A New Chlorine-Containing Elastomer

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A new elastomer, chlorobutyl rubber, has been introduced (*1, 2, 7*) into the expanding field of synthetic rubbers. Until the commercialization of brominated Butyl rubber (*6*), the only commercially available synthetic rubber based on isobutylene was the copolymer of isobutylene and isoprene. This Butyl rubber is produced in a range of molecular weights and unsaturation, with the unsaturation always at a low level, from about 0.5 to 2.5 mole % (*10*) so that the bulk of the polymer molecule is made up of saturated polyisobutylene units.

The new elastomer (*1*), known as MD-551 or chlorobutyl rubber, is a chlorine-containing isobutylene copolymer, best described through its vulcanization properties. The ratio of isobutylene to comonomer is about the same as for a common grade of Butyl rubber (Enjay Butyl 215), consequently, the major portion of the polymer chain is saturated. The polymer contains reactive allylic chlorine which is responsible for its versatility in vulcanization, which distinguishes it from Butyl rubber.

Typical inspections of the raw polymer are as follows: chlorine, 1.2%, corresponding to 1 chlorine atom per double bond; unsaturation, 1 to 2 mole % [the method of measuring unsaturation (5) is subject to interpretation]; specific gravity, 0.92, nearly the same as for polyisobutylene; color, amber, satisfactory for white stocks; Mooney viscosity, 52 ±5 at 8 minutes ML/212° F. and intrinsic viscosity measurements using the constants for polyisobutylene (*4*) correspond to about 450,000 viscosity average molecular weight.

The reactivity of the chlorine atom is typical of allylic chlorides, and not of alkyl chlorides which have been prepared by copolymerizing isobutylene with alkenyl chlorides (*3*). The allylic chloride structure in the comonomer unit imparts distinctly different vulcanization properties than is found in an all-hydrocarbon elastomer.

The allylic chlorine of MD-551 provides a wide variation in practical cure systems because it may react through either or both the unsaturation and chlorine atom. Moreover, the chlorine atom in the polymer molecule enhances compatibility between MD-551 and elastomers of higher unsaturation during vulcanization. For an isobutylene copolymer, MD-551 has a fast cure rate, and it cures to a high degree of cross links. Because it is fast curing and the cross links are thermally stable, many systems give broad flat cure plateaus. The efficient cure and the thermal stability of the cross links both contribute to give low compression set and excellent performance in compression flexing, as in the Goodrich Flexometer. Abrasion resistance of MD-551 tread stocks is good in the laboratory and on the road. Ozone resistance of MD-551 in sulfur cures is similar to Butyl rubber of comparable unsaturation. Nonsulfur cures of MD-551 are considerably more resistant to ozone.

VULCANIZATION CHARACTERISTICS

Six basic cure systems are illustrated in Figures 1 to 6. Each is a simple formulation containing 50 parts of HAF carbon black. In the first one, the only curative is zinc oxide. The cure is slow but the bonds formed are very stable and are postulated to be carbon to carbon cross links.

The addition of one part of tetramethyl thiuram disulfide increases the speed and degree of cross linking, as shown in Figure 2 where the modulus is higher and elongation is lower. This is a very useful cure system for MD-551 and can be modified in many ways.

The cure curves for a sulfur cure, as might be used in an all-hydrocarbon elastomer, are shown in Figure 3. The same high modulus is attained only at a somewhat slower rate than the compound without sulfur. No reversion is apparent. Although

