

Ameripol SN—A *Cis*-1,4-Polyisoprene

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THE important observation, made by Katz (6) in 1925 using x-ray diffraction technique, showed that the mere stretching of crude or soft vulcanized Hevea rubber caused at least a portion of the polymer to undergo crystallization. This and the subsequent experiments of Hock (4) emphasized the point that successful attempts to synthesize a polymer resembling Hevea rubber would have to take regularity into account. The situation is complicated in isoprene polymers by the variety of ways the monomer can enter the growing polymer chain.

The four isomeric forms of polyisoprene are shown in Figure 1. Since head-to-tail orientations must be considered because of the asymmetry of the isoprene molecule, there are eight possible arrangements of the units that can occur in polymerized isoprene. Sodium, potassium, emulsion, and alfin polyisoprenes have been shown to contain all four forms of the repeating units (8). All of these uncured polymers have poor tack and their pure gum vulcanizates show poor physical properties. They do not crystallize when stretched or cooled. It has long been recognized that polymers of conjugated hydrocarbon dienes would have to be very regular in structure before their properties would approach those of Hevea rubber.

Looking back over the last 15 to 20 years, there has been a slow development, almost imperceptible at first, of catalyst systems which produce polymers that in some degree show an oriented structure. This orientation could result if the monomer, during the propagation phase of the polymerization, is held in a definite position with respect to the growing chain, as by cybotactic forces where polymerization is initiated at the melting point of the monomer or as by adsorption of the monomer onto a solid surface—perhaps to the surface of the catalyst itself.

The work reported here deals primarily with the properties of a rubber made by directed polymerization.

POLYMER STRUCTURE AND PROPERTIES

Catalyst. Catalyst systems, based on polyolefin information purchased from Karl Ziegler, have been applied to isoprene monomer systems, and modifications have been developed such that either *cis*-1,4-polyisoprene or *trans*-1,4-polyisoprene can now be prepared at will.

Infrared Absorption Spectra. The effect of one of these catalyst modifications was first recognized when a modified olefin polymerization yielded an isolable unstabilized rubbery component which showed an infrared absorption spectrum (2- to 25-micron range) almost identical to that of Hevea rubber except for peaks due to oxidation at 2.8, 5.6, and 5.8 microns and, additionally, a slightly higher intensity in the peak at 11.25 microns. Subsequent samples of this rubber, a *cis*-1,4-poly-

isoprene, now called Ameripol SN, when protected by age resistors did not show these oxidation peaks (Figure 2).

Infrared absorption spectra indicate low maximum concentrations of 1,2- and 3,4- addition products in Ameripol SN. For these two isomeric units the discrimination in the presence of *cis*-1,4-polyisoprene units is good, being of the order $\pm 1\%$. The discrimination of small amounts of *trans*-1,4- units in the presence of a large concentration of *cis*-1,4- units is not good, for, if we add by common solvent technique 5 parts of balata to 100 parts of Hevea rubber, detection of the added balata is very difficult. In the region from 8.0 to 10.5 microns where the spectrum of amorphous balata is most unlike that of Hevea rubber, the spectra of Hevea rubber-balata mixtures are practically superimposable on that of Hevea rubber alone. At least 10 parts of balata per 100 parts of Hevea rubber are required for detection (Figure 3). Single isolated *trans*-1,4- polyisoprene units would not necessarily have the same set of absorption bands as totally *trans*-1,4- polymer chains. At least four *trans*-1,4- units in a block are required to produce a spectrum resembling that of balata. These limitations on the infrared absorption technique apply to both synthetic and natural polyisoprenes.

Since it has been noted in this work as well as in the previous work of Richardson and Sacher (8) and of Binder and Ransaw (1) that infrared absorption techniques do not offer sufficient discrimination for accurately measuring the concentration of *trans*-1,4- isomer in predominately *cis*-1,4- samples of polyisoprene, we concluded that such a quantitative analysis for characterizing a material having less than 10% *trans*-1,4- units was not feasible at this time. Instead, we estimated the maximum possible amounts of each isomeric impurity from the infrared spectra.

The spectrum of the Ameripol SN protected with an antioxidant duplicates that of the natural product except for the slight increase in intensity at 11.25 microns which may be attributable to the presence of about 1% more 3,4- addition product than is present in Hevea rubber. To the best of our knowledge, the origin of the 11.25-micron peak in the spectrum of Hevea rubber has not been established. Salomon and Van der Schuer (9) say it is tempting to assign the 11.25- μ peak to 3,4- addition structure, but they found it survived ozonization.

The spectra of Ameripol SN and of Hevea rubber in the region around 10.9 microns are very much the same, indicating very little difference in 1,2- addition product concentration. Thus the amount of side chains formed by 1,2- addition is estimated to be less than 1% for both Hevea rubber and for Ameripol SN.

It is not known what the differences in the infrared spectra of *cis*-1,4- head-to-tail polyisoprene and of *cis*-1,4- head-to-head polyisoprene would be like because polymers of the latter type are

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not available. It appears safe to assume that some of the skeletal vibrations would be affected, producing differences in the spectra. Since no differences except those already mentioned are apparent,

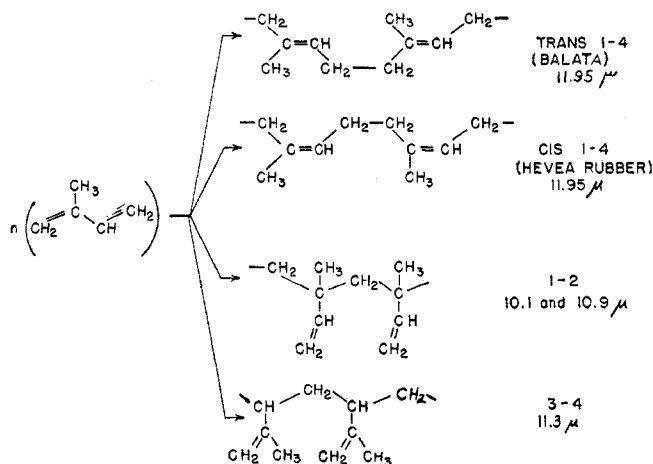


Figure 1. The four isomeric forms of isoprene and characteristic infrared absorption peaks

it is reasonable to say that no great differences in head-to-tail orientation exist between Ameripol SN and Hevea rubber.

