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A NEOPRENE WITH OPTIMIZED BONDABILITY FOR SONAR TRANSDUCER APPLICATIONS

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A neoprene compound has been developed for underwater acoustical applications that exhibits excellent bondability and very good engineering properties. This compound is based on Neoprene GRT cured with red lead and filled with carbon black. The dependence of the physical properties on the composition of the compound has been studied. Of particular importance is the effect of the type and amount of carbon black on a range of properties such as moduli and electrical resistivity. The processing and storage parameters necessary to produce a high-quality material are discussed. A quality control system based on compositional analysis is also described.

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A Neoprene with Optimized Bondability for Sonar Transducer Applications

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A NEOPRENE WITH OPTIMIZED BONDABILITY FOR SONAR TRANSDUCER APPLICATIONS

BACKGROUND

The applications of elastomers to underwater acoustical systems are many and varied. These include acoustic windows, acoustic baffles, acoustic or dynamic absorbers, cables and cable glands, and boots over acoustical devices. The engineering requirements placed on the elastomers are frequently severe. Not only are the elastomers required to have high strength and bondability, and appropriate acoustical properties, but most importantly they must maintain these properties for many years in a relatively hostile environment. The environmental factors may include temperature and pressure cycling in salt or fresh water, and biological growth as well as spurious changes in pH and transition-metal content.

In addition to the real engineering requirements of the elastomer component, there is also the additional burden of convenience in handling the material and ease-of-manufacture of the part. In the recent past these handling requirements have assumed increasing importance as device manufacturers have tried to cut costs. However, convenience in handling should not play the most important role in determining the elastomer formulation.

For sonar transducer applications, the elastomers presently used were developed without property optimization for short-term operation and with little consideration for long-term performance requirements. Furthermore, the elastomers have usually been purchased under a performance specification of limited scope. Consequently, the rubber manufacturer may well modify his formulation during the production--as long as it continues to meet the performance specification. Therefore an alternate but more fundamental approach was taken to the elastomer problem under tasks of the Naval Sea Systems Command's (NAVSEA) Sonar Transduction Sciences Program and the Sonar Transducer Reliability Improvement Program (STRIP). First, necessary research was carried out such that the performance of transducer elastomers was well understood as functions of elastomer composition, cure conditions, and environmental parameters. An optimized rubber formulation was then designed and quality-control techniques developed to guarantee the reproducibility of the produced elastomers. Specifications for transducer elastomers were then carefully prepared to ensure that the elastomers used in molding transducers would have the proper composition and be correctly processed, so that the reproducibility and the performance of the elastomers in sonar transducers may be assured.

DESIGN CONSIDERATIONS

Many decisions are necessary to arrive at an elastomer formulation that might be considered for general use in sonar transducers. This decision matrix is discussed as follows:

- Short-term (initial) property considerations will be stated as quantitatively as possible.

- Long-term property considerations will be discussed.

- The types of studies performed and their effect on the organization of the research will be described.

- Polymer selection will be discussed in terms of property requirements.

- General precepts for elastomer compounding, which lead to a narrowing of choices, will be discussed.

- Dependence of each property on the type and amount of compounding ingredient will be discussed.

- Tradeoffs in properties will be illustrated.

These will be followed by discussions of the issues of quality control and rubber processing.

Short-Term (Initial) Property Considerations

A rubber designed for general sonar-transducer use must meet a wide range of short-term requirements. If application of the rubber is as a transducer window for a sufficiently high-frequency sound that makes the rubber thickness become a significant portion (perhaps >0.10) of a wavelength, then the density and sound speed of the rubber must be near those of seawater, 1030 kg/m^3 and 1525 m/s, respectively. Furthermore, the rubber needs to be quite low in loss to the dilatational sound wave. Of course, these requirements are not as important when the applications are mainly in the audio-frequency range. For many other applications, the rubber serves as a mounting spring for transducer components, for which it may be necessary that the rubber have a given shear modulus. Sometimes it is even necessary to interpret this property over a given frequency and temperature range. Most commonly, however, shear modulus is judged by means of the elementary Shore hardness test. This value is typically specified in the 55 to 75 range of Shore A.

For most applications, the rubber forms a barrier to protect the sonar transducer from environmental effects. Consequently, some level of strength or toughness is necessary. This is typically expressed in the specification as a tensile strength of 18 MPa (2600 psi) and an elongation at break of perhaps 500% (minimum). Many times a tear strength is also specified, but this is susceptible to the particular type of measurement. A typical specified value would be 35 kN/m (200 lb/in.) for the minimum Die B tear strength.

Whether or not the rubber is in contact with an electrode, electrical resistivity must be considered carefully for transducer applications. It may be sufficient in the case where voltages are applied to require a

minimum-volume electrical resistivity of 10^9 Ω·cm. A minimum dielectric strength may also be necessary for higher voltages. In the case where electricalvoltage is not applied, it will still be important that the rubber have a resistivity of perhaps 10^5 or 10^6 Ω·cm. This latter requirement is to avoid the possibility of the rubber setting up an electrical cell with exposed metal in the presence of oxygenated seawater. Such an electrical cell will generate hydroxide ions that can rapidly destroy any rubber-to-metal bonds [1].

One short-term property that might be considered only incidentally is the rate-of-cure of the elastomer formulation. This might be monitored or specified by means of a commercial rheometer. One widely accepted type of rheometer is an oscillating disk instrument made by the Monsanto Company. On this instrument, the shear modulus of a rubber sample is monitored as it cures. One way of expressing the amount of premature curing of a rubber compound is to specify the time taken for the torque (the measure of shear modulus) to increase by a given amount from the minimum value. For rubber samples intended for transfer or injection molding, a requirement might be that the time to an increase of 10 in.-lbs of instrumental torque from the minimum torque must be greater than 4 min. For compression-molded samples, this time requirement can be relaxed considerably.

Long-Term Property Considerations

The first long-term property consideration is, of course, that the initial or short-term properties do not change with age and exposure to the environment. This might be a severe test of a formulation as the ingress of seawater into some rubber matrices may drastically change such properties as electrical resistivity. Exposure to heat, oxygen, or ozone will reduce the rubber strength.

The rubber must have relatively low water permeability since it always acts as a water barrier. A determination of the real requirement for the permeability constant also requires consideration of the window thickness and area, the internal fluid volume, and the exposure temperature. Detailed analysis of these requirements has been done in only a few cases [2,3], but for many applications a maximum value of 25 or 30 ng·cm/cm^2·h·Torr might be specified. It is also desirable that exposure to water not cause excessive swelling of the rubber. This is most commonly specified as a maximum increase in weight of perhaps 3% for a rubber sample exposed to seawater (for example, at 55°C for 14 days).

In some cases the rubber serves to contain an acoustic coupling liquid. It must be assured that the liquid will not degrade the rubber. This is typically done by specifying a maximum weight change of say 10% on exposure to the liquid for some short time at an elevated temperature to accelerate the test. A reasonable exposure condition might be 1000 h at 75°C.

The seal between the rubber and the remainder of the transducer is made by either clamping or bonding the rubber in place. In the former case, the rubber must obviously stay in place and resist the clamping forces.

Specifying this property is difficult because the mode by which the rubber creeps from under a clamp is ambiguous. Most specification writers have used compression set as a measure of clamping-force resistance. For the case where a banding clamp is used, a compression-set value of 15 to 20% after a 70-h exposure at 85°C is typically specified. For a clamp of larger area, a larger compression-set value should be specified.

Specification of bondability is fraught with even more uncertainty. Short-term tests, such as a peel test or a button test, do not give any assurance that a bond will survive exposure to water or extraneous ions. Even among the various peel and button tests there is so little agreement about test results that few specifications actually contain any information about bondability.

Material Optimization

The general approach is to first choose the base polymer by a simple consideration of the generic properties of commercially available materials. Once this selection is made, the compounding ingredients must be carefully chosen. The principle used in this study is that the compounding ingredients should be chosen first so as to provide the greatest improvement in the properties that are considered to be the most vulnerable. This choice may be made by preparing samples with a variety of ingredients, testing the vulnerable properties, and selecting the best combination. Such a parametric study should then be followed by a study to optimize the amount of each ingredient for a wider range of properties. This may be done by acquiring samples with a variation in the ingredient loading over a reasonable range and determining their pertinent physical properties. We have called such a test an "off-specification" test because in addition to information that helps to optimize the formulation, one also develops correlations that are useful in showing the results of manufacturing variations.

In addition to the above tests, it is necessary to determine the effect of changes in mixing and molding procedures. Such studies can take the form of either the researcher going to the rubber plant to mix the formulation or of contracting for such a study.

FORMULATION AND PROPERTIES

Neoprene elastomers have been used successfully for so long that many of the device specifications require their use. Careful analysis of the engineering requirements placed on the rubber reveals that the applications divide clearly into two classes. These classes are determined by whether the primary watertight seal depends upon the rubber being clamped or upon being bonded. In the case of a clamped seal, the implication is that a Neoprene W must be used. (The designations Neoprene WRT and Neoprene GRT are trademarks of the Du Pont Co.) When properly formulated, Neoprene W's (including Neoprene WRT) have better resistance to compression set than other neoprenes. On the other hand, however, if the primary water seal involves a bond between

the neoprene rubber and a substrate, a Neoprene G must be used. This class of neoprene provides much better bondability than other neoprenes [4].

All underwater acoustical applications require resistance of the elastomer to low-temperature crystallization and the attendant changes in dimension and modulus. The most crystallization-resistant of the neoprenes are the -RT types. Consequently Neoprene GRT is a crystallization-resistant rubber with optimum bondability [4].

Chemically, Neoprene GRT is a copolymer of chloroprene (2-chloro-1,3-butadiene) and 2,3-dichloro-1,3-butadiene modified by sulfur and containing a thiuram disulfide stabilizer and an antioxidant [5].

Elastomer Compounding

Compounding of the Neoprene GRT to make a practical elastomer requires a metal-oxide curing agent, stearic acid as a cure activator, a cure modifier, an antioxidant, and a filler to increase the modulus of the final product. There is little room for choice among the various metal oxides used for curing agents. Lead tetroxide (red lead, Pb_3O_4) is the only metal-oxide curing agent that does not promote swelling of the cured neoprene when it is submerged in water, as discussed in the section on compatibility [4]. 2-Benzothiazyl disulfide (called MBTS after its old name of mercaptobenzothiazyl sulfide) is included in the formulation to serve as a peptizer (viscosity reducer) and a cure retarder. Octylated diphenylamine (ODPA) is used as an antioxidant. A common, medium-size carbon black (FEF or ASTM N550) was chosen as a reinforcing filler.

A processing aid called TE-70, manufactured by Technical Processing, Inc., was included to improve the efficiency of the mixing process. This is a proprietary ingredient whose mode of action is uncertain. The amounts of most of these compounding ingredients were chosen initially by reference to previous compounds. Red lead is required at a level of about 12 parts of Pb_3O_4 per 100 parts of neoprene elastomer to promote a tight cure. Stearic acid is used at a level of 2 parts for all Neoprene GRT formulations. Used at its maximum concentration, MBTS is limited by solubility in the elastomer to approximately 1.5 parts per 100 parts rubber (phr). ODPA and TE-70 are both used for most applications at a level of 2 parts. The level of carbon black is an important variable and will be discussed in detail in the various sections relating to physical properties. The experimental measurements used for each of the following discussions are given in Appendix A.

Density and Sound Speed

An optimum condition for an elastomer used in sonar equipment would be to have a sound speed and density that match that of seawater. The measurement of sound speed and density as a function of variation in the type of component in the formulation led to the following observations:

- Samples containing a ZnO/MgO curing system have a lower density but a higher sound speed than corresponding samples cured with lead oxide. This is true for samples with carbon black and silica or hard clay fillers and for samples with just carbon-black filler.

- In lead-oxide-cured samples, substituting silica or hard-clay fillers for a portion of the carbon black lowers the sound speed.

- An increase in the proportion of ODPA causes a decrease in density to

  a minimum of 1450 kg/m^3 at 2 phr and above (see Fig. 1). This increase in ODPA has little effect on the sound speed.

- A deviation in the proportion of MBTS has little effect on the sound speed or density of the elastomer.

A formulation variation, such as an increase in the amount of lead oxide, does not affect the amount of crosslinking in the elastomer above a certain concentration and does not significantly affect the modulus. As the red-lead content increases, the density increases and the sound speed decreases due to the mass of the red lead (see Figs. 2 and 3). The specific acoustic impedance (ρc) and the adiabatic bulk modulus (ρc^2) change monotonically over a very narrow range (see Figs. 4 and 5). The low bulk modulus of the lowest red-lead-content sample in Fig. 5 is probably a result of slightly low crosslink density.

A formulation variation, such as an increase in carbon-black loading, increases the modulus of the sample, which causes an increase in density and an increase in sound speed as seen in Figs. 6 and 7. Figures 8 and 9, respectively, show the specific acoustic impedance and adiabatic bulk modulus of Neoprene GRT as a function of increasing FEF N550 carbon-black loading. Figures 10 and 11 also show a similar increase in density and sound speed with increasing concentration of SRF N774 black, a somewhat coarser black. Figures 12 and 13 show an increase in specific acoustic impedance and adiabatic bulk modulus with an increase in SRF N774 carbon-black loading.

