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NRL Report 5885

The Use of Polyalkylene Glycol in Sonar Transducers

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February 15, 1979



SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NRL Report 8283	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THE USE OF POLYALKYLENE GLYCOL IN SONAR TRANSDUCERS		5. TYPE OF REPORT & PERIOD COVERED Interim Report on a continuing NRL Problem
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) C. M. Thompson		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Underwater Sound Reference Detachment P.O. Box 8337, Orlando, FL 32856		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NRL Problem S02-43 Program Element 64503N Project NAVSEA 660-PT
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Naval Sea Systems Command Washington, DC 20362		12. REPORT DATE February 15, 1979
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 30
		14. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Polyalkylene glycol Materials PAG Resistivity Poly(propylene oxide) Phase diagram Transducer fill fluids Compatibility Acoustic fluids Compressibility		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Polyalkylene glycol (PAG) has been proposed as a sonar-transducer fill fluid with nearly ideal properties, but PAG is far from being a universal fill fluid. Its speed of sound and acoustic impedance are both about 13% lower than those of seawater at 20°C, causing internal reflections (sensitivity loss) and refraction (directivity loss). Low thermal expansion and moderate compressibility make PAG a good choice in a nonpressure-relieved design. The electrical resistivity of PAG is 1000 to 10,000,000 times lower than that of other common fill fluids, partly from high water solubility. Also, some of the large amount of water in PAG at equilibrium will precipitate if the temperature drops and may cause		

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20. Abstract (Continued)

Catastrophic failure. Another concern with PAG is low resistivity if exposed to tin salts or perhaps tin, which may cause electrical failure. PAG is in general compatible with fewer acoustic-grade elastomers than castor oil. An advantage of PAG is low viscosity. It is much easier than castor oil to degas; hence air bubbles are less likely. The toxicity of PAG is low, and poisoning by vapors from overheating is easily avoided. PAG is readily available and not costly. If the vendor ceased production, the synthesis and specifications in this report would let additional vendors become qualified. In conclusion, with care in avoiding water exposure and in choosing exposed materials, PAG may find use in several Navy sonar units.

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THE USE OF POLYALKYLENE GLYCOL IN SONAR TRANSDUCERS

INTRODUCTION

A liquid used for filling a sonar transducer must meet a wide variety of general qualifications in addition to those requirements peculiar to a given application. Compatibility with other components, resistance to degradation, and proper acoustic impedance are always important requirements. In specific applications density, viscosity, water solubility, electrical resistivity, or stability may be important properties. Since at present no fill liquid combines all the most important properties, the choice of material involves a consideration of the advantages and tradeoffs of the candidates.

Polyalkylene glycol (PAG) was proposed by Green in 1974 [1] as a substitute for castor oil to avoid its high viscosity. Use of PAG in sonar transducers was also patented by the same author [2]. Many of the data presented in that earlier report are valid. This present report contains additional data and an assessment of the advantages and disadvantages of the use of PAG. The next section is a discussion of the properties of PAG and the tradeoffs and qualifications which encumber its use. The third main section gives a method of synthesis, along with a set of specifications and tests for PAG. The concluding main section discusses the potential of PAG as a transducer fluid.

PROPERTIES OF PAG

Acoustic and Pressure-Volume-Temperature Relationships

Sound Properties

A material which is used as an acoustic medium must obviously have good acoustic properties. PAG was reported by Green [1] to have a close sound-speed match with seawater. He also reported no measurable signal attenuation in PAG. Sound speed was measured at the Underwater Sound Reference Detachment (USRD) of the Naval Research Laboratory on a sonic solution analyzer under a variety of conditions. Sound speed is shown as a function of temperature in Fig. 1. The equation for the line in Fig. 1 is

$$C = 1395.0 - 3.34T, \quad (1)$$

where C is the sound speed in meters per second and T is the temperature in degrees Celsius. Sound speed is also a linear function of water content. These data are best described by

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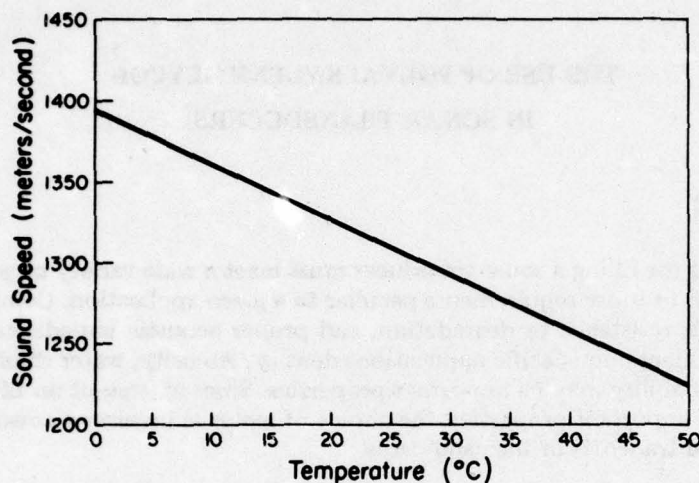


Fig. 1 — Sound speed of polyalkylene glycol (PAG) as a function of temperature

$$C = 1323.1 + 12.16\psi, \quad (2)$$

where ψ is the percent water (weight/weight) up to the saturation limit of 1.8%. Equation (1) is strictly applicable only to PAG with low water content (around 0.1% H_2O). Equation (2) was obtained for PAG at 22°C.

These results are considerably different from those of Green. His data were represented by

$$C = 1408 - 2.9T. \quad (3)$$

The difference in intercept and slope is well outside the limits of error of the USRD velocimeter. The difference in intercept for Green's data is best explained by assuming his sample contained approximately 1% water. The difference in slope remains unexplained.

Density of PAG

The density measured for PAG at USRD differs slightly from that previously reported [1]. The change in density with temperature may be described by the equation

$$\rho = 996.2 - 1.1T + 6.2 \times 10^{-3}T^2, \quad (4)$$

where ρ is the density in kilograms per cubic meter and T is the temperature in degrees Celsius. The density of PAG also changes regularly with changing water content. This change is described by

$$\rho = 971.4 + 1.6\psi, \quad (5)$$

where ψ is the percent of water (weight/weight) measured by Karl Fischer titration up to saturation limit of 1.8%. A combination of Eqs. (4) and (5) is not strictly permissible because of possible cross terms. However, the first equation is suitable for low water content (0.12% H_2O), and the second equation is suitable for ambient temperatures ($23^\circ C$).

These equations should be useful for the design of transducers containing PAG. Sound-speed and/or acoustic-impedance (product of sound speed and density) matching will improve the directivity and decrease internal reflections in a sonar transducer. For accurate acoustic-impedance matching the water content of the fluid during its lifetime should be considered in calculating both density and sound speed.

Compressibility

The adiabatic compressibility of PAG as a function of temperature and hydrostatic pressure was reported recently by Boles, Timme, and Shelton [3]. These data are plotted in Fig. 2. The isothermal compressibility data in Green's report [1] when expressed in SI units is $2.22 \times 10^{-10} \text{ m}^2/\text{N}$. Work under way at USRD will measure the parameter more accurately and as a function of temperature and pressure.

