Received from Dick Fezatte of Dow Chemical 6/27/68, with regard to Dowtherm 209.

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The Effect of Ethylene Glycol and Methoxypropanol-Based Coolants on Elastomers

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SEALING THE COOLANT PASSAGES in a liquid-cooled internal combustion engine is becoming more and more difficult as coolant temperatures and pressures increase and as the expected service life from all engine components is extended. This paper attempts to explain what happens when different coolants contact nonmetallic components of the cooling system and how this relates to field performance.

Of particular concern in this paper is the effect of alternate exposure of elastomers to water and to antifreeze/coolant solutions. Year-around use of an antifreeze/coolant is the exception rather than the rule in heavy-duty equipment such as trucks, buses, and off-highway vehicles, so this alternate exposure must be considered.

In 1965 an antifreeze/coolant based on methoxypropanol rather than the traditional ethylene glycol or methanol was introduced for use in heavy-duty equipment under the name Dowtherm* 209 coolant. During the development of Dowtherm 209 coolant, the effect of solutions of methoxypropanol on commonly used hose and seal materials was thoroughly studied. This investigation has continued and was expanded recently to include a re-evaluation of ethylene glycol - based antifreeze products with respect to the alternate use of water in warm weather and antifreeze/coolant in cold weather.

*Registered trademark.

THEORY BEHIND "RUBBER SWELL"

NONPOLAR ELASTOMERS - The simplest case is that of a nonpolar elastomer, such as natural rubber or GR-S, in contact with an organic liquid. The equilibrium swelling depends upon the degree of cross-linking of the rubber and upon the thermodynamic affinity of the liquid for the hydrocarbon chains.

The latter factor can be simply related to the solvent cohesive-energy-density (CED) or its square root, the "solubility parameter (SP)."

$$CED = \frac{\Delta E_{vap}}{\text{Molar volume}} = \frac{\Delta H_{vap} - RT}{\text{Molar volume}}$$

$$SP = (CED)^{1/2}$$

The best swelling agents for a given (nonpolar) elastomer are those which match the polymer in CED and hence in SP.

ABSTRACT

The effect of different coolants on common hose and seal formulations currently in use in heavy-duty engines has been studied. Water, ethylene glycol, and methoxypropanol coolants have been studied in contact with seven different types of elastomers. A brief discussion of the theory behind rubber swell is presented, as are laboratory and field test data. The data indicate that seasonal failure of hoses and seals may be caused by a sudden change in the composition of the coolant.

Swelling power decreases with increasing mismatch in SP between elastomer and liquid. With a given liquid, the degree of swelling decreases with increasing cross-linking of the elastomer. This dependency is particularly pronounced with powerful swelling agents, which have unlimited miscibility with the unvulcanized elastomer. For poor swelling agents, which are nonsolvents for the unvulcanized elastomer, the variation in equilibrium swelling resulting from differences in cross-link density is less pronounced, but still present. These effects are indicated schematically in Fig. 1. Table 1 lists the values of CED and SP for several typical solvents and elastomers. A more complete tabulation is available in the literature (1)*.

OIL RESISTANT ELASTOMERS - Some synthetic elastomers contain polar groups. This reduces their swelling by low SP liquids, such as hydrocarbons, but increases their swelling by many polar liquids.

The swelling behavior of a polar elastomer differs from that of a nonpolar elastomer in two important ways:

1. It has a higher value of SP.
2. Solubility parameter alone does not provide a satisfactory means of quantitatively explaining or predicting the degree of swelling by a wide variety of liquids.

The swelling of a polar polymer by a polar solvent involves specific interaction between polar groups -- not merely an overall match in SP. A number of approaches has been suggested to provide the necessary multiple characterization of a given liquid (2, 3, 4).

In particular, Beerbower, et al. relate the swelling of various elastomers to the solubility parameter, the dipole moment, and the hydrogen-bonding power of the liquid in question.

Every hydrogen bond involves a "Lewis acid" (that is, electron acceptor) and a "Lewis base" (electron donor). Some molecules can play the role of "base" in hydrogen bonding, but not that of "acid," for example, pyridine, or more weakly, ethers and ketones. Other molecules can act as "Lewis acids." And some molecules (for example, water, alcohols, primary amines, amides) possess both an "acidic" and a "basic" atom and thus can hydrogen bond to their own species. In terms of this terminology, an elastomer which possesses Lewis acid groups will exhibit a particularly strong affinity for solvents which contain Lewis base groups, and vice versa.