Figure 14 shows a decrease in adiabatic bulk modulus as the particle size of the carbon black increases over a wider range. All samples contained 30 phr of carbon black. The increase in carbon-black particle size has little effect on density while the sound speed decreases as shown in Fig. 15.
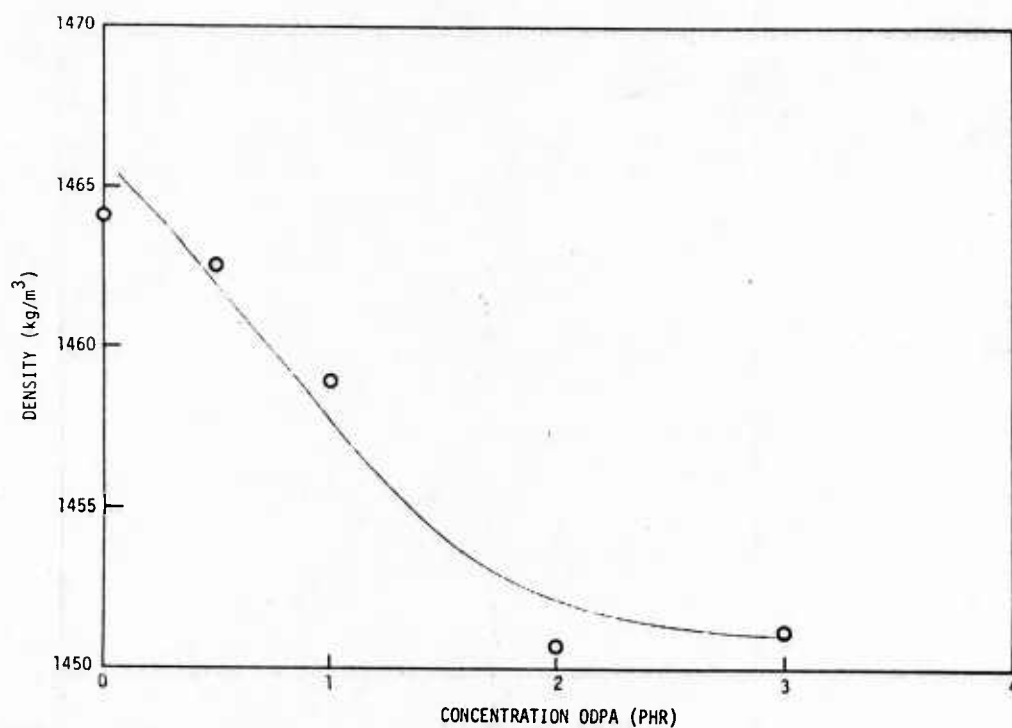
Fig. 1 - Density of Neoprene GRT with varying loading of antioxidant.
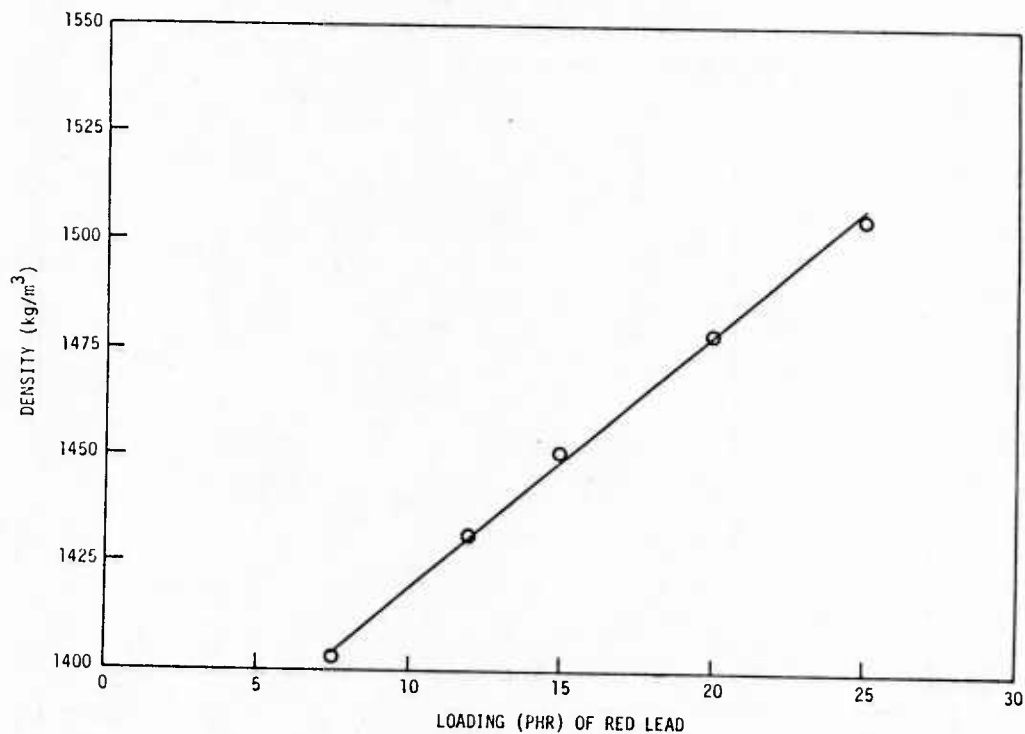
Fig. 2 - Density of Neoprene GRT with varying loading of
red-lead curing agent.
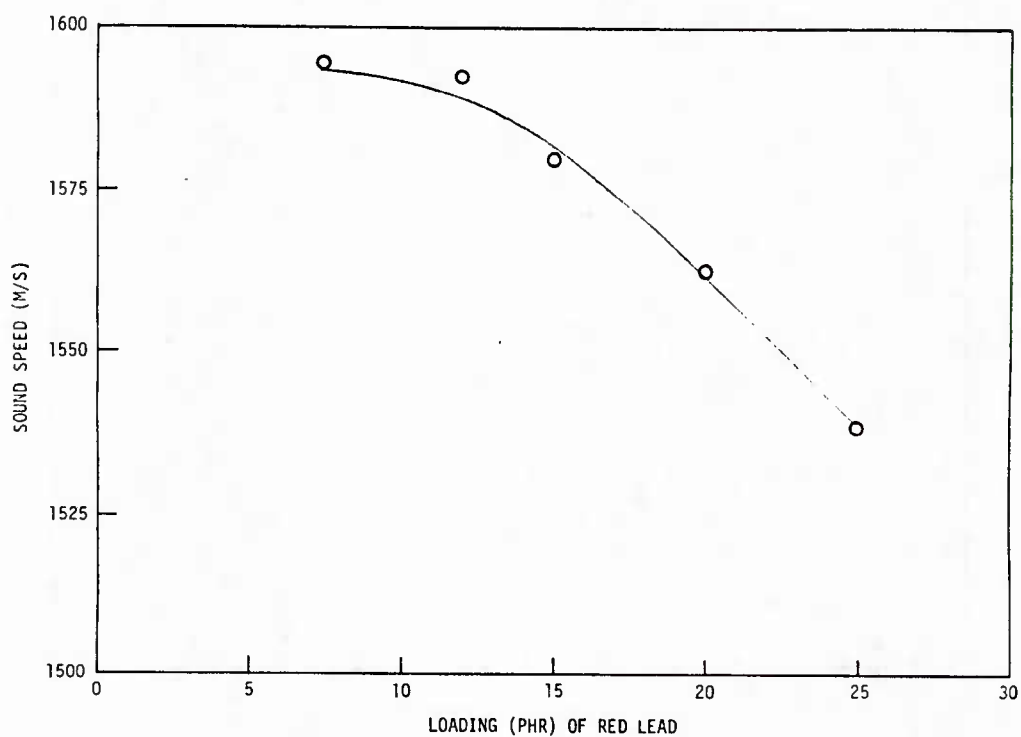
Fig. 3 – Sound speed of Neoprene GRT with varying loading of
red-load curing agent.
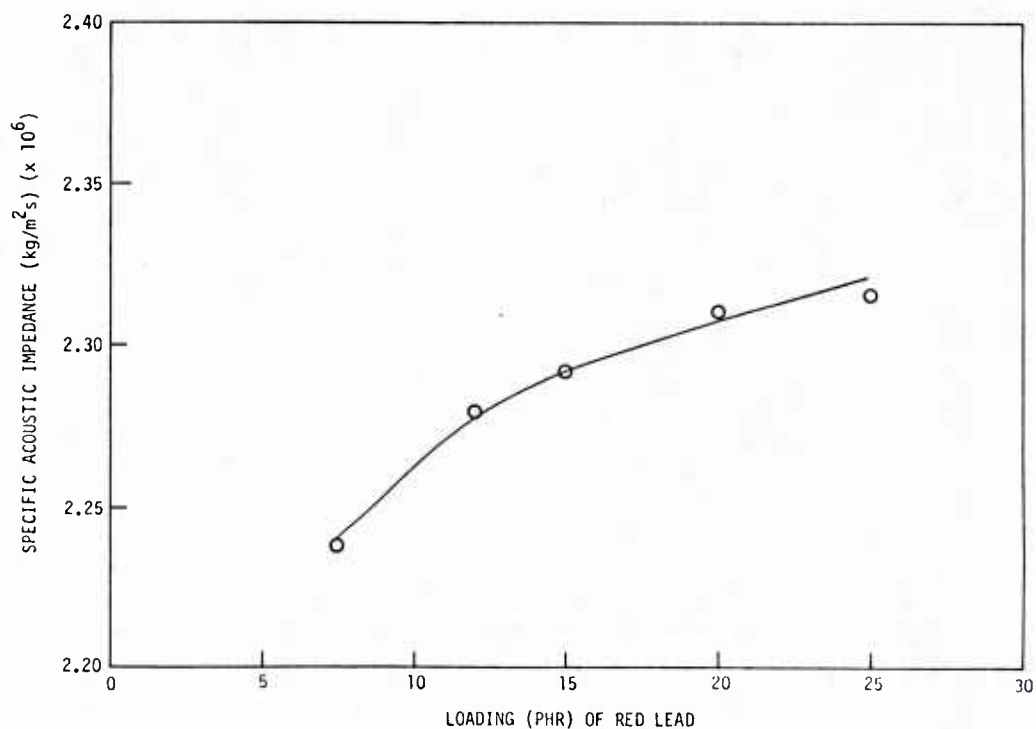
Fig. 4 – Specific acoustic impedance of Neoprene GRT with varying
loading of red-lead curing agent.
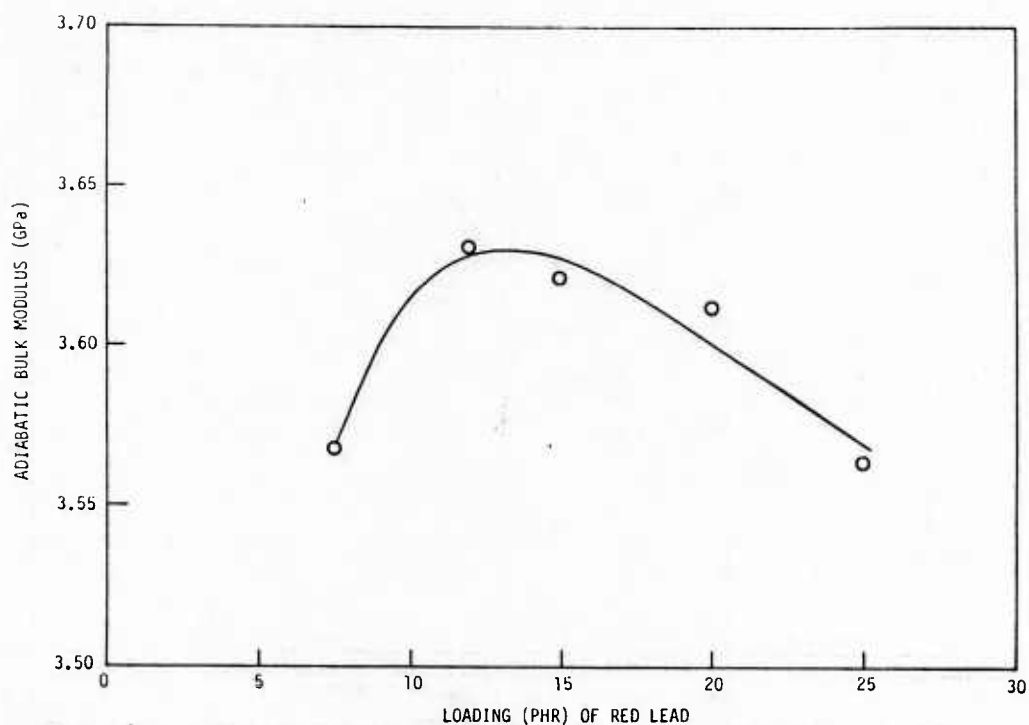
Fig. 5 – Adiabatic bulk modulus of Neoprene GRT with varying
loading of red-lead curing agent.
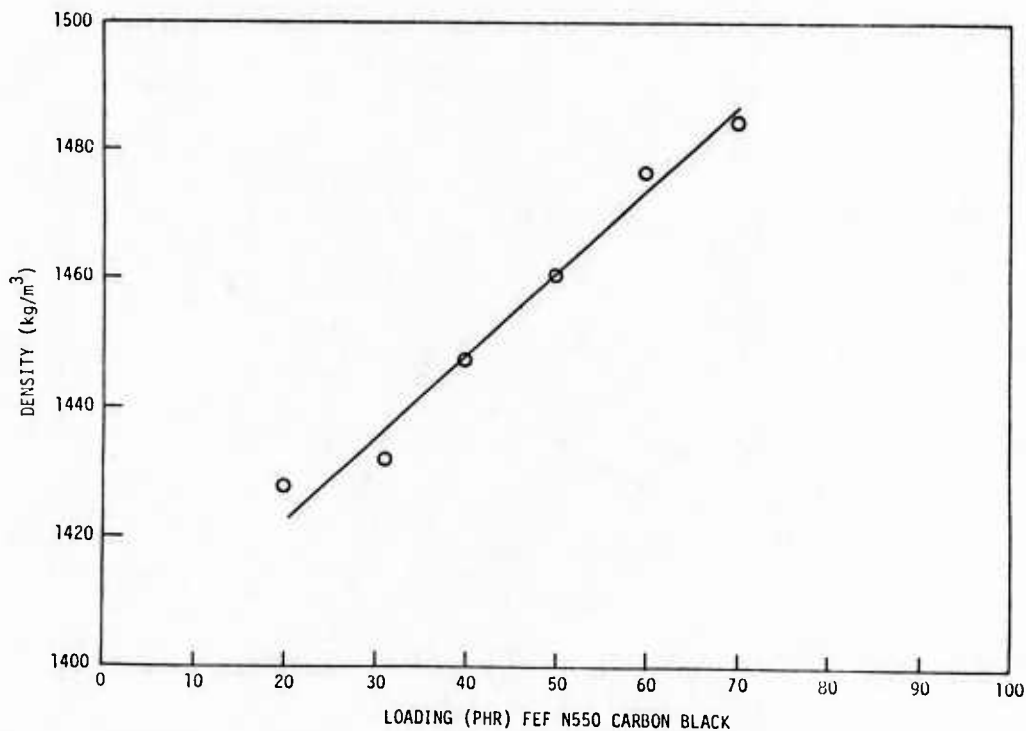
Fig. 6 – Density of Neoprene GRT with varying loading
of FEF N550 carbon black.