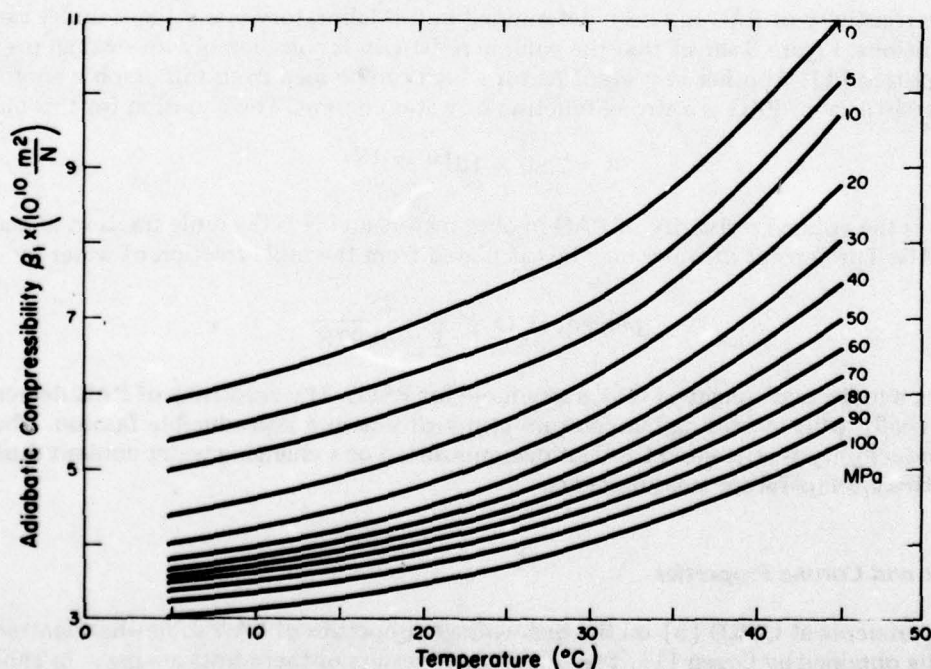


Fig. 2 — Adiabatic compressibility of PAG as a function of temperature and pressure

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The compressibility and rate of thermal expansion when taken together allow calculation of the pressure built up within a nonpressure-compensated transducer with a given increase in temperature. Such calculations must take into account thermal expansion of the case, flexing of the case under pressure, and expansion of other components. The increase of volume with temperature of PAG is slightly less than that of castor oil and considerably less than that of silicone transducer fluids. The reported isothermal compressibility of PAG is considerably lower than that of castor oil or silicone fluids. Calculations using these properties of PAG yield the result that in a noncompensated sonar transducer PAG will produce a smaller pressure increase with a given temperature increase than will either castor oil or silicone fluid. This conclusion is borne out in work reported by Green [4].

Electrical Properties

Dielectric Constant

Any fluid used in an electrical device must have a good dielectric constant and volume resistivity under a variety of conditions. The dielectric constant of PAG has been reported as 5.0 (compared to 4.5 for castor oil) [1].

Resistivity

The resistivity of PAG has been determined in this laboratory many times under various conditions. Figure 3 shows that the volume resistivity is considerably lower than previously reported [1]. Another important factor which can be seen from this graph is that the volume resistivity of PAG is a strong function of water content. The equation for this line is

$$\Phi = 7.80 \times 10^{10} e^{6.1N}, \quad (6)$$

where Φ is the volume resistivity of PAG in ohm-meters and N is the mole fraction of water in the PAG. The percent of water may be calculated from the mole fraction of water by

$$\text{percent H}_2\text{O} = \frac{3N}{1 - 0.97N} \quad (7)$$

(assuming a molecular weight of 600 grams/mole for PAG). The resistivity of PAG decreases monotonically with increasing temperature although not in a reproducible fashion. The nonreproducibility is attributed to slight decomposition or a changing water content during the resistivity/temperature measurements.

Arc and Corona Properties

Experiments at USRD [5] on the high-voltage properties of PAG somewhat contradict the results obtained by Green [1]. The quantitative results of these tests are given in Table 1. Included there for comparison are values for castor oil and gaseous nitrogen. As can be noted, both corona and breakdown occur at 10 to 30% lower voltages for PAG than for castor oil.

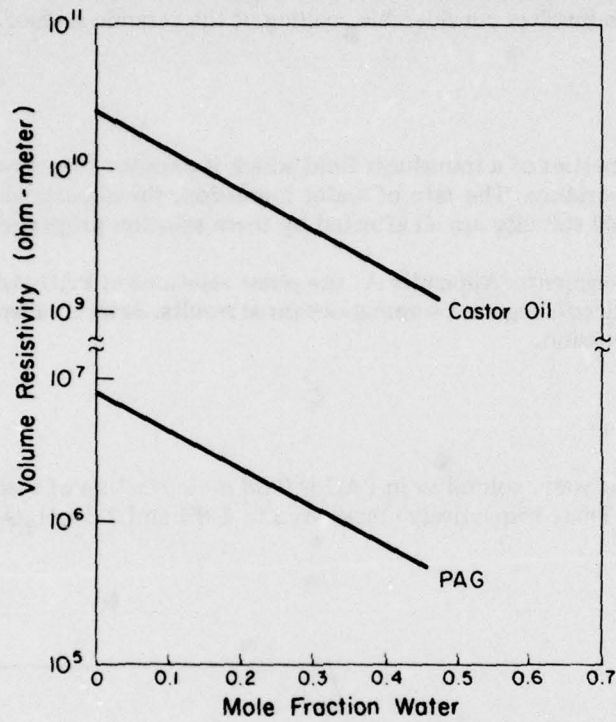


Fig. 3 — Resistivity of transducer fluids as a function of water content

Table 1 — Corona and Flashover Properties of Transducer Fill Fluids

Distance (mm)	PAG		Castor Oil		Nitrogen Flashover V_f (kV)
	Corona V_c (kV)	Flashover V_f (kV)	Corona V_c (kV)	Flashover V_f (kV)	
2	7.5	8.0	9.0	11.0	3.8
4	10.0	10.5	11.0	14.0	3.5
6	11.0	12.0	15.0	18.0	4.2
8	—	—	—	—	4.5

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Both PAG and castor oil form carbon tracks and gas bubbles on flashover. In PAG, however, flashover also involves considerable spalling of the ceramic surface.

Solution Properties

The solution properties of a transducer fluid which is exposed to seawater or moist air are of paramount importance. The rate of water ingress, the acoustical and electrical properties, and the fluid stability are all affected by these solution properties.

In a series of experiments (Appendix A) the phase relations of PAG-water solutions were studied in some detail. Figure 4 summarizes these results. Several salient features are worthy of further discussion.

Water Solubility

The upper limit of water solubility in PAG is 0.38 mole fraction of water at 25°C and 0.48 at 50°C (Fig. 4). These respectively correspond to 1.8% and 2.8% H₂O by weight.

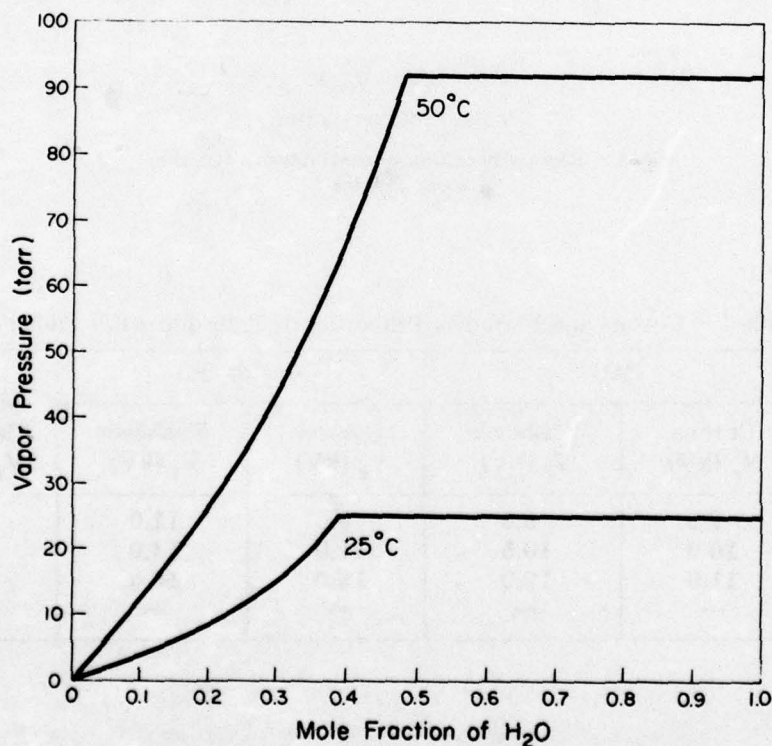


Fig. 4 — Vapor pressure of PAG-water solutions as a function of the fraction of water

Silicone oil, by comparison, dissolves only 0.03% water at 20°C. PAG has a high solubility limit for a material which is, of necessity, exposed to water. As already pointed out, this water degrades the electrical resistivity as well as changing the acoustic and pressure-volume-temperature properties. A more acute danger, however, is that when the temperature of saturated PAG decreases, water will precipitate. When this occurs in a sonar transducer, the water will precipitate onto the interior surfaces. Water on an electrical surface will cause catastrophic failure if high voltage is applied. This problem is not unique to PAG. The difficulty in this case lies in the relatively large amount of water which will precipitate from PAG. For example, if 0.4 liter of PAG cools from 50 to 25°C, as much as 3.6 ml of water could precipitate onto the interior surfaces. Depending on the configuration, this could effectively wet all the exposed surfaces.

