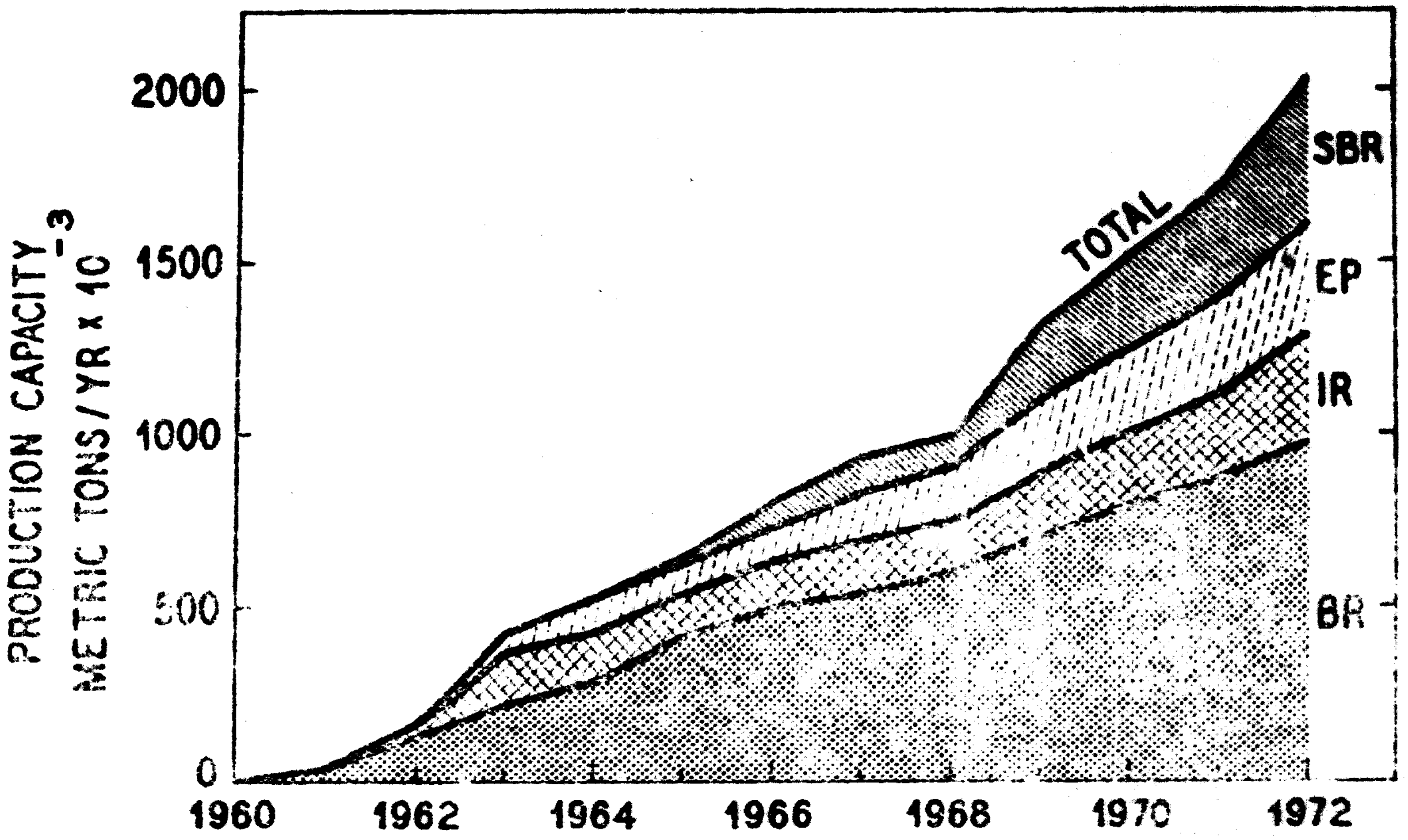
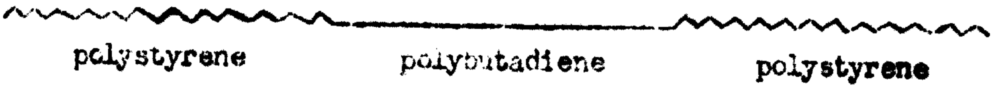