Examination by Phase Microscopy. Crystalline and amorphous balata are insoluble in Hevea rubber and Ameripol SN.

Concentrations as low as 2% of balata in either of these polymers are detectable by phase microscopy in the mixtures. Since gel-free fractions of Ameripol SN and Hevea rubber hydrocarbon show a single phase by this method, we conclude that each contains less than 2% of trans-1,4- polymer chains. This technique is applicable only if all the trans-1,4- units are in separate polymer chains. If the trans-1,4- units are distributed along predominately cis-1,4- polymer chains, insolubility would not result and detection by this means would be impossible.

X-Ray Diffraction Patterns. Ameripol SN crystallizes when cooled as does Hevea rubber. The initiation period for Ameripol SN at -26°C . is much longer than that for acetone-extracted Hevea. This is believed to be due to the absence of impurities which furnish nuclei for crystal growth. Seeding with stearic acid greatly reduces the initiation time. The rate of crystal growth in Ameripol SN at -26°C . was slower than in the acetone-extracted Hevea rubber used. Crystallization rate is also affected by impurities. Figure 4 shows the x-ray diffraction patterns of unseeded Ameripol SN and of acetone-extracted pale crepe. The pale crepe was cooled at -26°C . for 24 hours and held at this temperature during exposure. The Ameripol SN was cooled at -26°C . for 140 hours and then photographed at this temperature. These ring diagrams are typical of nonoriented, finely divided crystals. The slightly mottled appearance of the rings is due to the Styrofoam frost shield used during the experiment. The ring diameters are the same in the two patterns, indicating identical crystal structures. The ratio of ring intensity to halo intensity is not quite the same in both patterns—the degree of crystallinity being somewhat higher in the Hevea rubber sample. Hevea rubber shows its maximum rate of crystalliza-

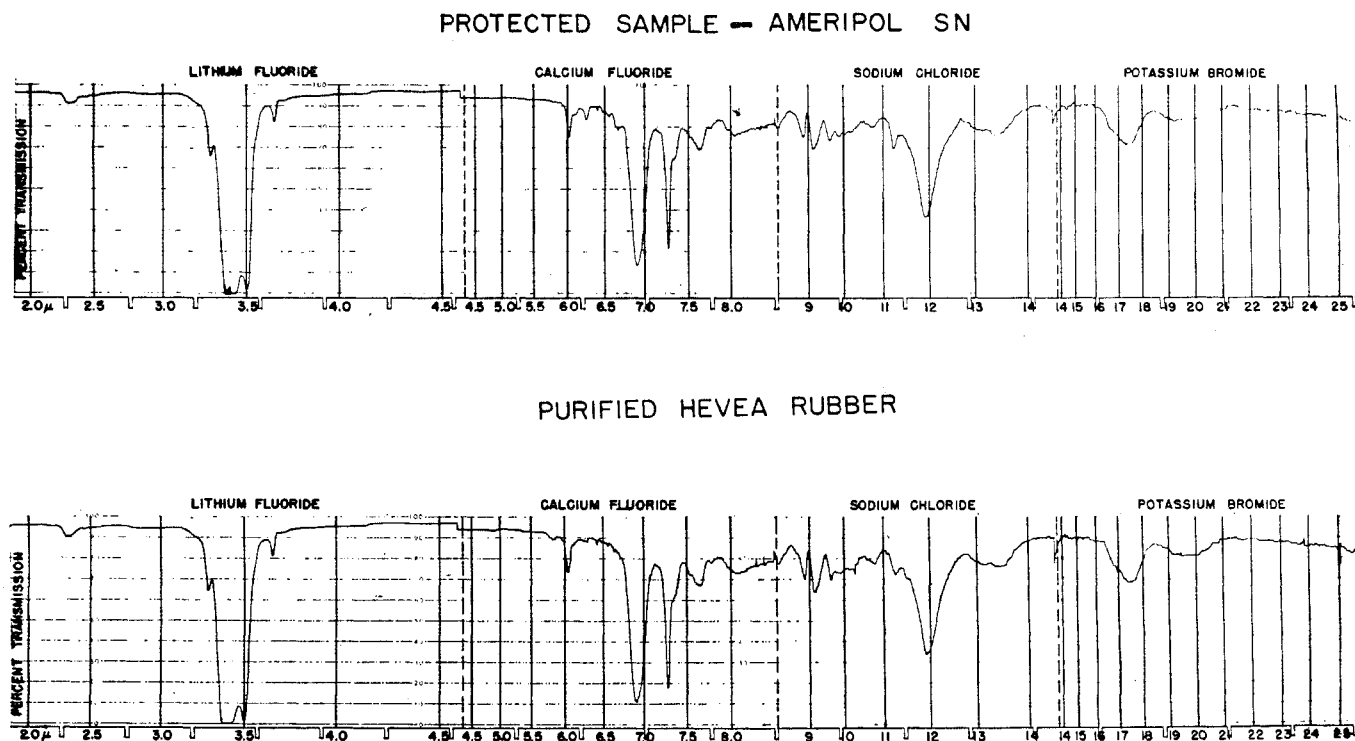


Figure 2. Comparison of the infrared spectra of Ameripol SN and Hevea rubbers

Films on potassium bromide disks

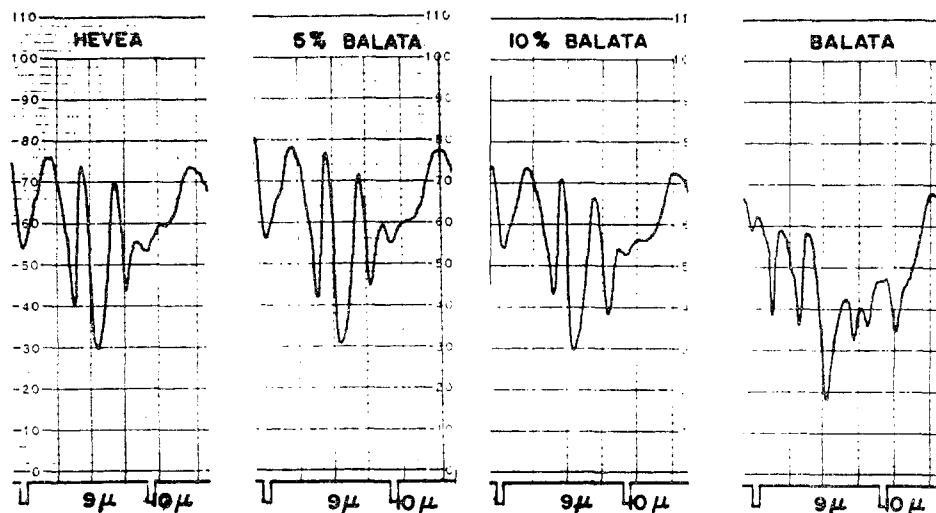


Figure 3. Infrared absorption spectra of Hevea rubber-refined balata mixtures

tion (10) at -26°C ., hence this temperature was used for these experiments. It is not yet known whether Ameripol SN shows its maximum rate of crystallization at this same temperature.