Vapor Pressure over Water-PAG Solutions

As can be seen from Fig. 4, at both temperatures PAG-water solutions exhibit simple, negative deviation from Raoult's law up to the solubility limit. The significance of this observation is that this curve largely determines the rate of water permeation into the sonar transducer. As discussed elsewhere [6,7], the lower the vapor pressure over solutions of water in oil, the faster the rate of water permeation into the transducer. This can be seen in the following equation, which relates the rate of water ingress to various parameters:

$$\frac{dm}{dt} = \frac{QA}{l} (P_o - P_i), \quad (8)$$

where dm/dt is the rate of water permeating the elastomer, Q is the permeability constant (an intrinsic property of the elastomer window), A is the area of the elastomer, l is the thickness of the elastomer, and P_o and P_i are the partial pressures of water outside and inside the transducer respectively.

Thus, as time passes and water permeates into the fluid, the water vapor pressure over the fluid will increase. As the water vapor pressure P_i over the fluid increases, the partial pressure difference $P_o - P_i$ between the outside and the inside of the transducer decreases and further permeation is retarded. From this viewpoint PAG also suffers by comparison to most other fluids. Castor oil for example exhibits a complex positive deviation from Raoult's law. Thus, it not only has a lower solubility limit, but the smaller vapor pressure difference between inside and outside the transducer means that the solubility limit will be reached more slowly.

Also important in considering the water permeation rate into a given oil is the solubility of the oil in water. Since a water-rich oil-water phase forms when the lower solubility limit is exceeded, its vapor pressure is expressed over the fluid in the entire heterogeneous range. Therefore when the transducer reaches saturation (the lower solubility limit) as it ages, the vapor pressure over the water-rich phase is the limiting vapor pressure. As can be seen from Eq. (8), net permeation ceases if this limiting vapor pressure is equal to that of pure water. If this vapor pressure is only very slightly less than that of pure water, permeation will cease when the hydrostatic pressure inside the transducer is slightly above that outside the transducer [7].

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There are severe experimental difficulties in measuring vapor pressures near that of pure water. Principally this is due to condensation on the hygrometer probe caused by slight temperature fluctuations. Because the probe material is porous, this condensation is reversible only over long time periods. Even if the temperature can be stabilized, the probe is very nonlinear near the saturation point. Since the vapor pressure near the saturation point cannot be measured accurately, it is preferable to calculate the saturation vapor pressure by other means.

The second phase which forms is in most practical cases a dilute solution of oil in water. In such a dilute solution Raoult's law will hold. By use of this approximation, the vapor pressure over the water-rich phase may be calculated. The solubility of PAG in water was measured to be 160 parts per million by weight at 25°C. This is equal to 0.0000048 mole fraction of PAG or 0.9999952 mole fraction of water. The vapor pressure of this solution is thus 99.9995% of that of pure water—effectively equal to it. Similar results are apparent if the data at higher temperatures are calculated. These results mean that in the absence of temperature fluctuations, no water-rich second phase will ever form in the transducer.

Solubility of Ionic Materials

Another concern about a transducer fluid which has a high water solubility is that the water will increase the solubility of metal ions. In a polyether such as PAG this is of special concern because of the potential of these compounds to form chelates with metal ions. In a brief study this property was investigated using volume electrical resistivity to indicate the presence of a significant quantity of metal ions. The salts of several metals which could be potentially found in a sonar transducer were chosen and exposed to water-saturated PAG. Some of these metal salts (aluminum and iron) showed little effect. Others such as magnesium, copper, and silver salts decreased the initial resistivity by about one half. Tin (II) chloride, however, decreased the resistivity by a factor of more than 10^2 . This means a change of about 4×10^3 from pure and dry PAG to wet, tin-containing PAG. Although this should be further tested with closer-to-life experiments, this would suggest catastrophic results if PAG should be exposed to tin-containing solder. Since the leads to the ceramic stack are soldered and the PAG is typically exposed to this connection, this could be of serious concern.

Confirmation of the complex-forming ability of PAG was recently provided by James, Wetton, and Brown [8]. These workers used density measurements and infrared spectroscopy as well as dielectric methods to prove the existence of relatively strong chelates between a compound similar to PAG and transition-metal salts. They found strong chelates with zinc and iron salts as well as with tin salts.

Chemical Properties

Compatibility with Elastomers

The question of the suitability of a given fluid-elastomer combination is fraught with many subjective judgments. No universal definition of compatibility seems possible due to

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the large variety of characteristics a sonar material is required to have. Some combinations are obviously not suitable, such as when the elastomer disintegrates or badly swells in a relatively short time. Other elastomers are just as obviously not affected by a given fluid. However, each of the many borderline cases must be judged on the basis of the intended end use.

The most frequently used indication of lack of compatibility between an elastomer and a fill liquid is the change in weight of the solid upon prolonged immersion. This test is an imperfect predictor, because it does not simulate any end-use test. However, *both* loss of weight (dissolving out the polymer or an additive) and gain of weight (liquid entering the polymer matrix) *indicate* some degradation of elastomer properties. Weight change was used by Timme [9] as an indicator of the compatibility of PAG with several elastomers. In addition he monitored dimensional changes and hardness changes on exposure.

Besides the previously mentioned deficiencies in the measurement, many elastomers show complex weight-change behavior with time, indicating several processes occurring simultaneously. This greatly complicates a unified scientific description of compatibility because of the likelihood that these different processes have different energies of activation. Fortunately two of the elastomers studied with PAG showed simple linear weight gain over a range of temperatures. A plot of the logarithm of the rate of weight change as a function of reciprocal absolute temperature gave an activation energy of approximately 50 J/mole (12 kcal/mole). Other studies at Texas Research Institute [10] gave similar results. If this value is accepted as applicable, the approximate degree of acceleration of degradation can be calculated.

As an empirical measure of the total change in an elastomer's properties a compatibility index is proposed which is to be the sum of the absolute values of all fractional weight changes that occur in a given short interval at an elevated temperature. Here a 40-day exposure (for convenience) at 90°C (the highest temperature generally accepted as not causing excessive polymer degradation) is used. By using the activation energy from the preceding paragraph, this exposure may be calculated to correspond to approximately 4.5 years of exposure at 25°C.

In Table 2 are listed the results of a study of compatibility of a variety of acoustic-grade elastomers with PAG. A more detailed description of the behavior of these elastomers is obtained by observing graphs of the results. These are given in Appendix B, with the tests at 25°C and 75°C extended to as long as 18 months. Examination of these longer term results lends support to the ratings suggested above, with one exception. Polychloroprene (Neoprene W), an important acoustic elastomer, was totally disintegrated after 13,700 hours (18 months) at 75°C. The sample exposed at 25°C was badly swollen and had obviously lost much of its physical strength.

A brief compatibility test was run between PAG and Lexan, a polycarbonate plastic commonly used in transducers. In an accelerated test, Lexan gained about 1% of its weight in PAG before degrading completely. This occurred in 85 days at 100°C. Although this exposure corresponds to long lifetime (again assuming an activation energy of 50 J/mole (12 kcal/mole)), the extent of the sample degradation casts serious doubt on the use of this material pair.

