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Development Of An EPDM Elastomer With Improved Bondability For Use In Sonar Transducers

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CONTENTS

INTRODUCTION.....	1
EXPERIMENTAL.....	2
Materials.....	2
Testing Procedures.....	4
TEST RESULTS.....	6
Elastomer-to-Metal Bondability and Tear Strength.....	6
Short-Term Properties.....	13
Density and Sound Speed.....	13
Dynamic Mechanical Properties.....	17
Hardness.....	18
Tensile Properties.....	21
Electrical Resistivity.....	26
Cure and Storage Parameters.....	29
Long-Term Properties.....	32
Compression Set.....	32
Compatibility and Water Permeation.....	35
DESIGN OF EPDM FOR TRANSDUCER USE.....	36
Physical Property Trade-Offs.....	36
Quality Control.....	38
Cold Bonding of EPDM.....	39
PROCESSING STUDY.....	39
CONCLUSIONS.....	40
ACKNOWLEDGMENTS.....	41
REFERENCES.....	42
APPENDIX A - Applications of EPDM-RLE.....	45
TR-317R Transducer.....	45
TR-242/316 Nodal Mount Grommet.....	45
TR-302 Depth Sounder Window.....	46
TR-330A Transducer.....	46
H52 Standard Hydrophone.....	47
APPENDIX B - Procurement Specification for EPDM-RLE.....	49

TABLES

Table	Page
1 Compounding Ingredients Used in EPDM Elastomers.....	3
2 Adhesive Systems Used for Elastomer-to-Metal Bonding.....	6
3 Effect on Bondability and Tear Strength of EPDM Elastomers by Changing Only Polymer Type.....	7
4 Bondability and Tear Strength of EPDM Elastomers With Varying Loadings of Only DCP.....	8
5 Effect of Changing Curing Coagents Only on the Bondability and Tear Strength of EPDM Elastomers.....	9
6 Effect of Curing Agent and Coagent Loading on EPDM Elastomer-to- Metal Adhesion and Tear Strength.....	9
7 Effect of Varying Only Carbon Black Size and Loading on the Bondability and Tear Strength of EPDM Elastomers.....	11
8 Effect of Variations in TMDQ and Zinc Oxide Loading on Adhesion of EPDM to Metal and Tear Strength.....	12
9 Effect of Changing Curative Type on the Tensile Properties of EPDM.....	22
10 Effect of Seawater Exposure at 40°C on the Tensile Properties of EPDM.....	26
11 Cure Times for EPDM Based on DCP Half-Life.....	31
12 Physical Properties of Plant-Mixed EPDM Formulations.....	40

FIGURES

Fig.		Page
1	Elastomer-to-metal bondability of EPDM exposed to seawater at 25°C.....	4
2	Tear strength of EPDM with varying loading of N660 carbon black....	12
3	Density of EPDM with varying loading of DCP curing agent.....	13
4	Density of EPDM with varying loading of N660 carbon black.....	14
5	Sound speed of EPDM at 1.5 MHz and 25°C with varying loading of N660 carbon black.....	15
6	Specific acoustic impedance of EPDM with varying loading of N660 carbon black.....	15
7	Adiabatic bulk modulus of EPDM with varying loading of N660 carbon black.....	16
8	Density of EPDM containing Nordel 1070 with varying loading of N660 carbon black.....	16
9	Sound speed of EPDM at 1.5 MHz and 25°C containing Nordel 1070 with varying loading of carbon black.....	17
10	Dynamic Young's modulus and loss tangent of EPDM at 10°C as a function of frequency.....	18
11	Shore A hardness of EPDM with varying loading of N660 carbon black.....	19
12	Shore A hardness of EPDM containing Nordel 1070 with varying loading of N660 carbon black.....	19
13	Shore A hardness of EPDM with varying loading of DCP curing agent.....	20
14	Shore A hardness of EPDM with varying loading of antioxidant TMDQ.....	21
15	Tensile properties of EPDM with varying loading of DCP curing agent.....	22
16	Tensile properties of EPDM with varying loading of N660 carbon black.....	23

17	Tensile properties of EPDM containing Nordel 1070 with varying loading of N550 carbon black.....	24
18	Tensile properties of EPDM with varying loading of antioxidant TMDQ.....	25
19	Log volume resistivity of EPDM with varying loading of N660 carbon black.....	26
20	Log volume resistivity of EPDM with varying loading of DCP curing agent.....	27
21	Log volume resistivity of EPDM with varying loading of antioxidant TMDQ.....	28
22	Effect of seawater exposure on log volume resistivity of EPDM.....	29
23	Effect of varying loading of DCP curing agent on the t_{10} of EPDM.....	30
24	Effect of varying loading of antioxidant TMDQ on the t_{10} of EPDM.....	30
25	Compression set of EPDM with varying loading of DCP curing agent.....	33
26	Compression set of EPDM with varying loading of antioxidant TMDQ.....	34
27	Effect of compression time on compression set of EPDM.....	34
28	Compatibility of EPDM with castor oil. Fractional mass change of EPDM with immersion in castor oil.....	35
29	Compatibility of EPDM with Isopar M. Fractional mass change of EPDM with immersion in castor oil.....	36

DEVELOPMENT OF AN EPDM ELASTOMER WITH IMPROVED BONDABILITY FOR USE IN SONAR TRANSDUCERS

INTRODUCTION

The designation EPDM has been given by the ASTM D1418 [1] to the class of elastomers that is composed of terpolymers of ethylene, propylene, and a non-conjugated diene, such as 1,5-hexadiene. These materials have achieved wide acceptance by designers of commercial products because of their generally excellent environmental resistance and low cost [2]. Since EPDM polymers remain rubbery to quite low temperatures, this suggests that the material has a very low glass-transition temperature. For ordinary sonar applications, one would operate in temperature and frequency ranges far above those for EPDM's glass transition and, therefore, expect the material to exhibit very low dynamic loss. Indeed, EPDM's were tested as sonar windows in 1969 [3]. The reasons they were never used are obscure but probably were based on the grave difficulty of forming reliable bonds of EPDM with metals. In this report we present the development of an EPDM formulation for sonar window applications.

An enumeration of both the short-term and long-term property requirements for an elastomer has been given elsewhere [4]. Briefly, however, the following properties are required for an elastomer to be used in a sonar transducer:

Short-Term Properties

- Sound speed and density match with seawater
- Low dynamic loss
- Moderate moduli (or Shore hardness)
- Good strength
- High electrical resistivity
- Convenient cure schedule

Long-Term Properties

- Retention of short-term properties with age
- Low water permeability
- Low swell in water
- Compatibility with acoustic coupling fluids
- Either good bondability or good resistance to creep.

As a class of elastomers, EPDM's are known to have a good sound speed and density match with seawater, low dynamic loss, and good retention of properties during environmental exposure. With some care in their compounding, they also may have an adjustable static modulus, low water permeability, and low swell in water. It was shown earlier that EPDM's exhibited an excellent compatibility with some acoustic coupling fluids [5]. Of the remaining properties, the gravest weaknesses of EPDM elastomers were perceived to be in bondability and strength. Thus, our research effort was initially focussed on bondability and strength, wherein we studied a range of polymer types, cure types, coagent types, and filler types. Only after the ingredients were optimized for bondability and tear strength were the concentrations of these ingredients adjusted to improve other properties.

EXPERIMENTAL

Materials

The compounding ingredients used to optimize an EPDM elastomer for use in transducers are outlined in Table 1. The brand name and manufacturer are given. The exact chemical equivalent may be substituted with confidence for those listed in this table.

Nordel 1070 has a higher Mooney viscosity and, is therefore, a higher molecular weight terpolymer than Royalene 521 [6,7]. Elastomers containing either of these polymers were cured with either a sulfur or a peroxide curing agent. Tetramethyl thiuram monosulfide (TMTM) and 2-mercaptobenzothiazole (MBT) were used as curing coagents to accelerate the sulfur-cured elastomers. The remaining curing coagents listed in Table 1 were used to improve the cure rate in the peroxide-cured systems. Stearic acid was used in the sulfur-cured samples as an activator of the cure system. Polymerized trimethyldihydroquinoline (TMDQ) was used as an antioxidant in all samples cured with peroxide. Zinc oxide was added to all samples but one. Zinc oxide apparently functions as a cure activator for both types of curing agents. Laboratory samples of the formulations were compounded by Technical Sales and Engineering Company, Inc. of St. Petersburg, Florida, and Burke Rubber Industries of San Jose, California. A typical formulation for an EPDM elastomer usually contains 100 parts-per-hundred rubber (PHR) of the polymer and may be cured with 3 to 7 PHR of a curing agent. A curing coagent may be used in the range of 1 to 3 PHR. The loading of filler in the elastomer may range from 20 to 70 PHR. An antioxidant might be included in the formulation up to 2 PHR. If a cure accelerator is present in the elastomer, the loading typically does not exceed 5 PHR.

Table 1 - Compounding Ingredients Used in EPDM Elastomers

FUNCTION	INGREDIENT	BRAND NAME	MANUFACTURER
polymer	ethylene-propylene-diene terpolymer	Royalene 521	Uniroyal Chemical
	ethylene-propylene-diene terpolymer	Nordel 1070	
curing agent	dicumyl peroxide (40% solution on clay) (DCP)	DiCup 40KE	Hercules Inc.
	2,5-bis(tertbutyl peroxy)-2,5-dimethylhexane (DBPH)	Varox DBPH	
	a-a'-bis(tertbutyl peroxy)diisopropylbenzene (DBPB)	Vul Cup 40KE	Hercules Inc.
	sulfur		
curing coagent	trimethylolpropane trimethacrylate (TMPTMA)	Sartomer SR350	Sartomer Company
	ethylene dimethacrylate (EDMA)	Sartomer SR206	
	1,2-polybutadiene (PB)	Ricon 151	Colorado Chem. Spec. Inc.
	N,N'-m-phenylenediamaleimide (PDMI)	HVA-2	
	triallycyanurate (TAC)	TAC	American Cyanamid Co.
	2-mercaptobenzothiazole (MBT)	Mastermix MBT	
	tetramethyl thiuram monosulfide (TMTM)	Monex	Uniroyal Chemical
filler	carbon black 21-nm particle size (N220)	Philblack N220	Phillips Petroleum Co.
	carbon black 41-nm particle size (N550)	Philblack N550	
	carbon black 52-nm particle size (N660)	Philblack N660	
	carbon black 60-nm particle size (N774)	Philblack N774	
	carbon black 27-nm particle size (N327)	Neotex 100 (N327)	
cure activator	zinc oxide (ZnO)		Various
	stearic acid		
antioxidant	trimethyldihydroquinoline (TMDQ)	Naugard Q	Uniroyal Chemical

Testing Procedures

This section will explain the methods used to measure the physical properties of the elastomers. The bondability of the elastomer to mild steel was measured using a 90° static peel test. The mild steel substrates were sanded in one direction with 120-grit silicon carbide sandpaper. The substrates were then carefully degreased with trichloroethane. One coat of the primer was applied to the substrate and allowed to dry. This was followed by a coat of adhesive. The elastomer was vulcanized to the substrate at an elevated temperature and pressure. One end was left unbonded. A mass was suspended from the free end of the rubber to place stress on the bond line. The bond line was submerged in 3.5% saltwater at 25°C. The peel rate of the bond was determined by periodically measuring the distance of the bond line from a reference point on the substrate using a Gaertner Traveling Microscope. The peel rate is theoretically constant and is the slope of the line obtained by plotting the distance of the bond line from the reference point vs the elapsed exposure time. Figure 1 is an example of such a plot. The data points curved up away from the line late in the test because the bond began to deteriorate from the sides as well as in the direction of the peel. Therefore, the length of the bond line was shortened and the peel rate was increased.

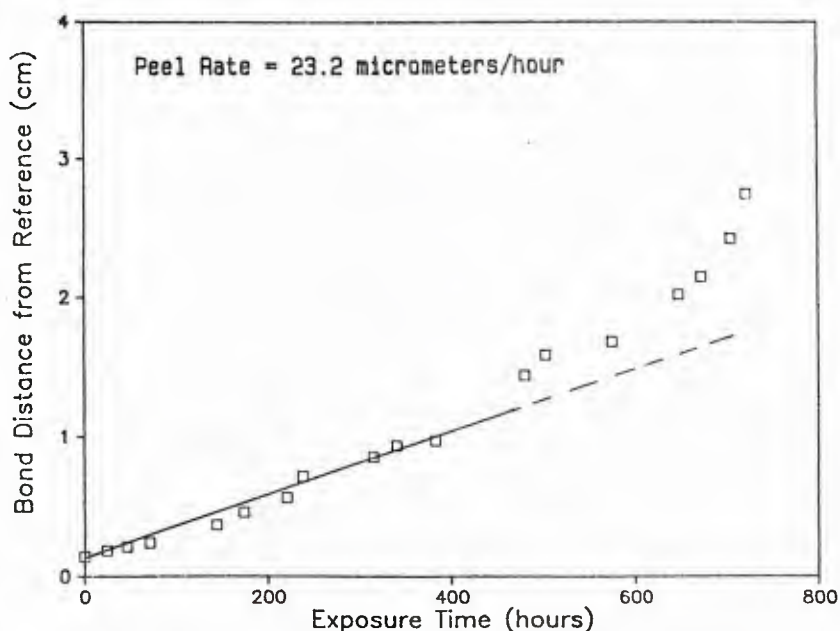


Fig. 1 - Elastomer-to-metal bondability of EPDM exposed to seawater at 25°C.

The tear strength was measured at 25°C using a constant-rate Instron testing machine and a method described by ASTM D624 [8]. The specific gravities were measured by Archimedes Principle given in ASTM D297 [9]. Densities were calculated from the specific gravities and handbook values of the density of water. Sound speeds were measured in a Mapco Corp. Sonic Solution Monitor by a method similar to that of Zacharias, *et al.* [10]. In this method, the time of flight of a 1.5-MHz sound pulse through pure water

and through the sample in water was measured at 25°C. The sound speed, or more properly longitudinal wave speed, was calculated from these time readings. Dynamic mechanical measurements were carried out on EPDM over a range of temperatures and frequencies using a resonant string instrument. This method was discussed by Capps [11]. The hardness was measured at 25°C with a constant-rate, constant-load, Shore A durometer 15 seconds after application of load. The tensile strength, tensile modulus at 200% elongation, and ultimate elongation were measured according to ASTM D412 (Die C) [12]. These measurements were made on the Instron Universal Instrument.

The volume electrical resistivity was measured at 25°C by the ASTM D991 method [13] using a Hewlett Packard Resistivity Cell Model 16008A. The vulcanized samples, approximately 4 mm in thickness and at least 10 cm in diameter, were degreased and placed in a desiccator for 24 hrs prior to testing. The sample was charged with 100 V for 25 seconds. The volume resistance was measured after another 35 seconds. Volume resistivity was calculated using the following equation:

$$\text{resistivity} = \frac{A \times 19.635 \text{ cm}^2}{B}, \quad (1)$$

where A = volume resistance (ohm)
 B = sample thickness (cm)
 19.635 = cell factor.

The cure schedules of the EPDM elastomers were established with a Monsanto rheometer at 155°C [14]. The rheometer gave a continuous curve of the elastomer's modulus vs cure time. The elastomer was placed between two platens that maintained a constant pressure and the preset temperature. Within the platens, the elastomer covered a disk that oscillated through a 3° arc. The force required to oscillate the disk was proportional to the shear modulus of the elastomer. This force was monitored by the rheometer as torque and was plotted vs the time elapsed. As the elastomer warmed, it reached a minimum in modulus--shown by a decrease in torque on the rheometer curve. This was followed by a rapid rise in torque as the elastomer flowed and began to cure. The time taken for a 10-point rise above the minimum viscosity is the t_{10} . The total cure time for a given elastomer is the time (t_{90}) to reach 90% of the maximum torque on the rheometer curve.