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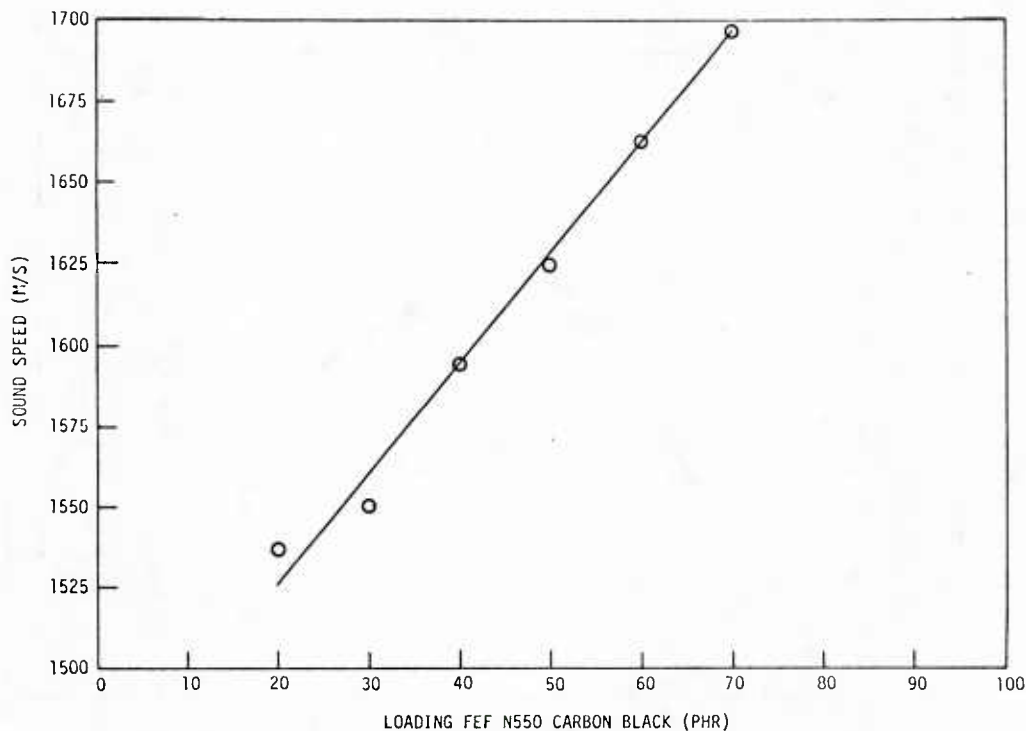
Fig. 7 – Sound speed of Neoprene GRT with varying loading
of FEF N550 carbon black.
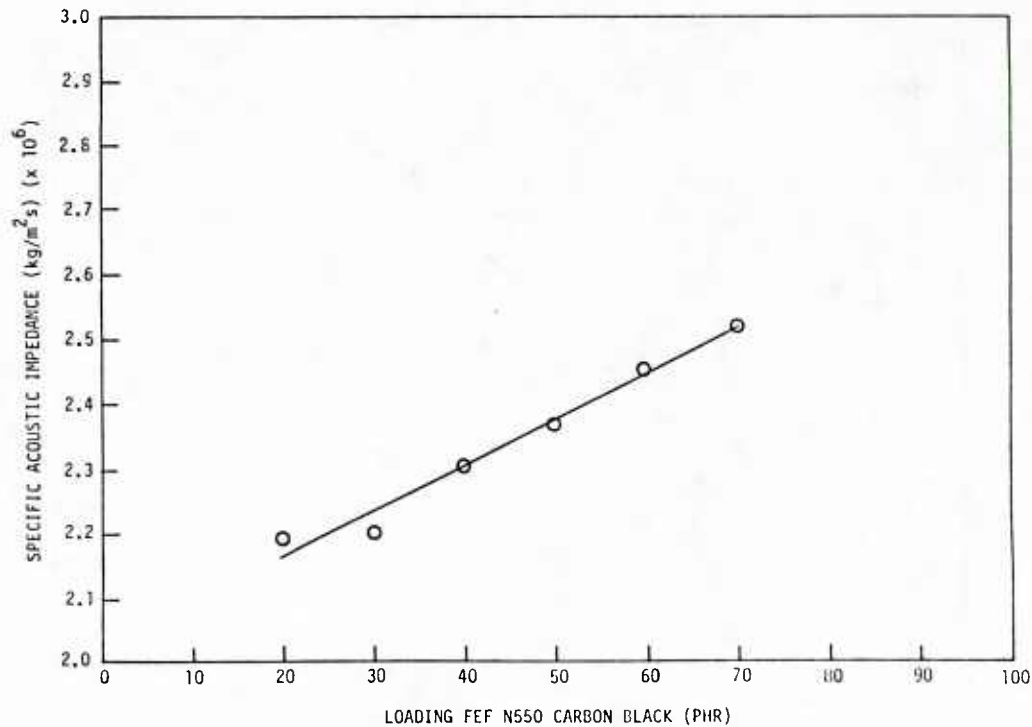
Fig. 8 – Specific acoustic impedance of Neoprene GRT with varying
loading of FEF F550 carbon black.
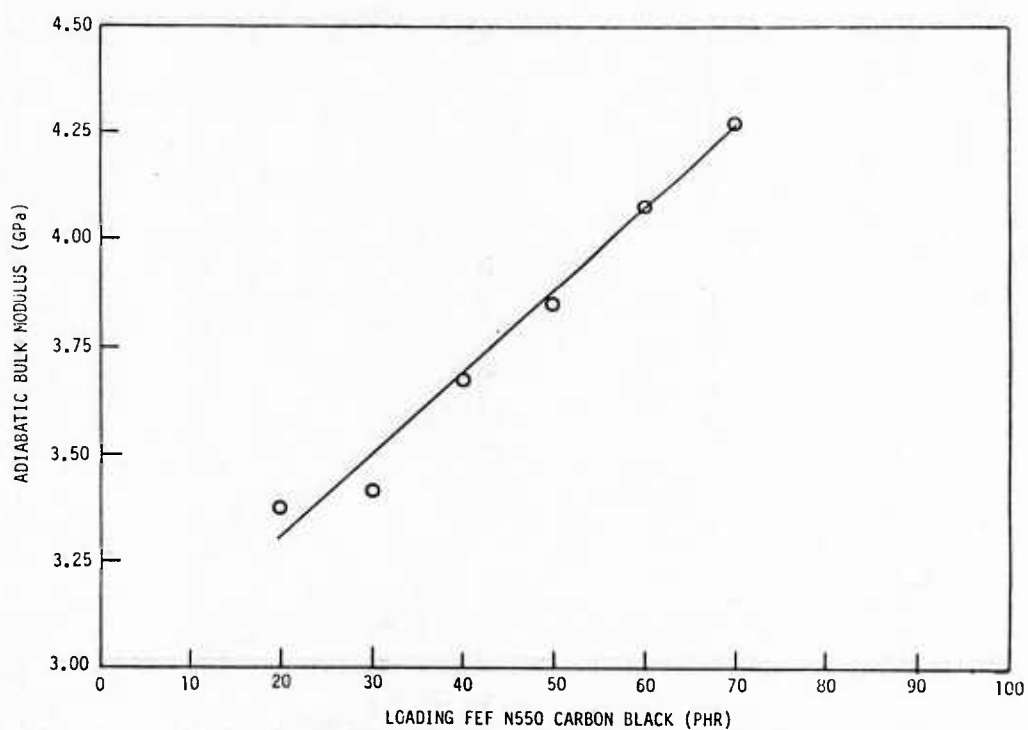
Fig. 9 – Adiabatic bulk modulus of Neoprene GRT with varying
loading of FEF N550 carbon black.
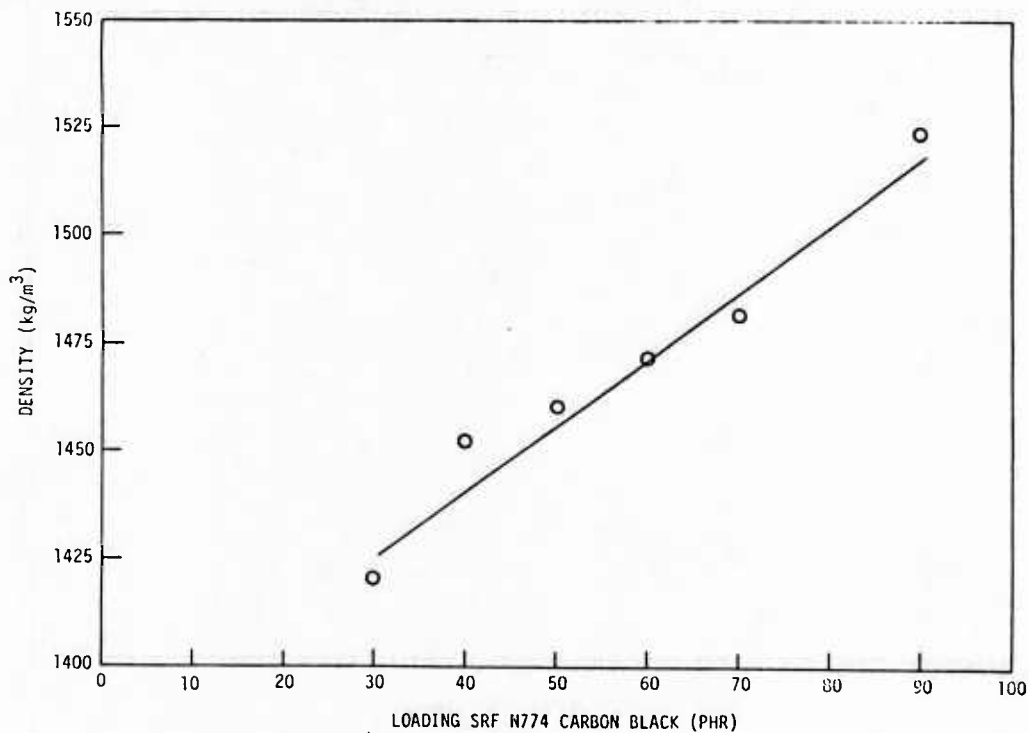
Fig. 10 – Density of Neoprene GRT with varying loading of
SRF N774 carbon black.
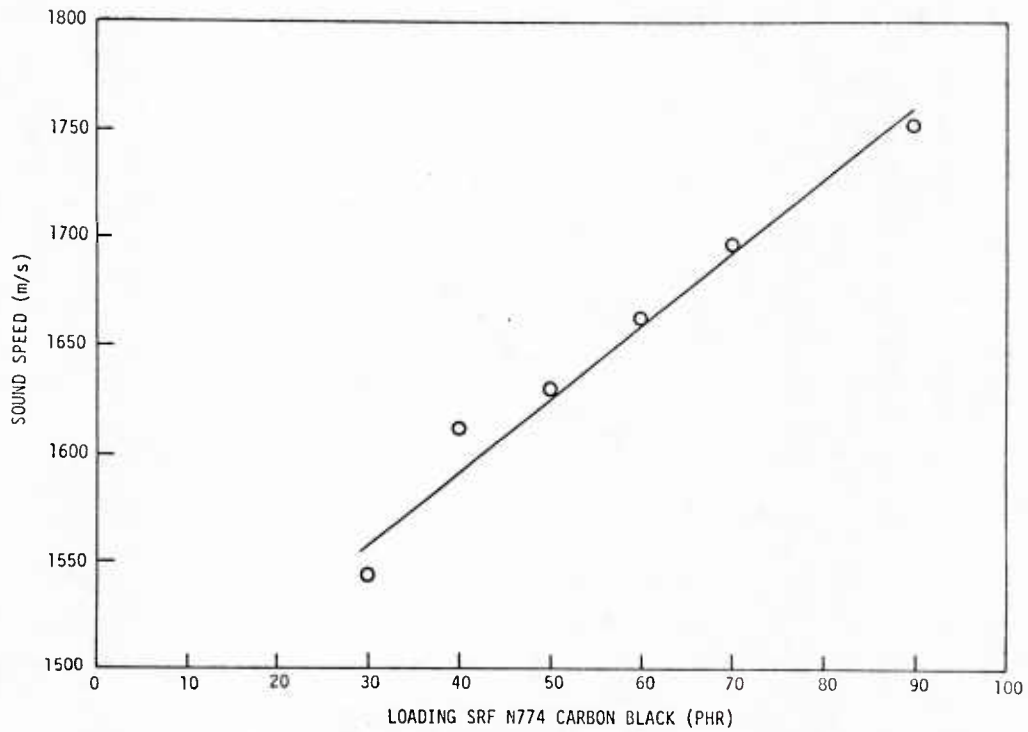
Fig. 11 - Sound speed of Neoprene GRT with varying loading
of SRF N774 carbon black.
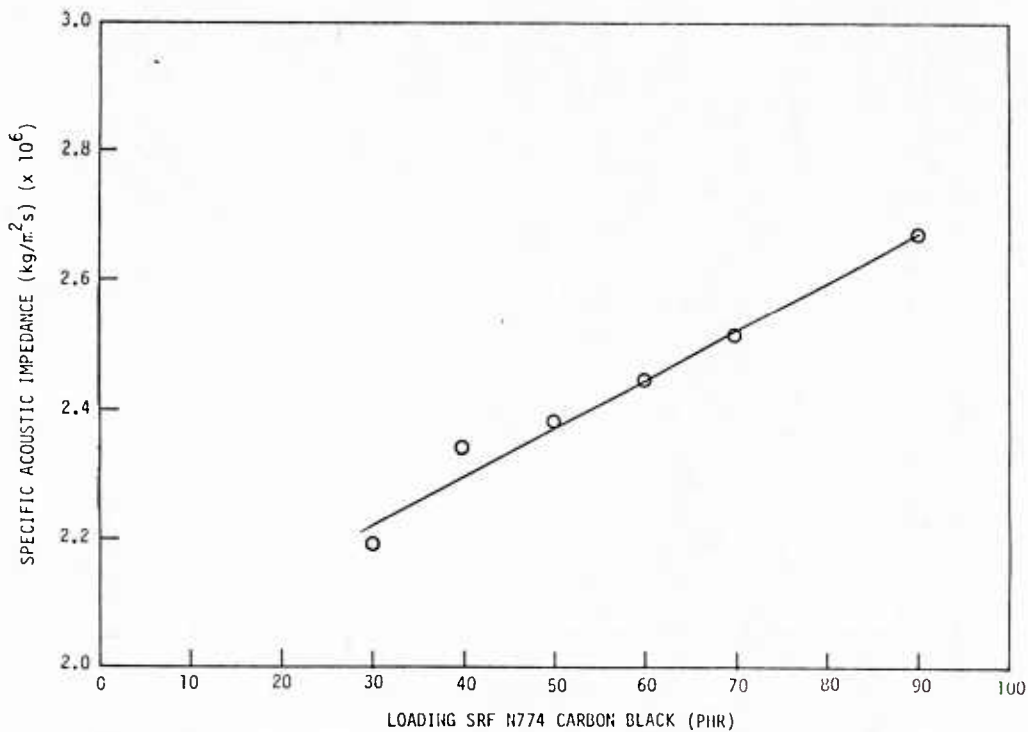
Fig. 12 - Specific acoustic impedance of Neoprene GRT with varying
loading of SRF N774 carbon black.
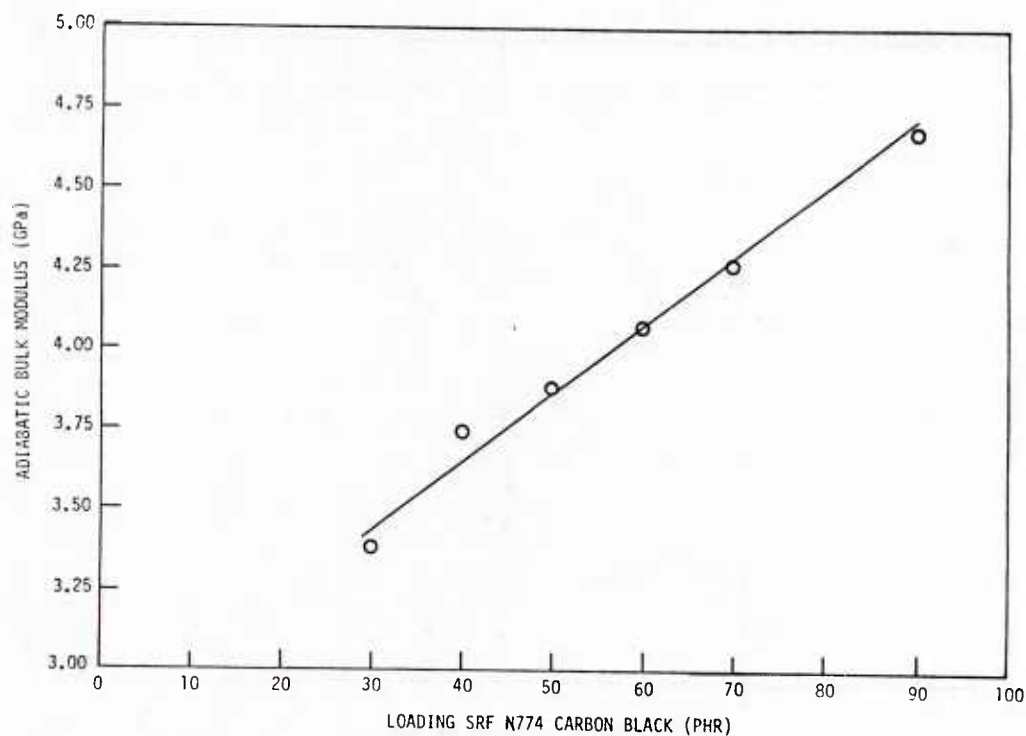
Fig. 13 – Adiabatic bulk modulus of Neoprene GRT with varying
loading of SRF N774 carbon black.
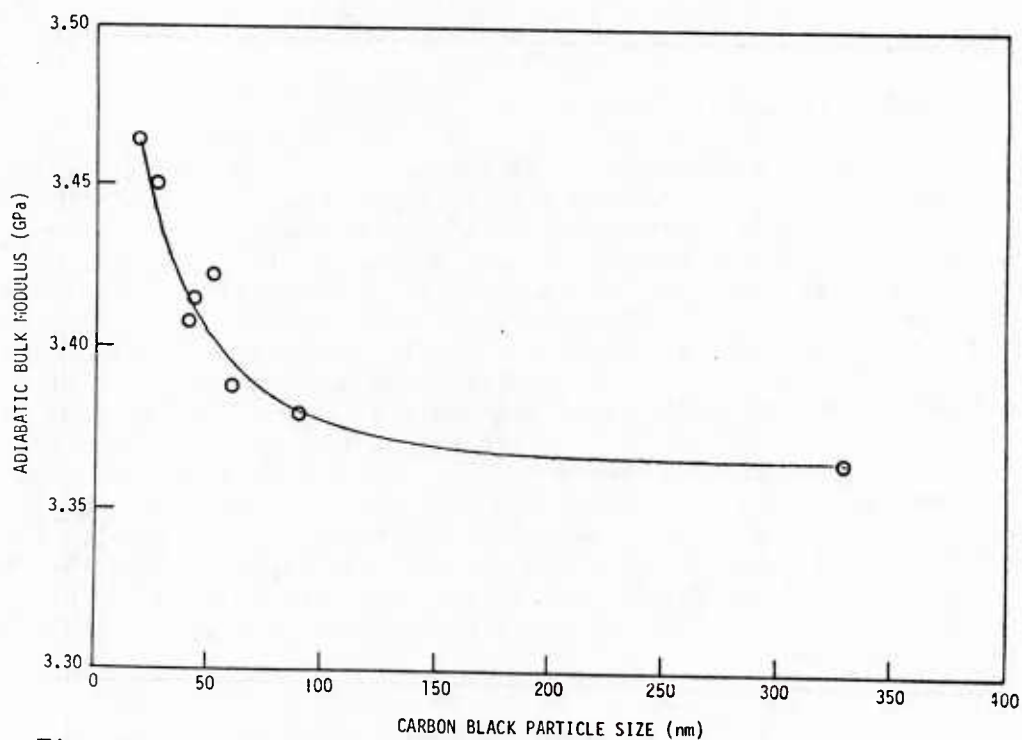
Fig. 14 – Adiabatic bulk modulus of Neoprene GRT with varying
particle size of carbon black (30 phr loading).
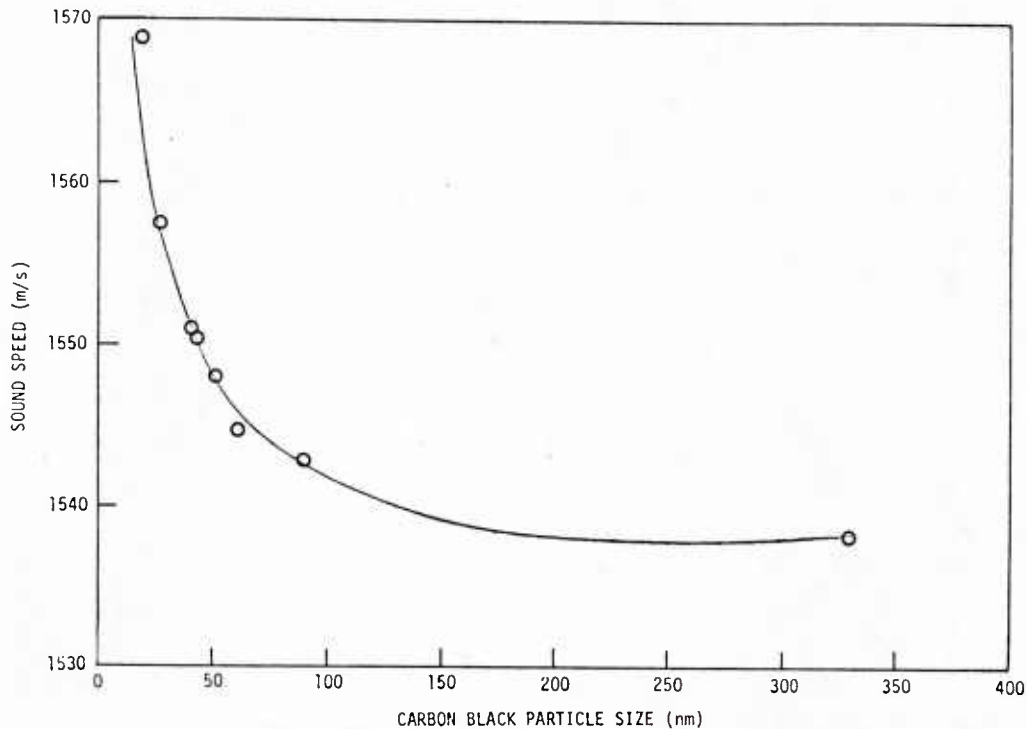
Fig. 15 – Sound speed of Neoprene GRT with varying particle
size of carbon black (30 phr loading).

Dynamic Mechanical Properties

Dynamic mechanical measurements were carried out on some of these Neoprene GRT's to determine their performance over a range of temperatures and frequencies. The Young's storage modulus E' and the mechanical loss tangent were determined by using a resonant string instrument [6]. The Young's storage modulus E' is a measure of the ratio of in-phase stress to strain for a type of tensile relaxation. The loss modulus E" is defined as the stress that is 90 deg out of phase with the strain, divided by the strain. The loss modulus is an indication of the energy dissipated as heat per cycle of sinusoidal deformation when different systems are compared at the same strain amplitude. The ratio of E" to E', the mechanical loss tangent, is a measure of the mechanical hysteresis of the material. All measurements were made at low strain amplitude, and the conclusions from these measurements should not be extrapolated to a high- strain-amplitude environment. The results for a Neoprene GRT with 40 parts of FEF black are shown in Fig. 16 where the Young's storage modulus E' and mechanical loss tangent are plotted at 2 kHz as functions of test temperature. A glass transition temperature of –14°C was identified at that frequency.