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Table 2 — Compatibility of Elastomers with PAG

Generic Type	Formulation	Compatibility Index*	Assessment†	Remarks
Chlorobutyl	H862A	1.6%	Very good	—
Nitrile-butadiene	Buna N	2.3%	Very good	—
Silicone	V121	2.7%	Very good	—
Butyl	B252	3.6%	Very good	—
Fluoroelastomer	Viton A	3.5%	Good	—
Polychloroprene	Neoprene W	9.5%	Fair	—
EPDM	Nordel 1070	15%	Poor	—
Natural	BFG 35001	12%	Poor	33 days at 50°C 20-day test performed at Texas Research Institute
Polychloroprene	(from Ametec Straza)	5.8%	Poor	
Polychloroprene	BFG 35003	30%	Poor	—
Natural	BFG 35007	53%	Poor	—
Castable rho-C	BFG 35075	93%	Poor	—
Polyurethane	PRC 1538	93%	Poor	—

*Sum of weight changes $|\Delta m/m_0|$ during 40 days at 90°C.

†Qualitative descriptions are:

excellent = $\sum |\Delta m/m_0| < 1.5\%$,
 very good = $1.5\% < \sum |\Delta m/m_0| < 3\%$,
 good = $3\% < \sum |\Delta m/m_0| < 6\%$,
 fair = $6\% < \sum |\Delta m/m_0| < 12\%$,
 poor = $12\% < \sum |\Delta m/m_0|$.

PAG is thus seen to be relatively incompatible with a variety of commonly used acoustic-grade materials. However, by proper care in choice of elastomers, this difficulty may be avoided.

Stability

Unlike ester-type fluids PAG is very resistant to hydrolysis. This is an important property for a material which will inevitably become saturated with water. The products of such hydrolytic degradation are much more likely to attack elastomeric, metallic, and ceramic components of the transducer.

Of lesser importance for sonar applications is the question of oxidative stability. As a test of this property PAG was aerated while being stirred at 100°C for 48 hours. The product of this air and heat aging proved to undergo slow hydrolysis on exposure to water at room temperature. As will be explained later in this report, this hydrolysis may be carried out at an elevated temperature (100°C) and the product measured by titration with aqueous base solution. In the tests run at USRD, no sample of PAG from Union Carbide (LB135Y3) showed more oxidation than 0.2 mole percent. This is an acceptably small amount and indicates the efficacy of Carbide's antioxidant additive.

Miscellaneous Properties

Viscosity

The viscosity of a transducer fluid must be low enough to permit its easy flow into recesses in the transducer and to allow easy removal of air. Too low a viscosity allows the fluid to leak through seals in the transducer. PAG has been reported to have a viscosity of 68 centistokes at room temperature [1]. The variation of viscosity with temperature is expressed as

$$\eta = 190 e^{-0.0513T}, \quad (9)$$

where η is the viscosity in centistokes and T is the temperature in degrees Celsius.

Cavitation Level

A high value of cavitation threshold is a necessity for an acoustic fluid which will be used in a high-power projector. Green [1] reported a much higher level of cavitation threshold for PAG than for castor oil. In a recent work Moffett [11] has quantified and somewhat contradicted those results. PAG had an initial cavitation threshold of approximately 240 dB re 1 μ Pa compared to 233 dB re 1 μ Pa for castor oil. The high cavitation level for PAG quickly falls off to approximately 227 dB re 1 μ Pa after cavitation has begun. In this regard therefore PAG is seen to be comparable to castor oil.

Environmental and Toxicity Considerations

PAG is perhaps the most easily handled of common transducer fluids. Surfaces contacted with it are readily cleaned with acetone, acetone-alcohol, or methyl ethyl ketone. No skin or eye irritations have been reported after several months of laboratory handling. In one incident PAG was accidentally heated to 250°C to 300°C for an extended time after being spilled into the coils of an oven. The fumes given off by this material apparently produced sinus headaches with subsequent flulike symptoms in a technician who was exposed for several hours. For further applications such overheating of PAG must be avoided.

Cost

Because of its widespread use in other applications, the price of PAG remains relatively low compared to other transducer fluids. Union Carbide quoted a price of \$5.28 per gallon in October 1977 for their transducer quality PAG (LB135Y23) purchased in 55-gallon drums.

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SPECIFICATION, TESTS, AND PROPOSED PREPARATION

This section will provide a series of specifications and tests suitable for quality assurance of PAG to be used in sonar transducers. In addition a method of preparation of PAG is proposed for use in the event that the current single source (Union Carbide) ceases production or that sole-source procurement must be avoided.

Specifications and Tests

This subsection is arranged with statements in italics with wording appropriate for the specifications of a polyalkylene glycol to be used as a transducer fluid in a transducer procurement package. After each statement follows the test and an explanation of why that specification is important to the transducer operation.

Identity: The transducer liquid shall be a single-capped poly(propylene oxide). The liquid shall be a polymer of 1,2-propylene oxide, initiated by an alcohol with suitable catalysis.

Identity of a fluid from a proposed new source can best be established by reference to the infrared spectra (Fig. 5) and the proton NMR spectra (Fig. 6). The NMR spectrum is especially suitable as a means of identifying the polymer. From Fig. 6 the assignment is straightforward. The shoulder at 3.52 ppm δ (relative to tetramethylsilane: TMS) is the hydrogen on the methyne carbon of the polymer chain. The peak at 3.43 ppm δ is from the hydrogens on the methylene carbon. The peak at 1.13 ppm δ is from the hydrogens on the methyl group on the chain. Approximate integral intensities of those peaks supports those assignments. Importantly, the peak at 1.47 ppm δ is apparently from the hydrogens of the end-group methyl. If this peak can be cleanly separated by the use of somewhat more sophisticated instrumentation, the ratio of its intensity to that of the methyl on the chain will provide a measure of the molecular weight of the material.

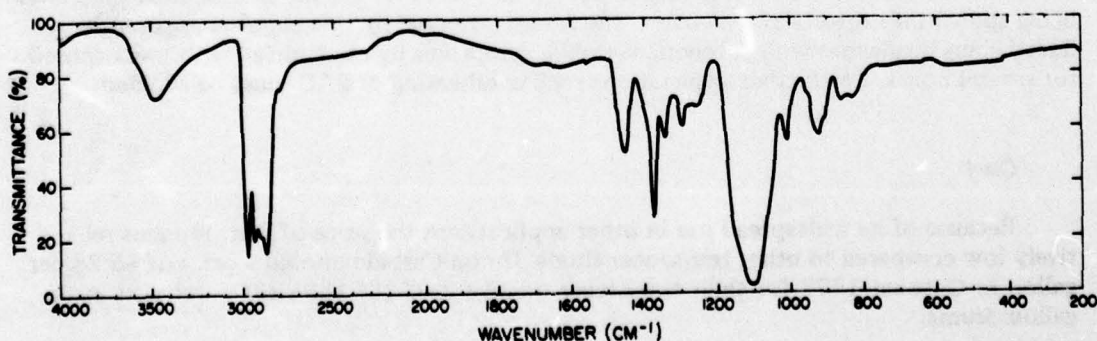


Fig. 5 — Infrared spectrum of PAG

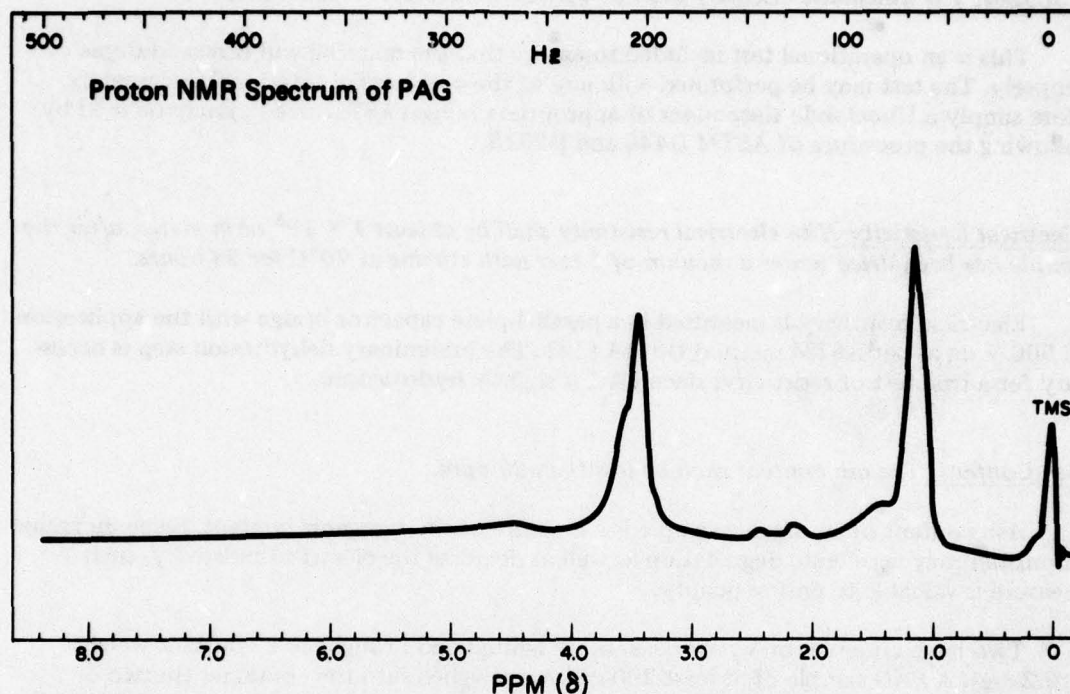


Fig. 6 — Proton NMR spectrum of PAG

Molecular Weight: The transducer liquid shall have a number average molecular weight in the range 570 to 630 grams per mole.