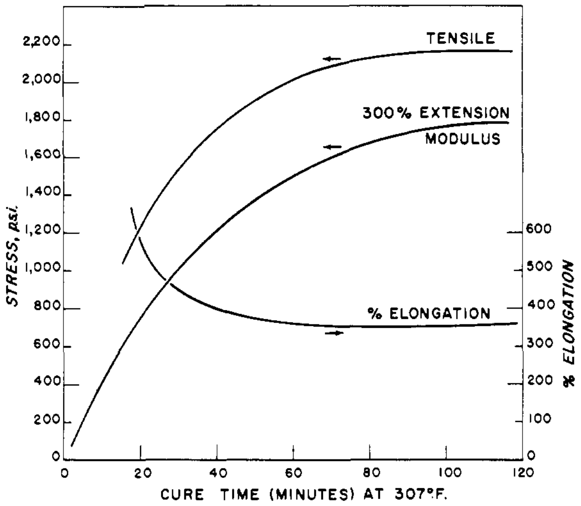


Figure 1. Zinc oxide cure

MD-551	100
HAF black	50
Antioxidant 2246	1.0
Stearic acid	1.0
Zinc oxide	5.0

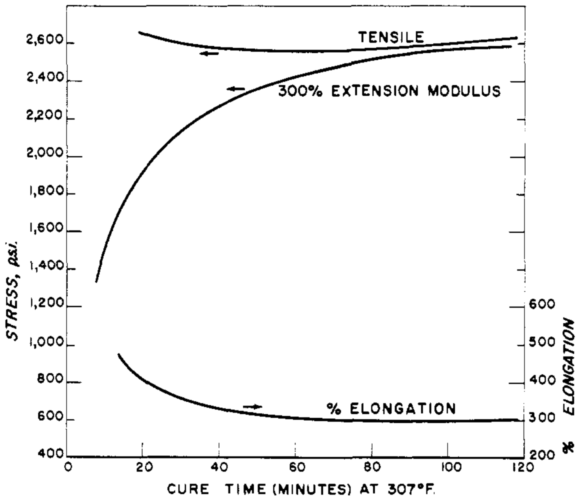


Figure 2. Thiuram disulfide cure

MD-551	100
HAF black	50
Antioxidant 2246	1
Stearic acid	1
Zinc oxide	5
Tetramethylthiuram disulfide	1.0

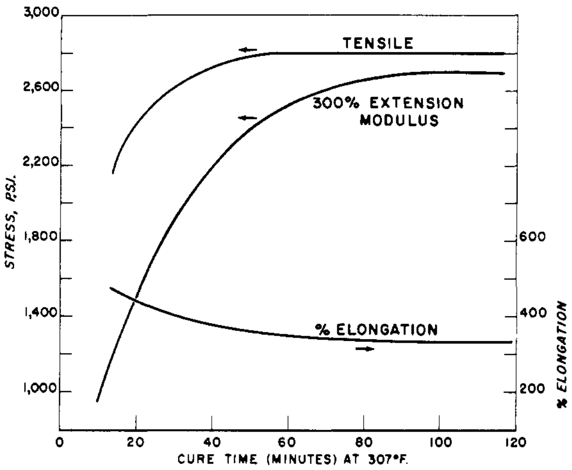


Figure 3. Sulfur cure

MD-551	100
HAF black	50
Stearic acid	0.5
Zinc oxide	5.0
Sulfur	2.0
Tellurium diethyl dithiocarbamate	1.0

these vulcanizates are not as stable to heat as without free sulfur, they are much more stable to heat than Butyl rubber in the same recipe.

A quinone dioxime cure system is applicable to MD-551, as illustrated in Figure 4 for a relatively nonscorchy recipe. Its physical properties are similar to those of a Butyl rubber–quinone dioxime cure.

A compound with two primary amino groups such as hexamethylene diamine or diethylene triamine, as shown in Figure 5, will cure MD-551 rapidly. It is very scorchy, and can be retarded by replacing the magnesium oxide with magnesium stearate. This illustrates the reaction of the halogen in the polymer with a bifunctional compound for cross linking. The vulcanizate is not very stable under severe compression flexing, but has excellent ozone resistance and ease of cure in the press or in open steam.