The viscoelastic properties of vulcanizates are affected by the addition of carbon-black filler. Certain predictions can be made concerning the effect of increasing carbon black on crosslink density. From molecular considerations, one would anticipate an increase in the storage modulus with an increase in the loading of the black or an increase in crosslink density in the rubbery, transition, and glassy regions. The effect upon the loss tangent is not as clear-cut, particularly in the transition region between the rubbery and glassy regions. In the rubbery region, however, one would expect crosslinking to increase hysteresis; and in the glassy region, little effect might be predicted. Likewise, one would expect increasing carbon-black loading to increase hysteresis in the rubbery region (the entanglement plateau). As the filled elastomer undergoes deformation, the increase in hysteresis in the rubbery region probably arises from molecular friction during deformation of the gum phase, interactions at the carbon-black elastomer interfaces, and interactions between agglomerates of carbon black and occluded elastomers. Work at this laboratory has shown that the effect of increasing the carbon-black loading in the transition region between the rubbery and glassy states is to decrease the loss tangent.
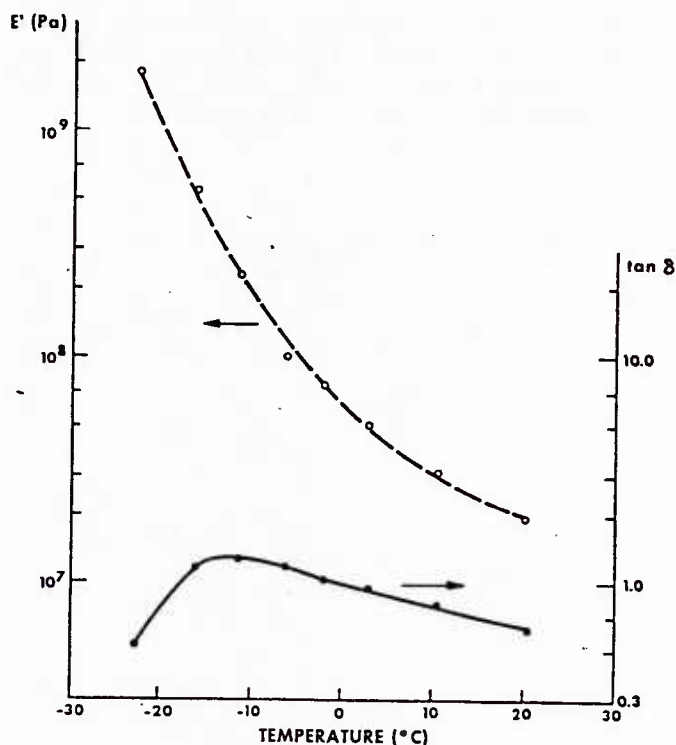
Fig. 16 - Dynamic properties of Neoprene GRT with
40 phr FEF carbon black at 2 kHz.

Hardness

Considerable work has been done to discover the relationships among the moduli of neoprene elastomers with various compounding ingredients. A common method of measuring the shear modulus of elastomers is the Shore hardness test. Shore A hardness, which is related to the shear modulus, is a strong function of the amount of carbon-black loading. This dependency is illustrated in Fig. 17. Increasing the FEF N550 carbon-black loading by 10 phr causes an 8-point increase in hardness. An increase of 10 phr of SRF N774 carbon black causes a 6-point increase in hardness. Hardness is also dependent on the particle size of the carbon black. Figure 18 shows the hardness of several Neoprene GRT samples with 30 phr of carbon black of varying particle size. The hardness decreases as the particle size of the carbon black increases. Therefore, a higher loading of a coarser carbon black is necessary to obtain the same modulus as would be produced by a specified loading of medium carbon black. The effect of changing the cure system of the elastomer from a Pb_3O_4 cure to a ZnO/MgO cure on the hardness is minor.

A word of caution is in order about Shore hardness. The device samples an area of only about 1 mm^2. The devices are notoriously dependent on load and rate-of-load applications. Furthermore, devices drift and require frequent recalibration. Individual readings also drift so that the time-after-load application must be specified. All of these factors mean that some care must be taken before the Shore hardness requirement becomes really meaningful.
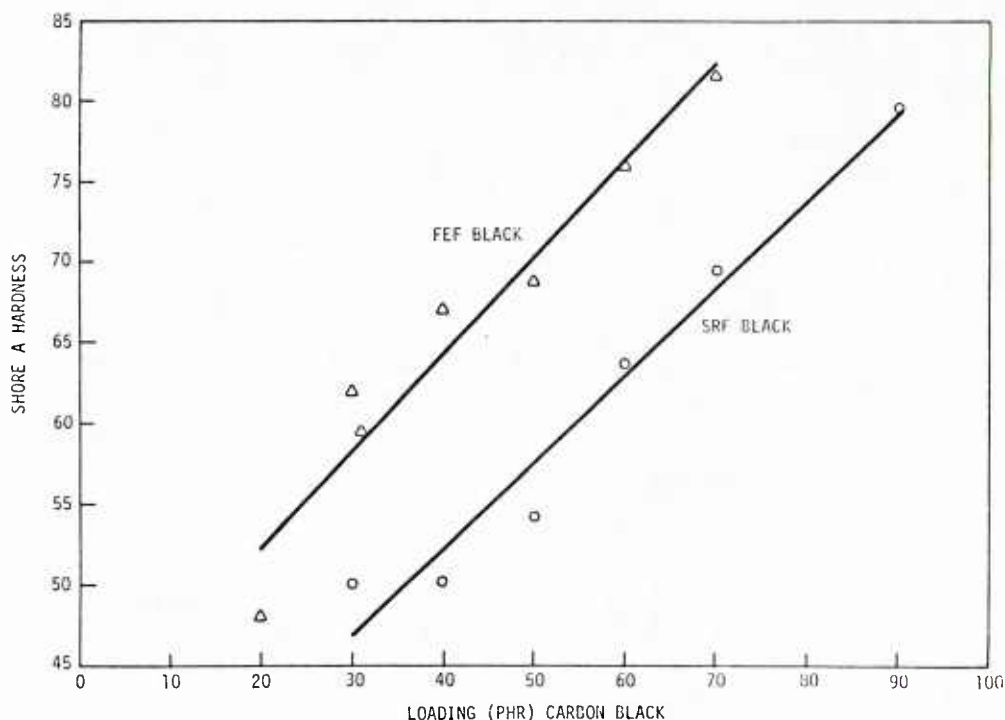
Fig. 17 - Shore A hardness of Neoprene GRT with varying loading
of FEF N550 and SRF N774 carbon black.
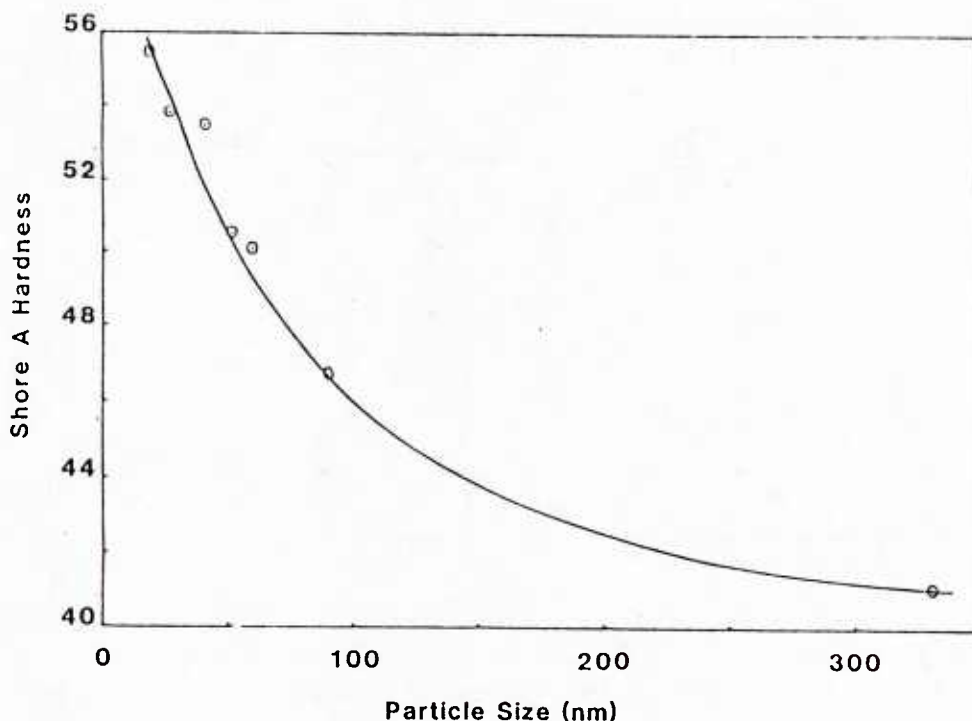
Fig. 18 - Shore A hardness of Neoprene GRT with varying particle size of carbon black (30 phr carbon black).

Tensile and Tear Properties

The tensile properties of an elastomer are greatly dependent on the type and proportion of carbon black in the sample. Figure 19 shows an increase in the tensile modulus at 300% elongation as the amount of FEF N550 carbon black increases. A decrease in ultimate elongation is shown in Fig. 19. The tensile strength changes little with increasing carbon-black content over the range studied. These same trends in tensile properties were observed for increases in the proportion of SRF N774 carbon black (see Fig. 20). For samples formulated with the same loading (30 phr) of carbon black, the tensile strength and the tensile modulus at 300% elongation decrease as the particle size of carbon black increases. This is shown in Fig. 21. The ultimate elongation of the elastomer increases as the carbon- black particle size increases. The tear strength of Neoprene GRT with 31 parts of FEF black is 85 kN/m. When the black content is raised to 40 parts, the tear strength increases to 96 kN/m.
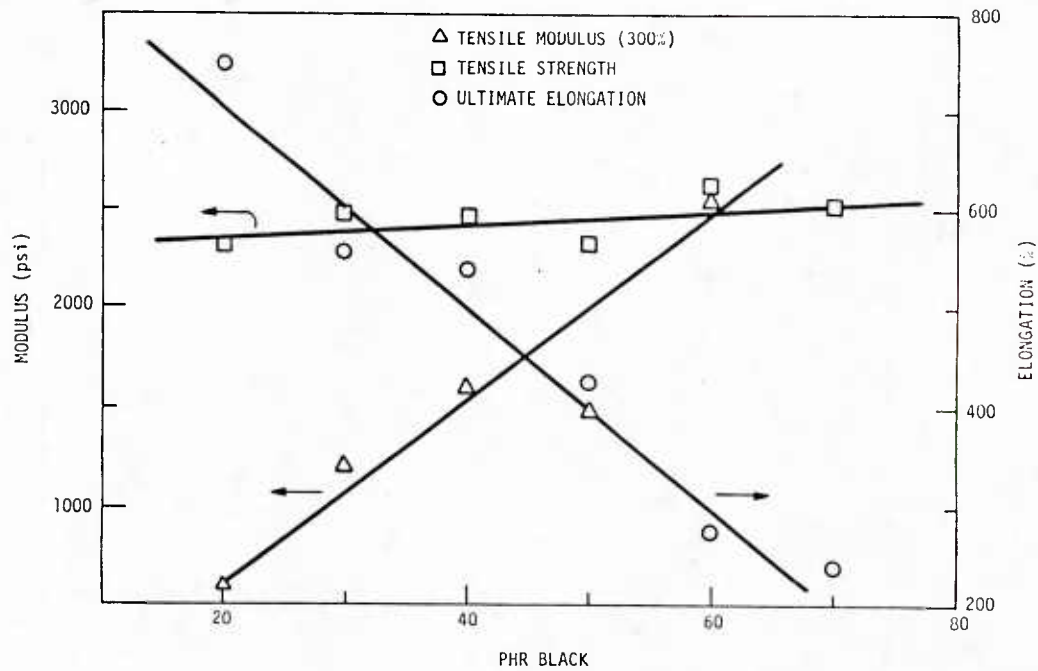
Fig. 19 - Tensile properties of Neoprene GRT with varying
loading of FEF N550 carbon black.
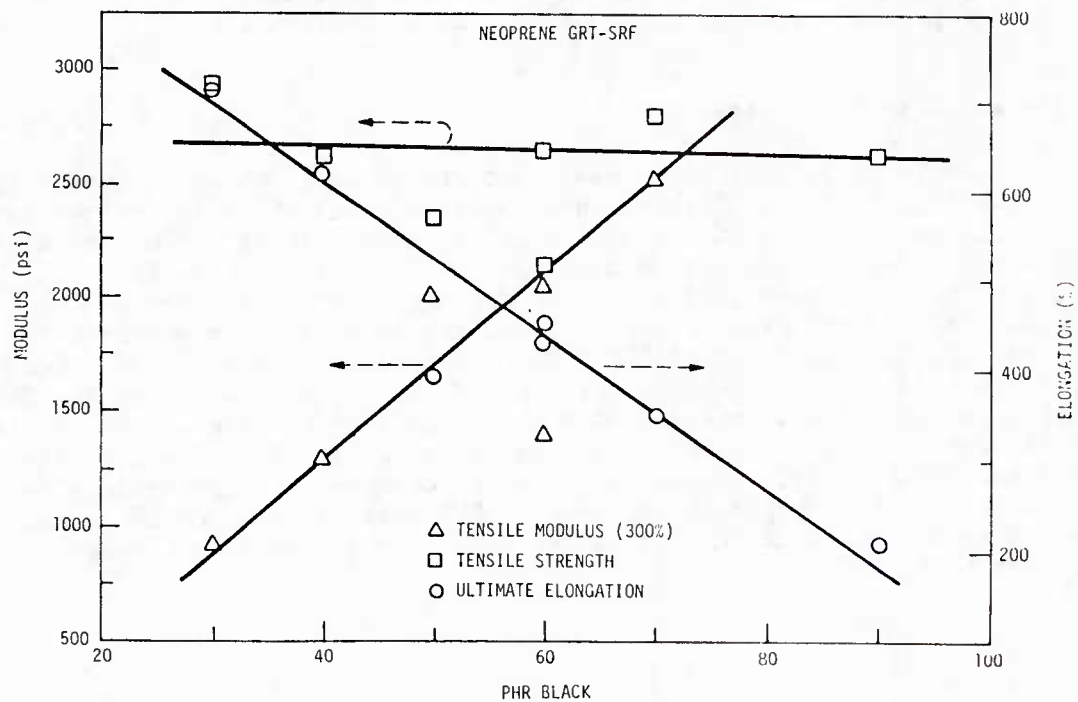
Fig. 20 - Tensile properties of Neoprene GRT with varying
loading of SRF N774 carbon black.
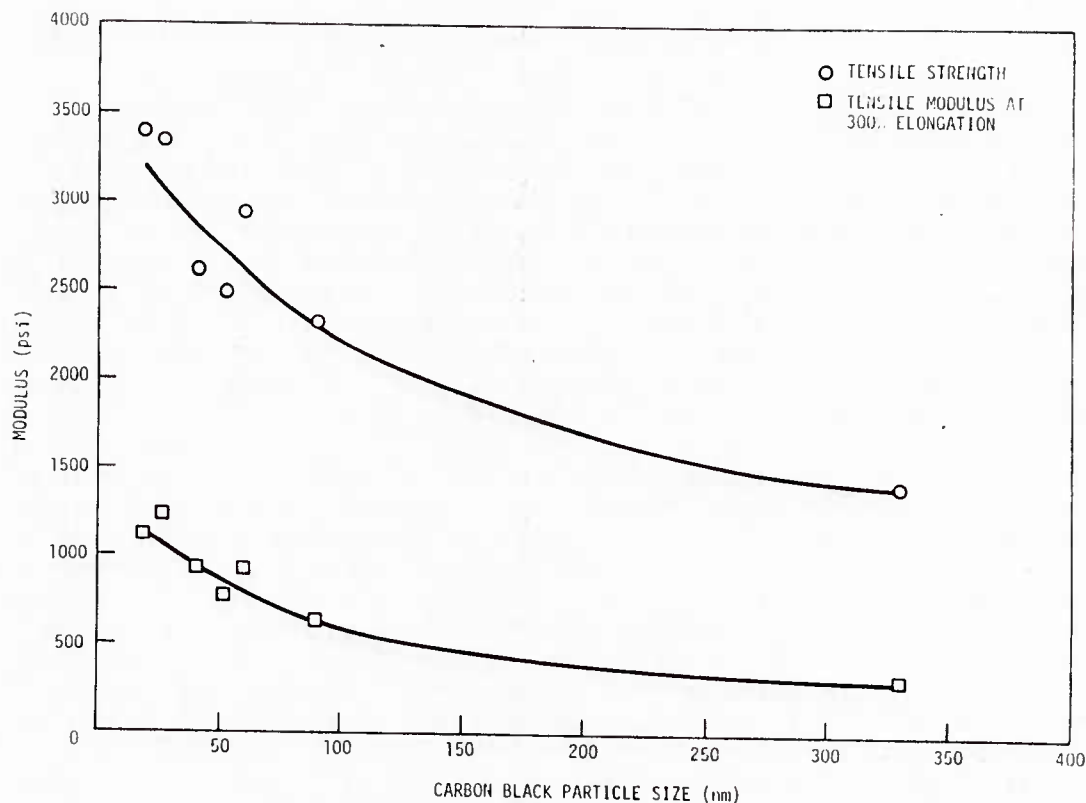
Fig. 21 - Tensile properties of Neoprene GRT with varying
particle size of carbon black (30 phr loading).