Molecular weight may be measured by a simple cryoscopic method using benzene as the solvent. After the freezing point ($\pm 0.01^\circ\text{C}$) of the pure benzene is measured, PAG should be accurately weighed in at the rate of 1.5 to 4.0 g for 20 g of benzene. The freezing point of the solution is measured in the standard way. The determination should be repeated. Molecular weight is calculated by

$$MW \text{ (g/mole)} = \frac{5120 \times \text{weight of PAG}}{\Delta T \times \text{weight of benzene}}, \quad (10)$$

where ΔT is the change in freezing point of the benzene. Agreement between the duplicates should be 25 g/mole or a third determination should be run. Molecular weight may also be measured to similar precision using any of the commercially available vapor pressure instruments.

More suitably for critical applications, molecular-weight distribution should also be measured using gel permeation chromatography equipment. Any sample from a new source with a relatively broad molecular-weight distribution must be viewed with some concern.

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Viscosity: *The kinematic viscosity shall be between 1.3 and 1.4 stokes at 25°C.*

This is an operational test included to ensure that the material will flow and degas properly. The test may be performed with any of the commercial rotational viscometers. More simply a Ubbelohde viscometer of appropriate range (ASTM size 2c) may be used by following the procedure of ASTM D445 and D2515.

Electrical Resistivity: *The electrical resistivity shall be at least 1×10^6 ohm-meter, after the sample has been dried under a vacuum of 1 torr with stirring at 70°C for 24 hours.*

Electrical resistivity is measured in a parallel-plate capacitor bridge with the application of 500 V dc as per ASTM method D3114 [12]. The preliminary dehydration step is necessary for a true test of resistivity, since PAG is slightly hygroscopic.

Ash Content: *The ash content shall be less than 20 ppm.*

Ash content of an organic sample is a measure of the inorganic content. Since inorganic impurities may accelerate degradation as well as decrease the electrical resistivity, such a measure is valuable to ensure quality.

Two large crucibles or Vycor beakers are ignited and brought to a constant weight (± 0.2 mg). A PAG sample of at least 200-g size is weighed into the container (in two or three batches if necessary) and ignited. After burning has ceased, the temperature should be increased until no carbon residue remains. The crucible is accurately reweighed. Ash content is calculated as follows

$$\text{ppm ash} = \frac{\text{gain in weight}}{\text{sample weight}} \times 10^6 \quad (11)$$

Acidity and Stability: *The initial acidity shall be less than 0.05% (expressed as acetic acid). The sample shall contain a stabilizer to inhibit oxidative degradation. When the sample is heated at 100°C in air for 48 hours with vigorous stirring, the acidity shall not increase to greater than 0.10% (as acetic acid).*

The end result of oxidative degradation of a compound such as this is an organic carboxylic acid. A specification of initial acid content thus ensures that the sample has no extensive degradation as received. A measure of acidity after heating also indicates how effectively the stabilizer prevents oxidation of the sample. Such an acidity test is used in the check on the stabilizer.

The acidity test is performed as follows: Accurately weigh (± 10 mg) approximately 50 g of the PAG sample into a titration flask (perform in duplicate). Add approximately 25 ml of distilled water. Add ethanol until the solution becomes clear, and then add an additional 15 ml of ethanol. Add 5 to 7 drops of a mixed indicator (0.1% bromothymol blue plus 0.1% phenol red) and titrate with accurately standardized 0.02-molar NaOH solution.

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The stabilizer test is performed as above except that after the heated PAG is added to the flask and the water is added, the mixture is heated to 100°C for 2 hours. The ethanol is added after cooling.

Acidity is calculated from

$$\text{percent acidity (as CH}_3\text{COOH)} = \frac{(\text{ml NaOH}) \times (\text{molarity NaOH}) \times 6}{\text{g sample}} \quad (12)$$

For both tests the higher value of the two duplicate determinations should agree within 5% of the lower value or a third determination should be run.

Proposed Method of Synthesis of PAG

PAG may be synthesized on a laboratory scale by the following procedure.

1. Fit a large three-necked flask or reaction vessel with a controllable heating mantle, a thermometer, an addition funnel, a stirrer (magnetic or shaft), and a condenser with flowing chilled (5 to 10°C) water.
2. Into the container weigh 3.42 g of sodium methoxide (0.063 mole) and 3.04 g of methyl alcohol (0.095 mole). Quickly purge with nitrogen or dry air and begin stirring. Add 90 g of propylene oxide (1.55 moles) to the additional funnel.
3. Apply heat to the mixture in the reaction flask until the temperature is near 35°C. Ensure that chilled water is circulating through the condenser and begin adding the propylene oxide dropwise. Continue the addition slowly over a period of 4 to 8 hours.
4. Continue boiling the reaction mixture until the temperature increases to approximately 80°C. This increase will occur rapidly after 24 to 48 hours and signifies the depletion of unreacted propylene oxide.
5. As soon as the temperature increases to 80°C, remove the heat and allow the reaction mixture to cool to room temperature. Add 1.5 ml of water to the flask and stir vigorously.

All of the preceding quantities may be appropriately scaled upward for production. The molar ratio of sodium methoxide to methanol may be decreased for economy, with a possibly longer reaction time. Other catalysts that conceivably could be used in the reaction are ethoxide, propoxide, or butoxide salts or Lewis acids such as AlCl_3 or ZnCl_2 . The products from these catalysts must be qualified carefully, as they produce a wider molecular-weight distribution than the methoxide specified.

The product from the synthesis must be purified by vacuum distillation. A column with a large number of theoretical plates is not necessary. Typically a 15-cm Vigreux column is adequate. This distillation should be carried out at a regulated pressure of 0.1 to 0.2 torr. The product distilling over about 160°C is collected. A boiling point range of up to 25°C is permissible.

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The product so collected should be stabilized to prevent oxidative degradation by the addition of a stabilizer. Approximately 0.5 to 1.0% of BHT (2, 6-di-tert-butyl-p-cresol) is suitable. Other stabilizers such as the secondary amine type are also suitable. Union Carbide's LB135Y23 PAG contains an excellent oxidative stabilizer whose identity is considered to be proprietary.

SUMMARY AND CONCLUSIONS

Discussions of the different aspects of the use of polyalkylene glycol (PAG) make clear that PAG is far from being a universal transducer fluid. Although there are advantages to the use of PAG, they must be balanced against its undesirable properties.

The speed of sound and acoustic impedance (product of density and sound speed) of PAG are both approximately 13% lower than those of seawater at 20°C. This difference between the inside and the outside of the transducer will result in internal reflections, which produce a loss of sensitivity, and in refraction, which produces a loss of directivity. However, the difference in acoustic impedance is only slightly greater than that of castor oil and is much less than that of silicone oil—two other commonly used transducer fluids. By these criteria PAG is effectively equal to or superior to other transducer fluids.