Vulcanizates of Ameripol SN and Hevea rubber crystallize when stretched. Figure 5 shows the x-ray diffraction patterns of the stretched vulcanizates at room temperature. The spot diagrams are essentially identical, indicating the same crystal structure and about the same degree of crystallinity in each case. The agreement here is as good as for two different samples of Hevea rubber. The fact that the two materials form crystals of identical structure precludes any large differences in head-to-tail orientation. It is impossible for head-to-tail oriented polymer of isoprene to form crystals of the same type and dimensions as a head-to-head polymer even though the repeating units are otherwise identical.

From the infrared data, phase microscopy examination, and the x-ray diffraction data, we conclude that Ameripol SN and Hevea rubber are essentially similar in molecular structure and both contain less than 2% predominantly trans-1,4- polymer and probably less than 10% distributed trans-1,4- units. This concentration or higher of distributed trans-1,4- units in the polymers would be expected to seriously interfere with their ability to crystallize which, actually, neither polymer lacks.

Second-Order Transition Temperature. The second-order transition temperature (T_g) of a sample of SN rubber was measured in a differential expansion apparatus similar to that described by Floyd (3) and was found to be -70°C ., which is the same as that obtained for smoked sheet and pale crepe in the same apparatus. The coefficients of expansion below and above the second-order transition temperatures agree also with published values within the 5 to 10% reproducibility of the experiment.

The second-order transition temperature is roughly the temperature at which segmental motion of the polymer chain ceases. The balance between thermal disordering forces (moving the chain) and van der Waal (or intermolecular) forces is fairly critical to changes in polymer or copolymer composition. (A few per cent of most comonomer units will change the second-order transition temperature by several degrees.) Hence, the identity of T_g values is another indication of the identity of chain composition.

Polymer Properties of Ameripol SN and Hevea Rubber Samples. Using toluene as the solvent, sol-gel measurements were carried out at room temperature (in the dark) employing essentially the procedure recommended by the Office of Rubber Reserve, Committee on Standardization of Methods and Apparatus for Determining Molecular Weights of Polymers.

Intrinsic viscosity measurements were made at $25.00^{\circ} \pm 0.01^{\circ}\text{C}$. over a concentration range and were extrapolated to zero concentration to obtain the limiting intrinsic viscosity value which is designated by the symbol $[\eta]_0$. Cannon-Fenske type viscometers (50 Series) were employed for the viscosity determinations.

Using the toluene solutions of the polymers, osmotic pressure measurements were made at $25.00^{\circ} \pm 0.01^{\circ}\text{C}$. Regenerated cellulose film was employed as the semipermeable membrane.

It is of interest to compare a few of the polymer properties of SN rubber with Hevea rubber. Some of the pertinent data relating to polymer properties such as gel content, swelling index,

M_n (number-average molecular weight), M_v (viscosity-average molecular weight), $[\eta]_0$ and μ_1 values are summarized in Table I.

Table I. Polymer Properties of Ameripol SN

	$[\eta]_0$ = limiting intrinsic viscosity value M_n = number-average molecular weight M_v = viscosity-average molecular weight μ_1 = measure of degree of solvation of polymer molecules by solvent molecules						
Sample	Gel, %	Swelling Index	$[\eta]_0$	M_n	M_v	M_v/M_n	μ_1
Ameripol SN	6.3	126	3.80	230,000	658,600	2.86	0.398
Ameripol SN	0	..	1.32	77,200	135,000	1.75	0.406
Milled pale crepe	0	..	1.47	118,700	157,700	1.33	0.431
Unmilled pale crepe	11.6	127	8.30	838,000	2,126,000	2.54	0.434

A sample of Hevea (pale crepe) was found to have a gel content of 11.6% with a swelling index of 137. The toluene-soluble portion yielded an $[\eta]_0$ value of 8.30 and an M_n value of 838,000. Using the equation of Carter, Scott, and Magat (2) of $[\eta] = 5.02 \times 10^{-4} M^{0.697}$, an M_v value of 2,126,000 was calculated. The ratio of M_v/M_n was 2.54 which indicated a wide distribution of molecular weights.

A sample of moderately high molecular weight Ameripol SN rubber contained 6.3% gel with a swelling index of 126. The toluene-soluble component had an $[\eta]_0$ value of 3.80. The high swelling index value of 126 encountered for a gel content of 6% was similar to sol-gel data obtained for some natural rubber samples. This type of a gel structure is easily broken down by normal milling and processing operations. M_n and M_v values of 230,000 and 658,600 were obtained for this SN rubber. The ratio of M_v/M_n was 2.86 which suggests a wide distribution of molecular weights similar to that indicated for the unmilled pale crepe rubber.

Hevea (pale crepe) rubber was milled on a cold mill for 20 minutes. It was totally soluble in toluene. The $[\eta]_0$, M_v , and M_n values were, respectively, 1.47, 157,700, and 118,700. This gave a ratio of 1.33 for M_v/M_n . Cold milling of the Hevea rubber resulted in a polymer with a narrower distribution of molecular weights compared to the original pale crepe rubber.

A low molecular weight Ameripol SN rubber was found to be totally soluble in toluene. The $[\eta]_0$, M_v , and M_n values were, respectively, 1.32, 135,000, and 77,200. The ratio of 1.75 for M_v/M_n indicated a broader distribution of molecular weights than that encountered in the milled pale crepe rubber.

A comparison of the μ_1 values of the rubber-toluene systems is of interest. The μ_1 value is a measure of the degree of solvation of polymer molecules by solvent molecules. For the binary system of natural rubber-toluene at 27° C. a μ_1 value of 0.43 was reported by Huggins (5).