Electrical Resistivity

A study was conducted to determine the effect of formulation variations on the electrical resistivity. Figure 22 shows the volume resistivity of Neoprene GRT as a function of the concentration of FEF N550 and SRF N774 carbon black. As the FEF carbon-black content exceeds 40 phr, the resistivity decreases very rapidly. A definite disadvantage is evident when formulating the rubber in the concentration region corresponding to the rapid decrease in resistivity. Small errors by the rubber manufacturer in proportion or homogeneity would cause a drastic change in resistivity. The region of rapid decrease in resistivity falls at a much higher carbon content for SRF-filled neoprenes. This observation is of little value for an elastomer designer because a higher SRF content is required to achieve a given modulus. The volume electrical resistivity was measured on test samples of rubber manufacturers' actual production runs of a GRT formulation having an FEF concentration near the transition region (i.e., 40 parts). Variations from 10^{11} to 10^{7} $\Omega \cdot cm$ were observed. Because of this inconsistency in the materials, the carbon-black concentration region corresponding to the rapid change in resistivity should be avoided when formulating rubber.

To study the dependency of resistivity on carbon-black particle size, the volume electrical resistivity was measured for a series of Neoprene GRT samples that contained the same loading (30 phr) of different types of black. The results, shown in Fig. 23, show that after an initial increase with carbon-black particle size, the electrical resistivity reaches a plateau for a given loading of black. Further increase of carbon-black particle size does not cause any further increase in resisitivity. The difference in electrical resistivity between neoprenes filled with FEF or SRF black having average particle sizes of 41 and 62 nm, respectively, is not seen in this figure because a loading of 30 phr of these blacks gives electrical resistivities on the plateau of Fig. 22.

The effect that seawater exposure has on the electrical resistivity of the Neoprene GRT formulations was measured. Multiple runs were necessary due to large experimental scatter. Figure 24 shows an initial increase in electrical resistivity of a Neoprene GRT with 40 parts of FEF black exposed to seawater. The decrease in resisitivity after 100 hours at 60°C has been observed repeatedly but is yet unexplained. The significant question is, "Is there some process being accelerated by the elevated temperature that does not occur at the environmental temperatures?" Furthermore, if the process does occur at environmental temperatures, how long will it be before resistivity starts to decrease and how low will it go? Despite these questions, it can be stated that even under the harshest conditions, the electrical resistivity of this neoprene formulation decreases only by a factor of 10 after 1000 h. This study was repeated on two other Neoprene GRT's, one of which was lead-oxide cured and filled with silica (25 parts) and N550 black (15 parts); the other was cured with a ZnO/MgO system and filled with silica (10 parts) and N550 black (30 parts). In Fig. 25 the volume resistivity of the lead-oxide-cured Neoprene GRT decreased after 10 h of exposure at 60°C to a plateau of 10^9 Ω·cm at 200 h. Samples exposed at 25°C decreased after 30 h of exposure to a plateau of 10^{10} Ω·cm at 200 h.

Figure 26 shows that a 100-h induction period is also observed for a ZnO/MgO-cured Neoprene GRT filled with silica and carbon black. However, the decrease in resistivity after that time is far greater than for the Neoprene GRT cured with Pb_3O_4 and filled with FEF black.
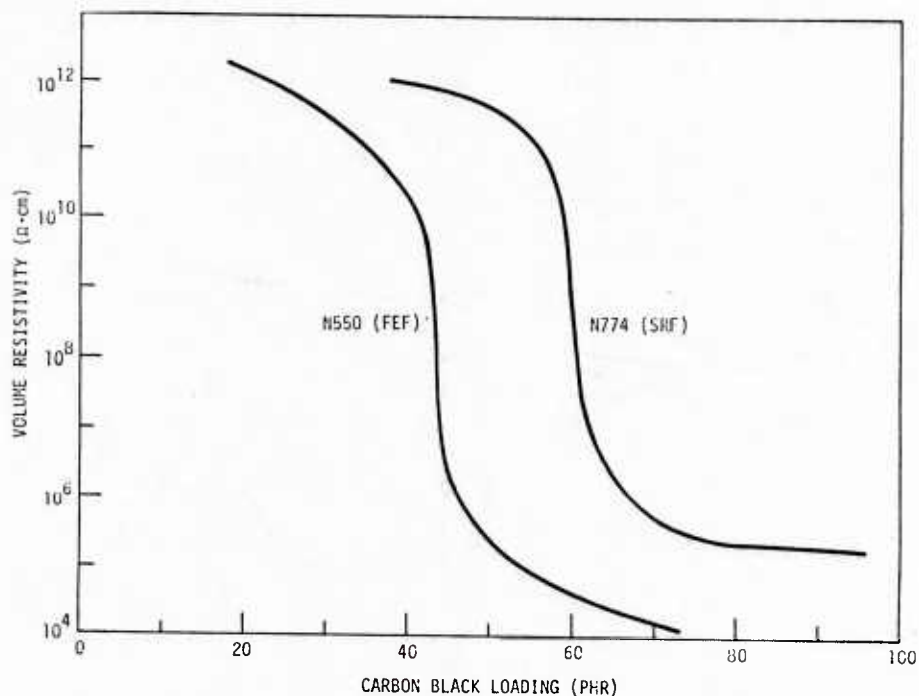
Fig. 22 - Volume electrical resistivity of Neoprene GRT
filled with FEF N550 and SRF N774 carbon blacks.
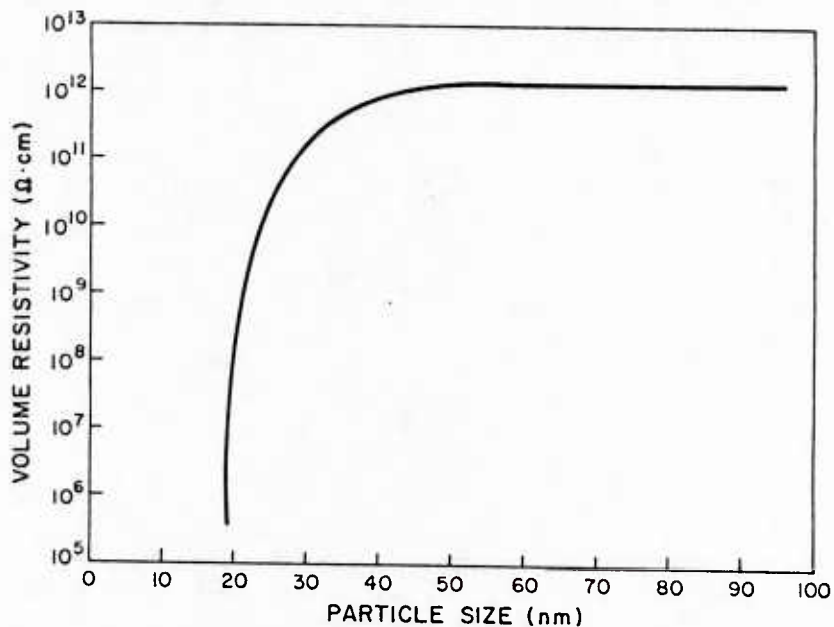
Fig. 23 - Volume electrical resistivity of Neoprene GRT with varying
particle size of carbon black (30 phr carbon black).
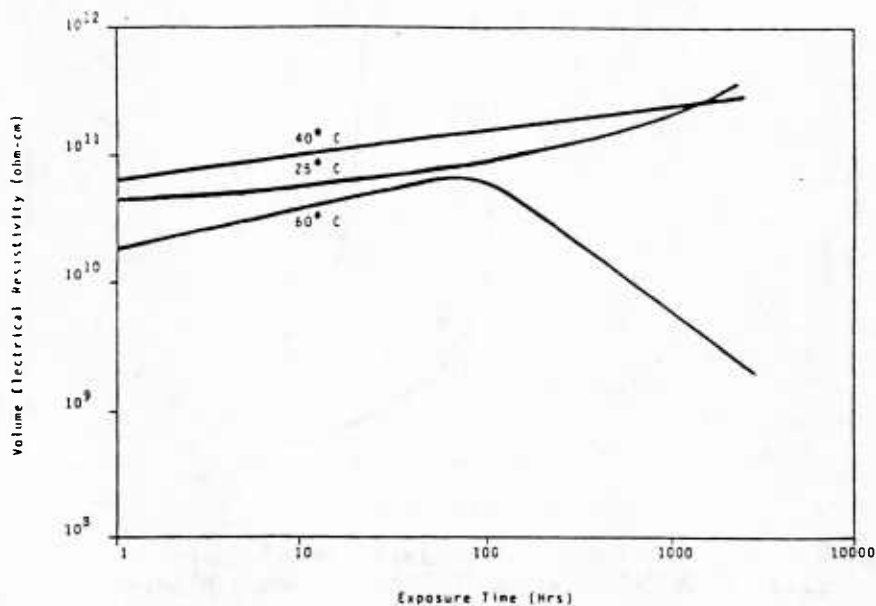
Fig. 24 - Volume electrical resistivity of Neoprene 5109 exposed to seawater.
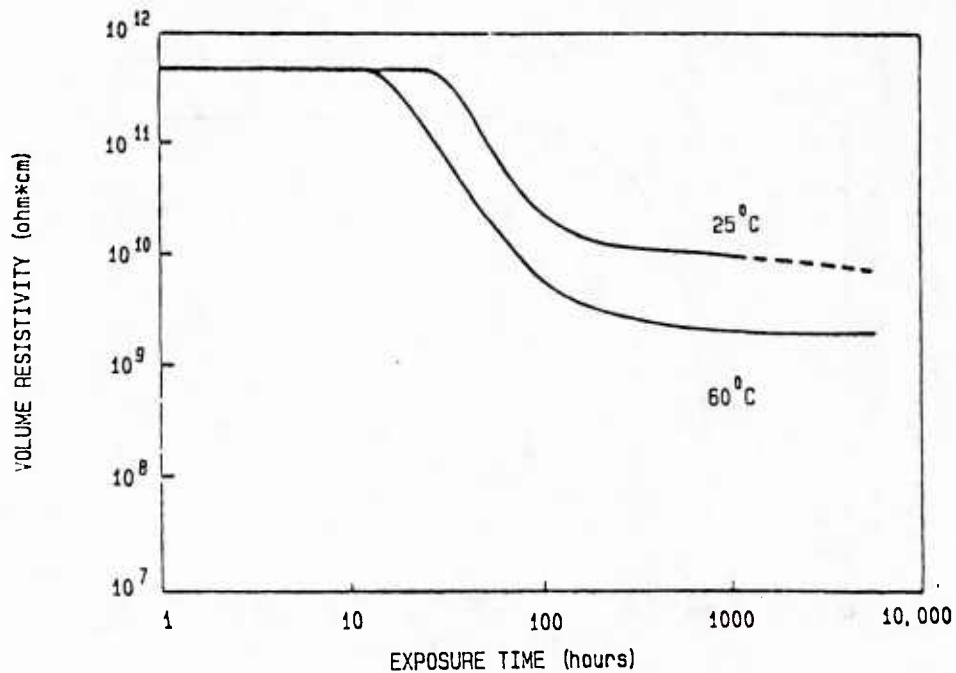
Fig. 25 - Seawater-exposed volume electrical resistivity of a Neoprene GRT cured with red lead and filled with silica (25 parts) and FEF N550 black (15 parts).
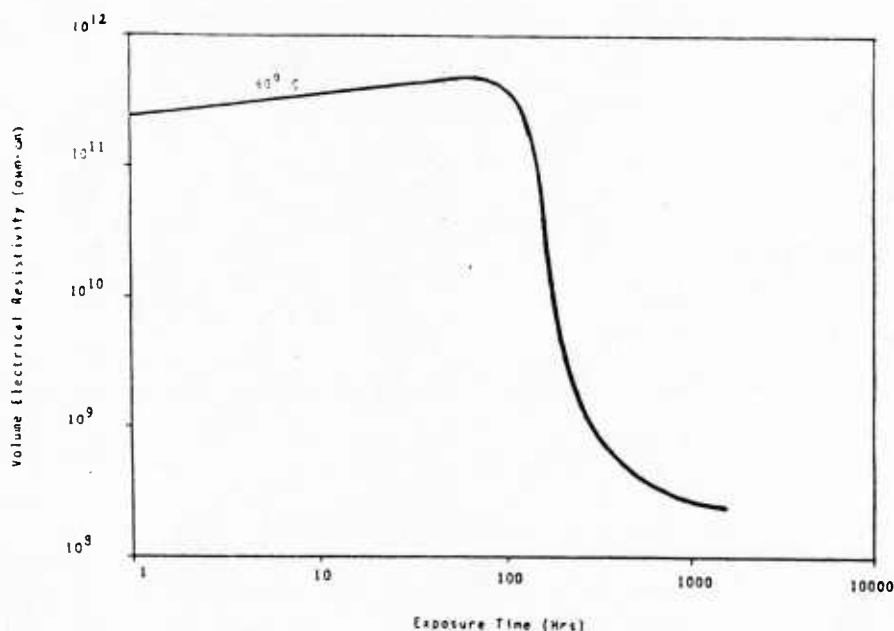
Fig. 26 – Seawater-exposed volume electrical resistivity of a
ZnO/MgO-cured Neoprene GRT filled with FEF N550 black
(30 parts) and silica (10 parts).

Bondability

The elastomer-to-metal bond is very important if it provides the primary
seal of the transducer. The bond must not fail when exposed to environmental
stresses. The strength of an elastomer-to-metal bond was measured as a
function of both the elastomer composition and the adhesive systems and has
been reported elsewhere by R. Y. Ting [7]. The technique employed for this
test was the ASTM-D429-81 Method C [8] using a 45-deg conical-button specimen
replicated eight times.

Eight commercial adhesive systems were examined, both for initial bond
strength and for bond strength after aging for 200 h in 50°C salt water and in
distilled water. These results are summarized in Table 1.

All of the failures in the control samples occurred entirely by rubber
tear except for the Chemlok 205/234B in which some failure was at the
rubber/adhesive interface. In only two cases did any significant degradation
in bond strength occur with exposure to distilled water. Marginal decreases
in bond strength occurred in three cases with exposure to seawater. Coupled
with this reduction it was observed that the fracture surface showed
increasing adhesive/metal interface failure as a result of saltwater exposure.

Table 1 – Effect of 200-h Wet-Aging at 50°C on the Bond-Strength
Failure Load of Conical-Button Specimens*

ADHESIVE	CONTROL (kg)	DISTILLED WATER (kg)	3.5% SALT WATER (kg)
Chemlok 252	353	356	351
Chemlok 205/220	339	347	350
Thixon P6-1/OSN-2	336	346	350
Thixon D21243/508	329	328	295
Chemlok 205/236A	321	285	307
Thixon OSN-2	314	327	310
Chemlok 205/234B	310	271	302

*Room temperature – dry

A separate peel test was performed in seawater in which a weight of 30 lbs was suspended from the elastomer bonded to a mild steel substrate. The Chemlok 205/234B bond showed no sign of bond degradation after 6 months. In addition to these, extensive work has been done to elucidate the failure modes of adhesives used with Neoprene GRT formulations (FY85/FY86 STRIP data).