Styrene-butadiene rubber, for example, has a rather low SP, and no tendency for hydrogen bonding; the most powerful swelling agents are liquids with solubility parameters in the range of 8.0-10.0.

Neoprene rubber is somewhat more polar than SBR; and nitrile rubber still more polar. Nitrile rubber acts both as a Lewis acid and as a Lewis base, and is strongly swelled by intermediate SP liquids, particularly those containing "base" or "acid" groups. Viton rubber (a fluorine-containing elastomer) acts as a Lewis acid and, consequently, is preferentially swelled by intermediate SP liquids which possess Lewis base groups.

SPECIAL ROLE OF WATER - Compared with all these elastomers, water has a very high cohesive energy density and, on the basis of the above discussion, would be expected

*Number in parentheses designates References at end of paper.

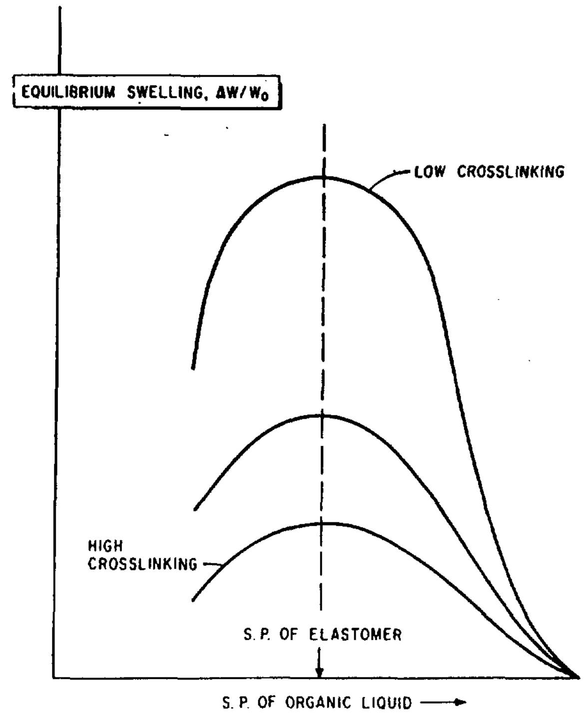

Fig. 1 - Equilibrium swelling as function of SP

Table 1 - Cohesive Energy Density (CED) and Solubility Parameter (SP) for Typical Liquids and Elastomers

Substance	CED	SP
n-Octane	58	7.6
n-Decane	61	7.8
Cyclohexane	67	8.2
Propylbenzene	76	8.7
Toluene	81	9.0
Ethyl Propionate	81	9.0
Dioxane	94	9.7
Butanol	117	10.8
Ethanol	170	13.0
Methanol	210	14.5
Ethylene-Propylene Rubber	64	8.0
Styrene-Butadiene Rubber	69-74	8.3-8.6
Neoprene	77	8.8
75/25 Butadiene/Acrylonitrile	88	9.4
70/30 Butadiene/Acrylonitrile	92	9.6

to exhibit a very low swelling power. And yet many elastomers in contact with liquid water for long periods of time, particularly at high temperatures, can absorb very large amounts. The explanation of this apparent anomaly lies in the fact that typical vulcanizates contain small amounts of extremely hydrophilic materials. Water can be imbibed to form a colloidal dispersion of droplets, which also contain hydrophilic impurities. The osmotic action of these hydrophilic materials within the water droplets provides the driving force for entry of more water. The elastic properties of the elastomer matrix provide some resistance to continued enlargement of the droplets. Different elastomers vary widely in their tendency to imbibe water by this two-phase mechanism (5).

LEAKAGE PROBLEM

Ever since ethylene glycol was first used as an antifreeze/coolant for internal combustion engines about 40 years ago, the problem of "glycol creep" has been a major concern to engine operators. "Glycol creep" may be defined as the common tendency of coolant leaks to appear in a seemingly "tight" cooling system shortly after the installation of ethylene glycol-based antifreeze.

External coolant leakage resulting from "glycol creep" is at best a costly nuisance, resulting in high coolant make-up and requiring tightening or replacement of hose clamps. Since external leakage of glycol antifreeze can often go undetected by the operator for long periods of time, there is a very serious danger that coolant loss will continue until there is insufficient coolant in the engine and severe overheating occurs with resulting engine damage.