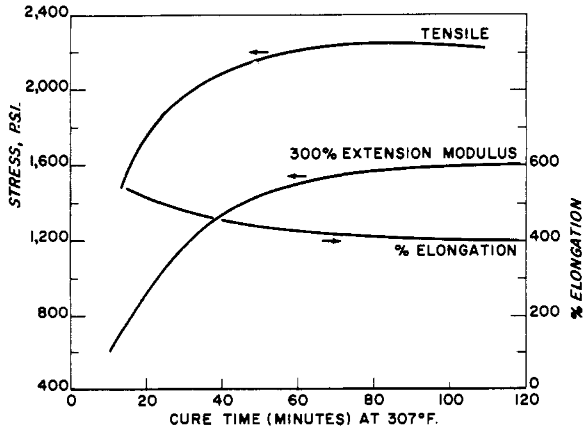


Figure 4. Quinone dioxime cure

Chlorobutyl MD-551	100
HAF black	50
Stearic acid	1.0
Zinc oxide	5.0
Lead dioxide	2.0
Quinone dioxime (GMF)	2.0
Benzothiazyl disulfide	4.0

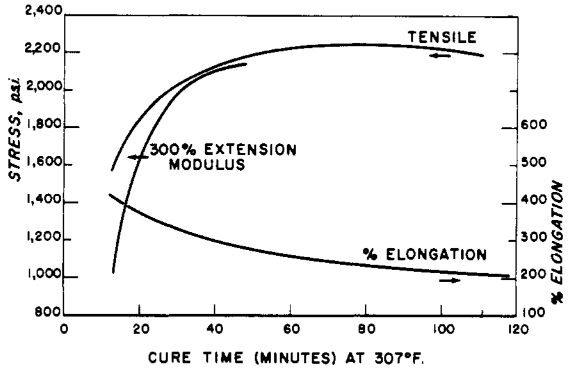


Figure 5. Amine cure

MD-551	100
HAF black	50
Antioxidant 2246	1.0
Magnesium oxide	5.0
Diethylene triamine	2.0

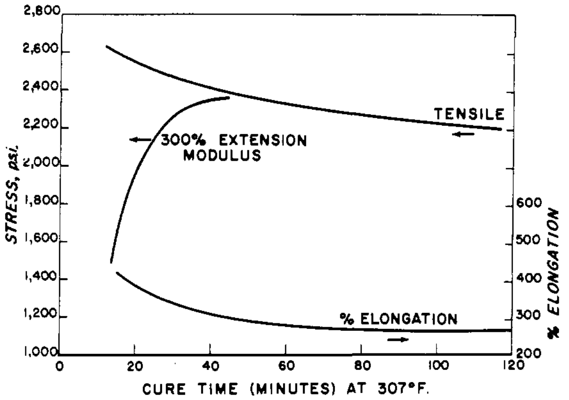


Figure 6. Methylol phenol resin cure

MD-551	100
HAF black	50
Antioxidant 2246	1.0
Stearic acid	1.0
Zinc oxide	5.0
Methylol phenol resin	7.0

MD-551 is unlike Butyl rubber in several respects. It cures very rapidly with polymethylolphenol resins. The simple recipe with no plasticizer (Figure 6) has remarkably good scorch safety (15 minutes to a 5-point Mooney rise at 260° F.) for such a fast cure. The optimum resin concentration may be 3 to 7 phr, while in Butyl rubber it is 10 to 15 phr which at best gives a very slow cure under ordinary vulcanization conditions. No halogen activator is required, and the polymethylolphenol resin may be used with other cures in MD-551, such as the sulfur cure. These two cures are not compatible in Butyl rubber, although they are in highly unsaturated rubbers. Excellent compression set and compression flexing are obtained from these resin cures of MD-551. Ozone resistance is also outstanding. Its main shortcoming is its shortness. On aging, the ultimate elongation becomes shorter while other good heat-resistant vulcanizates like the thiuram disulfide–zinc oxide maintain original elongation.