The low thermal expansion and moderate compressibility of PAG make it one of the best choices for use in a nonpressure-relieved design. Pressure changes with changing temperature will be slightly smaller than with castor oil and considerably smaller than with silicone oil. PAG in a transducer with a metal window may thus not build up damaging pressures. A metal window will also avoid the problem of water permeation.

The electrical resistivity of PAG is probably its poorest property. The value of resistivity is from 10^4 to 10^7 times lower than that of castor oil or silicone oil (both of which are approximately $10^{11} \Omega \cdot \text{m}$). In a transducer of moderate or high electrical impedance design PAG will offer a significant parallel current path with a resulting loss of power output or sensitivity.

PAG is the poorest of proposed or currently used transducer fluids with regard to its water solubility properties. The low resistivity just mentioned is partly a result of the high water solubility in PAG. In addition, however, a portion of the water in PAG at equilibrium at a given temperature will precipitate when the temperature is lowered, as is true for any liquid. But the large amount of water in PAG at equilibrium means that a much larger amount of water will precipitate than with other fluids. If, as is likely, the water precipitates onto the surface of the electrical elements, catastrophic failure will result. An additional concern with PAG is the possibility of its low resistivity on exposure to tin salts or perhaps tin, which may lead to electrical failure.

PAG is in general compatible with fewer acoustic-grade elastomers than castor oil. A sonar designer contemplating the use of PAG thus must simply choose materials which are compatible. These may well not be the same elastomers which might be used with a castor-oil-filled transducer. For example, in place of the neoprene window commonly used one may use a butyl or a chlorobutyl (or perhaps a bromobutyl) window.

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PAG has the advantages of low cost and ready availability. Should the current source cease production, the synthesis and specifications contained in this report will allow qualification of additional vendors.

The low viscosity of PAG is a real advantage of its use. It is much easier than castor oil to degas; hence there is less chance of air bubbles inside the transducer. The toxicity of PAG is quite low, and any possibility of poisoning by the vapors from overheated material is easily avoided.

In conclusion, although PAG is not a universal transducer fluid, with proper care in avoiding water exposure and in choosing exposed materials, PAG may find applications in several Navy sonar units.

ACKNOWLEDGMENTS

The helpful discussions with Dr. R. W. Timme and the able assistance of Misses D. P. Todd, L. A. Williamson, and S. K. Riesen and Messrs. E. W. Thomas and M. P. Shaver are gratefully acknowledged. Appreciation is also given to Messrs. L. P. Browder and L. A. Boles for information provided on their phase of this work.

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APPENDIX A

EXPERIMENTAL TECHNIQUES

The speed of sound was measured in the PAG samples with a NUS Corp. model 6105 laboratory velocimeter. It was calibrated with distilled water immediately prior to the measurements and certified to an accuracy of $\pm 0.05\%$. The model 6105 velocimeter employed a transducer which transmitted a 3.6-MHz sound pulse through the fluid under test to a second transducer which was separated from the first by a fixed distance in the fluid. With an electronic counter the pulse repetition rate (the inverse of the pulse transmit time) was determined and converted to sound speed. The temperature of the fluid was controlled by a thermoelectric cold-hot plate with magnetic stirrers. The fluid was stirred at the rate of 100 ml/min, and the temperature which was measured with two precision thermistors, was calibrated to $\pm 0.05^\circ\text{C}$. The total uncertainty of any single measurement of sound speed was $\pm 0.1\%$.

The water content of PAG was monitored throughout using Karl Fischer titration. A majority of these determinations were performed using a Fisher Scientific model 390/392 K-F titrator. Standardization was performed periodically with weighed samples of deionized water. Precision was measured to be less than $\pm 2\%$ relative (σ). The possibility of side reaction with the ether bond was investigated by determining H_2O content of a PAG sample by both KFR and Dean-Stark azeotropic distillation. The Dean-Stark distillation gave 0.14%—an insignificant difference from the 0.15% result for the KFR titration.

The pycnometers used to measure the density of PAG were calibrated with freshly boiled deionized water. The change of density of PAG with temperature was measured using a Cassia flask that had also been calibrated with boiled deionized water.

The adiabatic compressibility of PAG was measured at USRD by Boles Timme, and Shelton [3]. A reciprocity-coupler method is used to measure the sensitivity of a hydrophone to 500 Hz over a temperature range of 5 to 45°C and a pressure range of 0 to 100 MPa gage. The adiabatic compressibility can be obtained by comparing the sensitivity measured for a material whose acoustic properties are known to the sensitivity for the material in question.

The electrical resistivity of PAG was measured using a General Radio model 1644-A megohm bridge with a parallel-plate electrode. This electrode was constructed from copper imbedded in poly(methyl methacrylate) plastic. The electrode and cable were electrically shielded. The cell geometry was used to calculate the cell constant. In a parallel-plate configuration this is simply the area of the plates divided by the distance between them. This yielded a constant of 3.66 for the cell used in this work.

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The arc and corona tests of PAG and the other transducer fluids were performed with a Velonex model 360 high-power pulse generator. The pulse voltage was applied across silver electrodes on a lead zirconate-titanate piezoelectric ceramic (PZT-4). The onset of corona and arcing was detected by both visual examination and observation of current traces on an oscilloscope.

The water partial pressure over solutions of water in PAG was measured with a Panametrics model 2000 hygrometer. This instrument uses aluminum-aluminum oxide-gold sponge electrodes whose capacitance is a function of the partial pressure of water in the surrounding atmosphere. These electrodes were calibrated using saturated solutions of salts as suggested by NBS.*

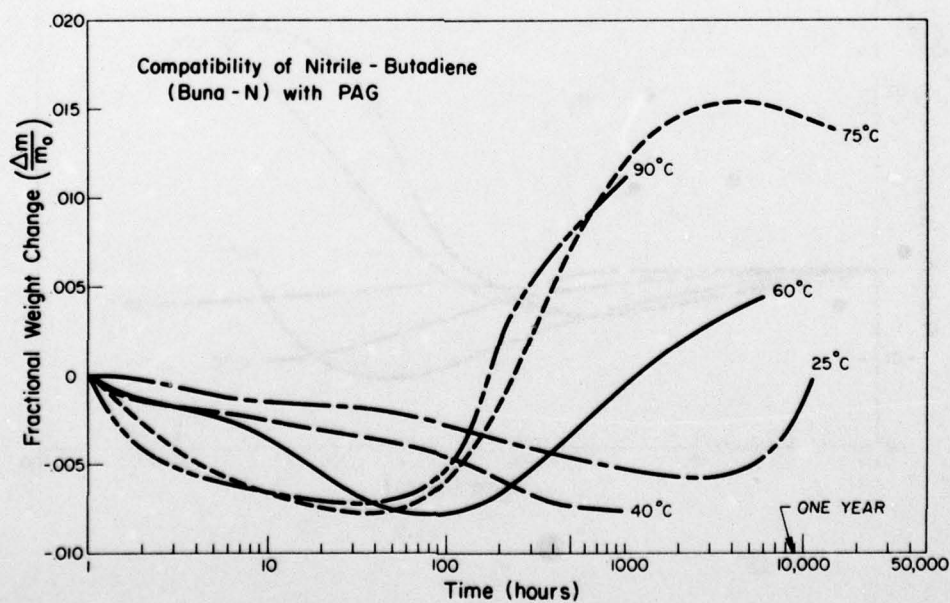
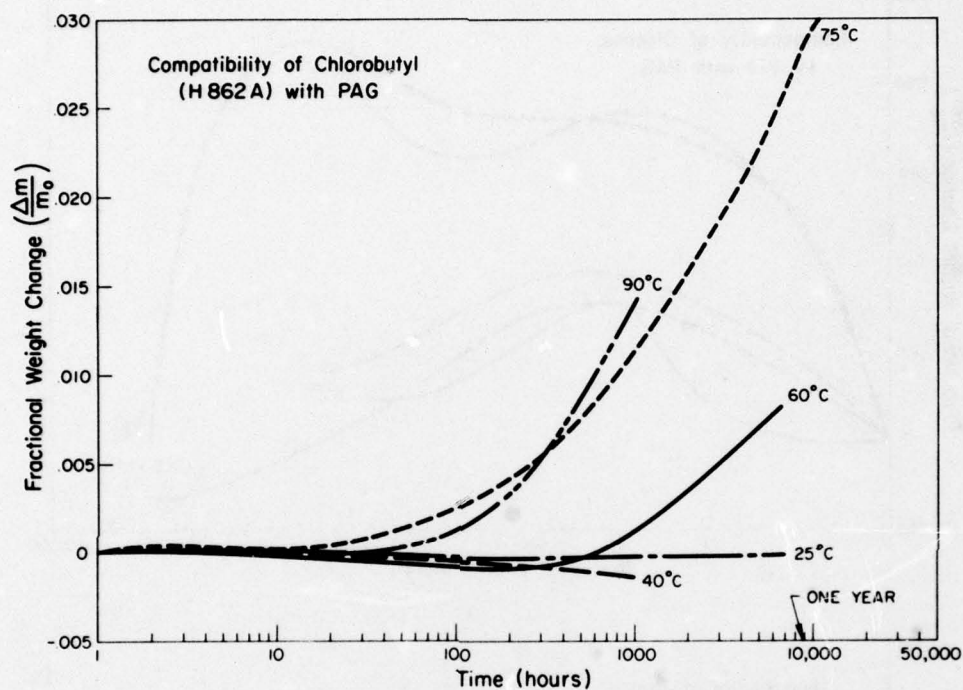
Saturated solutions of water in PAG at different temperatures were prepared by vigorously stirring water with PAG at approximately 25°C above the temperature of interest. After the phases separated, the PAG was decanted. The temperature of the PAG was decreased slowly until a slight precipitate appeared. The temperature was then increased until the cloudiness just disappeared. At this point the water content was measured by KFR titration.