The test membranes for the water permeability study were approximately 0.7 mm in thickness. They were mounted on a stainless-steel cup filled with deionized water. The cup was sealed with a thin layer of silicone adhesive and a stainless-steel flange. The cup was placed in a 0%-humidity environment and was weighed periodically to determine weight loss.

Samples for the compatibility study were 25-mm squares of approximately 4-mm thickness. Two pieces of the same formulation were exposed in each test. Prior to exposure, both samples were degreased and weighed, and the thickness of one sample was measured at the center. The test liquid was equilibrated at the test temperature before the samples were exposed to it. Both samples were periodically wiped dry with paper towels and then weighed together. The thickness was measured on the same sample measured initially.

The compression set of the elastomers was measured according to method B of ASTM D395 [15]. The thickness was measured at the center of each sample prior to testing. The samples were compressed to a specified thickness and exposed to 85°C for 70 hrs. The pressure was then released from the sample. The thickness was measured after the sample was allowed to rest for one-half hour. The compression set was calculated using the following equation:

$$cs = [(t_i - t_f)/t_d] \times 100 , \quad (2)$$

where cs = compression set

t_i = initial thickness of elastomer

t_f = final thickness of elastomer

t_d = amount elastomer is deflected during test.

TEST RESULTS

Elastomer-to-Metal Bondability and Tear Strength

Elastomers are often used in applications where they must be bonded to a metal surface. Commonly this bond provides the only watertight seal on the transducer. The strength of an elastomer-to-metal bond is thus a very important aspect when considering the long-term properties of the elastomer. The bond must be maintained after exposure to harsh environmental stresses. An elastomer intended for long-term use must also maintain a certain toughness. The toughness was measured by the tear strength of the rubber. A study to improve the tear strength was, therefore, performed in conjunction with a study to improve the bondability of the elastomer to metal.

Two major adhesive manufacturers were contacted for their recommendations about possible adhesive systems for use with EPDM's. The materials given in Table 2 were suggested as candidates for further testing. System A is intended to be used with peroxide-cured elastomers. Systems B and C are intended for sulfur-cured elastomers. The Thixon samples were obtained from Whitaker Corporation, and the Chemlok samples were obtained from Lord Corporation. All samples were used as received.

Table 2 - Adhesive Systems Used for Elastomer-to-Metal Bonding

SYSTEM	PRIMER	ADHESIVE
A	Thixon P-6-1	Thixon 814-1
B	Chemlok 205	Chemlok 234B
C	Chemlok 205	Chemlok 238

It was found that, unless the elastomer has a tear strength of at least 45 kN/m, the test fails because of rubber tear (RT) when a 12-kg mass is suspended from it. Therefore, samples with tear strengths between 30 and 45 kN/m had to be tested with only a 10-kg mass suspended from the free end of the rubber. A mass of 7 kg was suspended from samples with a tear strength

less than 30 kN/m. These bondability tests were, of course, of less value than those done at the maximum load, but did serve to indicate trends in bond strength.

The first compositional parameter investigated was a change in the polymer from Royalene 521 (R521) to Nordel 1070 (N1070). Six groups of samples that differ only in the type of polymer in the elastomer are shown in Table 3. The R521 samples had a slower peel rate for a longer period of time than the same samples containing N1070. There was no clear difference in the tear strengths of an elastomer with N1070 as compared to an elastomer with R521.

Table 3 - Effect on Bondability and Tear Strength of EPDM Elastomers by Changing Only Polymer Type

SAMPLE	POLYMER TYPE	TEAR STRENGTH (kN/m)	PRIMER/ADHESIVE SYSTEM TYPE (A OR B DEFINED IN TABLE 2) BONDABILITY RESULTS
201	R521	32.9	A 3 $\mu\text{m/hr}$ for 800 hr then RT
208	N1070	33.6	A 52 $\mu\text{m/hr}$ for 350 hr then RT
310	R521	46.0	B 2.2 $\mu\text{m/hr}$ for 25 hr
302	N1070	51.6	B immediate peel
311	R521	43.2	B RT
304	N1070	49.9	B 853 $\mu\text{m/hr}$ for 25 hr
312	R521	46.5	A 1.25 $\mu\text{m/hr}$ for 850 hr
305	N1070	42.8	A 5.2 $\mu\text{m/hr}$ for 525 hr
313	R521	48.9	A 8.8 $\mu\text{m/hr}$ for 850 hr
306	N1070	55.7	A 1.4 $\mu\text{m/hr}$ for 525 hr
314	R521	47.1	A 1.7 $\mu\text{m/hr}$ for 500 hr
308	N1070	38.7	A 2.0 $\mu\text{m/hr}$ for 400 hr

The bondability also was studied as a function of elastomer curative. Two types of curing systems were used: a sulfur cure and a peroxide cure. The peroxide cure used in this study was dicumyl peroxide (DCP). The Chemlok 205/234B adhesive system (B) was used to bond the samples with a sulfur cure. The Thixon P-6-1/814-1 adhesive system (A) was used to bond the peroxide-cured samples. The bondability and tear strengths were not affected by a change in the curative from peroxide to sulfur.

The bondability of EPDM elastomers with various peroxide-cured systems was studied. In addition to the DCP system mentioned above, 2,5-bis(tertbutyl peroxy)-2,5-dimethylhexane (DBPH) and a-a'-bis(tertbutyl peroxy)diisopropylbenzene (DBPB) were also included. Unfortunately, samples with these latter two curing systems had tear strengths below 30 kN/m; thus, their bondability could not be reliably measured. All of these samples exhibited RT and, thus, were not investigated further.

Table 4 shows the results of the bondability tests for samples varying only in the loading of DCP. The tear strength decreased as the loading of DCP was increased. The samples containing 5 PHR of DCP gave the best results in the bondability study. One of these samples withstood a mass of 12 kg for more than 16 months without peeling more than 1.5 cm.

Table 4 - Bondability and Tear Strength of EPDM Elastomers
With Varying Loadings of Only DCP

SAMPLE	LOADING OF DCP (PHR)	TEAR STRENGTH (kN/m)	BONDABILITY RESULTS PRIMER/ADHESIVE SYSTEM A
408	5	53.3	0.7 $\mu\text{m/hr}$ for 700 hr
906	5	50.7	60 $\mu\text{m/hr}$ for 400 hr
807	6	50.3	17 $\mu\text{m/hr}$ for 300 hr then RT
314	7	47.1	1.7 $\mu\text{m/hr}$ for 500 hr
908	3	49.3	6.6 $\mu\text{m/hr}$ for 250 hr
909	4	49.3	7.6 $\mu\text{m/hr}$ for 250 hr
901	5	45.3	0.6 $\mu\text{m/hr}$ for 400 hr
801	6	45.6	1.75 $\mu\text{m/hr}$ for 700 hr then RT
803	7	41.1	RT

A study was performed to determine the effect of changing the type and loading of curing coagents used with the DCP curative. The results can be seen in Table 5. Samples in the first group in Table 5 compare the curing coagents 1,2-polybutadiene (PB), trimethylolpropane trimethacrylate (TMPTMA), N,N'-m-phenylenedimaleimide (PDMI), and ethylene dimethacrylate (EDMA). These samples had tear strengths below 35 kN/m due to a small loading of carbon black. The sample with EDMA as the curing coagent had the slowest peel rate for this series. The second and third groups of samples in Table 5 are formulated with either triallyl cyanurate (TAC) or TMPTMA as the curing coagent. The samples in the second group differed by having a larger particle size of carbon black than the samples in the third group.

Table 5 - Effect of Changing Curing Coagents Only on the Bondability and Tear Strength of EPDM Elastomers

SAMPLE	TYPE AND LOADING CURE COAGENT (PHR)	TEAR STRENGTH (kN/m)	BONDABILITY RESULTS PRIMER/ADHESIVE SYSTEMS A
202	2 PB	29.9	11 $\mu\text{m/hr}$
203	1 TMPTMA, 2PB	32.2	3 $\mu\text{m/hr}$ for 300 hr then RT
204	2 PDMI	27.8	RT
207	2 EDMA	31.9	2 $\mu\text{m/hr}$ for 350 hr then RT
1001	2 TAC	34.1	RT
1004	2 TMPTMA	47.9	516 $\mu\text{m/hr}$ for 55 hr
1002	2 TAC	48.8	246 $\mu\text{m/hr}$ for 100 hr
1003	2 TMPTMA	47.8	160 $\mu\text{m/hr}$

A study was performed in which the loading of DCP and the loading of TMPTMA were both varied in the elastomer. The results of the bondability tests and the tear strengths are in Table 6. The DCP was present in levels of 3, 5, and 7 PHR. Within each level of DCP were samples containing 1, 2, and 3 PHR TMPTMA. The formulation that gave the best adhesion to metal was the sample with 5 PHR of DCP and 2 PHR of TMPTMA.

Table 6 - Effect of Curing Agent and Coagent Loading on EPDM Elastomer-to-Metal Adhesion and Tear Strength

SAMPLE	TMPTMA (PHR)	DCP (PHR)	TEAR STRENGTH (kN/m)	BONDABILITY RESULTS PRIMER/ADHESIVE SYSTEM A
912	1	3	54.9	12.5 $\mu\text{m/hr}$ for 75 hr
908	2	3	49.3	6.6 $\mu\text{m/hr}$ for 250 hr
913	3	3	49.7	7 $\mu\text{m/hr}$ for 450 hr
910	1	5	45.6	RT
901	2	5	45.3	0.6 $\mu\text{m/hr}$ for 400 hr
911	3	5	48.9	3 $\mu\text{m/hr}$ for 300 hr then RT
914	1	7	41.6	RT
903	2	7	41.1	RT
915	3	7	35.9	RT

Changing the amount or particle size of carbon black in an elastomer is a common way to change a rubber's modulus. These variations in the carbon black filler may also change the tear strength. The tear strength was measured on a number of EPDM elastomers with variations in composition including polymer type, curing system, and carbon black particle size. Within each elastomer formulation were elastomers that contained varying amounts of the carbon black. The peel rate was also measured to determine if the change in carbon black would affect the adhesion of the rubber to a metal substrate. Table 7

shows the results of these compositional changes on tear strength and bondability. The tear strength increases as the loading of carbon black increases in all but one case in Table 7.

The first two groups of formulations in Table 7 have N1070 as the polymer. The first group had a sulfur-cure system. Although their tear strengths were very high, the peel rates were very fast. The second group of samples had a peroxide cure. Their bondability results were very good but their tear strengths were too low. The remaining formulations contain R521 as the polymer.

The third and fourth groups had the same cure system as the second group. The two samples with the N550 carbon black had good adhesion to metal and high tear strengths. The formulations containing N774 carbon black had low tear strengths. The rates of peel were too fast for these formulations to be favorable.

Groups 5 and 6 contained N660 carbon black and differed in the amount of DCP curative used. Group 5 formulations had 6 PHR of DCP. The formulations in group 6 were cured with 5 PHR of DCP. The tear strengths were slightly higher for elastomers with 5 PHR of DCP. The elastomer cured with 5 PHR of DCP and filled with 45 PHR of N660 carbon black showed the best adhesion to the metal substrate. Figure 2 is a graph of these data and shows that increasing the carbon black by 5 PHR increases the tear strength by 3 kN/m.

The last group of samples had a smaller particle size of carbon black than the elastomers in group 6. Less carbon black was required to achieve a given tear strength for samples with this smaller particle-size black. The peel rate was very fast for the elastomer with 45 PHR of N327 carbon black.

Table 7 - Effect of Varying Only Carbon Black Size and Loading on the Bondability and Tear Strength of EPDM Elastomers

GROUP/ SAMPLE	FORMULATION CHANGE FOR GROUP	CARBON BLACK (PHR)	TEAR STRENGTH (kN/m)	PRIMER/ADHESIVE SYSTEM BONDABILITY RESULTS
1/301	N1070	35	49.1	B 1330 $\mu\text{m/hr}$
302	sulfur cure	40	51.6	B immediate peel
303	N550 C.B.	45	60.2	B 5852 $\mu\text{m/hr}$
2/307	N1070	40	34.1	A 3.8 $\mu\text{m/hr}$ for 550 hr
308	7 PHR DCP	50	38.7	A 2.0 $\mu\text{m/hr}$ for 400 hr
309	N660 C.B.	60	33.7	A 23 $\mu\text{m/hr}$ for 170 hr
3/003	R521	35	45.2	A 6 $\mu\text{m/hr}$ for 600 hr
	7 PHR DCP			B 34 $\mu\text{m/hr}$ for 50 hr then RT
312	N550 C.B.	40	46.5	A 1.25 $\mu\text{m/hr}$ for 850 hr
4/002	R521	30	35.2	B 40 $\mu\text{m/hr}$ for 50 hr then RT
	7 PHR DCP			
001	N774 C.B.	40	43.9	B 187 $\mu\text{m/hr}$ for 170 hr then RT
5/806	R521	40	39.4	A RT
801	6 PHR DCP	45	45.6	A 1.7 $\mu\text{m/hr}$ for 700 hr then RT
807	N660 C.B.	50	50.3	A 17 $\mu\text{m/hr}$ for 300 hr then RT
404		55	51.1	
6/904	R521	35	40.5	A RT
905	5 PHR DCP	40	42.1	A RT
901	N660 C.B.	45	45.3	A 0.6 $\mu\text{m/hr}$ for 400 hr
906		50	50.7	A 60 $\mu\text{m/hr}$ for 400 hr
907		55	52.0	A 0.96 $\mu\text{m/hr}$ for 400 hr
7/1102	R521	25	35.3	
1103	5 PHR DCP	30	38.0	
1003	N327 C.B.	45	47.8	A 160 $\mu\text{m/hr}$

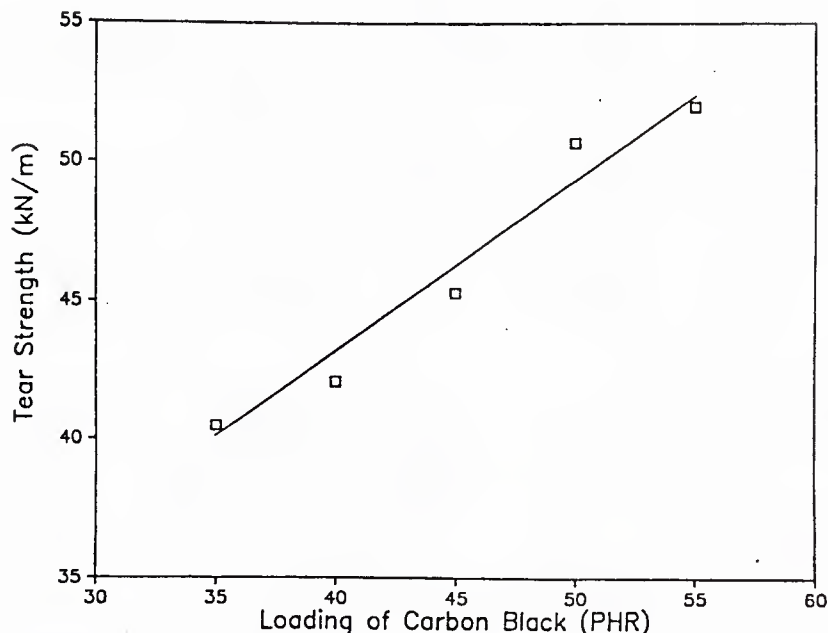


Fig. 2 - Tear strength of EPDM with varying loading of N660 carbon black.