FIGURE 1

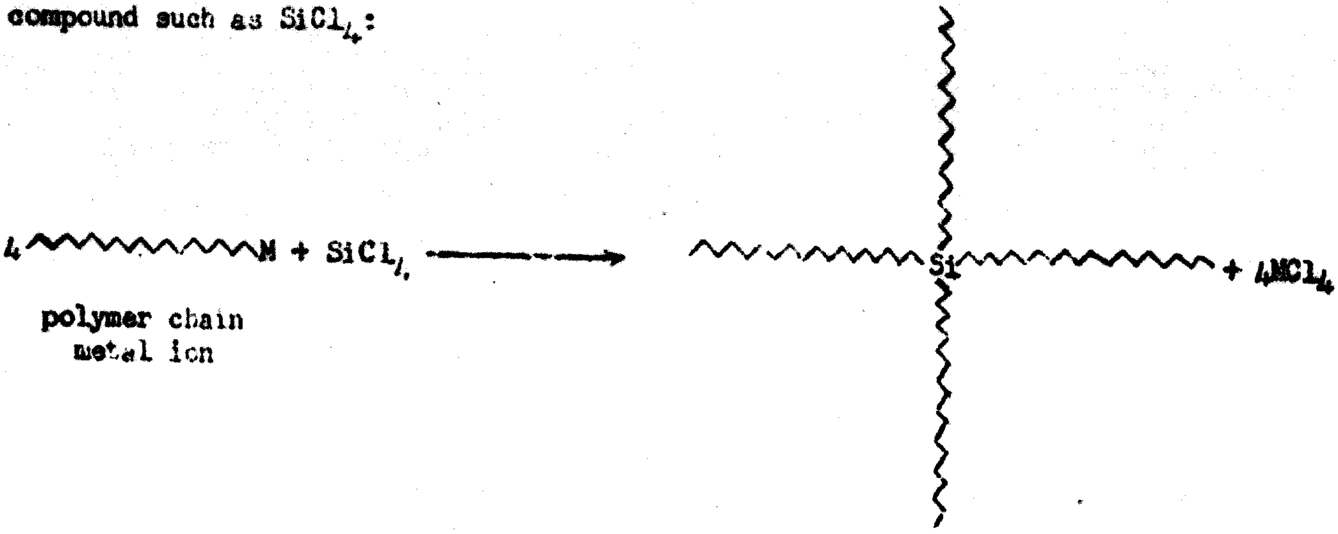
WORLD CAPACITY FOR SOLUTION RUBBERS
(EX COMMUNIST BLOC)

II. VERSATILITY OF THE PROCESS

A process employing an anionic catalyst in a solution system is by far the most versatile method known to produce synthetic elastomers. Dozens of different polymers can be produced. The polymerization occurs in a "living" reaction in which millions of polymer chains are initiated simultaneously and grow to high polymers over a period of time that might run for several hours without termination. At the end of that time a terminating agent is added to inactivate the growing polymer. If a lower molecular weight polymer is desired, more catalyst is used, producing more chains, each having a shorter length. If desired, a second monomer may be added during the reaction, producing "block" copolymers, consisting of polybutadiene on one end and polystyrene on the other. The process can be extended a step further to produce polymers having polystyrene ends and a polybutadiene center. These are the so-called ABA copolymers, thermoplastic rubbers, which have green strength without vulcanization.



Alternatively, it is possible to produce "radial" polymers in which three or four polymer chains radiate out from a central hub like the spokes of a wheel. This can be done by coupling living polymer chains with a compound such as $SiCl_4$:



Under some conditions, if two monomers are charged to the process initially, one will react first then the second. This produces a block copolymer. However, additives have been discovered that can be introduced at low levels into the reaction mixture which will force the monomers to enter the polymer chains in a random manner.

The versatility of the process is illustrated by the list of products shown in Table I which shows twelve Solprene® rubbers which are typical of those produced by Phillips and its licensees. The list includes polybutadienes, random copolymers, block copolymers, oil-extended random copolymers and several radial block copolymers (thermoplastic rubbers). They are used in tires, footwear, mechanical rubber goods, as a plastic (impact polystyrene) additive and in adhesives. Some of the thermoplastic rubbers are used in injection molding without vulcanization.