Because of the enhanced activity of these vulcanization systems with MD-551, in some instances scorch safety is limited. For practical applications, a cure system usually needs good resistance to scorching to make processing possible. Mooney scorch data for the different unplasticized and unmodified vulcanization systems given in Figures 1 to 6 are shown in Table I.

Generally, 10 to 15 minutes to scorch in the Mooney plastometer at 260° F. is required for good factory processing safety.

Many retarders give extended scorch safety for some cure systems without adversely affecting cure rates (Table II).

No satisfactory retarder has been found for the GMF cure, but the scorch time shown for this system may be sufficient for certain applications, such as wire insulation and molded goods.

Table I. Mooney Scorch Properties of MD-551 Vulcanization Systems

	Mooney Scorch at 260° F.	
Vulcanization System [a]	MI [b]	MS [c]
ZnO	55	30
Thiuram disulfide	38	7
Sulfur	55	2
Quinone dioxime	62	7
Amine	< 95	0
Methylol phenol resin	38	15

[a] Recipes for these compounds are shown in Figures 1 to 6.
[b] MI = initial Mooney reading.
[c] MS = minutes to a 5 point rise above minimum reading.

The amine cure, interesting because of its outstanding ozone resistance, is still too scorchy for most applications.

VULCANIZATE PROPERTIES

An outstanding characteristic of MD-551 vulcanizates is stability at elevated temperature in the presence of air. The manner of aging depends in some degree on the type vulcanization system employed. Heat aging data for the six recipes given are reported in Figure 7. For this, dumbbells from 0.075-inch pads cured 45 minutes at 307° F. were aged in a circulating air oven at 300° F. for 72 hours. There is good retention of physical properties for all cures in comparison with ordinary elastomers. Retention of elongation is good for the thiuram disulfide cure, while the presence of free sulfur in the recipe has some softening effect so that the aged tensile is low and ultimate elongation is higher. However, even this is a good aging stock. Best tensile retention was noted with the resin cure, but it is typical for this vulcanizate to become shorter on aging. These are not necessarily the best compounds for heat aging, but they are good for comparison of basic properties.

Table II. Scorch Retarders for MD-551 Cure Systems

Principal Curing Agent	Retarder	Comments
Thiuram disulfide	Benzothiazyl disulfide	At 1 phr concn. extends time to scorch 10 to 15 min. and gives improved vulcanizate properties.
Thiuram disulfide	MgO or Mg stearate [a]	Increase time to scorch and aids processing, but also may retard cure depending on concentration.
Sulfur and dithiocarbamate accelerators	4,4'-Dithiodimorpholine	At 1 phr extends time to scorch 10 to 15 minutes and causes only a slight retardation in cure at the low cure times (<20 min. at 307° F.).
Amine	Mg stearate	Extends scorch time by 2 min.

[a] Special consideration should be given to addition of Mg compounds.