To complete the study of the effect of compositional changes on tear strength and elastomer-to-metal adhesion, the loading of antioxidant TMDQ and the loading of zinc oxide were varied. The measured tear strengths and peel rates for these samples are given in Table 8. Increasing the TMDQ in EPDM increased the tear strength. However, this same increase in TMDQ was seen to be detrimental to the elastomer-to-metal adhesion. Sample 1004 shows that zinc oxide (ZnO) is a necessary component for the elastomer to have good adhesion to metal.

Table 8 - Effect of Variations in TMDQ and Zinc Oxide Loading on Adhesion of EPDM to Metal and Tear Strength

SAMPLE	TMDQ (PHR)	ZnO (PHR)	TEAR STRENGTH (kN/m)	BONDABILITY RESULTS PRIMER/ADHESIVE SYSTEM A
902	0.0	5.0	39.8	RT
901	0.8	5.0	45.3	0.6 $\mu\text{m/hr}$ for 400 hr
903	1.6	5.0	56.8	23 $\mu\text{m/hr}$ for 400 hr
1004	0.8	0.0	47.9	516 $\mu\text{m/hr}$
901	0.8	5.0	45.3	0.6 $\mu\text{m/hr}$ for 400 hr

Short-Term Properties

Density and Sound Speed

The density and the sound speed are very important properties of an elastomer used in underwater acoustical applications. A match of these properties with seawater is desired so that the elastomer does not affect the performance of the transducer. A density and sound speed match eliminates reflection and refraction at the interface. One of the inherent properties of EPDM elastomers is that the density is close to 1000 kg/m^3 . The density (ρ) and sound speed (c) of EPDM were measured for several samples with variations in composition. The specific acoustic impedance (ρc) and the adiabatic bulk modulus (ρc^2) were calculated from the measured values.

Both the density and the sound speed were greater for an elastomer with R521 polymer than for an elastomer with N1070 polymer. Changing the type of curative from sulfur to peroxide had little effect on density or sound speed. A change in peroxide curative from DBPH to DBPB resulted in a lower density and a lower sound speed. Figure 3 shows that the density increased as the amount of peroxide cure DCP increased. The increase in DCP loading leads to an increase in the number of crosslinks in the elastomer. This effect made the elastomer more dense but did not affect the sound speed. Therefore, an increase in DCP loading caused an increase in specific acoustic impedance and the adiabatic bulk modulus. Varying the loading of TMPTMA curing coagent in EPDM did not affect the sound speed or density.

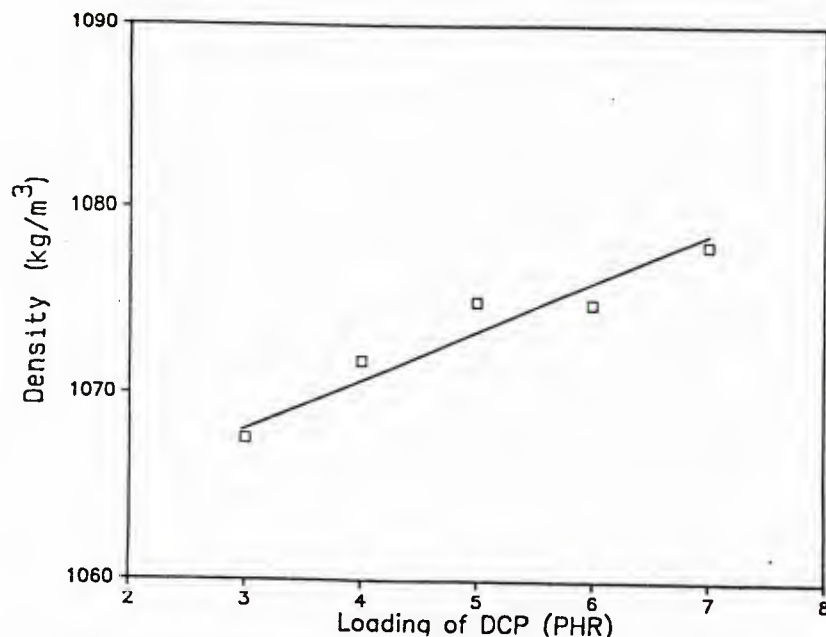


Fig. 3 - Density of EPDM with varying loading of DCP curing agent.

The density and sound speed are greatly dependent on the loading of carbon black in the elastomer. An increase in loading of N660 carbon black increased the modulus of the rubber and caused an increase in the density and the sound speed, as seen in Figs. 4 and 5. Figures 6 and 7 show the increase in the specific acoustic impedance and the adiabatic bulk modulus caused by an increase in carbon-black loading. The increase in density and sound speed that resulted from an increase in carbon black loading is shown in Figs. 8 and 9 for an EPDM elastomer with N1070 as the polymer in place of R521.

Finally, the amount of the antioxidant TMDQ was varied from an omission of it to a doubling of the usual amount of 0.8 PHR. This variation caused only a very minor change in density and sound speed.

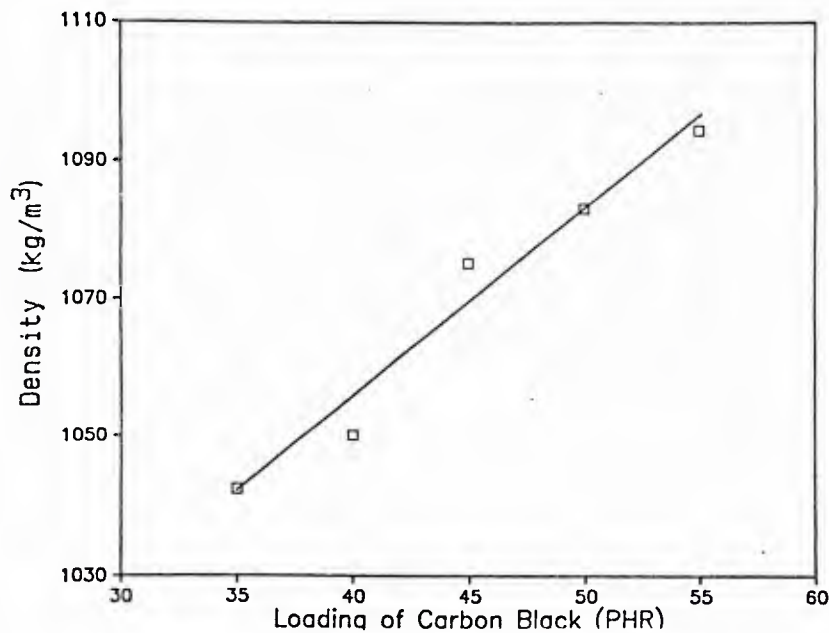


Fig. 4 - Density of EPDM with varying loading of N660 carbon black.

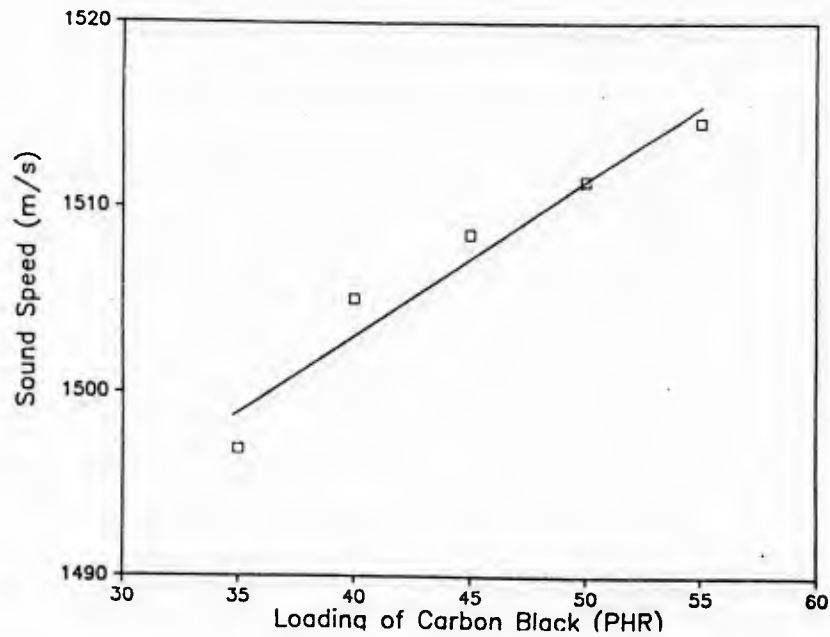


Fig. 5 - Sound speed of EPDM at 1.5 MHz and 25°C with varying loading of N660 carbon black.

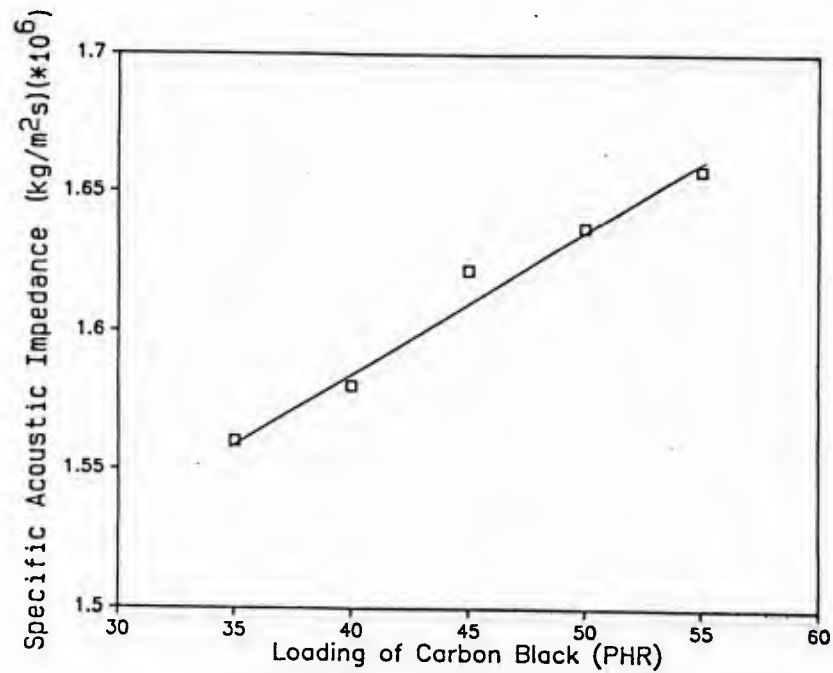


Fig. 6 - Specific acoustic impedance of EPDM with varying loading of N660 carbon black.

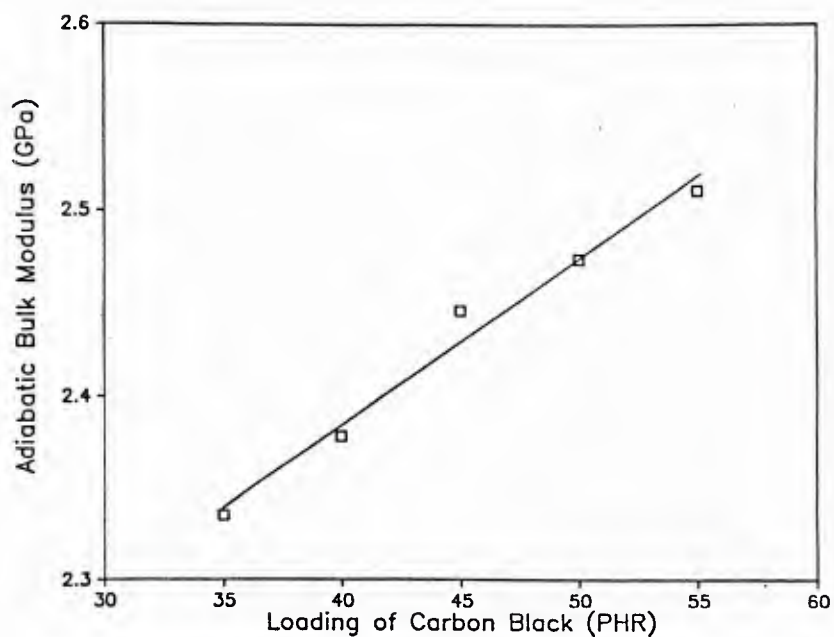


Fig. 7 - Adiabatic bulk modulus of EPDM with varying loading of N660 carbon black.

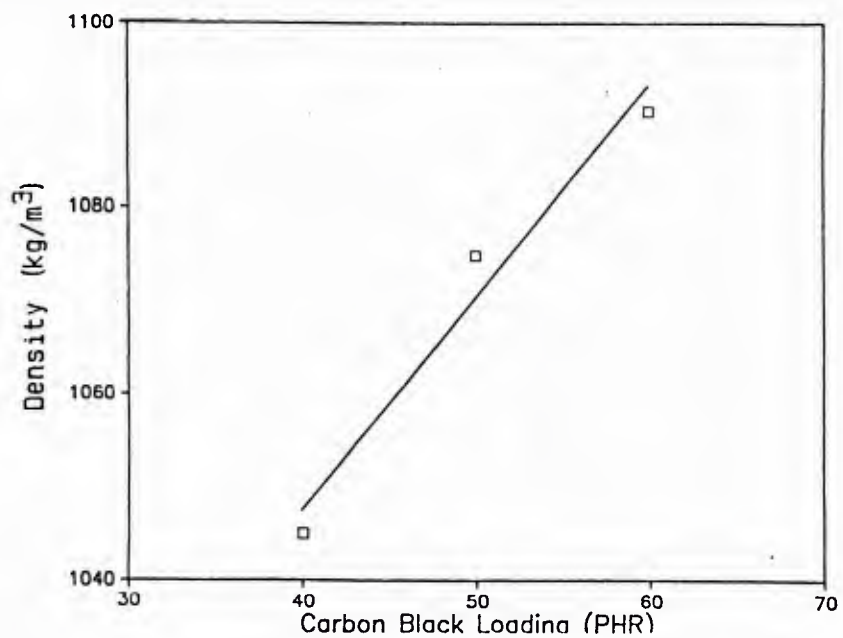


Fig. 8 - Density of EPDM containing Nordel 1070 with varying loading of N660 carbon black.

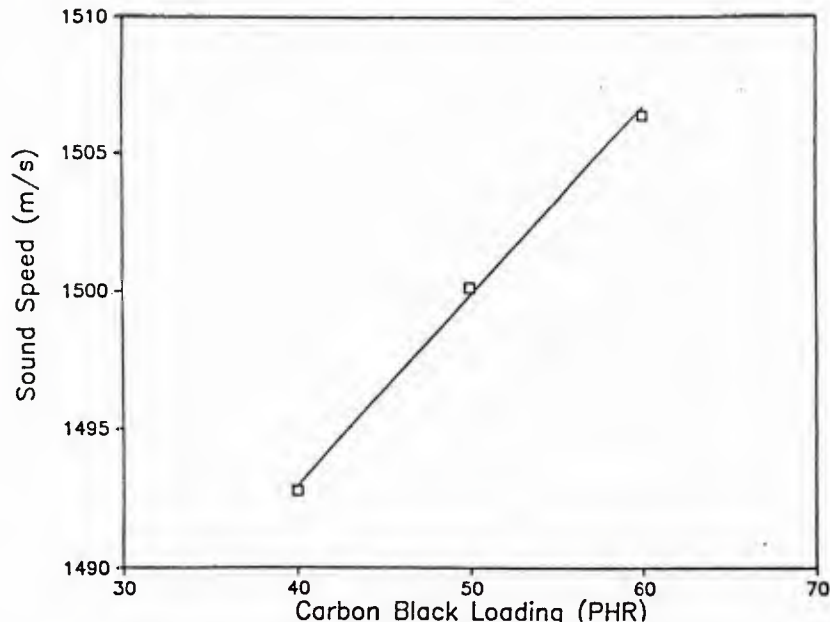


Fig. 9 - Sound speed of EPDM at 1.5 MHz and 25°C containing Nordel 1070 with varying loading of carbon black.