The high and the low molecular weight Ameripol SN rubber samples yielded μ_1 values of 0.406 and 0.398 at 25.00° C. Unmilled pale crepe and milled pale crepe had μ_1 values of 0.434 and 0.431, respectively, at 25.00° C.; this represents a good check on the value of 0.43 reported by Huggins.

At the present time, it is believed that the difference in the μ_1 values of Ameripol SN and Hevea rubber is real. These data imply that the Hevea rubber molecules are less solvated by toluene than the Ameripol SN rubber molecules. This may be due to the presence of a more highly branched structure in the Hevea molecule as compared to the SN molecule, or it may be a reflection of the presence of a small amount of nonrubber constituents in the Hevea samples.

Solvents having solubility parameter values of 8.6 ± 1.35 appeared to be good solvents for both Ameripol SN rubber and milled pale crepe rubber. Carbon tetrachloride was the best solvating agent for both materials. Other good solvents were chloroform, cyclohexane, carbon disulfide, chlorobenzene, toluene, and benzene.

Stabilization of Ameripol SN. Freshly made polymer must be stabilized to protect it from degradation and softening by atmospheric oxidation. Illustrative of some of the early results of screening tests are the examples in Table II. Aliquots of a polymer charge were mill mixed (eight passes) with the materials shown and exposed as 0.015-inch-thick sheets both at room temperature (unheated) and (heated) in a circulating air oven for 8 hours at 100° C.; specific viscosities (at 1/2% concentration in toluene) were then determined. As one would expect, some materials and combinations were more effective than others in stabilizing the raw polymer. The effectiveness of the stabilization of some of these Ameripol SN rubber samples prepared by the addition of the more promising commercial stabilizers or antioxidants was further determined by measurements of the rate at which various polymer samples reacted with oxygen at elevated temperatures. An apparatus that permitted measurements of the volume of oxygen consumed at constant pressure and temperature was employed. All measurements were made at a temperature of $100^\circ \pm 0.2^\circ$ C. and at approximately 760 mm. of mercury pressure.

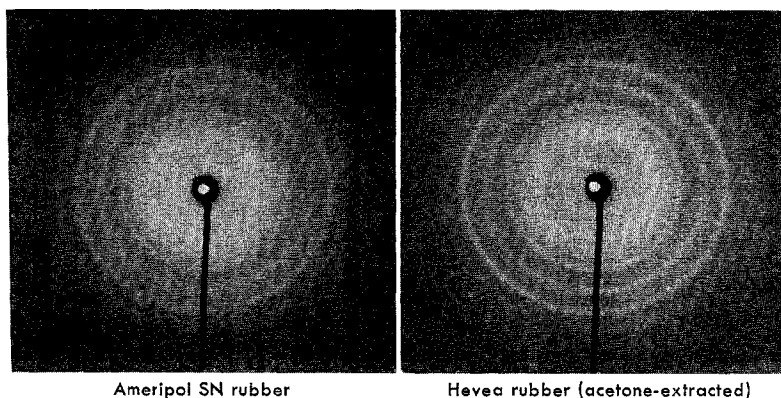


Figure 4. X-ray diffraction patterns of frozen but unstretched specimens

Table II. Stabilization of Ameripol SN Rubber Qualitative Screening Test

Stabilizer	Parts/ 100 Parts Rubber	η_{sp} (0.5% in Toluene)	
		Un- heated	Heated 8 hr. at 100° C.
Diphenyl- <i>p</i> -phenylenediamine	0.25	3.39	2.51
2:5 Di- <i>tert</i> -butylhydroquinone (Santovar O)	0.2		
Bis(dimethylthiocarbamyl) disulfide (Tuads)	0.2	3.40	1.08
Mercaptobenzothiazole (Captax)	0.2	2.87	1.02
Bis(2-benzothiazyl) disulfide (Altax)	0.2	2.68	1.30
Sulfur	0.2	3.04	1.08
Polymerized trimethyldihydroquinoline (AgeRite resin D)	1.0	3.27	1.20
1,2-Dihydro-2,2,4-trimethyl-6-phenylquinoline (85%)	1.0	3.04	1.84
Diphenyl- <i>p</i> -phenylenediamine 15% (Santoflex BX)			
<i>sym</i> -Di- <i>β</i> -naphthyl- <i>p</i> -phenylenediamine (AgeRite white)	0.5	3.43	2.34
Diphenyl- <i>p</i> -phenylenediamine	0.25		
<i>sym</i> -Di- <i>β</i> -naphthyl- <i>p</i> -phenylenediamine (AgeRite white)	0.5	2.60	1.92
2,5-Di- <i>tert</i> -butyl hydroquinone (Santovar O)	0.2		

The curves of oxygen consumed versus time were all of an autocatalytic nature, oxidation rate increasing with time. Two parameters can be obtained from such curves: The first is the initial rate of oxidation, designated r_0 , and the second is a factor designated by k which is a measure of the autocatalytic nature or self-acceleration of the oxidation. Table III shows typical data from a series of oxidation rate measurements. Decreased values of r_0 , of course, correspond to more efficient stabilization as do decreased values of k . For this series, AgeRite white is the most efficient stabilizer, Santovar O being next. Both AgeRite white and the combination of AgeRite white and Santovar O shown have stabilized the Ameripol SN to a degree equivalent to or better than that shown by pale crepe. The unstabilized Ameripol SN polymer is quite susceptible to oxidation at 100° C.

The addition of stabilizers decreased the initial rate of oxidation by a factor of approximately 20, whereas k was decreased by a factor of almost 100.

PROCESSING AND VULCANIZATION

Ameripol SN, as ordinarily made, looks and handles much like masticated Hevea rubber.