The solubility of PAG in water was determined by a gravimetric procedure. A large sample of water (about 200 ml) was warmed and stirred with PAG. After cooling, the last traces of PAG were removed by blotting with phase-separation filter paper (Whatman 1-PS). The solution was weighed and evaporated with gentle heating to near dryness. The last traces of water were then removed with more gentle heating but under an air flow to avoid burning.

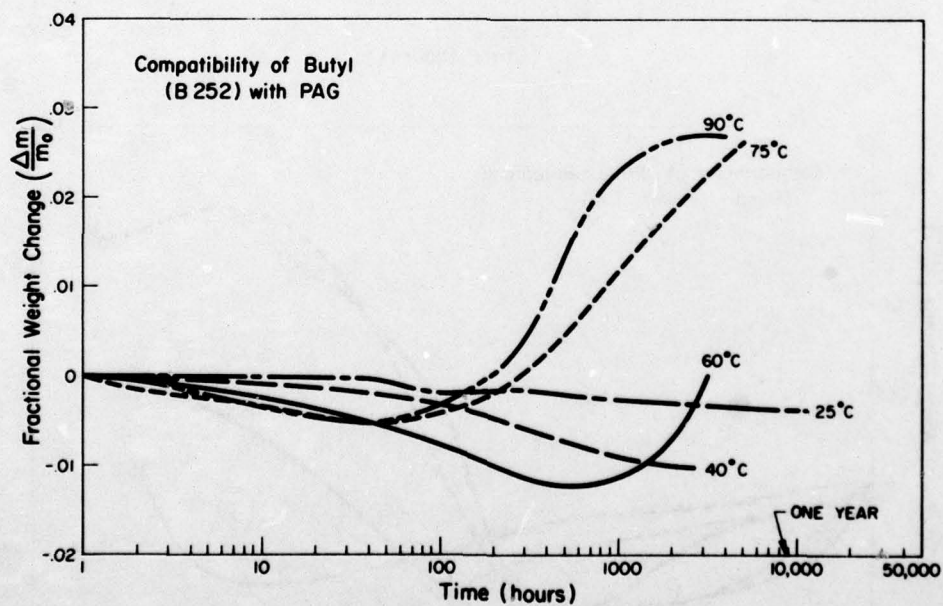
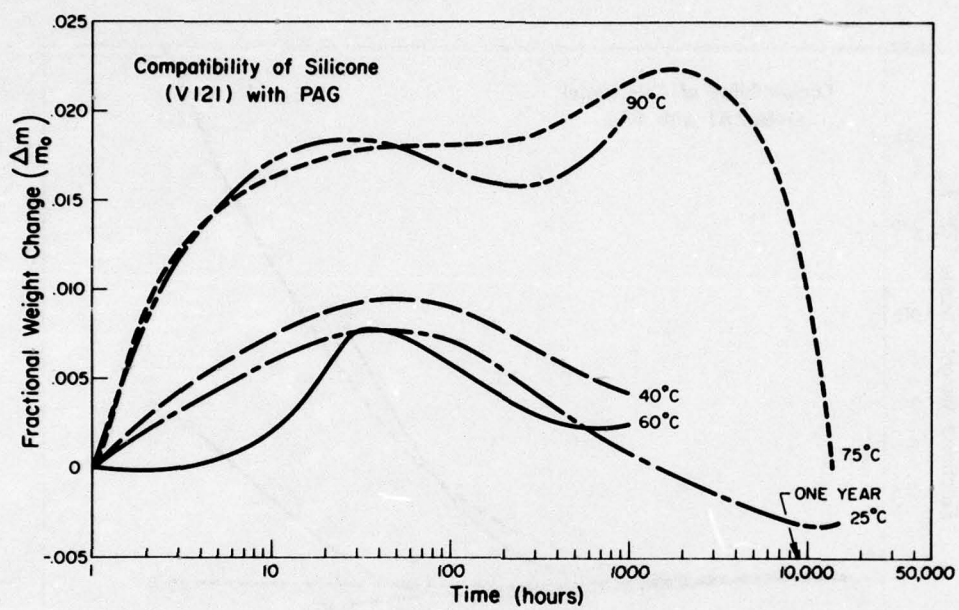
The compatibility tests were performed by immersing weighed samples of the elastomer in PAG that was maintained at the test temperature. A minimum of four samples of each elastomer at each temperature was used. The samples were 25 by 25 by 3.94 mm. This provided a surface-to-volume ratio of 0.666 mm⁻¹. When samples of this specific size were not available, others with similar surface-to-volume ratio were used.

*L. Greenspan, J. Res. National Bur. Stds. 81A, 89-96 (1977).

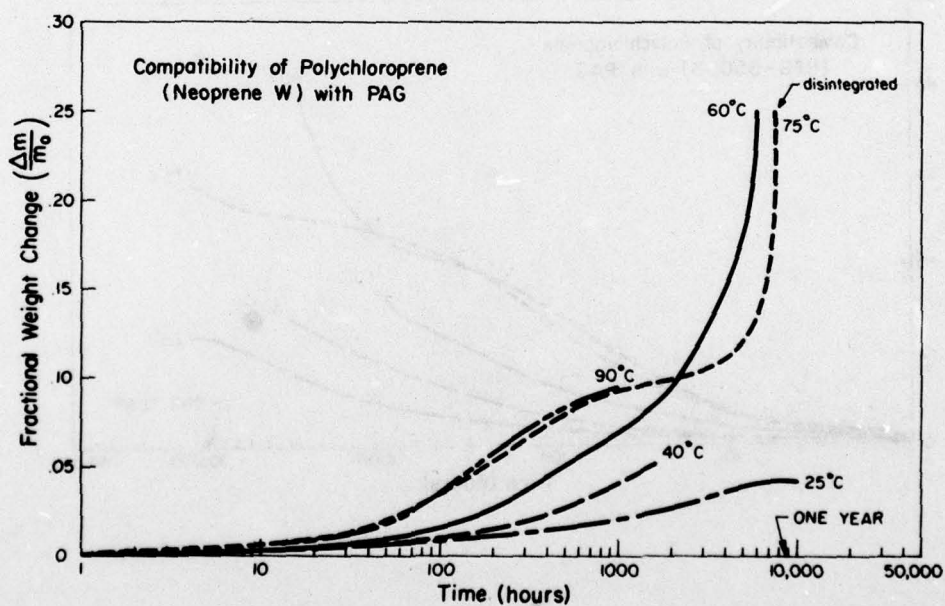
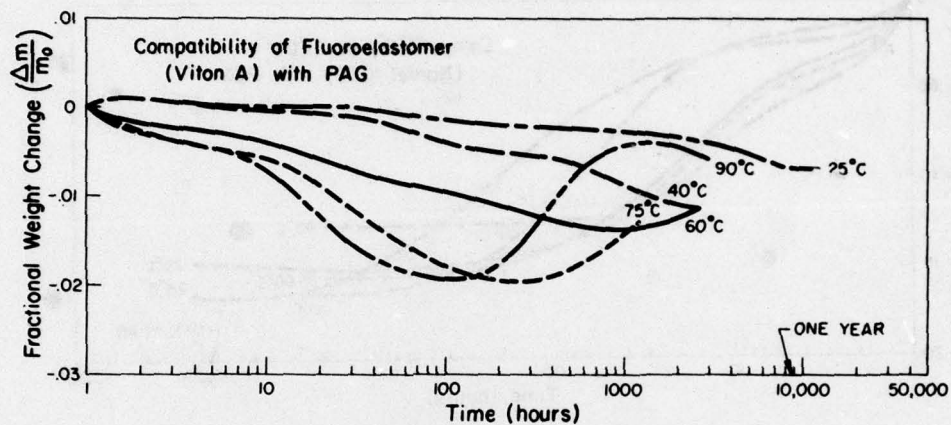
APPENDIX B **COMPATIBILITY GRAPHS**