TABLE I

TYPICAL SOLPRENE* RUBBERS PRODUCED BY PHILLIPS AND ITS LICENSEES

Rubb.	Type	Mooney ML-4	Oil, parts	Uses
Solprene 201	polybutadiene	55	none	plastic additive
Solprene 250	polybutadiene	50	"	tires, belting
Solprene 277	polybutadiene	40	37.5 HA	tires
Solprene 1204	75/25 copolymer random	56	none	tires, footwear, M.R.
Solprene 1206	"	33	none	rug underlay, sponge
Solprene 1205	75/25 copolymer block	47	none	footwear, flooring, processing aid
Solprene 303	52/48 copolymer block	48	none	shoe soles, flooring
Solprene 380	75/25 copolymer	53	37.5 HA	tires
Solprene 384	85/15 copolymer random, controlled microstructure	50	37.5 HA	tires
Solprene 411	70/30 radial block copolymer	-	none	adhesives
Solprene 406	60/40 radial block copolymer	-	none	injection molding, adhesives
Solprene 475	60/40 radial block copolymer	-	50 naph.	injection molding, M.R.G.

*A trademark

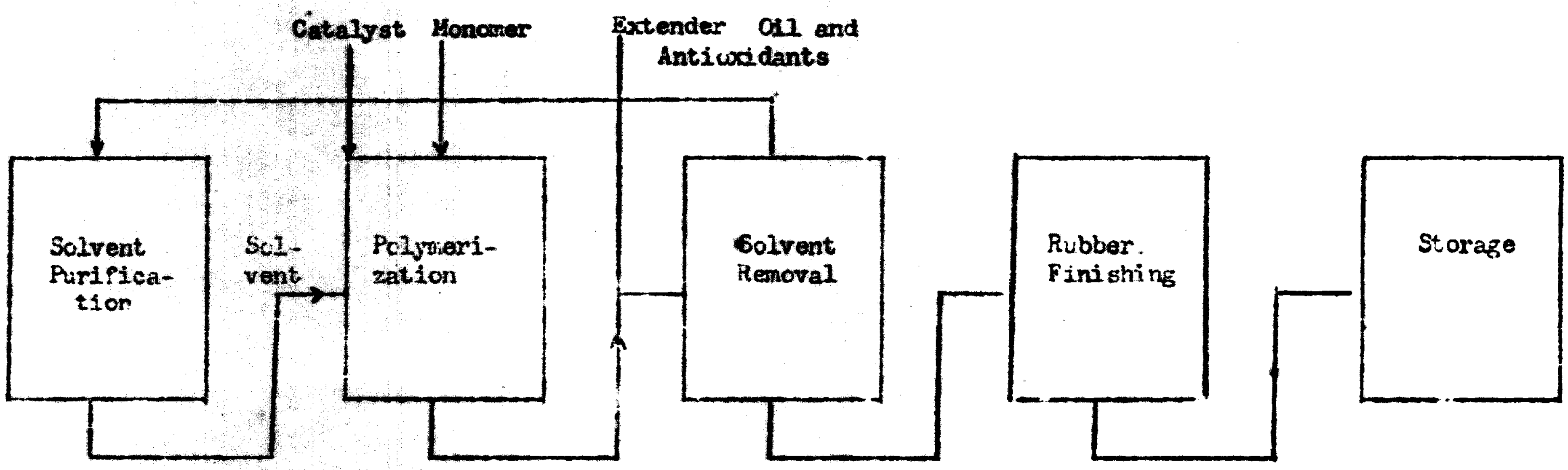
III. THE SOLUTION SBR PROCESS

A brief outline of the steps in a solution SBR process is shown in Figure 2. A hydrocarbon solvent is employed, usually one of about 5 to 7 carbon atoms such as n-hexane, cyclohexane, benzene or toluene. Geometrical structure of the polymers may be affected by the choice of solvent, and viscosity of the polymer solutions may also be affected. The principal object of the solvent purification system is to remove all traces of water since a bone-dry system is necessary to prevent waste of catalyst. The polymerization is conventionally done in stirred autoclaves of 4,000 to 8,000 gallons capacity. Continuous or batch operation may be used; however, the latter may be preferred in a small or medium sized plant producing a family of products. Polymerization reactions are highly exothermic, and some provisions must be made to remove the heat of reaction; however, unlike emulsion polymerization, in this process critical control of temperature is not required. When the polymerization is complete the product is in the form of a viscous cement of 10 to 20% rubber content, containing catalyst residues but almost completely free of monomer. In this process reaction of the monomer is almost 100% and recovery and recycle of the monomer is usually not necessary. This is another significant advantage over emulsion processes in which conversion of the monomer is only about 60 to 70% and from which the unreacted monomer must be recovered, purified and recycled.