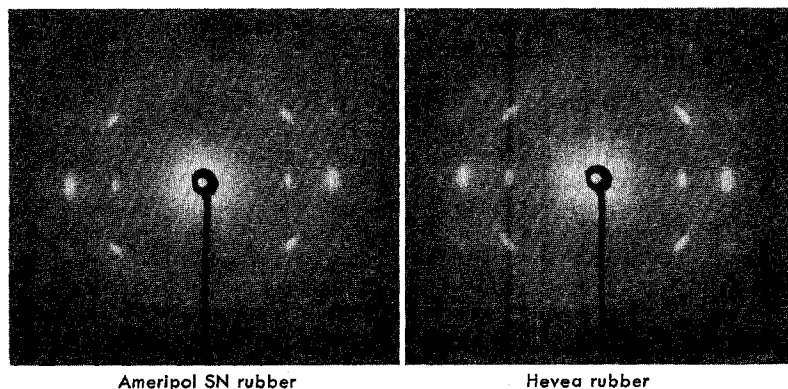


Figure 5. X-ray diffraction patterns of pure gum vulcanizates at 1000% elongation

Table III. Stabilization of Ameripol SN Rubber Oxygen Absorption at 100° C.

r_0 = initial rate of oxidation, mole O_2 /gram⁻¹ min.⁻¹
 k = measure of autocatalytic nature of oxidation, min.⁻¹

Polymer	Stabilizer	r_0	k
Ameripol SN	None	5.0×10^{-7}	96×10^{-4}
Ameripol SN	2,5-Di- <i>tert</i> -butyl hydroquinone (Santovar O), 0.5% on rubber	0.25×10^{-7}	6.3×10^{-4}
Ameripol SN	Diphenyl - <i>p</i> - phenylenediamine, 0.2% on rubber	0.40×10^{-7}	21×10^{-4}
Ameripol SN	<i>sym</i> - Di - β - naphthyl - <i>p</i> - phenylenediamine (Age-Rite white), 0.5% on rubber	0.10×10^{-7}	0.64×10^{-4}
Ameripol SN	<i>sym</i> - Di - β - naphthyl - <i>p</i> - phenylenediamine (Age-Rite white), 0.5% on rubber 2,5-Di- <i>tert</i> -butyl hydroquinone (Santovar O), 0.2% on rubber	0.10×10^{-7}	~ 0
Hevea pale crepe	None added	0.19×10^{-7}	2.2×10^{-4}

Table IV. Physical Properties of Vulcanizates—Gum Stock

(Room temperature tests)

	Ameripol SN		Hevea Rubber		
	No additive	Plus 1.5 parts of additive ^a	Tech. Red O	Classified Yellow O	Grades Blue O
Cure, min. at 280° F.	Tensile, Lb./Sq. Inch				
15	No cure	2840	800	2540	2900
30	1400	3550	2680	3150	3970
45	2030	3440	2970	3850	3810
60	2380	3200	3090	3450	4000
90	2250	3210	3110	3600	3730
600% Modulus, Lb./Sq. Inch					
15	..	350	260	380	500
30	120	700	550	790	970
45	280	800	700	1110	1200
60	350	800	930	1280	1320
90	430	700	1040	1400	1520
Elongation at Break, %					
15	..	930	870	890	860
30	990	850	820	800	830
45	910	880	790	780	760
60	860	750	760	750	770
90	800	820	750	700	750

^a Lecithin (95%) and TEA (5%).

ACS II Recipe: Rubber 100, zinc oxide 6, stearic acid 4, Captax 0.5 sulfur 3.5; ACS tensile sheets.

It has excellent tack and good "tooth." The Mooney viscosity (ML-4' at 212° F.) of the polymer is in the 50 to 75 range.

Processing Properties. Ameripol SN requires no preliminary breakdown and bands smoothly on a laboratory mill by the time the rolls have made three or four revolutions. This is partly due to the excellent natural tack of the polymer. Like natural rubber, Ameripol SN breaks down rapidly on a cold mill, so mill mixing is usually carried out at temperatures around 180° F. Compounding ingredients then added are accepted as readily and dispersed as well as they would be in Hevea rubber.

Laboratory Banbury mixing is usually run at 220° to 260° F. where the stocks handle well, but batches have been discharged satisfactorily at 325° F. Factory Banbury mixing presented no problem and Ameripol SN stocks processed well on factory calendars and in extruders. In fact, extruded treads showed less linear shrinkage and less extrusion porosity than ordinary Hevea rubber treads. The carcass plies and the treads handled well in the factory tire-building operation, and the building tack of the Ameripol SN was equivalent to that of similar Hevea rubber stocks.

Compounding. Freshly made Ameripol SN lacks three kinds of materials (naturally present in Hevea rubber) that are known to have an important influence on the technical quality of vul-

canizates—antioxidant for polymer stabilization, nonrubber constituents (such as ash, protein, and protein decomposition products), and fatty acid material which affect the state of vulcanization. These deficiencies are corrected by additions of suitable materials. The antioxidant is added at once to every lot of the freshly made polymer accordingly as a nonstaining or staining type polymer is required. Addition of fatty acid and a material simulating the nonrubber constituents is made by the compounder as required. Some buffer material (7) is needed to help adjust the rate of cure of Ameripol SN, and in the tests reported the additive, soybean lecithin (95%) with triethanolamine (TEA) (5%), was used (1½ parts of this mixture to 100 parts by weight of polymer). Otherwise, Ameripol SN is compounded and handled like Hevea rubber.

Pure Gum Stocks. Ameripol SN with additive shows good properties in the ACS II test recipe (Table IV), approximating those shown by the Hevea rubber test blend of ribbed smoked sheets and pale crepe. In a low sulfur, pure gum recipe, (Table V), Ameripol SN containing both additive and extra fatty acid gives a vulcanizate quite comparable to that of the Hevea rubber control.

Heavy-Duty Tire Stocks. It was a natural anticipation that this new polymer, Ameripol SN, so much like Hevea rubber in chemical structure, milling, compounding, and vulcanizing characteristics, should show low hysteresis values, as well, in heavy-duty truck tire stocks. Extended tests have amply borne this out.

Table V. Physical Properties of Vulcanizates—Low-Sulfur Gum Compound

(Room temperature tests)

	Ameripol SN ^a	Hevea Rubber ^b
Cure, min. at 260° F.	Tensile, Lb./Sq. Inch	
10	2420	No cure
20	2900	2880
30	3180	3280
40	3100	3300
600% Modulus, Lb./Sq. Inch		
10	200	..
20	420	420
30	400	500
40	400	350
800% Modulus, Lb./Sq. Inch		
10	1100	1720
20	1900	1900
30	2200	1900
40	2000	1550
Elongation at Break, %		
10	930	..
20	860	920
30	830	900
40	860	980

Recipe: Rubber 100, zinc oxide 1, AgeRite White 0.5, fatty acid activator 2.5, Captax 0.4, Altax 0.35, sulfur 1.5; ACS tensile sheets.