Dynamic Mechanical Properties

The dynamic mechanical properties were measured for EPDM over a range of temperatures and frequencies. The Young's storage modulus, E' , is a measure of the in-phase stress-to-strain experienced by the sample. The loss modulus, E'' , is defined as the stress that is 90° out of phase with the strain, divided by the strain. The ratio of E'' to E' is the loss tangent ($\tan \delta$). This is a measure of the lag in change of mechanical stress in the elastomer when the stress acting on it is changed. The results for EPDM are shown in Fig. 10 where the Young's storage modulus E' and the mechanical $\tan \delta$ are plotted as a function of frequency. This EPDM sample contained R521 as the polymer, DCP as the curing agent, TMPTMA as the curing coagent, TMDQ as the antioxidant, and ZnO as the cure activator. The sample was filled with N660 carbon black. The dynamic data show that the sample exhibits very low loss under dynamic strain for frequencies below 10 kHz.

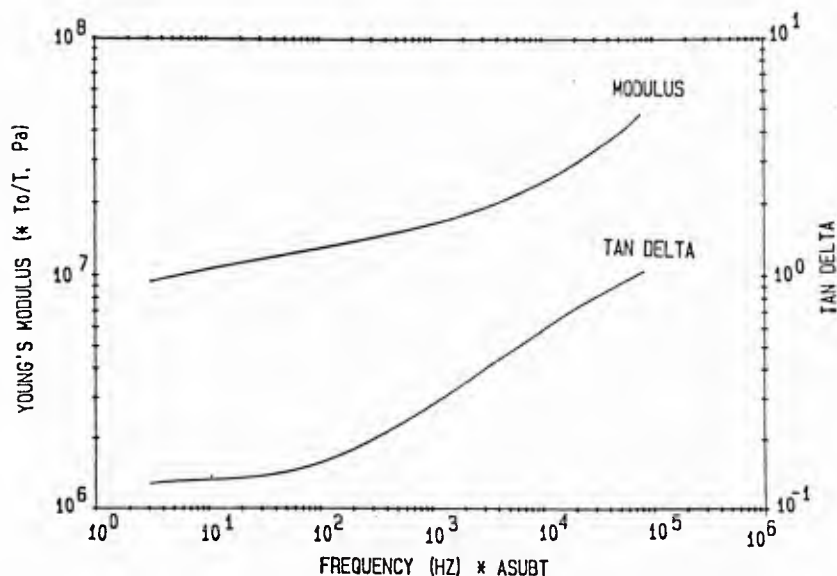


Fig. 10 - Dynamic Young's modulus and loss tangent of EPDM at 10°C as a function of frequency.

Hardness

A study was performed to discover the relationship between the modulus of EPDM elastomers and a change in composition. Shore A hardness, which is related to shear modulus, is dependent on the carbon-black filler. Figure 11 shows that the hardness increased by 8 as the carbon-black loading was increased from 35 to 55 PHR. An EPDM elastomer with N1070 polymer in place of R521 gave a 10-point rise in hardness with a 20-PHR increase in carbon black. This is shown in Fig. 12.

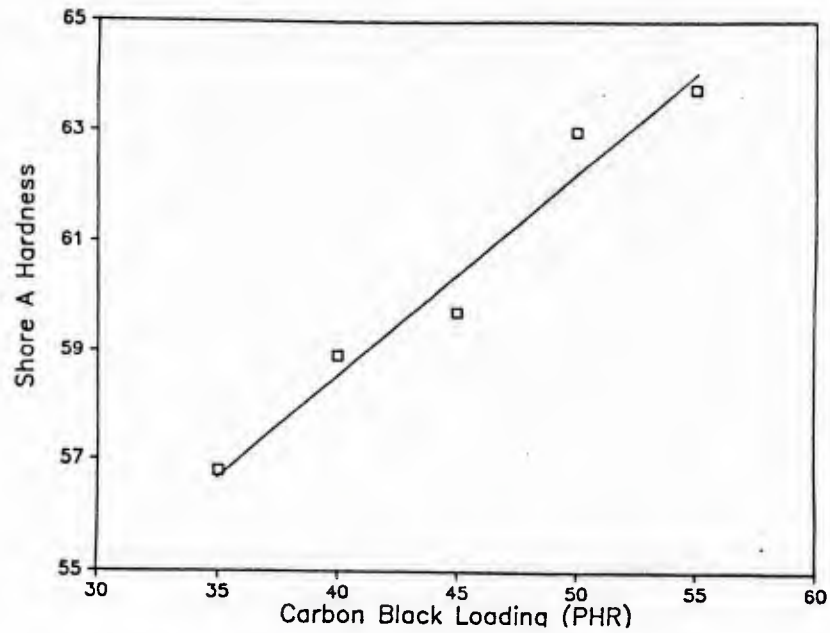


Fig. 11 - Shore A hardness of EPDM with varying loading of N660 carbon black.

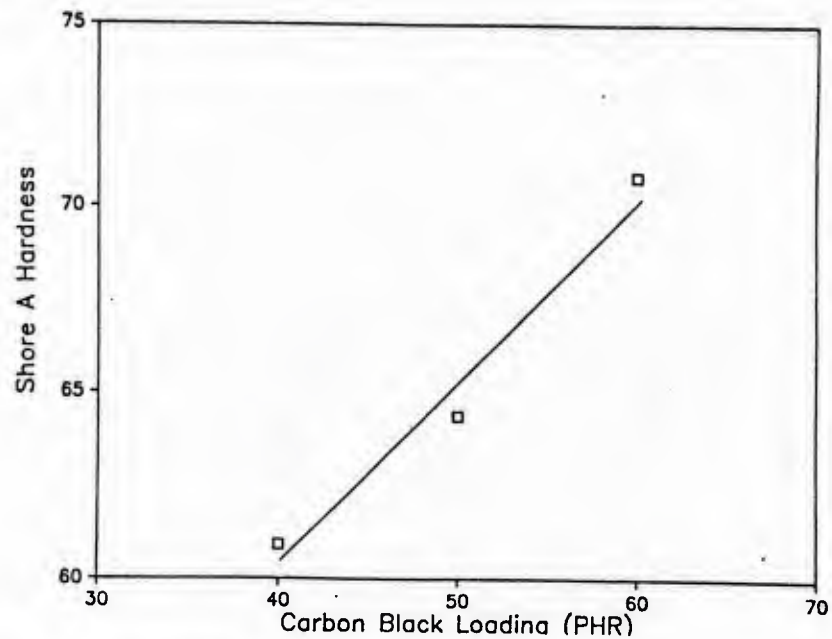


Fig. 12 - Shore A hardness of EPDM containing Nordel 1070 with varying loading of N660 carbon black.

A change in the type of curative present in the elastomer, from a sulfur to a peroxide cure, did not affect the hardness. Of the formulations containing the three peroxide cures, the one containing DCP gave the highest hardness. The hardness was shown to be dependent on the amount of peroxide curing agent. As the amount of curing agent increases, the number of crosslinks in the elastomer increases. The increase in the number of crosslinks causes the elastomer to be held together more tightly and increases the hardness. Figure 13 shows that an increase in DCP by 1 PHR caused an increase in hardness of 1.5.

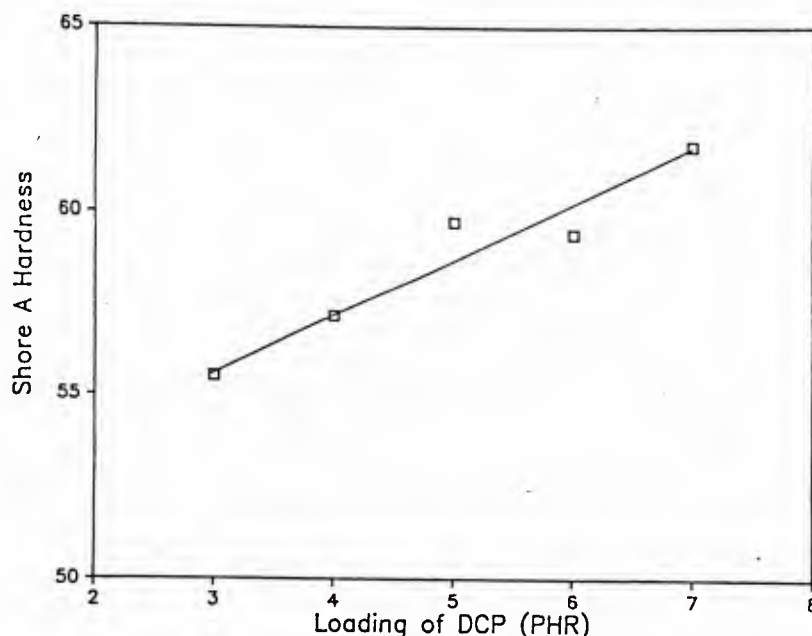


Fig. 13 - Shore A hardness of EPDM with varying loading of DCP curing agent.

Increasing the amount of the TMPTMA curing coagent had little effect on hardness. When the only difference in the composition was the polymer type, there was no significant difference in hardness. The last two compounding ingredients to be studied were the antioxidant TMDQ and ZnO. Figure 14 shows that the hardness increased as the amount of TMDQ was decreased. Omitting the ZnO had no effect on the hardness of the elastomer.

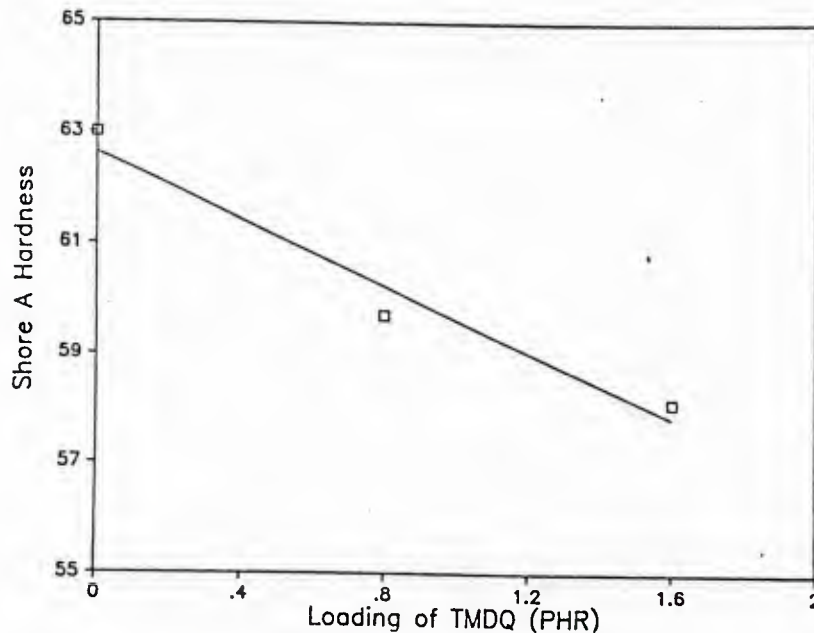


Fig. 14 - Shore A hardness of EPDM with varying loading of antioxidant TMDQ.

Tensile Properties

The tensile properties are very important when considering the performance of an elastomer that will be stretched during use. The tensile properties that were measured on the EPDM samples were the tensile modulus at break (tensile strength), tensile modulus at 200% elongation, and the ultimate elongation. These properties are dependent on the type of curing system used. Table 9 shows the effect of changing the curative from a sulfur cure to a peroxide cure. The tensile strength and the tensile modulus at 200% elongation are greater for samples containing the peroxide curative. The ultimate elongation, with the exception of one set of samples, was lower for samples cured with peroxide.

Table 9 - Effect of Changing Curative Type on the Tensile Properties of EPDM

CURATIVE	TENSILE MODULUS 200% ELONGATION (MPa)	TENSILE STRENGTH (MPa)	ULTIMATE ELONGATION (%)
sulfur	4.6	11.6	461
peroxide	10.5	11.3	215
sulfur	5.6	12.6	384
peroxide	12.2	13.3	195
sulfur	6.4	13.8	425
peroxide	8.5	15.6	293
sulfur	7.0	9.5	240
peroxide	9.1	14.2	273

It was shown that it took more force to stretch the samples a given distance as the amount of curative was increased. The sample did not stretch as far before breaking as the amount of curative was increased. Figure 15 shows the effect of increasing the loading of DCP in EPDM. As the amount of DCP curative was increased, the tensile modulus at 200% elongation increased. The ultimate elongation decreased as the loading of DCP was increased. The tensile strength showed only a slight decrease.

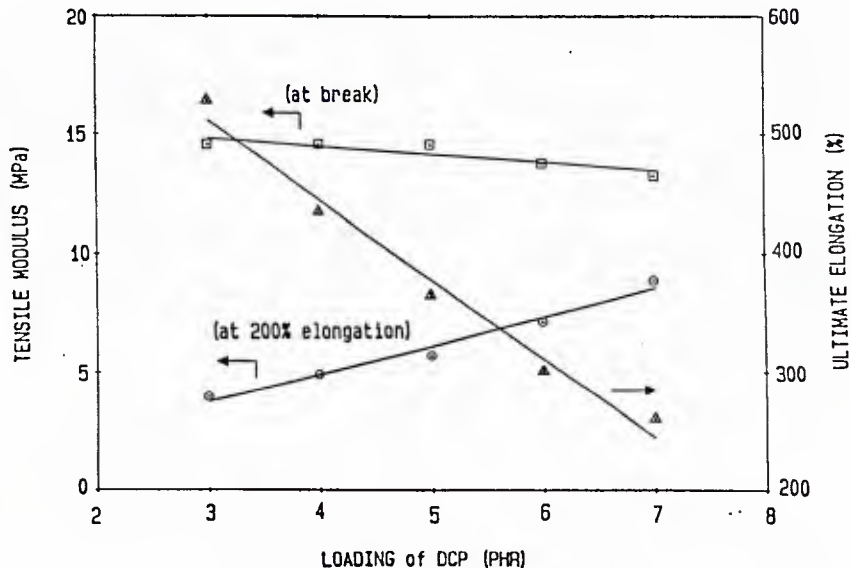


Fig. 15 - Tensile properties of EPDM with varying loading of DCP curing agent.

The tensile properties of an EPDM elastomer were also shown to be dependent on the amount of filler present in the formulation. Figure 16 shows the effect that increasing the loading of N660 carbon black had on the tensile properties of EPDM. The tensile modulus at 200% elongation and the tensile strength increased and the ultimate elongation decreased as the loading of carbon black was increased. These same trends were seen for samples with a finer particle-size carbon black of N327. Figure 17 gives the tensile properties for elastomers with N1070 as the polymer instead of R521. These samples had a sulfur curative and contained N550 carbon black.