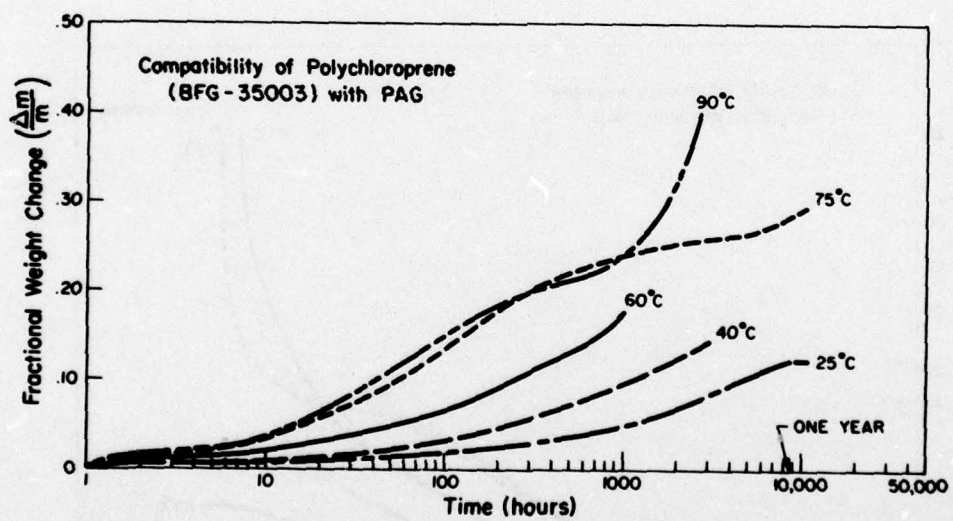
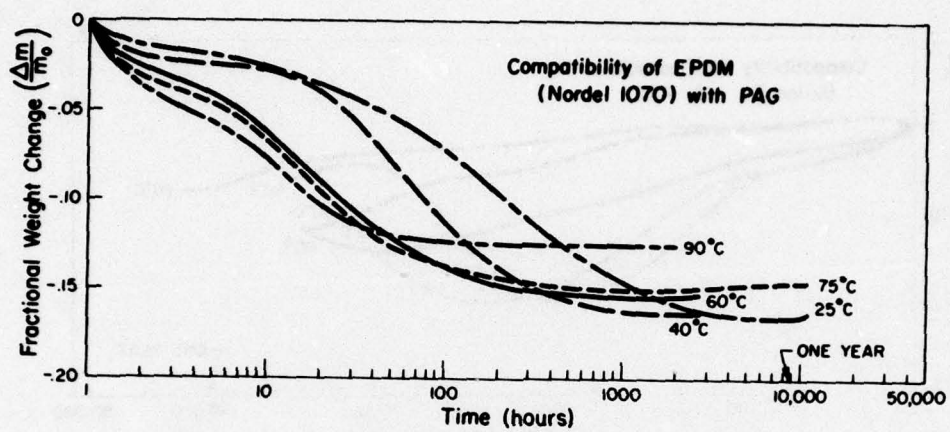
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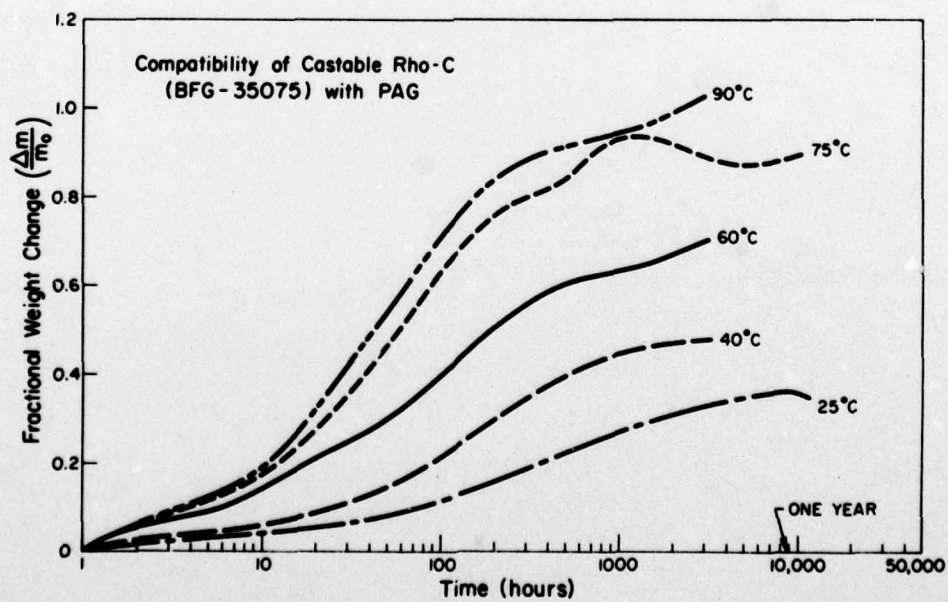
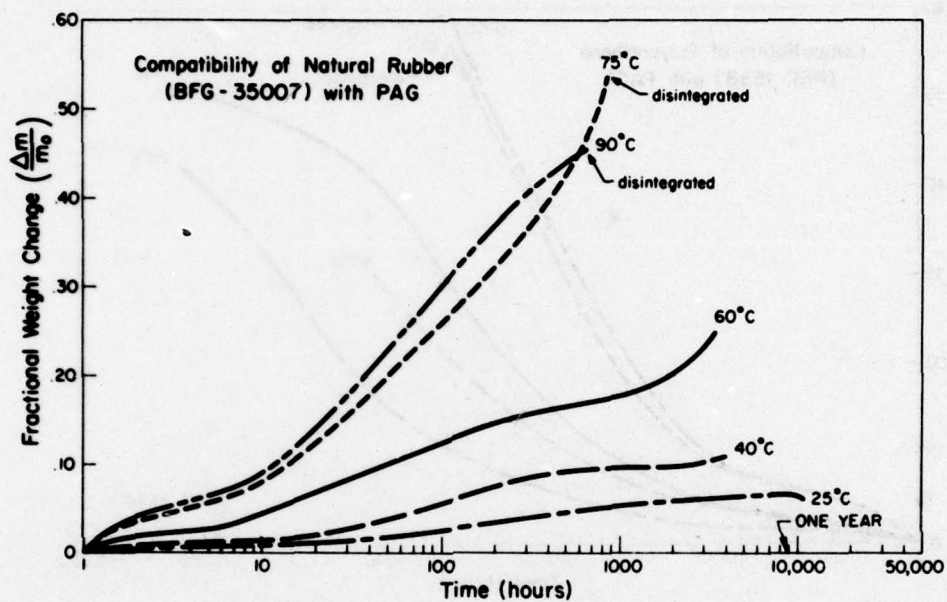
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