Water Permeation

Many transducer failures have been attributed to ingression of water into the transducer which results in corrosion and change in electrical resistivity. Water may enter the transducer through a bonding failure between the case and the elastomer, or the water may permeate through the elastomer itself. It is therefore important to know the water permeation rate of the elastomer that was used. The water permeability of elastomer membranes was measured as a function of several compositional parameters. This research yielded a number of important results. The permeation constant for a wide variety of Neoprene GRT materials has been determined to be near 20 $ng\cdot cm/cm^2\cdot h\cdot Torr$ at 25°C. This value is significantly lower than published values for other neoprene formulations [9]. Both Pb_3O_4- and ZnO/MgO-cured Neoprene GRT give permeability constants of this magnitude. This seems to suggest that neoprene-rubber permeability constants are independent of the type of curing agent. The permeability constant is, however, related to the proportion of carbon black in the rubber. An increase from 40-phr FEF carbon black to 60-phr FEF black causes the permeability constant to decrease from 21 to 18 $ng\cdot cm/cm^2\cdot h\cdot Torr$ (see Fig. 27). A similar effect is seen in Fig. 28 when SRF N774 black is substituted for FEF N550 black.
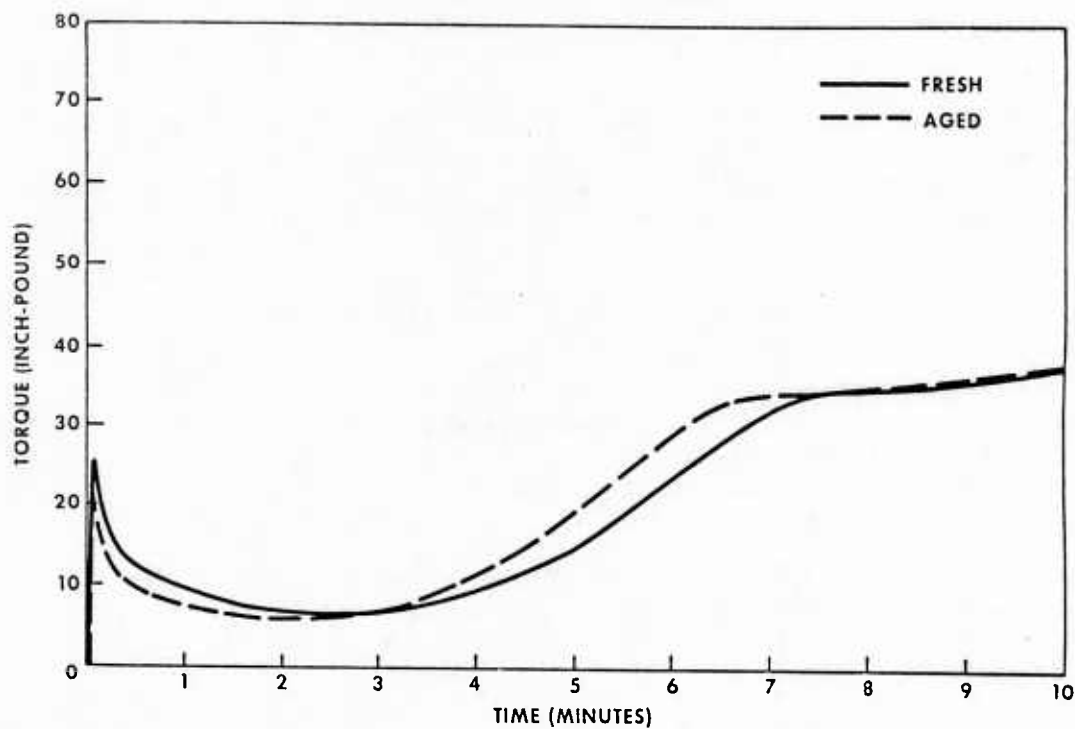
Fig. 27 – Water permeation (at 25°C) of Neoprene GRT with varying loading of FEF carbon black.
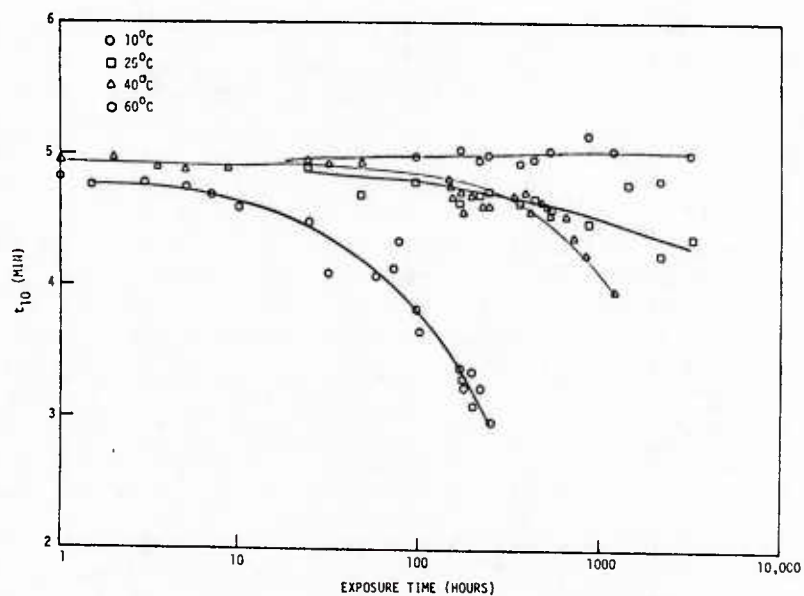
Fig. 28 – Water permeation (at 25°C) of Neoprene GRT with varying loading of SRF carbon black.

The effect of temperature on the permeability constant of elastomers is of great importance because of the interest in the application of accelerated life testing for sonar transducers. It has long been observed empirically that the acceleration of a process with temperature follows the rate law:

$$k = A \cdot \exp[-(E_a/R)(1/T)], \qquad (1)$$

where k = the rate constant,
    A = a constant called the frequency factor,
    E_a = the activation energy,
    R = the universal gas constant, and
    T = the absolute temperature.

This equation was first stated by Arrhenius and is commonly called the Arrhenius equation. Subsequent theoretical development led to equations similar in form to Eq. (1). Taking the natural log of Eq. (1) gives:

$$\ln k = \ln A - (E_a/R)(1/T). \qquad (2)$$

The equation in this form shows clearly why a plot $\ln k$ versus $1/T$ gives the activation energy from the slope of the line.

The magnitude of the Arrhenius activation energy for water permeation has been used in contradictory ways to explain permeation phenomena. Specifically, the low values measured for the activation energy (compared with most chemical processes) have been attributed to both the existence of extensive convective diffusion in one case [10] and to the significance of surface effects vs. bulk diffusion in another case [11].

Studies were designed and conducted to test these two concepts to better interpret permeability data. In the first case [10], the lower apparent activation energy for permeation was ascribed to the convective diffusion that was caused by the silica content of the tested rubber. This explanation relied on the fact that the activation energy for a pure convective diffusion is less than that for a pure activated diffusion (E_a for a pure convective process may be less even than zero--i.e., a temperature increase may slow down convective diffusion). To study the validity of this concept in interpreting the permeability data of elastomers, a series of Pb_3O_4-cured Neoprene GRT's

was obtained that contained a constant loading of filler (to assure nearly equal permeability at ambient temperatures) but varied only in relative proportion of carbon black and silica. Loading ranged from 40 parts FEF black with no silica to 7 parts FEF black and 33 parts silica. These data are given in Table 2. The permeability constants at 25°C for all of these samples (all of which contain 40 parts of filler) are virtually identical. The calculated activation energy reveals no significant trend. Since this series changes only in relative proportion of silica, which should increase the relative proportion of the permeability that is convective, the constancy of the activation energies indicates that for a neoprene rubber the magnitude of activation energy does not depend on the nature of the diffusion process.

Table 2 - Effect of Silica on the Activation Energy of Permeation

FILLER	PERMEABILITY CONSTANT $(ng \cdot cm/cm^2 \cdot h \cdot Torr)$				ACTIVATION ENERGY (kcal/mole)
	25°	40°	60°	75°	
40 phr FEF black	27	36	62	88	9.8
30 phr FEF, 10 phr Silica	25	37	54	78	9.4
23 phr FEF, 17 phr Silica	24	33	60	–	10.6
15 phr FEF, 25 phr Silica	24	47	61	–	10.2
7 phr FEF, 33 phr Silica	25	39	62	–	10.2

A similar study was conducted on samples of Neoprene GRT cured with ZnO/MgO with variations in filler loading as above. The Arrhenius activation energy in all cases was determined to fall between 8.6 and 12.0 kcal/mole.

In a study of the effect of surface phenomena on water permeation, membranes of a Pb_3O_4-cured Neoprene GRT were prepared that varied only in thickness. The process of water dissolving into the rubber at the water-vapor interface has a negative activation energy. Diffusion through the bulk of the material has a positive activation energy. Since permeability is the product of these processes, its activation energy is the sum of their activation energies. As the test membranes get thinner, however, the contribution from bulk diffusion may decrease and thus lower the overall activation energy. Determination of the permeation activation energy over a range of specimen thicknesses thus provides a measure of the effect of surface phenomena as well as of the validity of permeability measurements. Data from this test are given in Table 3

Table 3 - Effect of Specimen Thickness on the Activation Energy for Permeability of a Neoprene

THICKNESS (mm)	PERMEABILITY CONSTANT $(ng \cdot cm/cm^2 \cdot h \cdot Torr)$				ACTIVATION ENERGY (kcal/mole)
	25°	40°	60°	75°	
0.1	23	27	47	56	8.0
0.4	22	28	37	79	9.8
0.8	21	28	46	–	8.8
1.5	22	39	48	77	9.6

Again, no trends are obvious in the activation energy. It is obvious that over the range of thicknesses studied, the effects of surface phenomena are unimportant. It should be pointed out, however, that the thinnest of the membrane thicknesses studied here are significantly greater than those from which conclusions have been drawn in the literature [11]. However, they are significantly thinner than any that might be encountered in acoustical use. Consequently, the constancy of the observed permeability constants does much to demonstrate the validity of the measurements and the degree of acceleration that would be produced by a given temperature rise.

Compatibility

Regardless of whether an elastomer used in underwater sonar equipment is clamped or is bonded to the device, it must be resistant to both water and any acoustic fill fluid. The degradation of the elastomer exposed to a fluid can be approximated by making a few assumptions. The first is that the rate-determining step in the degradation of an elastomer is the diffusion of the fluid into the matrix. The second is that a change in the physical properties of the elastomer is approximated by a change in mass or thickness. The third is that an increase in temperature will accelerate the diffusion process. The resistance of an elastomer to the diffusion of a fluid as a function of formulation variations was measured by monitoring the volume and weight changes of a variety of elastomers submerged in the fluid. The following observations have been made for elastomers submerged in fresh and salt waters:

- Typical ZnO/MgO-cured neoprenes absorb water eight times as rapidly as lead-oxide-cured neoprenes.

- Inclusion of silica fillers in ZnO/MgO-cured neoprenes changes the rate of water absorption only slightly but allows salt ions to migrate through the rubber [12].

- Finer carbon blacks promoted a somewhat greater rate of water absorption.

- The effect of varying concentrations of carbon black on the water absorption is minor.

A lead-oxide-cured Neoprene GRT was exposed to castor oil (Baker dB grade), polyalkyleneglycol (PAG) (UCON LB135Y3), and silicone oil (Dow Corning 100.100) at 25, 40, 60, 75, and 90°C for up to 1000 h. Figure 29 shows a typical example of the fractional weight change that occurs in the elastomer with time. A fractional weight change of 0.10 after 1000 h was observed for this Neoprene GRT in castor oil at 90°C. A similar exposure to PAG (Fig. 29) gave a fractional weight change of 0.17. Exposure to silicone oil produced a fractional weight change of −0.016. These data show that this formulation is moderate in its compatibility with castor oil and PAG and excellent with silicone oil. The Arrhenius plot in Fig. 30, of the rubber exposed to PAG, gives a reasonably straight line with an activation energy of 8.2 kcal/mole. That is, the compatibility process is predictably accelerated by an increase in temperature.
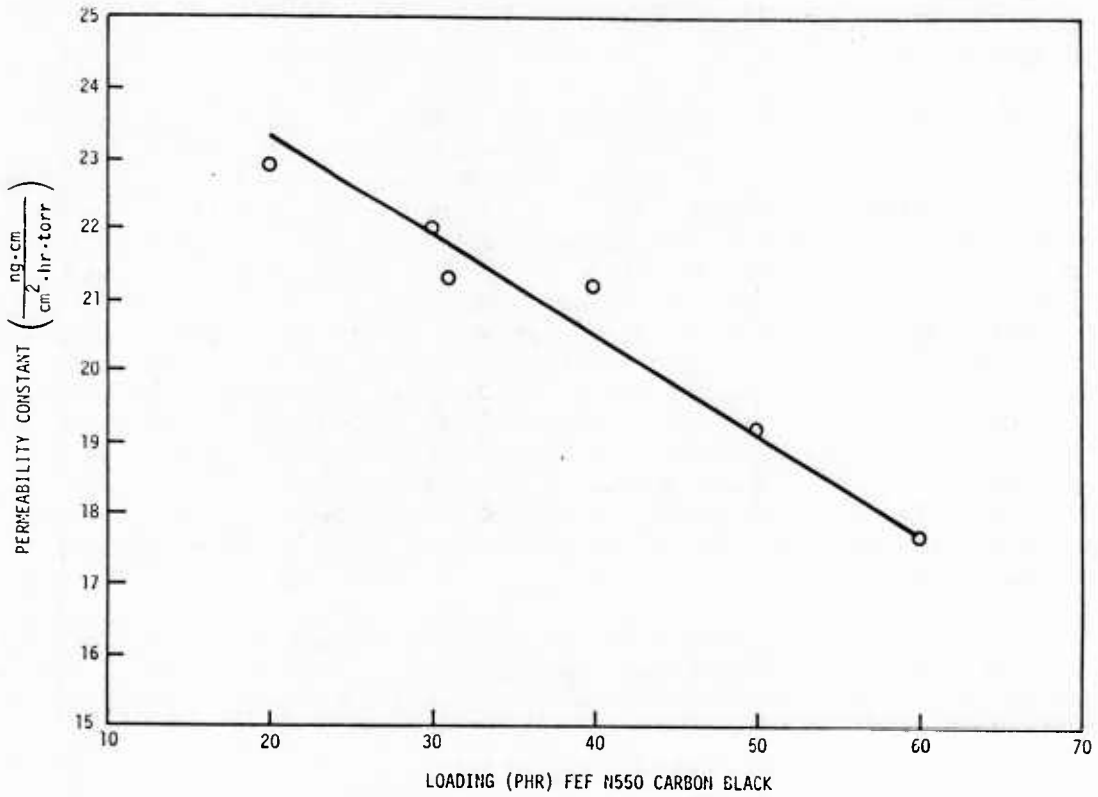
Fig. 29 - Fractional change in mass of lead-oxide-cured Neoprene GRT exposed to PAG.
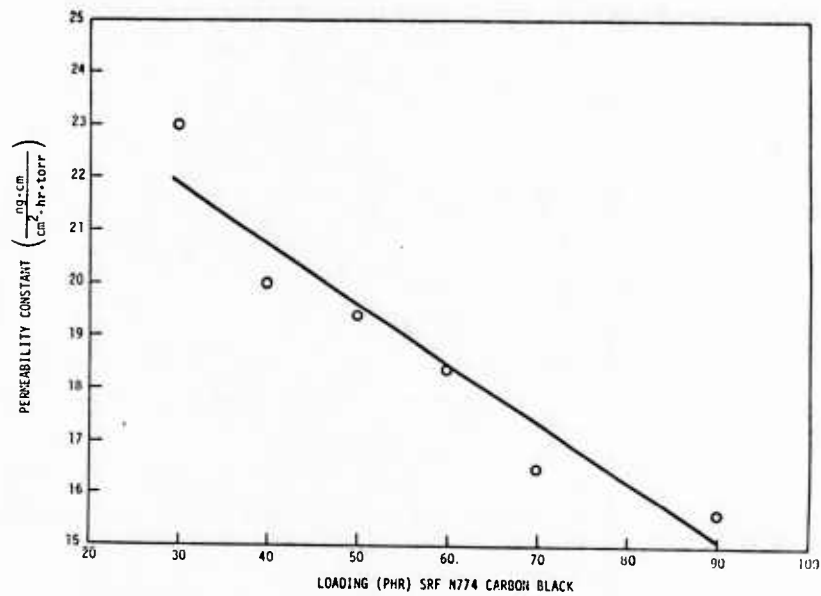
Fig. 30 - Arrhenius plot of the rate of change is mass of lead-oxide-cured Neoprene GRT in PAG.

Compression Set

Compression set is one measure of the ability of rubber compounds to retain elastic properties after prolonged compression at a specified deflection. The compression set improves when the ability of the elastomer to rebound to original dimensions after being compressed improves. Because compression is a measure of the difference between the thickness of the sample before and after compression divided by the deflection thickness, an improvement in compression set is expressed by a smaller value. The compression set may also be used as a measure of the cure state (crosslinking density) of the elastomer. The compression set of one red- lead-cured Neoprene GRT (cured for 45 min at 155°C) is 75%. Figure 31 shows the results of a study of the compression set of this same formulation as a function of cure time and cure temperature. At each individual temperature the compression set improves (crosslinking density increases) as the cure time is increased. Figure 32 is an Arrhenius plot of compression-set data taken over a range of temperatures. The slope of the line gives an activation energy of 21.6 kcal/mole.