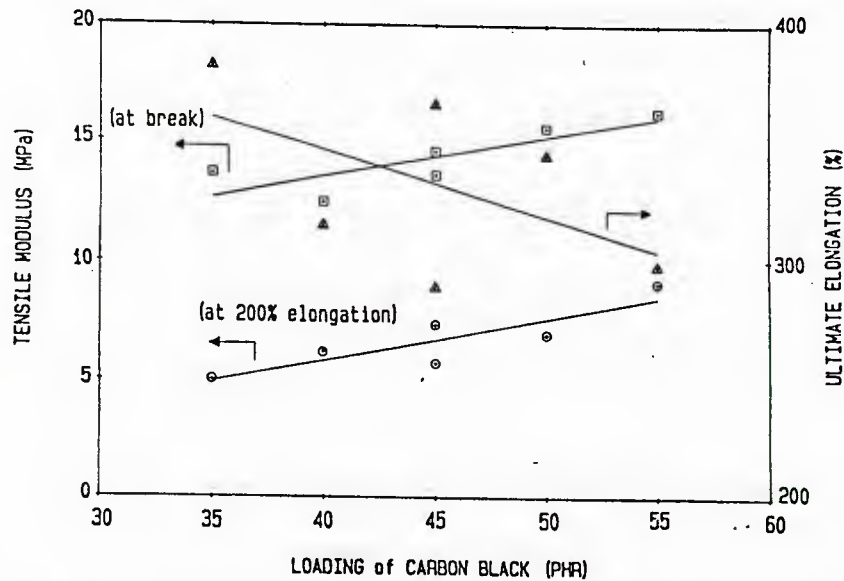


Fig. 16 - Tensile properties of EPDM with varying loading of N660 carbon black.

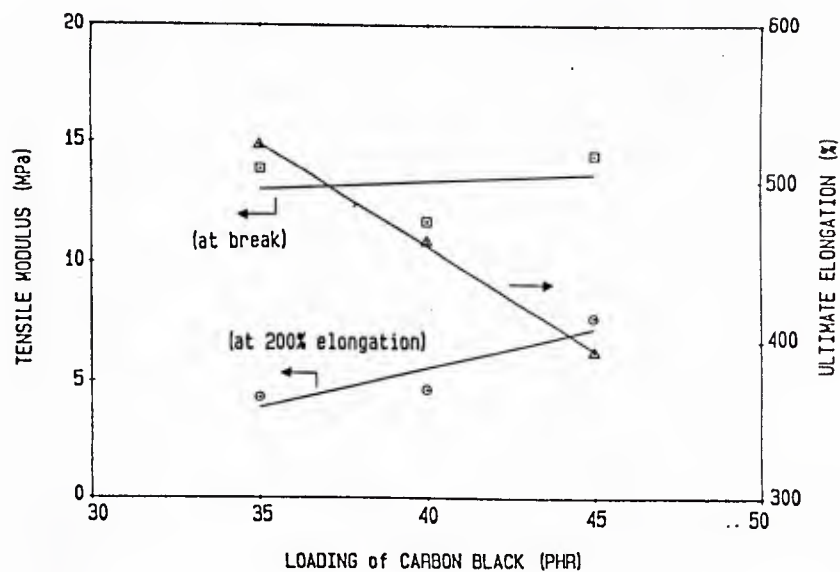


Fig. 17 - Tensile properties of EPDM containing Nordel 1070 with varying loading of N550 carbon black.

Another compositional parameter varied to determine the effect on the tensile properties was the amount of antioxidant TMDQ. Figure 18 shows that the tensile modulus at break (tensile strength) and the ultimate elongation increased as the loading of TMDQ was increased. The tensile modulus at 200% elongation decreased as the loading was increased.

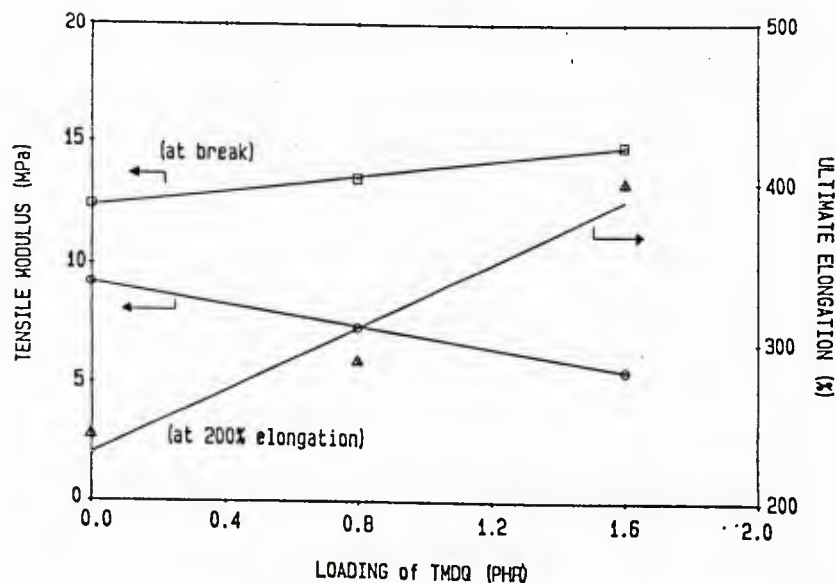


Fig. 18 - Tensile properties of EPDM with varying loading of antioxidant TMDQ.

Changing the polymer from R521 to N1070 did not affect the tensile properties of EPDM. Increasing the loading of the curing coagent TMPTMA increased the tensile modulus at 200% elongation and decreased the ultimate elongation. This increase had no effect on the tensile strength. Omitting the ZnO from EPDM increased the tensile strength and the ultimate elongation and caused the tensile modulus at 200% elongation to decrease.

It is very important that the EPDM elastomer retain its tensile properties after exposure to various environmental conditions. A study was performed on EPDM to determine if it would maintain the tensile properties measured initially after prolonged exposure to seawater. The initial tensile properties were measured for a single formulation of EPDM. Several samples of the same formulation were exposed to seawater at 40°C. The tensile properties on four samples were measured periodically. The results of this study are shown in Table 10. The exposure to seawater had little effect on the tensile properties of EPDM over the course of one year.

Table 10 - Effect of Seawater Exposure at 40°C on the Tensile Properties of EPDM

EXPOSURE TIME (HRS)	TENSILE MODULUS AT 200% ELONGATION (MPa)	TENSILE MODULUS AT 300% ELONGATION (MPa)	TENSILE MODULUS AT BREAK (MPa)	ULTIMATE ELONGATION (%)
0.0	7.2	12.9	15.6	337
840.0	6.7	13.4	15.3	327
2160.0	6.3	12.5	15.1	336
4632.5	6.4	12.1	15.0	339
8880.0	6.3	11.9	15.1	344

Electrical Resistivity

The importance of an elastomer having high electrical resistivity has been discussed by Thompson [4]. A study was conducted to determine the effect on electrical resistivity of formulation variations in EPDM elastomers. Figure 19 shows that the log volume resistivity vs presumed carbon-black content has the same sigmoidal shape with EPDM elastomers as seen with neoprene elastomers [4]. An EPDM formulation containing R521 had a higher volume resistivity than an EPDM with N1070.

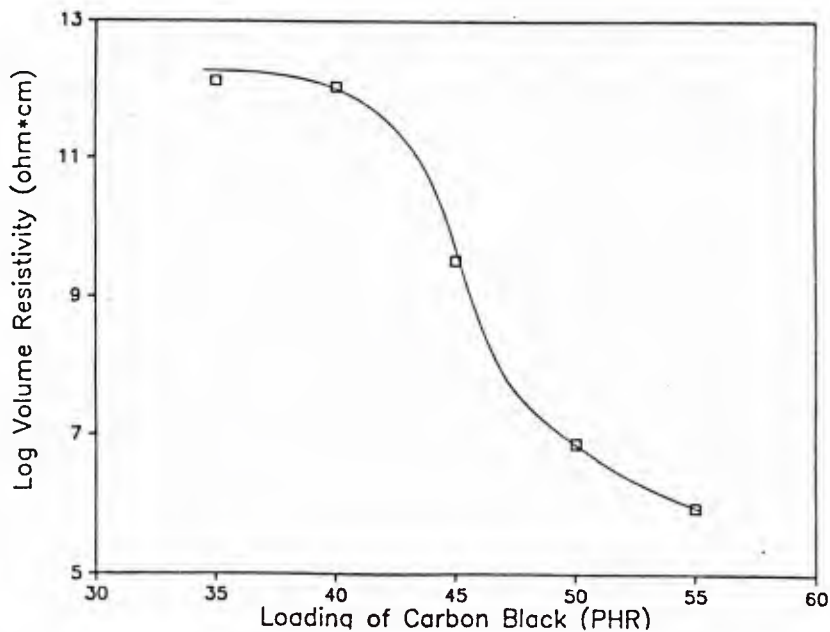


Fig. 19 - Log volume resistivity of EPDM with varying loading of N660 carbon black.

A study was performed in which the type of curative was changed to determine the effect on volume electrical resistivity. Changing the curative from a peroxide cure to a sulfur cure had a minor effect on the volume resistivity of EPDM. The volume resistivity was measured for samples containing 6 PHR of the peroxide curatives DCP, DBPH, and DBPB. The sample containing DCP had the highest volume resistivity. Figure 20 shows that the log volume electrical resistivity increased as the amount of DCP curative present in the elastomer was increased. Changing the type of curing coagent from TMPTMA to TAC did not change the volume resistivity of the elastomer. Increasing the amount of TMPTMA curing coagent in EPDM had little effect on the volume electrical resistivity.

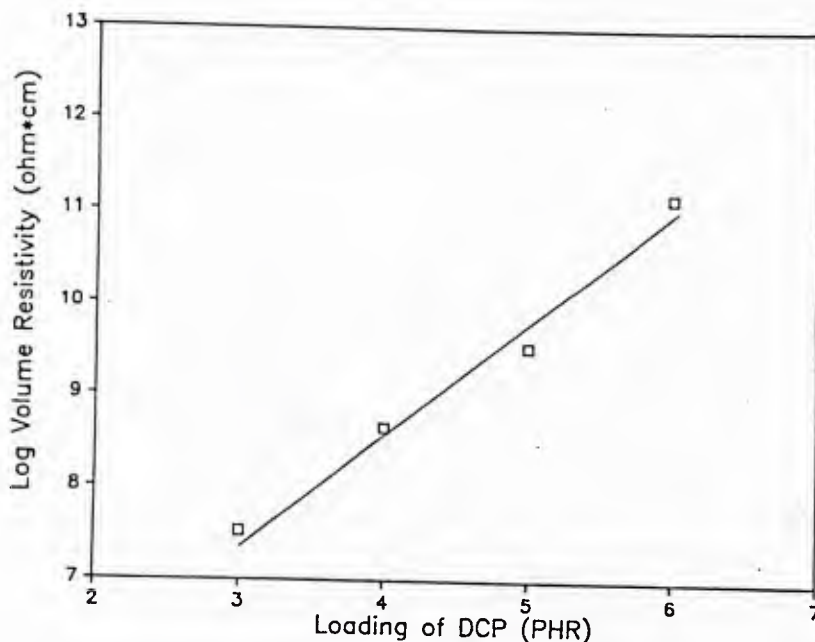


Fig. 20 - Log volume resistivity of EPDM with varying loading of DCP curing agent.

Figure 21 shows the effect that the antioxidant TMDQ had on the volume resistivity. Increasing the level of TMDQ from 0 to 0.8 PHR increased the resistivity of the EPDM. Any further increase has little effect on the resistivity. The omission of ZnO from EPDM increased the log volume resistivity from 9.5 to 11.7.

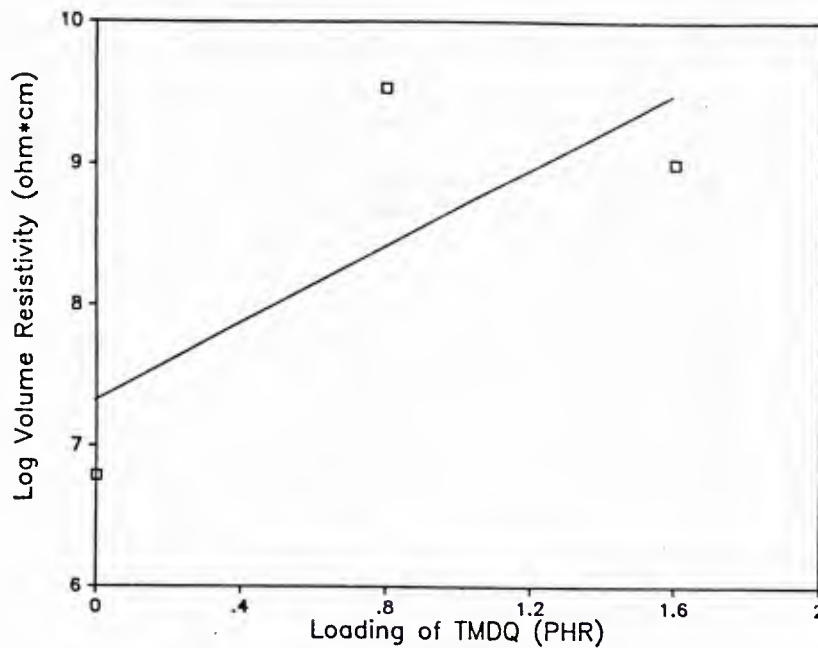


Fig. 21 - Log volume resistivity of EPDM with varying loading of antioxidant TMDQ.

As mentioned earlier, one of the most important properties possessed by an elastomer is the ability to retain its original physical properties after being exposed to various environmental stresses. A study was performed to determine the effect of seawater exposure on the volume electrical resistivity of EPDM. Vulcanizates of EPDM were exposed to synthetic seawater at 25, 40, and 60°C. The volume resistivity was measured periodically on the samples. The results of this study are shown in Fig. 22. The exposure to seawater did not have a detrimental effect on the electrical resistivity of the rubber. The volume resistivity increased in all three cases.

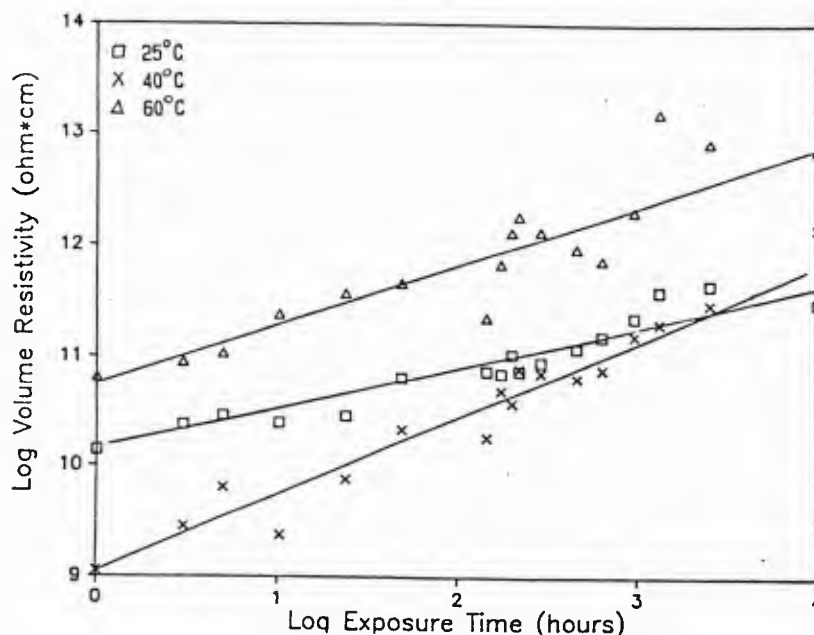


Fig. 22 - Effect of seawater exposure on log volume resistivity of EPDM.