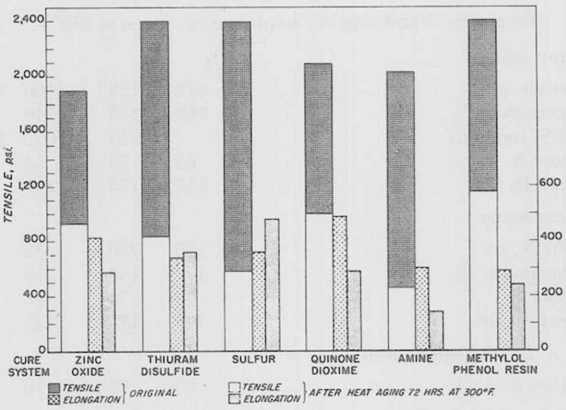


Figure 7. Heat aging properties of MD-551

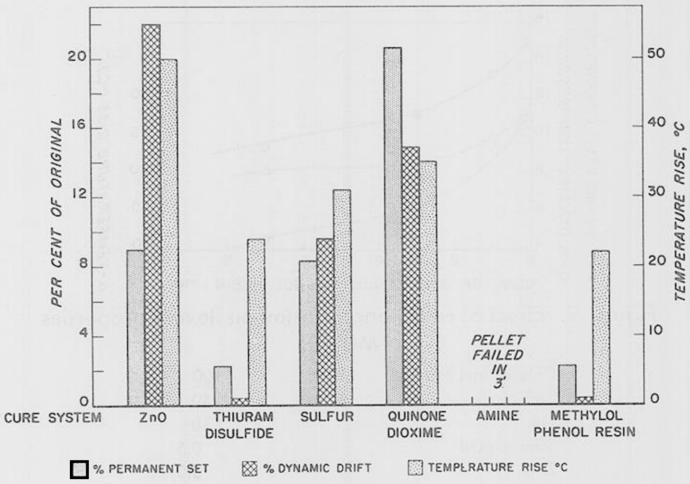


Figure 8. Goodrich flexometer properties of MD-551

Compression flexing at elevated temperatures requires a high degree of stability for good performance. For low permanent set and low dynamic drift, the stock must not continue to cure, nor can the cross links be fugitive. Temperature rise during flexing depends on the hysteresis properties and the degree of deformation as controlled by the softness of the vulcanizate. If there is breakdown during the test, the temperature may rise; otherwise it reaches a maximum and remains constant. Thus, temperature rise in itself has little meaning. The data illustrated in Figure 8 are for the same six compounds with pellets cured 45 minutes at 307° F. and tested in the Goodrich Flexometer at 32 cycles per second with an 0.25-inch stroke and an 89 p.s.i. load for 30 minutes at an ambient temperature of 212° F. These conditions were chosen to represent severe flexing of the type encountered in tires.

The very low dynamic drift and permanent set for the thiuram disulfide and resin vulcanizates demonstrates their outstanding stability under dynamic conditions. Even the sulfur cure is considered very good in this test. If the zinc oxide vulcanizate were cured longer, it would perform better under these dynamic conditions. Neither the quinone dioxime nor the amine cure is as stable as the other cure systems. Delamination occurred in the pellet cured with diethylenetriamine.

Both efficient utilization of cross-link sites and stability of cross links themselves are responsible for good low set properties, whether dynamic or static tests are employed. In Table III are shown very low static compression set data for simple unplasticized systems after 70 hours at 212° F. (ASTM D 395-55, Method B). The thiuram disulfide–zinc oxide system gives 12% set with an SRF black and 30% with 50 phr of HAF black. The resin cure is still lower over a wide range in resin concentrations, 3 to 9 phr.

The improvement in the Goodrich Flexometer data by addition of the polymethylol resin to sulfur cure is shown in Figure

Table III. Compression Set Properties of MD-551

Compound	A	B	C	D
MD-551	100	100	100	100
SRF black	50	. . .	. . .	. . .
HAF black	. . .	50	50	50
Stearic acid	1.0	1.0	1.0	1.0
Cyanamid antioxidant 2246 [a]	1.0	1.0	1.0	1.0
Tetramethyl thiuram disulfide	1.0	1.0	. . .	. . .
Amberol ST-137 [b]	. . .	. . .	3.0	9.0
Zinc oxide	5.0	5.0	5.0	5.0
Cure time, min., and temp., ° F.	40 at 310°	40 at 310°	25 at 320°	25 at 320°
% compression set B (70 hr. at 212° F.)	12.0	30.2	16.0	20.0

[a] American Cyanamid Co.
[b] Rohm & Haas.