The compression set of this rubber was also studied as a function of the total time compressed and the temperature to which the compressed sample was exposed. Figure 33 shows that the compression set increases as the exposure temperature increases.
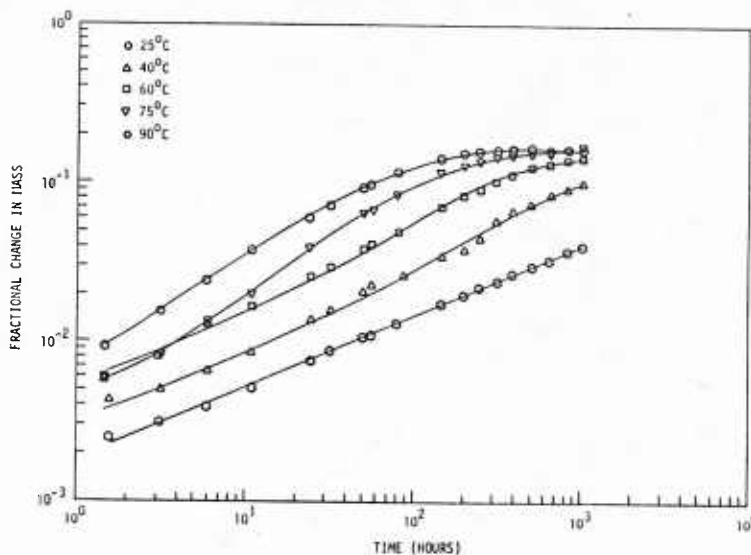
Fig. 31 - Effect of exposure time and temperature on compression set of red-lead-cured Neoprene GRT.
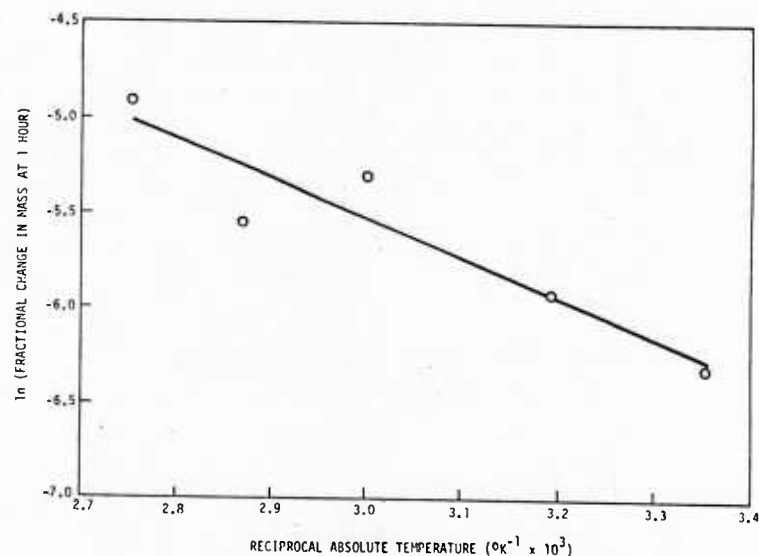
Fig. 32 - Arrhenius plot of the effect of temperature on the rate of improvement of the compression set of red-lead-cured Neoprene GRT.
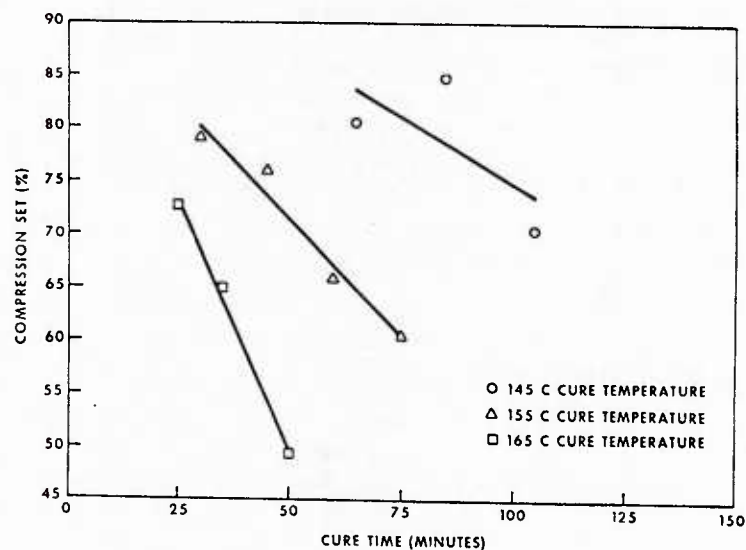
Fig. 33 - Effect of compression time on the compression set of red-lead-cured Neoprene GRT.

Cure Conditions

Before the measurement of engineering or physical properties could begin on the elastomer samples, the cure conditions of the elastomers were established. A rheometer gives a continuous curve of the elastomers modulus versus cure time. The elastomer is placed between two platens that maintain a constant pressure and preset temperature. As the elastomer warms, it flows to cover a disk that oscillates through a 3-deg arc. The force, recorded as torque, required to oscillate the disk is proportional to the shear modulus of the elastomer. As the elastomer warms and flows, it reaches a minimum in viscosity shown by a minimum in torque on the rheometer curve. As the crosslinks are formed during cure, the shear modulus of the sample increases. Based on the isothermal curve at 155°C for Neoprene GRT with FEF black, the time to reach 90% of the maximum torque development (t_{90}) was determined to be 38 min for compounds mixed in an internal (Banbury) mixer and 35 min for compounds mixed in an open mill. The cure for these neoprene formulations is specified as follows for thick sections where temperature control is difficult: 45-min cure in a pressurized mold at 155°C followed by a 60-min post cure of the elastomer at 177°C. The post-cure treatment is to ensure that the entire sample has come to temperature to allow total cure of elastomer and bonding system.

Storage

One of the disadvantages of red-lead-cured Neoprene GRT is that cold storage is necessary for the uncured rubber. Extended storage and exposure to heat will cause an increase in the amount of early cure of the stored material. Rheometer curves for a fresh sample and one that has been aged for 1 week at 25°C are shown in Fig. 34. Most notable here is the more rapid rise above the minimum viscosity shown in the aged sample. This indicates that the aged sample would flow into a mold cavity less readily and would not "knit" as well as a fresh sample would. Figure 35 shows the change in the time (t_{10}) for a 10-point rise from minimum viscosity as a function of storage time for elastomers at the specified temperatures. Samples stored at 10°C experienced little change in t_{10}. The rate of t_{10} degradation of the sample increases as the storage temperature increases to 60°C. A t_{10} of at least 4.0 min is desirable to allow for rubber flow into the mold cavity to ensure molding reproducibility. From Fig. 35 it can be seen that samples stored at 60°C become unacceptable after less than 100 h of storage. These data indicate that red-lead-cured Neoprene GRT should be stored cold. A rheometer test should be performed on samples of the rubber before use to determine any degradation of cure properties.
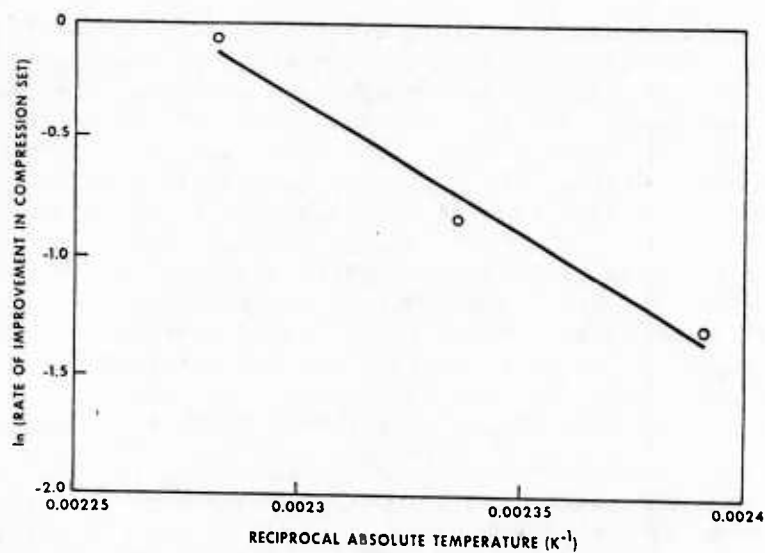
Fig. 34 - Rheometer test on fresh Neoprene GRT and on aged Neoprene GRT.
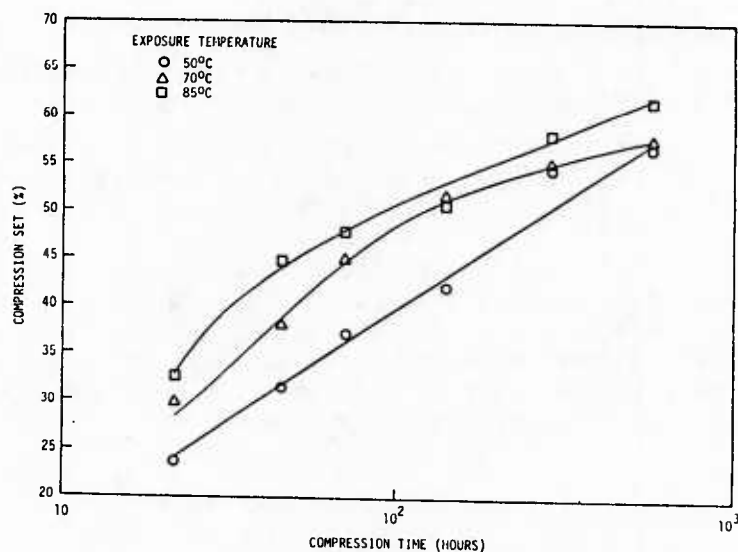
Fig. 35 - Effect of storage on the t_{10} of Neoprene GRT.

PROPERTY TRADEOFFS

In determining an elastomer formulation best suited for specific underwater applications, the physical and engineering properties required of the elastomer must be specified. These properties are then measured for elastomers with variations in the type and the amount of components. In the study of Neoprene GRT, it became evident that some changes in formulation are beneficial to some properties of the elastomer but detrimental to others. Therefore some compromises were made in selecting the final formulation.

There have been a number of cases of significant property tradeoffs as a function of formulation in this study. One of the most important is the effect of carbon-black loading on modulus (as measured by hardness) and electrical resistivity. In order to achieve a hardness of 70, it is necessary to use nearly 50 phr of FEF N550 black in Neoprene GRT (see Fig. 17). The important tradeoff here is that 50 phr of FEF N550 black in Neoprene GRT implies an electrical resistivity of 10^6 $\Omega \cdot cm$ (Fig. 22). This value is too low for most practical underwater applications. One way of examining this tradeoff is to observe the interdependency of hardness and resistivity for many carbon-loaded Neoprene GRT samples. Figure 36 is such a plot. The curve on this plot may be looked at as the highest hardness that can be achieved for a given resistivity. Points may fall below this curve because of poor homogeneity or other reasons but may not fall above it. Thus, necessary hardnesses may be reached only by the addition of silica or clay fillers to the compound. However, these types of fillers should not be considered for use since they have been reported to increase salt-ion migration and to cause failure of rubber-to-metal bonds (FY83 STRIP data).

Another example of a property tradeoff lies in the use of a ZnO/MgO-cured elastomer instead of a Pb_3O_4-cured elastomer to achieve a stronger adhesive bond to metal. This choice would prove disastrous if the elastomer were exposed to water because the ZnO/MgO-cured Neoprene GRT absorbs water eight times as rapidly as lead-oxide-cured Neoprene GRT.

Still another example of the property tradeoff becomes evident when considering the effect of lead-oxide content in Neoprene GRT on sound speed and density. Figures 2 and 13 show that although an increase in the amount of red lead in Neoprene GRT decreases sound speed, an increase in red-lead content causes an increase in density of Neoprene GRT, thus causing a net degradation of the acoustic impedance match with seawater.

Fig. 36 - Interfependency of hardness and resistivity for carbon-loaded neoprenes.

OPTIMUM FORMULATIONS

A careful review of the effects of the elastomer composition on the significant properties led to the following formulation as the best compromise for sonar transducer use.

	Parts
Neoprene GRT	100
Stearic Acid	1
Octylated Diphenylamine	2
Benzothiazyl Disulfide	1.5
Red-Lead Dispersion (90% in EPDM)	15
TE-70 processing Aid	2
N550 Carbon Black	31

This formulation has become known as Neoprene 5109S. In addition, for a few applications where a slightly higher shear stiffness (or Shore hardness) is desired, a version containing 40 parts of carbon black and designated Neoprene 5109 has been recommended. (A similar formulation, called 314-857, was developed at the Mare Island Rubber Laboratory in the early 1960's for use in special hull treatments. Burke Industries in San Jose, CA, subsequently added TE-70 processing aid and designated the formulation Neoprene 5109.)

The remainder of this report will deal with the steps that were necessary to make practical the applications of Neoprenes 5109 and 5109S. In addition, the properties of these formulations will be given and some of the applications discussed.

QUALITY CONTROL

In the past, rubber quality control has been attempted by means of a battery of physical tests. The selection of these tests has frequently been arbitrary; and even when the tests are pertinent to the application they have proved to be inadequate to assure that the Navy will get the same formulation every time elastomers are procured for use in sonar transducers. A research project [13] was carried out by approaching the problem of rubber quality control from a different perspective. It was proposed that rubber quality could be better assured by providing a means of determining whether the designated ingredients have indeed been used to compound the uncured rubber. The compositional analysis is intended to be used in conjunction with a few well-understood, supporting physical tests applied to the cured rubber. The compositional-analysis scheme involves dissolution of the uncured rubber in a solvent. The undissolved carbon black and red lead are filtered off, and the filtrate is chromatographed. High-performance liquid chromatography on the filtrate provides a means of determining the concentration of ODPA and the residue of MBTS in the rubber. Gel permeation chromatography on the filtrate is a way of determining the molecular weight distribution and, therefore, the quality of the polymer. When the red lead is dissolved away from the carbon black, it in turn can be determined by means of a complexation chromatographic technique. The carbon black remaining can be determined by weighing. Details of these procedures are given in a separate report [14].

The physical tests to be selected for use in conjunction with the compositional analysis were chosen based on the dual test of ease-of-performance and relationship to a recognizable compositional variable. Based on the procedures described in Ref. 14, the compositional variable whose interpretation is fraught with the greatest risk is the carbon-black loading. Consequently, volume electrical resistivity is important because it is the physical test providing the most direct information about the carbon black. Likewise, Shore A hardness responds to the level of curative and to the carbon-black content. In addition to these, the density of the cured rubber is a simple check of the carbon-black content, the red-lead content, and the nature of the polymer. Thus these three tests are used in determining where difficulties may lie in production batches of Neoprenes 5109 and 5109S.

RUBBER PROCESSING

Sample Buy

A draft military specification was developed for Neoprene 5109 to designate how this material might be reproducibly procured for transducer use. This draft was then exercised by procuring plant batches (i.e., large production batches) of Neoprene 5109 per this specification.

This so-called sample buy was conducted by purchasing the rubber from seven rubber-compounding companies. The batches were tested to determine if they had both the compositional and the physical properties that were expected. Compositional analysis was performed on each of four plugs removed from random locations within each sample batch. Each test plug was subjected to the chromatographic and wet-chemical analyses developed for Neoprene 5109 quality control. Some physical tests were also performed on multiple test plugs within each sample batch.

All of these test results are summarized in Table 4. Standard deviation values (σ) represent the dispersion of the results among the test plugs. It is thus considered as a measure of the inhomogeneity of the rubber batch. Results from sample G are incomplete because this sample was too scorched when received to permit meaningful chemical analysis.

Table 4 - Results of Sample Buy of Neoprene 5109

Test (Units)	MANUFACTURER MIXING METHOD						
	A Open Mill	B Internal Mixer	C Internal Mixer	D Internal Mixer	E Internal Mixer	F Open Mill	G Internal Mixer
MBTS (%) Anticipated Range: 0.10-0.13	0.112	0.098	0.137	0.155	0.130	0.203	--
Std. Dev. (σ)	0.027	0.042	0.004	0.025	0.050	0.005	--
ODPA or Octamine (%) Anticipated Range: 1.0-1.2	1.28	1.00	1.22	1.20	0.99	1.06	--
Std. Dev. (σ)	0.10	0.04	0.06	0.11	0.03	0.04	--
No. Aver. Molecular- Wt. (g/mole$\times 10^{-5}$) Anticipated Range: 0.8-1.2	0.92	0.79	0.80	0.95	1.27	0.99	--
Std. Dev. (σ) ($\times 10^{-5}$)	0.05	0.06	0.07	0.01	0.02	0.06	--
Polydispersity Anticipated Range: 2.0-3.2	2.9	3.4	3.22	2.33	2.95	2.87	--
Std. Dev. (σ)	0.2	0.3	0.06	0.22	0.10	0.17	--
Lead Oxide (% Pb_3O_4) Anticipated Range: 7.2-8.5	7.3	7.4	8.4	7.3	4.9	8.2	6.8
Std. Dev. (σ)	0.5	0.5	0.6	0.8	0.3	1.1	0.4
Carbon (%) Anticipated Range: 30-35	29.2	31.2	33.3	31.4	29.1	35.2	43.2
Std. Dev. (σ)	0.8	2.5	1.1	2.2	1.3	2.9	3.0
Log Volume Elect. Resistivity	7.732	11.175	7.626	10.540	10.276	8.625	5.75

(continued)

Table 4 (continued)

Test (Units)	MANUFACTURER MIXING METHOD						
	A Open Mill	B Internal Mixer	C Internal Mixer	D Internal Mixer	E Internal Mixer	F Open Mill	G Internal Mixer
Std. Dev. (σ)	0.793	0.915	0.350	1.189	0.216	0.53	--
Log Surface Elect. Resistivity	7.384	10.760	7.180	10.083	9.820	7.760	5.36
Std. Dev. (σ)	0.594	0.842	0.354	1.163	0.214	0.507	--
Shore Hardness	63.7	59.5	65.2	65.8	62.8	59.6	70.1
Std. Dev. (σ)	1.0	1.2	0.7	2.3	0.8	0.7	1.0
Density (kg/m^3)	1443.1	1446.8	1443.9	1456.7	1444.4	1446.7	1448.1
Std. Dev. (σ)	2.7	47.2	0.6	3.7	0.8	1.4	7.1
Sound Speed (m/s)	1607	1598	1615	1616	1603	1616	--
Rheometer-Minimum Viscosity (in.-lb)	7.2	6.8	8.4	--	7.5	5.9	12.8
Rheometer-time to 10-pt. rise (minute)	4.0	3.8	3.8	--	3.6	4.5	1.8
300% Tensile Modulus (psi)	1851	1730	1772	2017	1858	1605	--
Tensile Strength (psi)	2888	2959	2715	2940	2783	2923	--
Ultimate Elongation (%)	570	545	540	530	500	650	--

The most important question about such a large data compilation is whether or not the physical test results (performance) correlate with the chemical. In most cases, mathematical analysis of the results was confounded by sample anomalies. In addition to the scorched sample G, sample F showed an extra peak in the gel permeation chromatogram at a molecular weight of approximately 1100. Such a peak would be expected from a heavy plasticizer or a factice in the rubber, although the manufacturer has stated that no such additive was included. The low hardness and low tensile modulus of sample F would also be consistent with the presence of a plasticizer. The remaining five samples,

therefore, form a basis for mathematical correlation of the results, although with such few data sets, the possibility of coincidental relationships exists among randomly varying values. Examples of correlations found are:

- A linear correlation of tensile modulus with poly-dispersity (coefficient of correlation, R^2 = 0.995).