Cure and Storage Parameters

Measuring the cure characteristics of each elastomer sample is essential in order to ensure reproducible molding. The cure characteristics were measured at 155°C on a Monsanto rheometer for all EPDM formulations studied. The time (t_{10}) taken for a 10-point rise above minimum viscosity on a rheometer curve gives a rough estimate of the amount of time the rubber will have to flow into a cavity during molding. A t_{10} of at least 4 mins is desired to ensure good, reproducible moldings of the elastomer.

Several compositional parameters were changed to obtain an elastomer with a long t_{10} that also retained the other required physical properties discussed above. Peroxide cures DCP, DBPH, and DBPB were used in the EPDM compositional study. Of these three, DBPB had the longest t_{10} . The sample containing DBPH had a t_{10} almost equal to the sample with DCP. The fitted curve through the data in Fig. 23 shows that as the loading of DCP was decreased by 1 PHR, the t_{10} increased by about 0.7 mins. Decreasing the loading of TMPTMA used as a curing coagent with DCP resulted in an increase in t_{10} . Decreasing the loading of TMPTMA by 1 PHR had less of an effect on the t_{10} than a 1-PHR decrease in DCP. Samples that contained TAC as a curing coagent had a much higher t_{10} than samples with TMPTMA. Figure 24 shows that the t_{10} increased as the loading of the antioxidant TMDQ was increased. Omitting the ZnO from the elastomer formulation had little effect on the t_{10} . Replacing the R521

polymer with N1070 had little affect on the t_{10} . Increasing the loading of carbon black in EPDM also had a very minor effect on the t_{10} of the sample.

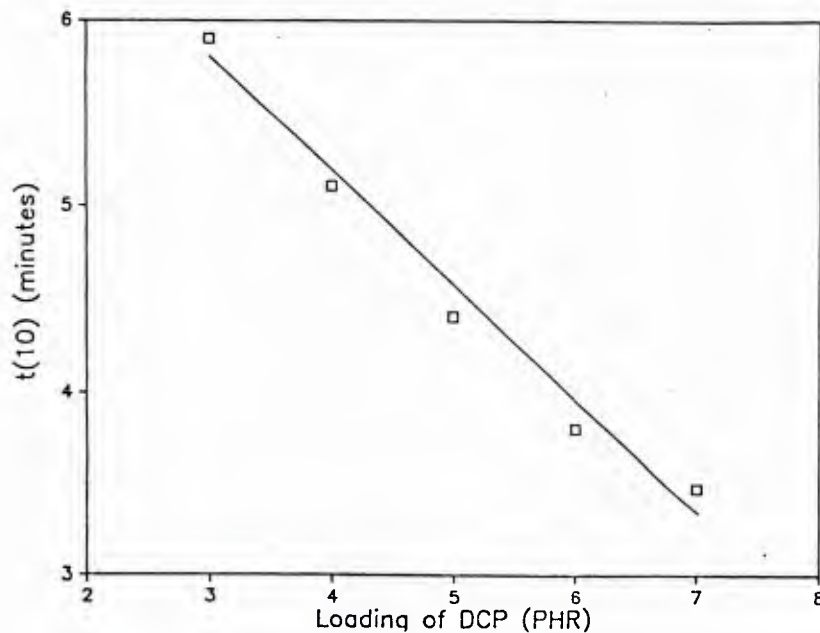


Fig. 23 - Effect of varying loading of DCP curing agent on the t_{10} of EPDM.

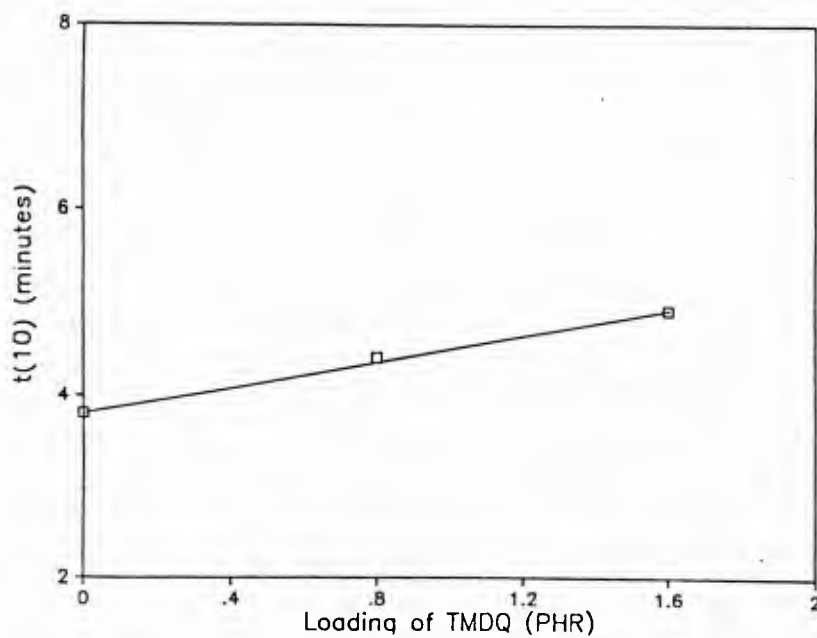


Fig. 24 - Effect of varying loading of antioxidant TMDQ on the t_{10} of EPDM.

Three methods are used to define an appropriate cure time for an elastomer. The rheometer curve previously discussed can give information about the time and temperature necessary to achieve viscosity or shear modulus that is a given percentage of the maximum value. With this method, 90% of maximum is commonly chosen. The time necessary to reach this value is called the t_{90} . For many applications, properties other than modulus might be of greater importance in defining the cure conditions. In these cases, it is necessary to study the critical property as a function of cure conditions. A third alternative for defining cure conditions is to consider the basic chemical kinetics of the curative. For many curatives, the kinetics are not well known. However, for the peroxide curatives used here, the kinetics have been well studied. Therefore, in this case, cure conditions might be defined as the time and temperature necessary to cause a given percentage of the peroxide to react.

Addressing this last method first, a description of the DCP curing of EPDM has been published [16]. The half-life of DCP is the time required for 50% of the available peroxide to decompose and react. From the kinetics for a first-order reaction, it is known that seven half-lives result in 99%--or essentially total conversion. Likewise, 90% conversion requires 3.33 half-lives. A study was designed for the physical properties of the rubber at several cure states as defined by the DCP kinetics. The half-life of DCP as a function of temperature was given by Hercules Incorporated [17]. These values are given in Table 11 for three temperatures. Table 11 also gives three of the four cure times studied. These cure times correspond to the time ($7 \times t_{1/2}$) necessary for a 99% conversion of DCP at the temperatures chosen. The fourth cure time studied was the time ($3.33 \times t_{1/2}$) necessary to achieve a 90% conversion of DCP at 155°C.

Table 11 - Cure Times for EPDM Based on DCP Half-Life

CURE TIMES	155°C	165°C	175°C
DCP half-life (min.)	12	4.7	1.75
t_{99} cure time (min.)	84	33	12.5
t_{90} cure time (min.)	40		

Three different formulations of EPDM were used in this study. All three contained R521 as the polymer, 5 PHR of ZnO, 50 PHR of N660 carbon black, and 0.8 PHR of TMDQ. Sample 403 was cured with 6 PHR of DCP and 2 PHR TMPTMA. Sample 405 contained 6 PHR of DCP and 1.2 PHR of TMPTMA. Sample 408 was cured with 5 PHR of DCP and 2 PHR of TMPTMA. The tear strength, hardness, and tensile modulus at 200% elongation were measured. The tear strength was greatest for samples cured at 155°C for 40 mins for the two samples containing 2 PHR of TMPTMA. The tensile modulus at 200% elongation was slightly lower for all samples when cured for a time corresponding to t_{90} instead of t_{99} . The hardness changed very little as the cure time and temperature were changed.

Because the tear strength was greater for samples cured to a 90% conversion of DCP, a study was performed in which the cure time was varied for

samples cured at 155°C. The EPDM samples were cured for 30, 40, 55, and 70 mins (corresponding to 2.5, 3.3, 4.6, and 5.8 half-lives or to 82, 90, 96, and 98% conversion of the DCP). The tear strength, hardness, and tensile properties were measured for several samples cured at the conditions stated above. Increasing the cure time from 30 to 70 mins had little effect on the tear strength, the hardness, or the tensile modulus at break. Increasing the cure time over this range increased the tensile modulus at 200% elongation but decreased the ultimate elongation. The cure time of 55 mins at 155°C gave the best compromise of these last two properties studied. This was chosen as the cure schedule for the remaining studies on this formulation. This cure schedule is equivalent to a 93% cure as interpreted from the rheometer curve.

Storage of uncured rubber has been a problem in the past. It has been shown that some Neoprene elastomers must be stored cold [4]. Storage in warm locations caused these elastomers to begin curing prematurely. This partial curing of the rubber is called "scorch" and can be detected by periodically analyzing the cure characteristics of the elastomer on a rheometer. If the rubber has begun to cure, there will be a decrease in the t_{10} . A study was conducted to determine the tolerance of EPDM rubber to storage. The cure characteristics were measured periodically for EPDM samples at 10, 25, 40, and 60°C. The t_{10} did not decrease at all for the samples stored at 60°C until after 3000 hrs. The t_{10} for samples stored at 60°C still had not fallen below 4 mins even after 8000 hrs. The t_{10} for samples stored at the other temperatures did not decrease at all after 8000 hrs. This implies that EPDM elastomers do not have to be stored cold and may be stored at room temperature.

Long-Term Properties

The first long-term requirement of an elastomer is that the short-term properties not change with age and exposure to the environment. Exposure to the environment may be a severe test of a formulation. Exposure to heat, oxygen, or ozone will reduce the rubber strength. The absorption of seawater into the rubber matrix may drastically change some properties, which could lead to transducer failure.

Compression Set

Another means for maintaining a seal between the elastomer and the transducer case is to clamp the elastomer in place. It is important that the force applied by the clamp remain fairly constant for the lifetime of the device or the seal may be broken. The elastomer must not become irreversibly compressed by the force of the clamp. It is difficult to predict how the elastomer will respond to being clamped for a certain length of time because the modes by which the rubber creeps out from under the clamp are not well understood. The accepted method of determining whether or not an elastomer will be useful in a clamped state is to measure the compression set of the elastomer. The compression set is a measure of the ability of the elastomer to retain its elastic properties after prolonged compression at a specified

deflection. An elastomer that rebounds closer to its original dimensions will have a smaller value for its compression set.

The compression set was measured on several EPDM elastomers with variations in formulation. The elastomers in Fig. 25 contain varying loadings of the DCP curative. The compression set improved as the amount of DCP was increased. Varying the amount of the curing coagent TMPTMA in EPDM does not improve the compression set unless the loading of DCP is low (3 PHR). An increase in the amount of carbon-black filler in the elastomer had little effect on the compression set. Figure 26 shows that a decrease in TMDQ from 1.6 to 0.0 PHR resulted in an improvement in compression set of 9%. However, it is important to note that the worst of these EPDM materials are still the equal of most neoprene elastomers and the best are significantly better than the best neoprenes.

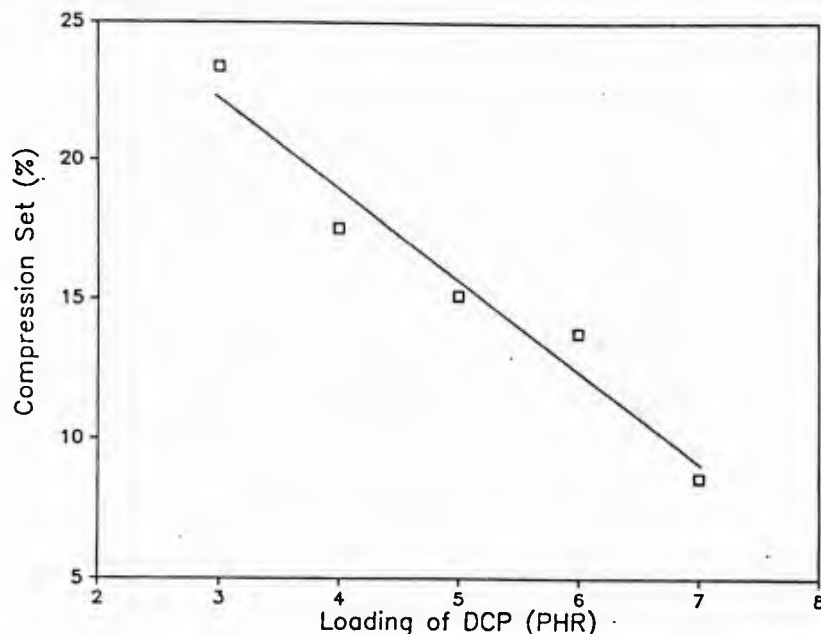


Fig. 25 - Compression set of EPDM with varying loading of DCP curing agent.

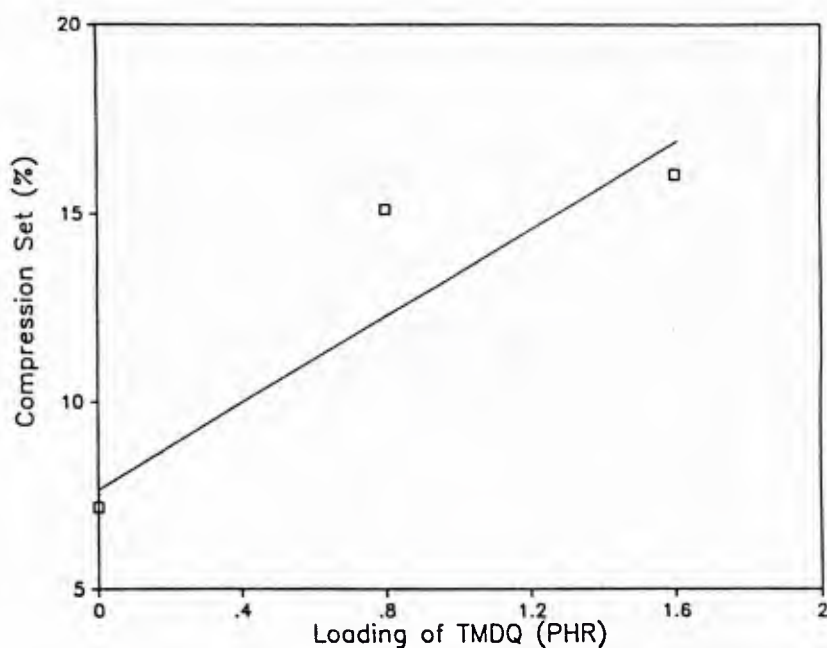


Fig. 26 - Compression set of EPDM with varying loading of antioxidant TMDQ.

A study was performed to determine if the time of compression affected the resulting compression set. Figure 27 shows that as the compression time was decreased, the compression set also decreased in a regular manner.