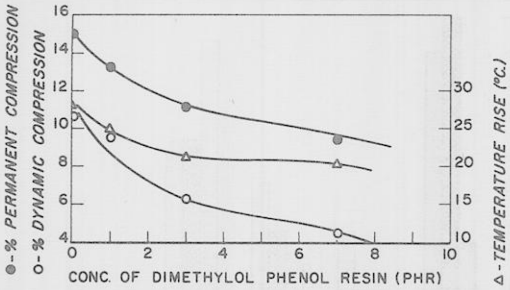


Figure 9. Effect of resin concentration on flexing properties of MD-551

Chlorobutyl MD-551	100
SAF black	40
Oil	10
Stearic acid	0.5
ZnO	5.0
Sulfur	1.5
Tellurium diethyl dithiocarbamate	1.0
4,4′-dithiodimorpholine	1.0
Resin	As shown

Cure 40 minutes at 307° F.

9. About three parts is optimum, although more may be used for even greater effect.

Figure 10 gives results of an accelerated ozone test on dumbbells from 0.075-inch pads which were press cured 45 minutes at 307° F. and from pads cured in open steam 20 minutes at 320° F. These are all the 50 phr HAF black compounds described in Figures 1 to 6. Minutes to the first observable crack in an ozone concentration of 0.2% in air, with the dumbbells extended 50% at room temperature is used as a measure of ozone resistance. In this test, the sulfur cure of MD-551 is about the same as Butyl rubber in the same recipe. The thiuram disulfide cure is about twice as good, and the resin cure lasts 5 to 10 times as long. The steam cure of the polymethylolphenol resin is not as good as the dry press cure in its physical properties, as well as its ozone resistance. The resin cure has a high modulus and low set properties, so this good ozone resistance can be attributed only to its chemical resistance and not to stress relaxation.

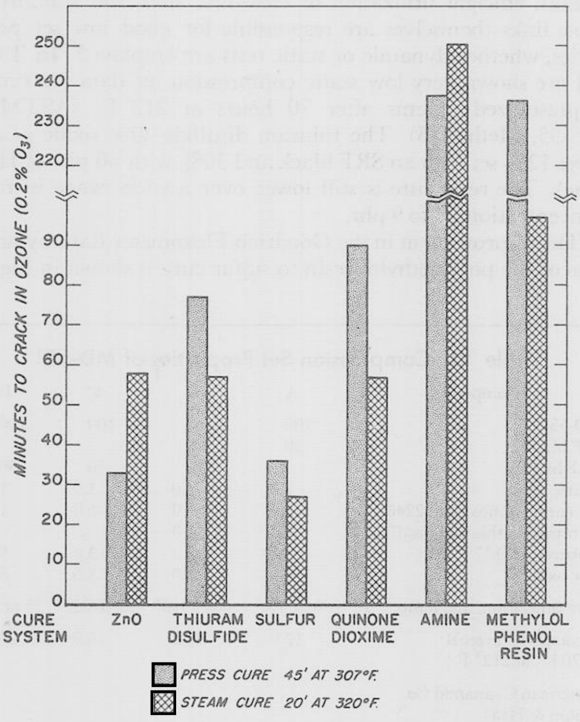


Figure 10. Ozone resistance of MD-551

Tear resistance of MD-551 vulcanizates vary as shown in Figure 11. ASTM D 624-54 procedure was used for tear resistance evaluation. Two additional compounds are included to show the effect of thiazyl compounds on tear strength. Replacing the tetramethyl thiuram disulfide in the recipe of Figure 2 with benzothiazyl disulfide gives a vulcanizate with good tear but poor physicals. Adding 1 phr of benzothiazyl disulfide to the recipe in Figure 2 gives both good physicals and good tear, and improves scorch safety.