- A parabolic equation relating tensile strength to carbon-black content (R^2 = 0.985).

- A parabolic equation relating the standard deviation of density to the ODPA content (R^2 = 0.99999).

Disappointingly, though, there did not at first appear to be any relationship between the measured carbon-black content or its standard deviation and the electrical resistivity of the samples. Since this is a rubber property of critical importance, additional effort was made to determine the reason for the more than three orders of magnitude spread among the samples. Inquiry to each of the rubber manufacturers revealed that five different brands of N550 carbon black were used in preparing the samples. Two of the manufacturers could narrow down to only two brands. Published data exist for the properties of commercial brands of carbon blacks [15]. Direct inquiry to the supplier provided information about one carbon black whose data were not found published [16]. There appears to be a very good correlation between the log volume electrical resistivity and the stated average particle size of the carbon black. In Fig. 37 the individual data points are coded according to the rubber manufacturer given in Table 4. The two horizontal lines represent the expressed uncertainty of rubber manufacturers about the brand (and therefore the particle size) of the N550 black that was used.

The ASTM specification for carbon-black classification [17] requires only that the particle size of N550 blacks should be in the range of 40 to 48 nm. The data in Fig. 37 show both that the actual particle size of different manufacturers' N550 black may be outside this range and that this wide variation in size may make a big difference in the final rubber product.

The important conclusion to be drawn from this study is that an additional requirement must be added to the procurement specification that requires an N550 black with a particle size of 48 ± 6 nm. This means that the carbon-black specification in Neoprene 5109 now dictates three carbon-black variables--percent of loading, homogeneity, and particle size. Each of these three variables affects the physical properties of the cured sample in different ways. It is believed that this variation in carbon black is the dominant reason that good correlations cannot be found between rubber composition and physical properties in this sample buy.
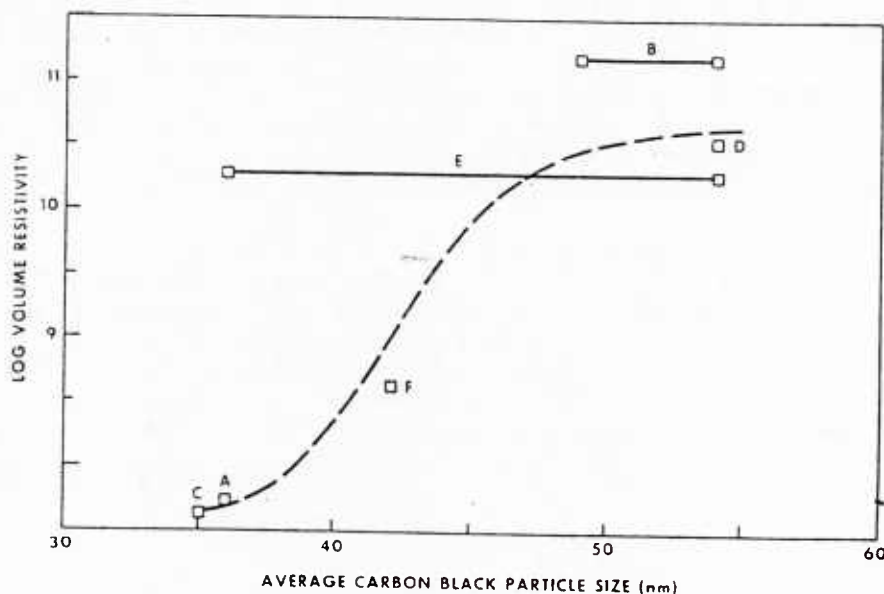
Fig. 37 - Electrical volume resistivity vs particle size of
N550 black in Neoprene 5109 samples.

Mixing Study

A detailed mixing study on Neoprene 5109 was done to further define the limits within which good-quality Neoprene 5109 can be made. The mixing study was carried out by NRL-USRD personnel using the facilities of the Associated Rubber Company in Tallapoosa, GA. Batches of raw materials were purchased by a special order for this mixing study.

The open mill used for the study was 60-in. wide and was water cooled. Six batches of 100 to 130 lb each were prepared on the open mill. The most important variable studied was the sequence and rate of addition of the additives. Addition of carbon black to the rubber matrix dries it and causes it to become friable. Stearic acid, MBTS, TE-70, and ODPA all melt during mixing and tend to counter the drying effect of the carbon black. Consequently, addition of alternate portions of carbon black and of one of the liquefying ingredients causes the rubber matrix to stay smooth during the mixing process. In all cases, the red-lead curing agent was added last in order to minimize premature vulcanization (scorch) of the rubber. After the red-lead addition, mixing was continued for the minimum time necessary (i.e., until no red streaks were visible) and the rubber was removed from the mill in slabs and placed on a cool, clean surface. After cooling to room temperature, the rubber was packed in dry ice for subsequent handling.

The order of addition of the liquefying additives was studied. For some of the batches, the MBTS was added first, followed by stearic acid, TE-70, and ODPA. For others the stearic acid was added first. The most effective

technique was to add alternate small portions of MBTS and carbon black after the rubber had already broken down on the mill. Part of the stearic acid may also be used near the beginning. After the rubber forms a smooth matrix on the front roller of the mill, the remaining ingredients, excluding the red lead, are thoroughly mixed into the remainder of the carbon black. This mixture is then added gradually to the rubber on the mill. After the addition is complete and the rubber has been cut and folded back 15 to 25 times, the matrix will be smooth and will appear homogeneous. At this point, the red lead is added in several small pieces.

The internal mixer study was carried out in a No. 3A Banbury mixer. This study was much less involved since all of the ingredients—except red lead—are generally added initially. The most important variables involved batch size and keeping the carbon black swept down into the mixer. Batch size is critical because the mixer will cease efficient mixing outside of a relatively narrow range of material volume. The Banbury batches were all dumped after 3 to 4 min of effective mixing and at a measured temperature between 104 and 110°C. The dumped rubber was placed on a 60-in. mill and was formed into a smooth matrix. This allowed significant cooling of the rubber to perhaps 65°C. The red lead was added as described above, and the rubber was removed from the mill and cooled.

Each of the nine batches successfully produced was subjected to a battery of tests. Complete compositional analyses were run on four random samples from each batch in order to obtain a measure of the homogeneity of the batch. In addition, the physical properties of each of these separate samples were also measured.

The results of all of these tests may be summarized as follows:

- The first batch showed too short a t_{10} (time to 10-point rise) on the rheometer. This occurred because the batch size was too large and therefore took too long to mix.

- The tenth batch showed a marginally low Shore hardness and a low percentage of carbon black. This may have resulted from too much of the carbon-black dust escaping from the Banbury mixer because of the absence of the TE-70 ingredient.

- The samples mixed in the Banbury mixer showed a slightly lower tensile modulus than those mixed on the open mill, but the values are still quite acceptable.

- Each sample except the first and tenth was totally acceptable from the standpoint of both physical tests and compositional analysis.

The conclusions of this study are thus that with a modicum of care, good-quality Neoprenes 5109 and 5109S may be mixed by either the open mill or the Banbury method.

CONCLUSIONS

The two formulations designated Neoprene 5109 and Neoprene 5109S are now being tested for use in a variety of underwater acoustical applications as shown in Appendix B. These formulations have the typical physical properties given in Table 5.

Table 5 - Typical Properties of Neoprenes 5109 and 5109S

Property	Neoprene 5109	Neoprene 5109S
Density	1450 kg/m^3	1430 kg/m^3
Durometer	67	58
Tensile Strength	2500 psi	2500 psi
Ultimate Elongation	550%	600%
300% Modulus	1550 psi	1200 psi
Tear (Die C)	96 kN/m	85 kN/m
Compression set	48%	43%
Volume Resistivity	1×10^{10} $\Omega \cdot$cm	1×10^{11} $\Omega \cdot$cm
Sound Speed	1580 m/s	1555 m/s
Water Permeability	20 ng$\cdot$cm/cm$^2 \cdot$h$\cdot$Torr	22 ng$\cdot$cm/cm$^2 \cdot$h$\cdot$Torr

Beside the physical properties, both formulations have excellent bondability and good environmental resistance. Additionally they have the overwhelming advantages of having a very good quality-control scheme and a military procurement specification. The marginal compression-set values imply that this formulation may not be suitable where a relatively small-area clamp or band on the rubber provides the water seal. For those applications, a formulation based on Neoprene WRT is desirable. Development of such a formulation is in progress and will be the subject of a future report.

REFERENCES

1. C. M. Thompson, "Electrolytic Effects on Bonds," presentation at the TR155F Workshop, Washington, DC, Feb. 1983.

2. C. M. Thompson, "Permeation into Containers Filled with Nonideal Oil," *J. Appl. Polym. Sci.* 26, 373-77 (1981).

3. P. E. Cassidy and R. B. Perry, "Analysis of Water Ingression into Rubber Sealed Systems," *SAMPE Quarterly* 6 (4) July 1975.

4. R. M. Murray and D. C. Thompson, *The Neoprenes*, (G.I. DuPont deNemours & Co., Inc., Wilmington, DE, 1963).

5. H. J. Stern, *Rubber: Natural and Synthetic*, 2nd Ed., p. 121 (Palmenton Publishing, New York, 1967).

6. R. N. Capps, "Dynamic Young's Moduli of Some Commercially Available Polyurethanes," *J. Acoust. Soc. Am.* 73 (6) (1983).

7. R. Y. Ting, "A Study on Elastomer/Metal Bonds Applicable in Underwater Sonar Systems," *Adhesive Joints*, (Plenum Publ. Corp., New York, 1984).

8. American Society for Testing and Materials, *1982 Annual Book of ASTM Standards*, Part 37, ASTM 429-81, Method C.

9. P. E. Cassidy, T. M. Aminabhavi, and C. M. Thompson, "Water Permeation Through Elastomers and Plastics," *Rubber Chem. & Tech.* 56 (3), 594 (1983).

10. W. J. Kass and W. J. Andrzejewski, "Water Permeation in Silicone Rubber," Report SLA73-0718, Sandia Laboratories, Albuquerque, NM, July 1973.

11. E. Sasher and J. R. Susko, "Water permeation of Polymer Film.1. Polyimide," *J. Appl. Polym. Sci.* 23, 2355-64 (1979).

12. A. Hallenbeck and S. W. Schmitt, "Compounding Neoprene for Water Resistance," Report NP-520.1, Du Pont Co., undated.

13. C. M. Thompson, M. E. Quinn, and W. W. McGee, "Compositional Analysis Procedures for Selected Elastomers Used in Sonar Transducers," NRL Memorandum Report 5746, Nov 8.

14. W. W. McGee, NRL Memorandum Report 5811, Nov 1986.

15. D. R. Smith, ed., *1981 Rubber World Blue Book* (Bill Communications, Inc., NY) 192-193 (1981).

16. David Young, Columbian Chemicals, Akron, OH, informal communication dated April 1983.

17. American Society for Testing and Materials, *1982 Annual Book of ASTM Standards*, Part 37, ASTM D1765.

Appendix A

TESTING PROCEDURES

The tear strength was measured according to ASTM D624 [A1]. The tensile strength, tensile modulus at 300% elongation, and ultimate elongation were measured as per ASTM D412 (Die C) [A2]. These measurements were made on the Instron Universal Testing Instrument Model 1122. The hardness was measured at 25°C with a constant rate, constant load, Shore A durometer 20 s after application of load. Densities were calculated from handbook values of the density of water and the specific gravities measured by an Archimedes Principle of ASTM D297 [A3]. Compression set was measured by Method B of ASTM D395 [A4]. Unless otherwise specified, the compressed sample was exposed at 85°C for 70 hours. Sound speeds were measured in a Mapco Corp. Sonic Solution Monitor by a method similar to that of Zacharias, et al. [A5]. In this method, the time of flight of a 1.5-MHz sound pulse is measured at 25°C both with pure water and with the sample in water. The sound speed is then calculated from these time readings.

Samples for the compatibility study were 1-in. squares of approximately 4-mm thickness. Two sample pieces of the same formulation were used in each test. Prior to exposure, both samples were degreased and weighed, and the thickness at the center of one sample was measured. The test liquid was brought to test temperature before the samples were submerged. Both samples were periodically wiped dry with paper towels and weighed, and the thickness was measured on the same sample that was measured initially.

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 and sealed with a thin layer of silicon adhesive and a stainless-steel flange. The cup was placed in a 0% humidity environment and weighed periodically to determine weight loss.

Volume electrical resistivity was measured at 25°C by the ASTM D991-82 [A6] method using a Hewlett Packard resistivity cell Model 16008A. The samples, approximately 4 mm in thickness and at least 10 cm in diam, were degreased and placed in a dessicator for 24 h prior to measuring. The sample was charged with 100 V for 25 s. The volume resistance was measured after another 35 s. Volume resistivity was calculated using:

$$\text{Volume resistivity} = \frac{A \times 19.635 \text{ cm}^2}{B} \qquad \text{(A1)}$$

where A = volume resistance (Ω), B = Sample thickness (cm), and 19.635 = cell factor.

In preparation for the adhesion study of Neoprene GRT rubber, the conical buttons and the static-peel substrates were degreased, sanded with 120-grit silicon carbide, and degreased again before being coated with adhesive. The manufacturers' suggestions were followed for the application of the adhesive systems. After sufficient drying time, the thickness of the adhesive on the

conical buttons was checked with a magnetic-type film-thickness gauge. An electrically heated transfer mold was used to fabricate the test specimens. An injection molding technique was applied for introducing the rubber into the mold for final vulcanization. The fully cured samples had a controlled distance of 11.5 ± 1 mm between the tips of the conical end pieces. The sample thickness for the static-peel test was maintained at 0.25 ± 0.02 in. The weights for the static-peel test, which were corrected for bouyancy (if they were to be suspended in seawater), were suspended from the free end of the sample. The rate of peel was obtained by measuring the distance of the bond line to a reference point, fixed on the substrate, using a traveling microscope.

REFERENCES

A1. American Society for Testing and Materials, *1982 Annual Book of ASTM Standards*, Part 37, ASTM D624 Die B.

A2. American Society for Testing and Materials, *1982 Annual Book of ASTM Standards*, Par 37, ASTM D412 Die C.

A3. American Society for Testing and Materials, *1982 Annual Book of ASTM Standards*, Part 37, ASTM D297, para 15.1.2.

A4. American Society for Testing and Materials, *1982 Annual Book for ASTM Standards*, Part 37, ASTM D395.

A5. E. M. Zacharias, M. W. Zacharias, and R. A. Parnell, Jr., "Measuring Sound Velocity and Bulk Modulus of Plastics," *Modern Plastics* 51, 88 (1974).

A6. American Society for Testing and Materials, *1982 Annual Book of ASTM Standards*, Part 37, ASTM D991-82.

Appendix B

APPLICATIONS OF NEOPRENE 5109 AND 5109S

TR-317R TRANSDUCER

The TR-317R is a tonpilz transducer mounted in a large spherical array on the front of U.S. Navy submarines of several classes. The design of this transducer requires a rubber face that protects the face from seawater and provides the spring mount between the radiating face and the steel shroud. Grave problems experienced in the past in transducers of similar design resulted in failure of the bond between the rubber and the shroud. Neoprenes 5109 and 5109S were attractive candidates for this application because of their excellent bondability. One of the possible mechanisms driving the failure of the earlier, similarly designed transducers required a low value of electrical resistivity in the face rubber. To provide additional processing latitude, the rubber with higher resistivity (Neoprene 5109S) has been specified for use. Many head-mass assemblies have been built using 5109S as the face rubber. One of the tests that samples of the head-mass production are subjected to is a push-out to destruction. This tests the bonding and tear strength of the rubber. The forces required with the 5109S head-mass assemblies have all exceeded the specified value, many by a great deal. Furthermore, no samples exposed to water have shown any rubber-to-metal debonds.

DT-276 HYDROPHONE

The DT-276 is a rubber-covered ceramic cylinder used as a passive listening device in an array on some submarines. The rubber is in direct contact with one of the electrodes and thus must function as insulation to the seawater ground. Neoprene 5109S has been selected for this application because of its good electrical resistivity and its excellent bond strength.

TR-316/TR-242 TRANSDUCERS

These transducers form a part of the under-ice navigational suites on some submarines. The face rubber is clamped in place by means of an ice shield with a relatively wide flange. Neoprene 5109 is now being specified for this application because it has been shown to not creep from underneath the wide clamping flange. Thus the clamping force has been predicted to persist for many years of life and maintain the seal between the fill oil and the seawater.

TR-330 TRANSDUCER

The TR-330 transducer is a moderately high-frequency sonar transducer used on class DDG surface ships. The moderate dynamic losses of Neoprene 5109S in this frequency range at ocean temperatures caused some initial concerns about its suitability. However, the advantages of the greater iability associated with 5109S more than outweigh the slight performance penalty, and it has now been specified for this application.

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