Following the polymerization reaction water or some other reactive material is added to inactivate the residual polymerization catalyst. Antioxidants are added and if the polymer is to be oil extended the oil is added at this point. The cement is then processed to remove the solvent and the residual rubber is recovered and baled.

FIGURE 2

THE SOLUTION SBR PROCESS



The above description is one example of the solution SBR process. There are many variations in order to produce the various products already described. For example, in some cases the monomers and the catalyst are added stepwise. For some products terminating agents such as silicon tetrachloride are used to give a radial or branched polymer. Some products are finished in crumb form rather than bales and are sold in bags or fiber drums.

Estimated investment for a new solution SBR plant, including necessary supporting facilities and working capital, are shown in Table II. These costs are for a plant built on the U. S. Gulf Coast and are shown in 1973 U. S. dollars.

TABLE II

SOLUTION SBR PLANT INVESTMENT AND OPERATING COSTS

(25,000 MT/yr., USA Gulf Coast, 1973 dollars)

Investment:	
Battery-limits plant	$7,300,000
All necessary supporting facilities	3,700,000
Total	$11,000,000
Manufacturing Costs:	Cost, $/MT
Feedstocks: Bd @ $0.09; Sty @ $0.075/lb.	194.13
Labor	32.30
Utilities	14.20
Catalyst and Chemicals	47.50
Supplies	15.40
Packaging and storage	11.60
Overhead and general expense	32.00
Taxes and insurance	15.40
Depreciation (15 yr. st. line)	29.40
Total manufacturing costs	391.93

IV. THE PHILLIPS SOLPRENE RUBBERS

Phillips Petroleum Company developed its solution SBR process during the late fifties, and its first commercial production was started in a 3000-ton per year unit at Borger, Texas, in 1962. Since that time Research and Development work on this process has been aggressively continued, and many new products and process improvements have been made. An active R&D program is still underway to determine the full potential of this prolific polymerization system.

Presently, seven plants operate under license from Phillips. They are listed in Table III, which also shows startup date and present capacity of each. Two of the plants have expanded production since startup and five of them have further expansions scheduled.

The Phillips process seems ideally suited for use in a situation where near self-sufficiency in rubber is desired at modest levels of production. As already discussed, a wide variety of products, including rubbers for tire treads and carcasses, footwear and mechanical rubber goods can be produced. The process is designed to permit production to be shifted from one of these products to another with minimum production of mixed, off-specification rubber. The process is adaptable to a small plant; in fact, as shown in Table III, the Phillips plant at Borger, Texas, had an initial capacity of only 3,000 tons per year, and only since 1970 has the capacity been expanded above 12,000 T/yr.