COMPOUNDING FOR HEAT RESISTANCE

A well designed heat-resistant compound is shown in Table IV. It employs some benzothiazyl disulfide to get good tear and scorch safety. Additional scorch safety is provided with magnesium oxide. This recipe utilizes the thiuram disulfide–

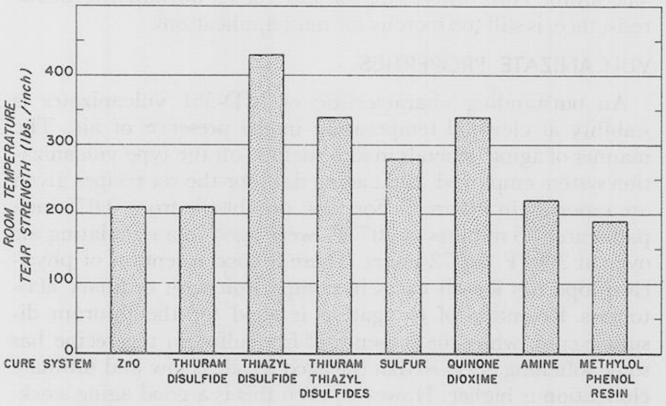


Figure 11. Tear strength of MD-551 vulcanizates

Table IV. Effect of Magnesium Oxide on MD-551 Heat-Resistant Compound

Light calcined magnesia	0	0.5	1	2
MD-551		100		
Antioxidant 2246		1		
HAF black		60		
Stearic acid		1		
Tackifier (Amberol ST-137X)		3		
Oil (Necton 60)[a]		5		
Benzothiazyl disulfide		2		
Tetramethylthiuram disulfide		1		
Zinc oxide		3		
Mooney viscosity ML 8 min. at 212° F.	84	83	86	81
Mooney scorch, min. to 5 pts./260° F.	15	30	30	30
Original Properties, 30 Min. at 320° F. Cure				
Tensile, p.s.i.	2130	2180	2120	2150
Elongation, %	520	560	570	520
300% modulus	1300	1140	1130	1300
Hardness, Shore A	66	64	66	65
Tear, lb./in.	335	355	360	415
Properties after Aging in Circulating Air Oven at 380° F.				
16-hour aging				
Tensile, p.s.i.	670	1130	1100	1040
Elongation, %	180	350	340	320
300% modulus	. . .	1020	1030	1010
Shore A	63	58	62	65
Tear, lb./in.	160	175	160	170
40-hour aging				
Tensile, p.s.i.	380	270	430	310
Elongation, %	170	150	250	250
Shore A	70	74	76	68
Tear, lb./in.	125	125	125	120
1/4 × 2 inch looped specimen				
Hours to crack	80	92	110	120

[a] Esso Standard Oil Co.

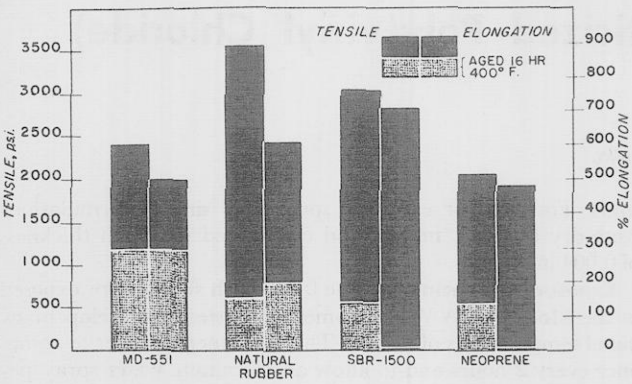


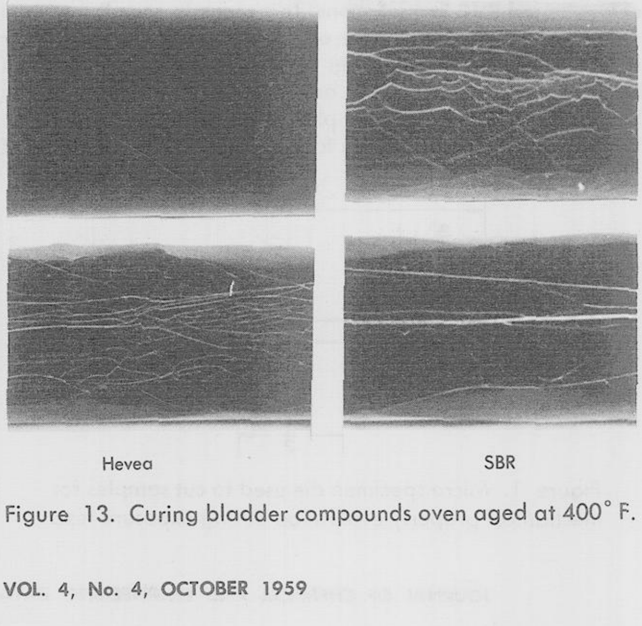
Figure 12. Comparison of heat-resistant compounds