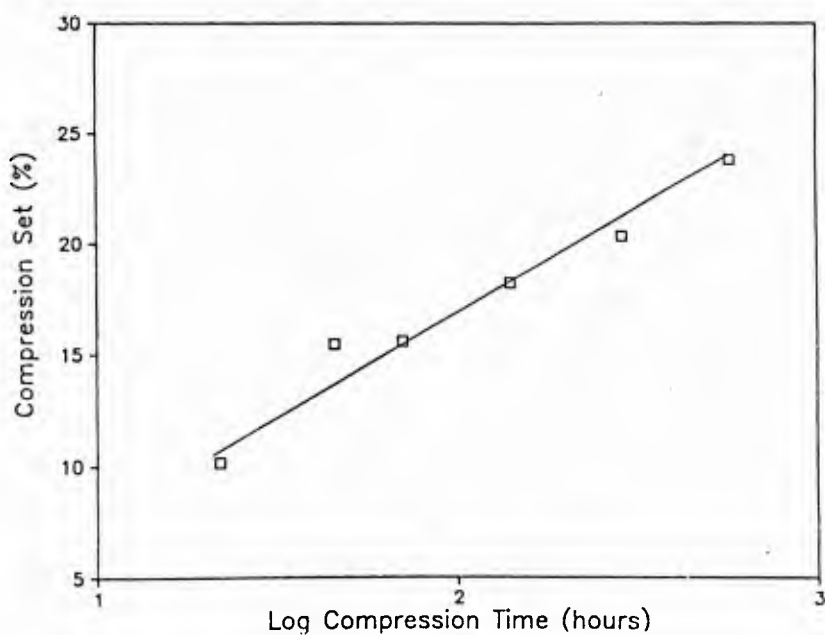


Fig. 27 - Effect of compression time on compression set of EPDM.

Compatibility and Water Permeation

Another important long-term property that an elastomer must possess is a resistance to degradation due to exposure to water or a transducer coupling fluid. The elastomer is very often used as a barrier between an acoustical fill fluid and seawater. Any rubber degradation will quickly lead to a failure in the seal formed by a clamp or a bond.

The resistance of EPDM elastomers to the absorption of several fill fluids was measured by monitoring the changes in mass and volume of the elastomers submerged in the fluids. The fluids were: castor oil (Baker dB grade), polyalkylene glycol (PAG) (UCON LB135Y3), polyalphaolefin (PAO) (Uniroyal 20-E), and an isoparaffinic hydrocarbon (Exxon Co.'s Isopar M). The submerged elastomers were exposed to temperatures of 25, 40, 60, 70, and 90°C.

Figure 28 shows the results of the compatibility study of EPDM with castor oil at 25, 40, and 70°C. Each sample of EPDM showed an initial decrease in mass. The sample exposed to 70°C had not returned to the original mass by 3000 hrs. The fractional change in mass for the sample exposed to 70°C was -0.005 after 1000 hrs--a very minor effect. EPDM is not compatible with a hydrocarbon fluid. Figure 29 shows that EPDM rapidly absorbed the Isopar M and then reached a point of saturation. As the temperature was increased, the sample reached the saturation point more quickly. The fractional change in mass after 1000 hrs of exposure to 70°C was 1.3. Exposure of EPDM to PAO at 70°C gave a fractional change in mass of 0.7 at 1000 hrs. A similar exposure to PAG gave a fractional change in mass of 0.035 after 1000 hrs of exposure. The EPDM shows superior resistance to absorption of castor oil and PAG but must not be used in contact with hydrocarbon fluids.

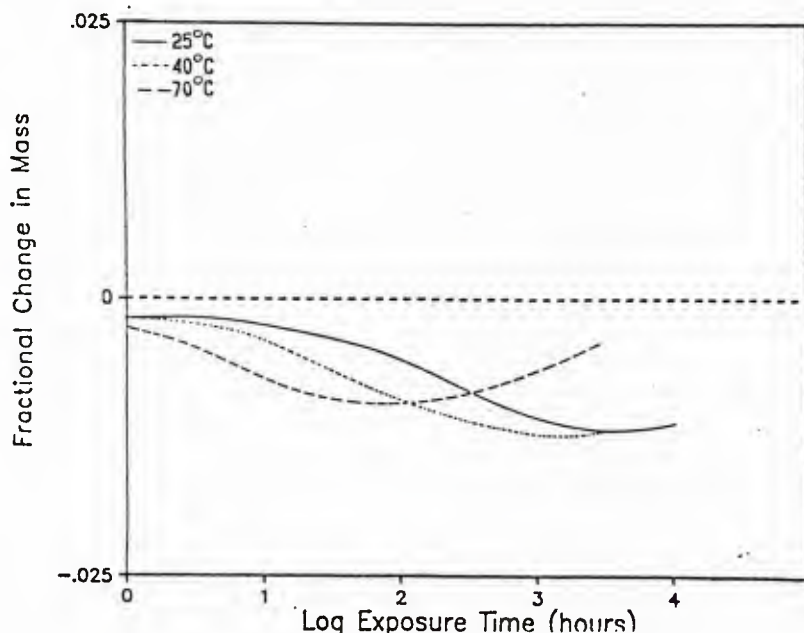


Fig. 28 - Compatibility of EPDM with castor oil. Fractional mass change of EPDM with immersion in castor oil.

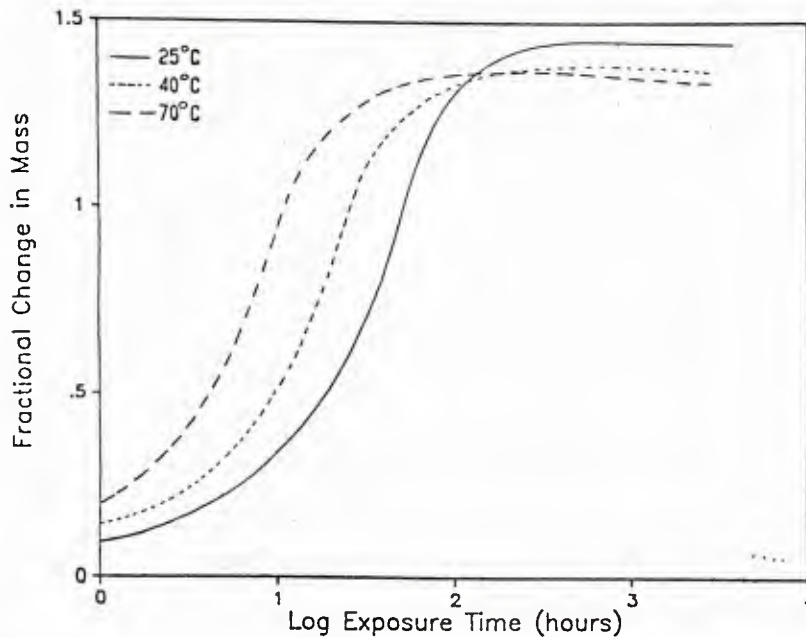


Fig. 29 - Compatibility of EPDM with Isopar M. Fractional mass change of EPDM with immersion in castor oil.

Because the elastomer may be used as a barrier between the transducer and seawater, the performance of the elastomer after exposure to seawater is an important aspect of the long-term use of the elastomer. It must not absorb water and swell. This would lead to a failure of the transducer. The elastomer must also be resistant to the permeation of water. Several samples of EPDM were submerged in seawater and exposed to 25, 40, 60, and 70°C. After 1000 hrs at 70°C, the elastomer had a fractional change in mass of -0.0005. The fractional change in thickness was only 0.007. The permeability of water through a membrane of the EPDM elastomer was measured at 25°C. The permeability constant of EPDM is $7.1 \text{ ng}\cdot\text{cm}/\text{cm}^2\cdot\text{hr}\cdot\text{torr}$. For purposes of comparison, the best neoprene formulations have permeability constants of $20 \text{ ng}\cdot\text{cm}/\text{cm}^2\cdot\text{hr}\cdot\text{torr}$. Butyl rubbers have values typically of $3 \text{ ng}\cdot\text{cm}/\text{cm}^2\cdot\text{hr}\cdot\text{torr}$. Thus EPDM's are a three-fold improvement over neoprene and approach butyl rubber in resistance to water permeation.

DESIGN OF EPDM FOR TRANSDUCER USE

Physical Property Trade-Offs

After examining the data given above for the various EPDM formulations, it is evident that no single sample possesses the best value for all properties measured. A compromise must be made to obtain the best overall formulation. There have been several examples of property trade-offs as a function of

formulation in this study. This section will discuss the decisions made in selecting the EPDM formulation best suited for use in sonar transducers.

Changing the polymer in EPDM from R521 to N1070 does not affect the tear strength, hardness, or tensile properties of the elastomer. Samples containing R521 were shown to have a slower peel rate for a much longer period of time than samples containing N1070. The volume electrical resistivity was higher for samples containing R521 in place of N1070. The density and sound speed were higher for samples with the R521 but still not far from an acoustic impedance match with seawater. Therefore, the R521 polymer was preferred over N1070.

Study of the EPDM curative effect on the physical properties of EPDM began by looking at the difference between a sulfur cure and a peroxide cure. Only the tensile properties were shown to be dependent on a change in curative from peroxide to sulfur. The tensile modulus at 200% elongation and at break were greater for samples with a peroxide curative. Therefore, the study of curing systems for EPDM was expanded to include three peroxide cures, of which DCP had the highest tear strength and resistivity. The property trade-off in choosing the DCP as the curative was a reduction in hardness. The bondability of EPDM cured with DCP far surpassed the bondability of other EPDM formulations.

After DCP was chosen as the curative for EPDM, an off-specification study was performed to determine the best loading of DCP. Choosing the amount of curative used in the elastomer led to another property trade-off. Decreasing loading of DCP to 3 PHR increased the tear strength. However, this decrease caused the hardness and resistivity to decrease. Furthermore, the adhesion to metal became unacceptable. As the loading of DCP was increased above 5 PHR, the t_{10} dropped below 4 mins. Therefore, the formulation containing 5 PHR of DCP, which showed excellent bondability and acceptable hardness and resistivity, was favored.

Five different curing coagents were studied to determine which was the best to use with DCP. As mentioned earlier, the tear strength and the adhesion-to-metal were the questionable properties of EPDM. Both of these properties were improved when TMPTMA was used as the curing coagent. At this point, another off-specification study was performed to determine the optimum loading of TMPTMA. As the loading of TMPTMA was increased, the tensile modulus at 200% elongation increased and the compression set improved but the t_{10} was reduced. Therefore, the formulation containing 2 PHR of TMPTMA, which gave the best bondability to metal and had a t_{10} above 4 mins, was favored.

The EPDM formulations were filled with various sizes of carbon black. The N660 carbon black was favored over the other carbon blacks for the following reasons:

Carbon black N774 had a lower tear strength and t_{10} .

Carbon black N550 had a lower t_{10} and a faster peel rate.

Carbon black N220 had a lower tear strength.

Carbon black N327 had a lower resistivity and a faster peel.

Varying the loading of N660 carbon black in EPDM presented another property trade-off. This was the effect of the loading of carbon black on modulus (as measured by hardness) and electrical resistivity. A loading of 55 PHR of N660 carbon black is necessary to achieve a hardness of 64 (see Fig. 11). The property trade-off in this case is that an EPDM elastomer with a loading of 55 PHR of N660 carbon black has an electrical resistivity of 10^6 ohm·cm (Fig. 19). This value is too low for most practical underwater applications. An EPDM formulation containing 45 PHR of N660 carbon black gave the best adhesion to metal. This sample had an acceptable electrical resistivity and the hardness was still 60.

The antioxidant TMDQ presented the same sort of trade-off between hardness and electrical resistivity that carbon black showed. Decreasing the loading of TMDQ increased the hardness, but it also decreased the electrical resistivity to 10^7 . Decreasing the loading of TMDQ to 0 also caused the peel rate to increase. A loading of 0.8 PHR of TMDQ gave the best combination of properties.

Omitting the ZnO from EPDM only affected two of the properties measured. The electrical resistivity was increased by two orders of magnitude but the peel rate was much too rapid. Therefore, the ZnO was retained in the final formulation.

The EPDM elastomer shown to have the best overall properties for use in sonar transducers has the following formulation:

INGREDIENT	PHR
Royalene 521	100.0
Zinc oxide	5.0
Trimethyldihydroquinoline (TMDQ)	0.8
N660 carbon black	45.0
Dicumyl peroxide (DCP)	5.0
Trimethylolpropane trimethacrylate (TMPTMA)	2.0

Quality Control

It is important that a practical elastomer system have a meaningful quality-control routine. In the past, this has been accomplished by means of a battery of physical tests. The difficulty with the approach is that definition of which tests are appropriate is frequently impossible. When an elastomer is defined by formula, the different possibility exists that quality control can be achieved by assuring that the formulation contains the ingredients specified. A method described by Quinn and McGee [18] has been developed that partially accomplishes this compositional analysis for these EPDM formulations. The method involves liquid-solid chromatography and has achieved satisfactory quantitation for each of the additives DCP, TMPTMA, and TMDQ. Methods to determine the molecular weight of the EPDM polymer using high-temperature gel permeation chromatography are now under development at this laboratory.

Cold Bonding of EPDM

There are few sites of chemical functionality available for bond formation on the surface of a cured piece of the EPDM formulation shown above. Furthermore, it is very difficult for an adhesive to wet the rubber since it has such a low critical surface energy. Several initial attempts to form bonds to a cured EPDM surface were unsuccessful. These involved a wide variety of common epoxy resins and curing agents. Even when the EPDM surface was pretreated with trichloro-isocyanuric acid (TCICA) in ethyl acetate [19], the epoxy failed to bond. A few attempts were made to use a mastic-like material as the adhesive. Although these would stick to the rubber, they always gave very low bond strengths (typically 0.5-kN/m peel strength).

A relatively new commercial material, called PRC944, was tried as a cold-bond adhesive. It is an epoxy but is based on an ether-thioether-backbone oligomer. This adhesive gave about a 70% yield of samples with moderate bond strengths. The successful samples of these have a 180° peel strength of 4 kN/m. However, the less-than-perfect yield provoked further investigation into the causes. Sample degreasing, abrasion, and adhesive-cure schedule were all tested with no improvement in yield. The problem was ultimately solved by pretreatment of the EPDM surface with a solution of TCICA. With this two-step cold-bonding operation, all of the test samples gave good bond strengths. However, it should be emphasized that these peel strengths of 4 kN/m are not adequate for many applications. These cold-bonded EPDM joints should be considered only where high strength is not an important requirement.

PROCESSING STUDY

A study was carried out on the mixing variables that might affect the quality of an EPDM elastomer. Five 90- to 120-pound plant batches were prepared, using both open-mill and internal mixers. The order of addition of the ingredients was studied as well as the mixing time. In the best mill-mixing procedure, the EPDM polymer was first milled together and then all of the ZnO, half of the TMDQ, and a small amount of the carbon black were added. This was allowed to stay on the mill for a total of 8 mins. During this time, the remaining ingredients (except for the DCP) were mixed into the remaining carbon black. About two-thirds of this mixture were then added gradually to the rubber on the mill, with frequent sweeping and re-adding of the unmixed materials. The DCP was then added to the remaining carbon-black mixture. This new mixture was added gradually to the rubber. It was necessary to carefully adjust the cooling-water flow and the spacing between the mill rollers (the nip width) to keep the rubber mixing properly. After all of the ingredients were added, the mixing was continued by cutting the rubber on the mill and sweeping and re-adding unmixed materials. A total mixing time of 20-25 mins was typically necessary. The rubber was cut from the mill and forced to cool either by vigorous air circulation or by placing it in contact with a heavy, cool surface.

The best procedure for mixing in a large internal mixer (a Banbury No. 3) was to simply charge all of the ingredients into the hopper and mix with full cooling-water flow. The ram was raised and swept down once during the process. The mixing was continued until the temperature of the mix reached 115°C, or approximately 4 mins. The mixture was then dropped from the

internal mixer, immediately placed onto a mill, and was mixed and cooled for 5 mins before being cut off. As before, the mixture was forcibly cooled immediately after coming from the mill.