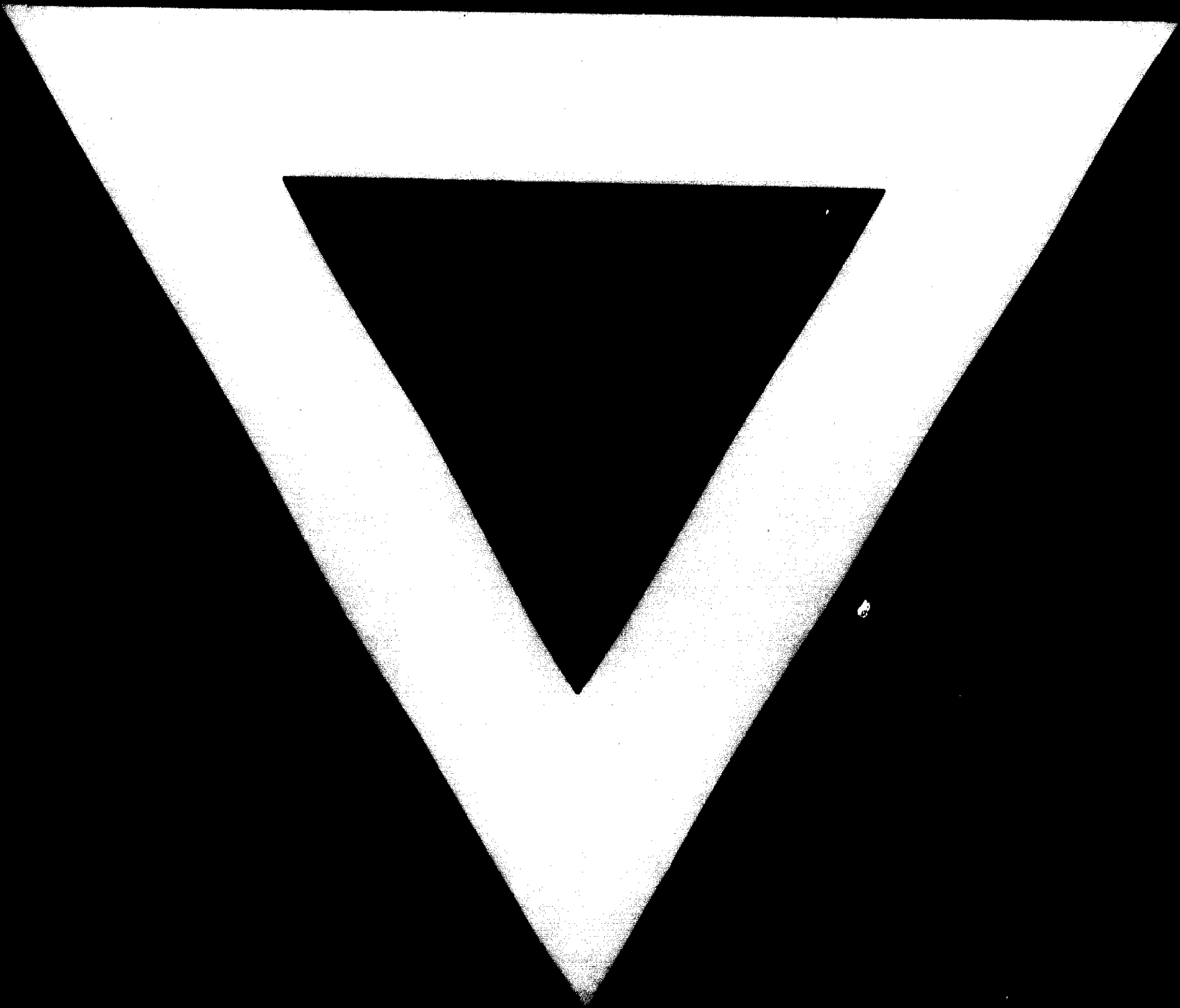
A very significant new development in this line of products has occurred in the past two years with the introduction of Solprene 384, shown in line 9 of Table I. This is an 85/15 oil-extended butadiene-styrene copolymer designed specifically for tire treads. This rubber is produced with a modified catalyst that gives a different microstructure (higher cis, higher trans, lower vinyl) than conventional solution SBR's. As a result of this fact together with its low styrene content, Solprene 384 has been found to provide better treadwear than the 65/35 blends of emulsion SBR and polybutadiene now conventionally used world-wide in premium tread compounds. For a number of years it has seemed that there was something unique in the high treadwear performance of SBR-polybutadiene blends that could not be equalled in a single polymer. This idea has now been refuted by the performance of Solprene 384 rubber. This rubber is still not in full-scale production and use, and only a few commercial plant runs of it have been made. We expect production to increase rapidly in the next year and anticipate that within a few years this rubber will become a major factor in the production of tire treads.

TABLE III

SOLPRENE RUBBER PLANTS
(metric tons per year)

Location	Initial Capacity	Present Capacity	Planned Expansion
Borger, Texas	3,000 (1962)	18,000	6,000
Santander, Spain	20,000 (1966)	75,000	30,000
Antwerp, Belgium	55,000 (1967)	55,000	27,500
Salamanca, Mexico	20,000 (1967)	20,000	8,000
Kurnell, Australia	20,000 (1966)	20,000	-
Oita, Japan	20,000 (1969)	20,000	20,000
Ravenna, Italy	25,000 (1972)	25,000	-
	TOTAL	233,000	91,000

[redacted]



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