zinc oxide cure. The zinc oxide may be varied from 3 to 20 parts without any appreciable effect, but magnesia should be kept at a low level because higher amounts will retard cure. The values shown are for a 30-minute cure; however, the cure curve is flat, and the physical properties change little between 20 and 100 minutes. Magnesium oxide helps in retention of both tensile and elongation during aging. Even after 40 hours of aging the dumbbells in a circulating air oven at 380° F., *good elongation* is maintained along with fair tensile strength. A Banbury mixing cycle for this stock is given in Table V.

Comparison of high-temperature air aging of MD-551 heat-resistant stock with other elastomers compounded in recommended recipes for high temperature service (*8, 9*) is seen in Figure 12. This extremely severe test involves aging dumbbells in a circulating air oven at 400° F. for 16 hours where even good heat-resistant compounds of rubber will rapidly degrade. Slabs were also aged under these same conditions and then wrapped around a mandrel to show surface appearance (Figure 13). Surface cracking with a soft interior is typical of natural rubber, while the SBR and neoprene stocks were brittle. The MD-551 vulcanizate maintained its original rubbery appearance.

Table V. Mixing Cycle for MD-551 Heat-Resistant Compound

Time, Minutes	Operation
	Masterbatching
0	Add polymer, MgO and antioxidant
1	Add half of black
3	Add all black and stearic acid
5-1/2	Add tackifier (if included)
6-1/2	Add processing oil
8 to 10	Discharge, stock about 300° F.
	Finalizing
0	Add masterbatch
1/2	Add Zno and accelerators
2-1/2	Discharge, stock about 210° F.



MD-551 Neoprene

Hevea SBR

Figure 13. Curing bladder compounds oven aged at 400° F.

One of the first applications to be developed for MD-551 was in curing bags. Butyl rubber bladders had a life of about 200 heats with a quinone dioxime cure, while an average of over 600 heats was obtained with a heat-resistant MD-551 compound. The resistance to softening from high pressure steam is characteristic of the MD-551 bladder. This is pictured by a measurement of Shore hardness on *the inside of a used bladder* section.

Adding a small amount of natural rubber or SBR to MD-551 is often beneficial by balancing the hardening effect of the highly unsaturated rubbers with the softening of MD-551 (Table VI). The addition of these highly unsaturated rubbers *does not* destroy the *ozone* resistance of this new synthetic rubber.

Table VI. Natural Rubber and SBR-1500 Added to MD-551

(50 phr HAF black compound)

Cure system	ZnO-thiuram disulfide				
MD-551	100	98	98	75	75
Smoked sheet	. . .	2	. . .	25	. . .
SBR	. . .	. . .	2	. . .	25
Original properties, 45 min. at 307° F.					
Tensile, p.s.i.	2630	2690	2750	1940	2400
Elongation, %	340	330	320	460	430
300% modulus	2290	2160	2400	1100	1500
Shore A	63	61	62	56	62
After aging 72 hr. at 300° F.Z					
Tensile, p.s.i.	830	1370	1370	760	810
Elongation, %	360	300	320	130	50
300% modulus	700	1370	1350	. . .	. . .
Shore A	58	74	72	83	54
Ozone resistance, 50% extension in 0.2% ozone					
Min. to crack	77	45	37	34	47
Min. to break	126	138	134	119	105

ACKNOWLEDGMENT

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