The measured physical properties of these plant-mixed EPDM samples were significantly better than those of the laboratory-size samples of the same formulation studied previously. The physical properties measured for the plant-mixed batches are shown in Table 12 compared to the physical properties measured for the laboratory-size sample 901. Specifically, the good plant samples all had a rheometer t_{10} of greater than 5 mins and tear

strengths of greater than 50 kN/m. Such results imply that molding or tearing will present little problem if some care is exercised in the preparation of the rubber batch.

Table 12 - Physical Properties of Plant-Mixed EPDM Formulations

PROPERTY	BATCH 1 MILL	BATCH 3 BANBURY	BATCH 4 MILL	BATCH 5 BANBURY	901
t_{10} (mins)	4.3	5.3	4.6	5.1	4.4
Density (kg/m^3)	1072.6	1050.6	1065.3	1045.6	1075.0
Log Vol. Resistivity (ohm·cm)	12.9	14.0	11.4	13.5	9.5
Tear Strength (kN/m)	51.9	55.8	53.1	53.2	45.3
Hardness	60.9	53.3	59.0	54.6	59.9
Sound Speed (m/s)	-	-	-	1053.0	1508.0
Tensile Strength (MPa)	15.5	14.0	16.4	15.8	13.5
Tensile Modulus 200% Elongation (MPa)	7.0	3.4	6.1	4.4	7.3
Ultimate Elongation (%)	315	504	364	438	288

CONCLUSIONS

The EPDM formulation that possessed the best overall physical properties proved to be processable and has reproducible quality-control analysis techniques established for the additives. This formulation was designated EPDM-RLE. It has the following physical properties:

Peel rate (microns/hr)	0.6
Tear strength (kN/m)	50.0
Density (kg/m ³)	1070.0
Sound speed (m/s)	1508.0
Log volume resistivity (ohm·cm)	11.3
Shore A hardness	60.0
Water permeability (ng·cm/cm ² ·hr·torr)	7.2
Compression set (%)	12.9
Tensile strength (MPa)	15.1
Tensile modulus at 200% elongation (MPa)	6.8
Tensile modulus at 300% elongation (MPa)	12.4
Ultimate elongation (%)	322
Superior castor-oil and PAG resistance	
Excellent environmental resistance	

EPDM-RLE is so named because of the near ρ -c (acoustic-impedance) match with seawater of its formulation. It has a low loss and is resistant to degradation when exposed to harsh environmental conditions. It also has excellent bondability to metal. Thus, the EPDM-RLE formulation is well suited for many uses in sonar transducers. Details of the application of EPDM-RLE to several transducers are given in Appendix A. A procurement specification for EPDM-RLE is given as Appendix B.

ACKNOWLEDGMENTS

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BEUMEL AND THOMPSON

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Appendix A

APPLICATIONS OF EPDM-RLE

Although EPDM-RLE has some excellent properties for sonar transducer use, its application should be considered on a case-by-case basis. For example, EPDM-RLE has acoustic properties superior to any neoprene formulation. However, it is inferior in strength to most neoprene formulations. Therefore EPDM-RLE should not be considered where strength requirements are significant--as when subjected to ice impact. Furthermore, its bondability is probably inferior to a good Neoprene GRT's such as Neoprene 5109S [4]. No EPDM formulation will be suitable for a fleet application where the transducer would be frequently exposed to hydrocarbon fluids such as diesel fuel.

TR-317R TRANSDUCER

The TR-317R transducer is a Navy-designed version of the spherical array transducer. Experimental TR-317 headmass assemblies were molded using EPDM-RLE bonded with the Thixon P-6-1/814-1 system. The push-out force on one sacrificed head mass was measured to be 18,000 pounds. This may be compared to a push-out force range of 18,000 to 24,000 pounds seen with a Neoprene GRT formulation developed for optimum bondability. Failure in this push-out may result from either rubber tearing or bond failure. The high push-out observed for the EPDM-RLE implies that this elastomer has very good bondability and tear strength. Furthermore, the rubber moldings were all smooth and well bonded with no visible defects.

TR-242/316 NODAL MOUNT GROMMET

Because of the excellent compatibility of EPDM with castor oil, an EPDM formulation was suggested for use as a stack-support grommet for the TR-242 and the TR-316 transducers. The previously used grommets were made of proprietary neoprene elastomers. These grommets increased in thickness after exposure to castor oil while they were in the assembled transducers. Fresh grommets made of this proprietary material were obtained from Hazeltine Corp. and C-Tech Inc. The grommets were exposed to castor oil at 90°C. After 1000 hrs of exposure, the Hazeltine grommets had a fractional change in thickness of 0.04 and the C-Tech grommets a fractional change of 0.07. A new formulation of EPDM elastomer was also exposed to castor oil at 40, 60, 75, 90, and 100°C. This EPDM was formulated to have similar physical properties to the proprietary neoprenes but have a better compatibility with castor oil. The formulation of this EPDM is presented in the following table.

BEUMEL AND THOMPSON

INGREDIENT	PARTS
R521	100
ZnO	5
N774	35
N990	30
TMDQ	0.8
TMPTMA	2
DCP	7

After 1000 hrs of exposure at 90°C, the fractional change in thickness was 0.004. This change is less than 10% of the change of thickness seen for the neoprene grommets. Because this sample had such a small change in thickness after exposure to castor oil and also had a low loss, it replaced the proprietary neoprene grommets in the TR-242 and the TR-316 transducers.

TR-302 DEPTH SOUNDER WINDOW

The TR-302 is a parametric sonar transducer used as a secure depth sounder. The window of this transducer must show minimum loss to the high frequencies employed. Therefore, this is a severe test of an elastomer's acoustical transparency. The insertion loss of a 0.5-in.-thick EPDM-RLE slab was measured from 200 to 300 kHz. The insertion loss over this range varied from 1 to 2.5 dB. This is a little higher than the current window. However, EPDM-RLE might still prove the better material choice since its low water permeability should allow it to be made thinner and consequently with lower losses.

TR-330A TRANSDUCER

The TR-330A transducer is a part of the SQS-56 system, a high-power projector and broadband receiver system for surface ships. The EPDM-RLE has a smaller modulus change with temperature than does neoprene. Therefore, it would be expected to produce a transducer with less performance change with temperature. The TR-330A is covered entirely with rubber. The watertight seal is formed between the rubber-covered body and a rubber skirt on the head. The requirements of this seal are not high strength but merely water resistance. A TR-330A transducer has been molded of EPDM-RLE with the seal made by bonding the two components together with PRC-944 adhesive. This transducer is still being evaluated.

H52 STANDARD HYDROPHONE

The USRD type H52 hydrophone is an underwater sound measurement standard for use in the frequency range 20 Hz to 150 kHz.*1 A substitution of EPDM-RLE for the usual butyl boot should improve performance in the higher frequencies. A hydrophone was calibrated with both a butyl and an EPDM-RLE boot. The performances were virtually identical up to 50 kHz, above which the EPDM-RLE booted unit gave about a 1-dB improvement in free-field voltage sensitivity. With this marginal improvement, no further effort is anticipated.

¹Underwater Sound Reference Detachment, "Underwater Electroacoustic Standard Transducer Catalogue," Apr 1982, pp. 107-110

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Appendix B

PROCUREMENT SPECIFICATION FOR EPDM-RLE

1.0. SCOPE

This document establishes the requirements for EPDM-RLE for use in sonar transducers.

2.0. APPLICABLE DOCUMENTS

ASTM D1765-82 "Standard Classification System for Carbon Blacks used in Rubber Products."

3.0. REQUIREMENTS

3.1. Raw Materials Description

3.1.1. Royalene 521: trademark of Uniroyal, Inc., for a terpolymer of ethylene, propylene, and a nonconjugated diene, with a Mooney viscosity (ML-1+4 @100°C) of 40-50.

3.1.2. Zinc oxide, treated with fatty acid. Brand names for this product include Protox 166 made by New Jersey Zinc Co. and St. Joe 42-21A zinc oxide made by St. Joseph Lead Co.

3.1.3. Polymerized 1,2-dihydro-2,2,4-trimethyl quinoline (TMDQ): brand names for this product include Naugard Q by Uniroyal Chemical.

3.1.4. Trimethylol propane trimethacrylate (TMPTMA): brand names for this product include Sartomer SR350.

3.1.5. Carbon black N660, as defined by ASTM D1765.

3.1.6. Dicumyl peroxide, 40%, absorbed on clay (DCP): brand names for this product include Di-Cup 40KE by Hercules, Inc. and Varox DCP-40KE by R.T. Vanderbilt Co., Inc.

3.2. Formulation

The formulation of this compound as follows.

Royalene 521	100 ± 1 parts by weight
Zinc Oxide	5 ± 0.5 parts
TMDQ	0.8 ± 0.1 parts
N660 black	45 ± 0.5 parts
TMPTMA	2 ± 0.1 parts
DCP	5 ± 0.1 parts

BEUMEL AND THOMPSON

- 3.3. Rubber Mixing
EPDM 521 may be mixed either on an open mill as in 3.3.1 Open Mill Mix or in an Internal Mixer as in 3.3.2. The open mill or the internal mixer shall be thoroughly cleaned prior to mixing EPDM 521.
- 3.3.1. Open Mill Mixing
 - 3.3.1.1. Batch size shall be chosen so as to produce a rolling bank of material during the mixing.
 - 3.3.1.2. All of the polymer shall be banded on the mill with water cooling. Modifications of the cooling water may be used to keep the rubber on the front roller.
 - 3.3.1.3. All the zinc oxide shall be gradually added across the bank of polymer.
 - 3.3.1.4. After the matrix has smoothed, add approximately 1/3 of the TMDQ.
 - 3.3.1.5. Add approximately 1 pound of N660 black, followed by additional TMDQ.
 - 3.3.1.6. Blend remainder of the black and TMDQ in a bin along with all of the TMPTMA.
 - 3.3.1.7. Add the blended ingredients gradually across the rubber band, with cutting. When 90% of the blended ingredients have been added, mix the DCP into the remaining 10%.
 - 3.3.1.8. Add the blended ingredients gradually to the rubber. Sweep the pan add the pan sweepings to the rubber. Cut the rubber 3/4 from each side until the matrix is smooth and there are no inhomogeneities visible.
 - 3.3.1.9. The rubber shall be cut from the mill in sheets convenient for handling and shall be kept separate until cooled to near room temperature. Laboratory samples shall be cut from a cut edge of the first, third, third-from-last, and last sheets. Other sampling may be used on approval of Government representative.
- 3.3.2. Internal Mixer
 - 3.3.2.1. The batch size shall be such as to maintain continual mixing throughout the cycle. Full cooling shall be maintained throughout the mixing.
 - 3.3.2.2. Add to the hopper, in order, all of the carbon black, all of the chemicals, and all of the polymer. Lower the ram.
 - 3.3.2.3. Continue mixing for from 3 to 4 minutes or until the temperature reaches 110°C. Raise and sweep down the ram as necessary during the mixing.

- 3.3.2.4. The compounded rubber shall be dumped from the mixer and within 3 minutes placed on an open mill with full cooling water. The rubber shall be banded and cut until a smooth matrix is formed and the temperature has dropped to 80°C.
- 3.3.2.5. The rubber shall be cut from the mill in sheets convenient for handling and shall be kept separate until cooled to near room temperature. Laboratory samples shall be cut from a cut edge of the first, third, third-from-last, and last sheets. Other sampling may be used on approval of Government representative.

3.4. Properties of Uncured Material

<u>PROPERTY</u>	<u>TEST METHOD</u>	<u>SPECIFIED VALUE</u>
Rubber scorch	ASTM D2084, 155°C 3" Arc, Microdie	At each test, the time required for the torque to increase by 10 inch-pounds shall be greater than 3.5 minutes.

3.5. Properties of Cured Material

3.5.1.	Density	ASTM D297 (para. 15.1.2)	1.07 ± 0.01
3.5.2.	Durometer (Shore A)	ASTM D2240	60 ± 5
3.5.3.	Tensile Strength	ASTM D412	14 MPa (min)
3.5.4.	Ultimate Elongation	ASTM D412	300% (min)
3.5.5.	300% Modulus	ASTM D412	12 ± MPa

4.0. QUALITY ASSURANCE PROVISIONS

- 4.1. Compositional accuracy and satisfaction of performance requirements will be monitored by the procuring activity. Compositional analysis will be performed by the Navy (or its designated agent). Documentation verifying conformance with specified property requirements and compliance with test plans and procedures as approved by the procuring agency is required.
- 4.2. For the purposes of this specification, a batch shall be considered to be that quantity of compound that is mixed at any one time. The product shall be sheeted on an appropriate size mill to a thickness specified by the procuring activity.
- 4.3. Quality Surveillance Plan
- 4.3.1.1. Production Approval
Inspection-Cured Provision of any compound intended to be in accordance with this specification, must be preceded by demonstration of compliance with the requirements of 3.4 and 3.5.1 through 3.5.5, as well as 4.3.1.2.

BEUMEL AND THOMPSON

- 4.3.1.1.1. Testing of this compound to satisfy 4.3.1.1 shall be documented so that procedures used and values obtained for each test are indicated.
- 4.3.1.1.2. Every batch of compound delivered to be in accordance with this specification shall be subjected to procedures outlined in 4.3.1.1.
- 4.3.1.2. Inspection-Uncured, Compositional Analysis
 - 4.3.1.2.1. Four sample plugs shall be removed from each batch as specified in 3.3.1.9 or 3.3.2.5. Each sample shall be a section through the thickness of the sheet and have a cross-sectional area of approximately 25 square inches.
 - 4.3.1.2.2. The sample plugs shall be wrapped separately in polyethylene film and shipped to: Naval Research Laboratory, Underwater Sound Reference Detachment, ATTN: TBQCL, 755 Gatlin Avenue, Orlando, FL 32806-6936.
- 4.3.1.3. Rubber manufacturer shall furnish certification of compliance stating that the compound meets the requirements specified herein.
- 4.4. Storage shall be made under conditions such that the rubber meets the requirements of 3.4 immediately before use. Recommended storage conditions are given in 6.0.
- 5.0. PREPARATION FOR DELIVERY
 - 5.1. Packing
 - 5.1.1. Uncured, compounded rubber shall be packed for shipment so as to meet the requirements of 4.4.
 - 5.1.2. A polyethylene film shall be used between the sheets extending over the full area of contact between the sheets. The inside height of the container shall not exceed 10 inches. The sheets shall be packed in such a manner that they will not become deformed or compressed in shipment or extended storage.
 - 5.2. Marking
 - 5.2.1. All marking of interior packages and shipping containers shall be done in accordance with MIL-STD-129 and the requirements herein.
 - 5.2.2. Each shipping container and each sheet of rubber shall be marked as follows.

Drawing No. _____
Vendor Code Ident. _____
Batch No. _____
Date of Manufacture _____

6.0. Storage

The uncured, compounded rubber from 3.3.1.9 or 3.3.2.5 will slowly cure or scorch under storage and handling conditions. The length of time before the material will fail the test of 3.4 depends upon the quality of the initial material. Storage at 25°C causes the t_{10} to decrease 0.1 minute for every month of storage. Storage at 10°C or below causes only a very slight decrease in t_{10} .

Freshening the uncured, compounded rubber on a small mill decreases t_{10} by 0.1 minute.

6.1. Vendor List

Identification of the suggested source(s) is not to be construed as a guarantee of present or continued availability as a source of supply for the item(s).

Associated Rubber Company
P.O. Box 245
Tallapoosa, GA 30176

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