^a Additives: 1 part stearic acid; 1.5 parts lecithin plus TEA.^b Additive: 1 part rosin oil.

Two different lots of Ameripol SN, labeled I and II, differing somewhat in gel content and in swelling index of the gel (determined on the unmilled polymer) were compounded in a typical carcass stock and in a tread stock along with a Hevea rubber test blend (ribbed smoked sheets and pale crepe) as a control. The recipes in each case are identical except for the lecithin-triethanolamine additive (1.5 parts/100 parts of Ameripol SN) and extra stearic acid (1 part/100 parts Ameripol SN) to approximate the amount naturally present in Hevea rubber. Comparative data on physical properties of the carcass stocks are shown in shown in Table VI and in Figure 6; those on the tread stocks are shown in Table VII and in Figure 7. The stress-strain properties at room temperature, at 212° F., and after aging are very similar on all the stocks and so are the Gehman low temperature moduli

Table VI. Physical Properties of Vulcanizates—Carcass Stocks

	Ameripol SN		Hevea Rubber			
	I	II		I	III	Hevea Rubber
Gel, %	14	31	..	Stress-Strain at 212° F.		
Swelling index	83	59	..			
$[\eta]$	3.17	3.45	..	Cure, min. at 280° F.		
Mooney viscosity, ML-4' at 212° F.	75	75	..			
Carcass recipe, Parts				10	Tensile, Lb./Sq. Inch	
Polymer	100.0	100.0	100.0	15	900	1200
Zinc oxide	3.0	3.0	3.0	30	1620	2180
Stearic acid	2.0	2.0	1.0	60	1500	2290
AgeRite powder (PBNA)	1.0	1.0	1.0	150	1330	1920
HMF black (Statex 93)	40.0	40.0	40.0		1320	1820
Pine tar	5.0	5.0	7.0	400% Modulus, Lb./Sq. Inch		
Lecithin + TEA (5%)	1.5	1.5	..	10	150	220
Altax	1.0	1.0	1.0	15	400	620
Sulfur	2.5	2.5	2.5	30	560	830
				60	700	750
				150	700	660
B. F. Goodrich plasticity, 85° C. (on compounded stock)	72.8	66.4	72.8	Elongation at Break, %		
Mooney scorch, 260° F. (large rotor)				10	1000	940
I.V., initial viscosity	36	42	34	15	800	900
V_m , min. viscosity	26	32	25	30	850	790
T_s , scorch time, min.	20.9	17.3	16.9	60	700	760
$T_c(T_s + T_{\Delta 20})$, cure time, min.	27.6	21.3	20.5	150	700	800
$T_{\Delta 20}$, min. for 20-point viscosity increase	6.7	4.0	3.6			
Gehman low temperature modulus (cure 30 min., 280° F.), ° C.				Aged in Test Tubes 24 Hours at 212° F. in Air; Stress-Strain at Room Temperature		
T_s	-33	-32	-34			
T_i	-48	-48	-49	Cure, min. at 280° F.		
Freeze point	-58	-58	-59			
				10	Tensile, Lb./Sq. Inch	
				15	1770	2680
				30	2220	3140
				60	2450	3080
				150	1880	2780
					2030	2380
				400% Modulus, Lb./Sq. Inch		
				10	700	1800
				15	800	1840
				30	1050	1450
				60	1280	1480
				150	1080	1120
				Elongation at Break, %		
				10	650	510
				15	680	590
				30	640	600
				60	520	600
				150	600	620
				Graves Angle Tear (212° F.)		
				Cure, min. at 280° F.		
				15	60	180
				30	210	220
				60	190	220

and freeze points. The heat rise in the B. F. Goodrich flexometer at both 0.175- and 0.225-inch strokes are likewise comparable. The Graves angle tear tests at 212° F. are somewhat lower than those for the Hevea stocks, but, on the other hand, the Ameripol SN stocks in the DeMattia flex crack-growth (initiated) tests appear on the whole to be more resistant than do those of the Hevea stocks.

Summary. The results of the laboratory comparative evaluation tests on pure gum carcass and tread stocks indicate a virtual identity in the performance of Ameripol SN rubber and of Hevea rubber. The comparative data suggest that Ameripol SN heavy-duty tires will perform as well as similar Hevea rubber tires.

TIRE TESTING

The possibility of using Ameripol SN rubber to replace Hevea rubber completely in the tread and carcass stocks of heavy-duty bus and truck tires has undergone extensive testing. The results reported here deal with a lot of sixteen 11.00 × 20 heavy-duty express tires which required about 1 ton of Ameripol SN for manufacture.

The procedure for evaluation of test tires is divided into three programs—namely, indoor wheel tests, where tires are run to destruction; test truck operation, where conditions such as speed, load, and inflation are closely regulated; and mileage contract busses, where tire maintenance is at a high level, but service conditions on the highways are very severe.

Indoor Wheel Test. Tires are run on smooth 67-inch-diameter wheels in an ambient temperature of 100° ± 5° F. at a speed of

B. F. Goodrich Flexometer (212° F.); 55-Lb. Load; 60-Min. Cure, 280° F.

Stroke, 0.175 inch			
Shore A hardness	48	52	49
ΔT , ° F.	27	25	25
Permanent set, %	10.4	6.7	7.5
Static compression at 55 lb., %	28.8	24.3	27.3
Duration of test, min.	25	25	25
Stroke, 0.225 inch			
Shore A hardness	47	52	48
ΔT , ° F.	52	41	45
Permanent set, %	15.3	8.5	10.5
Static compression at 55 lb., %	30.1	24.7	29.3
Duration of test, min.	25	25	25

50 miles per hour. This is a continuous 24-hour-per-day test with the load increased in increments amounting to 20% of the rated load capacity each 24 hours. The test is started at 80% of standard Tire and Rim Association load. This is a very severe accelerated test and usually is terminated by a carcass blowout due to heat build-up. Hysteresis of compounds used is a strong influential factor of the mileage obtained to failure. The heat build-up in Ameripol SN rubber tires, as measured by thermocouple needle and air pressure build-up in the tire, was slightly less than that in the Hevea rubber control tires. Tires evaluated by this method are always run to destruction. The mileages run by the Ameripol SN tires to failure were comparable to those shown by the Hevea rubber controls (Table VIII). Resistance to cut growth (standardized cuts are made in the tread grooves before the test is started) was somewhat better in the Ameripol SN tires (an average of 12% increase in cut growth) than in the