Internal leakage of glycol-based coolant can be catastrophic. The glycol reacts with lubricating oil to form sludge and varnish which increase oil viscosity, plug oil passages, cause piston rings and pins to "freeze," and, in many cases, cause seizure of the engine.

While it is certainly true that seals and sealing systems have been vastly improved in recent years, the problem of coolant leakage remains a serious one, particularly for the operator of heavy-duty equipment. For example, a 1966 survey conducted by the Regular Common Carrier Conference (RCCC) showed 74% of the truck operators surveyed considered internal leakage of coolant to be a serious maintenance problem in their operation. This internal leakage problem appears to occur in all types of diesel engines. Leakage is most common past cylinder head seals, injector tubes, and cylinder liners.

In the past few years, methoxypropanol-based antifreeze coolant has replaced glycol-based antifreeze in many truck and off-the-road fleet operations. Methoxypropanol has been shown to minimize the progressive engine damage associated with internal leakage of glycol-based coolant. Also, the distinctive odor of methoxypropanol makes detection of external leaks much easier.

While the movement from glycol to methoxypropanol coolant in heavy-duty equipment means less severe results

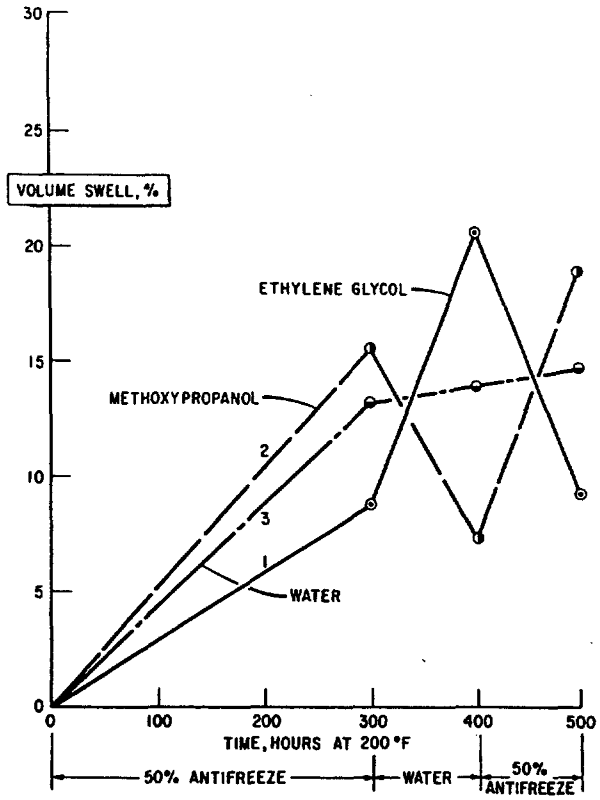

Fig. 2 - Buna-N "O" ring (engine manufacturer A)

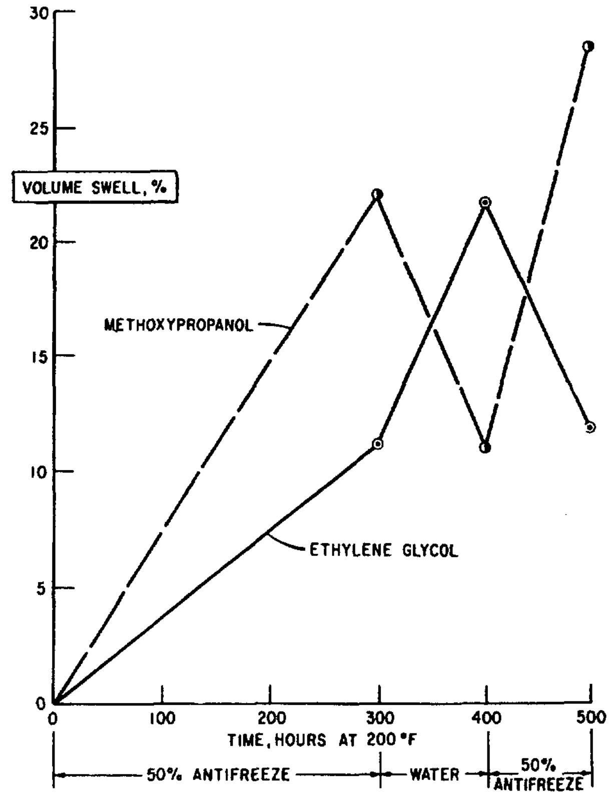

Fig. 3 - Buna-N "O" ring (engine manufacturer B)

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of leakage past seals and hose clamps, leakage still poses a problem and must be minimized.