Table VII. Physical Properties of Vulcanizates—Tread Stock

	Ameripol SN		Hevea Rubber		Ameripol SN		Hevea Rubber
	I	II			I	II	
Gel, %	14	31	..	Aged in Test Tubes 24 Hours at 212° F. in Air; Stress-Strain at Room Temperature			
Swelling index	83	59	..				
[η]	3.17	3.45	..				
Mooney viscosity, ML-4' at 212° F.	75	75	..	Cure, min. at 280° F.	Tensile, Lb./Sq. Inch		
Tread recipe, Parts				15	3120	2990	2950
Polymer	100.0	100.0	100.0	30	2890	2710	2810
Zinc oxide	3.0	3.0	3.0	45	2620	2570	2510
Stearic acid	4.0	4.0	3.0	75	2120	2110	1880
AgeRite powder (PBNA)	1.0	1.0	1.0	150	1430	1360	1550
BLE-25	1.0	1.0	1.0		400% Modulus, Lb./Sq. Inch		
ISAF black	42.0	42.0	42.0		1900	2780	2640
Pine tar	2.0	2.0	4.0	15	2100	2400	2660
Lecithin + TEA (5%)	1.5	1.5	..	30	2340	2570	..
Santocure	0.6	0.6	0.6	45
Sulfur	3.0	3.0	3.0	75
B. F. Goodrich plasticity, 85° C. (on compounded stock)	44.8	38.4	50.3	150	Elongation at Break, %		
Mooney scorch, 260° F. (large rotor)					600	530	450
I.V. ^a	52	56	56	15	550	470	440
V _m	35	40	36	30	450	400	380
T _s	12.8	11.3	12.25	45	380	330	300
T _c	15.0	13.4	13.8	75	280	270	290
T _{Δ30}	2.2	2.1	1.55	150			
Gehman low temperature modulus (cure 30 min., 280° F.), ° C.					Graves Angle Tear (212° F.)		
T ₂	-33	-32	-34	Cure, min. at 280° F.	Lb./Inch		
T ₅	-48	-48	-49	15	270	250	340
Freeze point	-58	-58	-59	30	270	240	360
				45	280	240	300
Stress-Strain at Room Temperature				B. F. Goodrich Flexometer (212° F.); 55-Lb. Load; 60-Min. Cure, 280° F.			
Cure, min. at 280° F.	Tensile, Lb./Sq. Inch			Stroke, 0.175 inch			
15	3810	3820	4040	Shore A hardness	62	64	61
30	4160	3810	4230	ΔT, ° F.	33	36	33
45	3900	3730	4080	Permanent set, %	10.8	10.3	9.4
75	3840	3700	3920	Static compression at 55 lb., %	19.2	17.9	20.1
150	3540	3150	3490	Duration of test, min.	25	25	25
	400% Modulus, Lb./Sq. Inch			Stroke, 0.225 inch			
15	1580	1890	2110	Shore A Hardness	61	63	62
30	2010	2300	2550	ΔT, ° F.	83	74	68
45	2250	2460	2370	Permanent set, %	20.0	18.2	16.7
75	2170	2360	2450	Static compression at 55 lb., %	20.4	19.1	21.3
150	1900	2010	2200	Duration of test, min.	25	25	25
	Elongation at Break, %			Pico Abrasion (B. F. Goodrich Research Center, unpublished method)	95	92	100
15	690	640	630	^a See Table VI for definitions.			
30	650	580	570				
45	600	550	570				
75	600	550	580				
150	630	570	560				
Stress-Strain at 212° F.							
Cure, min. at 280° F.	Tensile, Lb./Sq. Inch						
15	2700	2480	2860				
30	2450	2100	2480				
45	2220	2120	2490				
75	2210	2000	2480				
150	2170	1830	2400				
	400% Modulus, Lb./Sq. Inch						
15	880	1120	1140				
30	1150	1370	1290				
45	1300	1500	1420				
75	1290	1380	1500				
150	1150	1280	1220				
	Elongation at Break, %						
15	840	690	770				
30	700	580	600				
45	620	570	600				
75	600	520	600				
150	600	520	650				

Hevea rubber control tires (an average of 26% increase in cut growth).

Test Truck Operation. This is also an accelerated service test but of less severity than the indoor wheel test. The test trucks are operated in the Kerrville, Tex., area, on a 24-hour-per-day basis at 45 miles per hour. Tires are rotated to the four wheel positions at 700 mile intervals. Test conditions such as loads, speeds, and inflation pressures are closely regulated. The test is operated at standard Tire and Rim Association load for 2800 miles, followed by 2800 miles at 130% rated load, and then run to failure or completion of 19,600 miles (whichever occurs first) at 150% rated load.

The Ameripol SN rubber tires made a very creditable showing. Tread wear was 85% that of the standard Hevea control tires. (These particular Ameripol SN rubber treads were rerun several

Table VIII. Indoor Wheel Tests

(Tests run according to old [prior to April 15, 1955 revision] Tire and Rim Association load ratings)

Test Miles	Load		Inflation Pressure, Lb./Sq. Inch	Tire Temp., ° F.	
	On tire, lb.	% of standard		Crown	Shoulder
Ameripol SN tire No. 1					
0	3600	80	70		
0-1200	3600	80	85	210	187
1200-2400	4500	100	88	220	233
2400-3600	5400	120	89	235	249
3600-3675	6300	140	Tire failed at 3675 miles due to separation from carcass cord		
Ameripol SN tire No. 2					
0	3600	80	70		
0-1200	3600	80	83	204	186
1200-2400	4500	100	86	216	205
2400-3600	5400	120	86	233	261
3600-3788	6300	140	Tire failed at 3788 miles due to heat blowout		
Hevea rubber tire No. 1					
0	3600	80	70		
0-1200	3600	80	81	202	192
1200-2400	4500	100	80	220	246
2400-3600	5400	120	92	230	262
3600-3656	6300	140	Tire failed at 3656 miles due to heat blowout		
Hevea rubber tire No. 2					
0	3600	80	70		
0-1200	3600	80	91	213	223
1200-2400	4500	100	90	218	240
2400-3600	5400	120	91	236	272
3600-4051	6300	140	Tire failed at 4051 miles due to heat blowout		

times through the tube machine during efforts to obtain proper die distribution. This had a deleterious effect on the abrasion quality of the treads.)

Resistance to growth of initiated tread cuts was good—quite comparable to controls. Independent cracking was inferior to the control (Table IX).

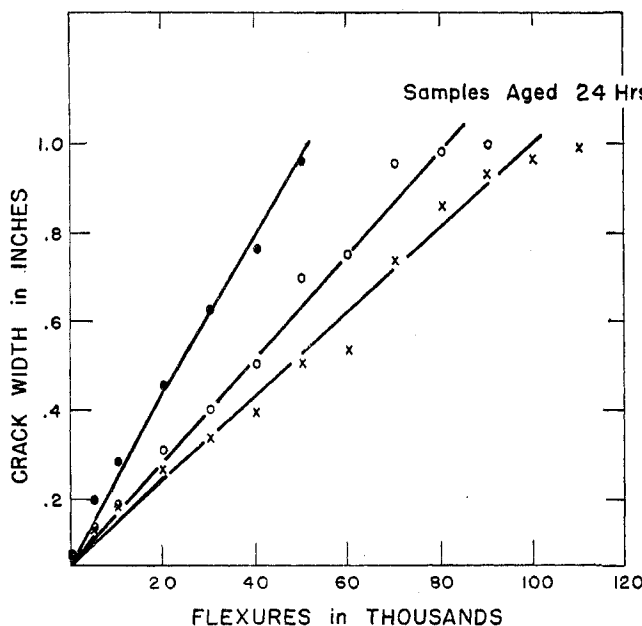


Figure 6. Carcass stock

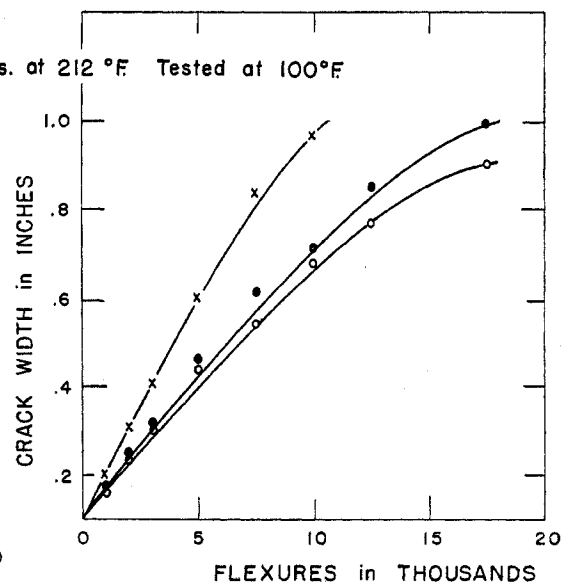


Figure 7. Tread stock

DeMattia flexing test initiated crack growth

○ Ameripol SN I (Gel 14% S.I. 83) × Ameripol SN II (Gel 31% S.I. 59) ● Hevea rubber

The carcasses of all the tires were sound after 19,600 miles of operation and have been recapped (a standard procedure) and placed in intracity bus operation service.

Mileage Contract Bus Operation. Tires have been placed in most rigorous intercity bus operational service. Speeds may be higher than 70 miles per hour. Loads naturally vary. The front wheel positions are usually overloaded (say, up to 130%) while rear wheel positions are reasonably close to rated loads. It is customary to apply new tires to the front wheel position, operate them for 15,000 to 25,000 miles, and then change tires to rear wheels. Such a routine is followed to obtain optimum service from the tires and to conform to the highest safety standards.

Ameripol SN rubber tires are operating very satisfactorily. The mileage on the individual tires naturally varies because they are running on different vehicles, but a particular lot of ten tires placed in intercity high speed bus service are all sound after accumulation of 600,000 miles of travel to the time of regrooving of the treads. Indications are that the tread wear index of Ameripol SN tires is about 85% that of the Hevea control tires. Independent tread cracking is inferior to that shown by the control tires but the severity is not alarming. These service

tests were initiated during the hot summer months, thus adding to the significance of the results obtained.

Summary. From a practical standpoint, Ameripol SN is equivalent in properties to Hevea rubber. This new development has solved the long-standing problem of producing by synthetic means a general-purpose polymer adequate as a complete replacement for Hevea rubber in heavy-duty tires.

ACKNOWLEDGMENT

The development and evaluation of Ameripol SN are a joint effort of the technical staffs of The B. F. Goodrich Company and Gulf Research and Development Co., on behalf of Goodrich-Gulf Chemicals, Inc., sponsor. The catalyst modification that produced the trans variety was developed by E. J. Carlson of this laboratory; Harold Gray directed the tire testing program. The authors wish to gratefully acknowledge major contributions to this study by other staff members as follows: M. L. Dannis, D. Diller, D. G. Frazer, R. G. Hay, A. M. Henke, H. M. Hoxie, J. E. Jansen, A. E. Juve, L. C. Kreider, R. E. Lynn, J. M. Madigan, F. F. Miller, M. G. Morningstar, H. Neff, R. F. Nichols, R. Shearer, A. G. Veith, J. S. B. Wolfe, G. V. Wootton, J. A. Yanko. General supervision: C. W. Montgomery, W. L. Semon.

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RECEIVED for review November 4, 1955. ACCEPTED January 30, 1956.
Presented for Goodrich-Gulf Chemicals, Inc., by F. K. Schoenfeld, vice president-research, The B. F. Goodrich Co., Brecksville, Ohio, before the Division of Rubber Chemistry, ACS, Philadelphia, Pa., November 1955.

Table IX. Texas Road Test

Conditions of test			
Speed: 45 miles per hour			
Tire size: 11.00 X 20 rayon construction			
Test Miles	Load on Tire, Lb.	% of Standard Load Rating	Inflation Pressure, Lb./Sq. Inch
0-2,800	5150	100	75 ^a
2,800-5,600	6700	130	75
5,600-19,600	7730	150	75
Results			
Tires made of	Inches of Cracking (Independent), Total Length	Initiated Cracks, % Growth	Tread Wear Index
Ameripol SN No. 1	64	245	85
Ameripol SN No. 2	98	265	
Hevea rubber No. 3	20 1/2	248	100
Hevea rubber No. 4	22 1/2	191	

^a Standard.