"CYCLING" EFFECT

Published data usually show the effect of a single immersion of a given elastomer in a solution of antifreeze. In actual practice many operators of heavy-duty equipment use inhibited water in the summer and antifreeze/coolant only in the winter or, at best, the concentration of antifreeze is allowed to vary significantly during the year. Thus, it was felt to be more realistic to measure the effect of alternate exposure of the same sample of elastomer to the antifreeze/coolant and to plain water.

EFFECT ON O-RINGS - Fig. 2 shows the per cent volume swell of a buna-N "O" ring after 300 hr at 200 F in a 50% solution of antifreeze, followed by 100 hr at 200 F in water, followed by an additional 100 hr at 200 F in a 50% solution of antifreeze. Curve 1 on Fig. 2 shows the data obtained with ethylene glycol antifreeze and curve 2 shows data obtained with methoxypropanol antifreeze.

Note the very pronounced "saw tooth" pattern which indicates a substantial reduction in volume when moving from water to glycol or from methoxypropanol to water. This, of course, corresponds to shrinkage of the rubber part in the "fall" with glycol and in the "spring" with methoxypropanol. In contrast, curve 3 in Fig. 2 shows the per cent volume swell resulting from immersion of the seal in water only.

The slow, smooth increase shown in curve 3 on Fig. 2 should help keep the seal pressed against the metal surfaces, extending the effective life of the seal. The sudden reduction of volume experienced when changing types of coolant, however, may cause the seal to fail if it has become hardened and lost its ability to conform to the new conditions.

Fig. 3 shows data obtained with buna-N "O" rings used by another engine manufacturer. The pattern is similar to the previous tests.

Fig. 4 shows the same "cycling" pattern obtained with neoprene "O" rings. In this case, water alone results in more swelling than either type of antifreeze, but the swelling is uniform in contrast to the saw-tooth pattern obtained when the antifreeze/coolant is alternated with water.

Fig. 5 shows data obtained with ethylene-propylene (EPT) "O" rings. The saw-tooth pattern is the same as for buna-N and neoprene although the absolute volume changes are different.

Silicone "O" ring formulations used by several different engine manufacturers were also tested. The volume change caused by immersion in any of the coolants tested was so slight, however, that no meaningful pattern was detectable.

EFFECT ON HOSES - The same testing was done on seven different types of cooling system hoses. The tests were carried out with transverse sections cut from commercially available heater hoses.

The types of hose tested were butyl, neoprene, Hypalon rubber (chlorosulfonated polyethylene), ethylenepropylene

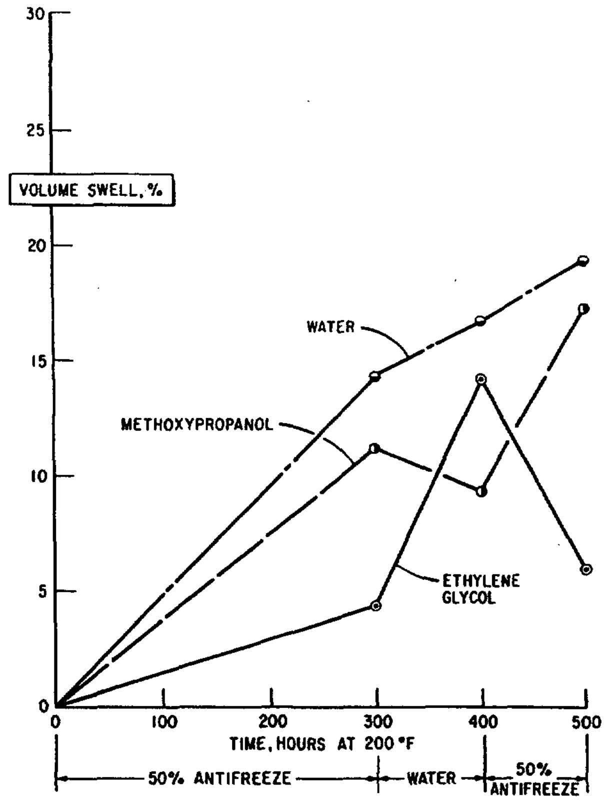

Fig. 4 - Neoprene "O" ring

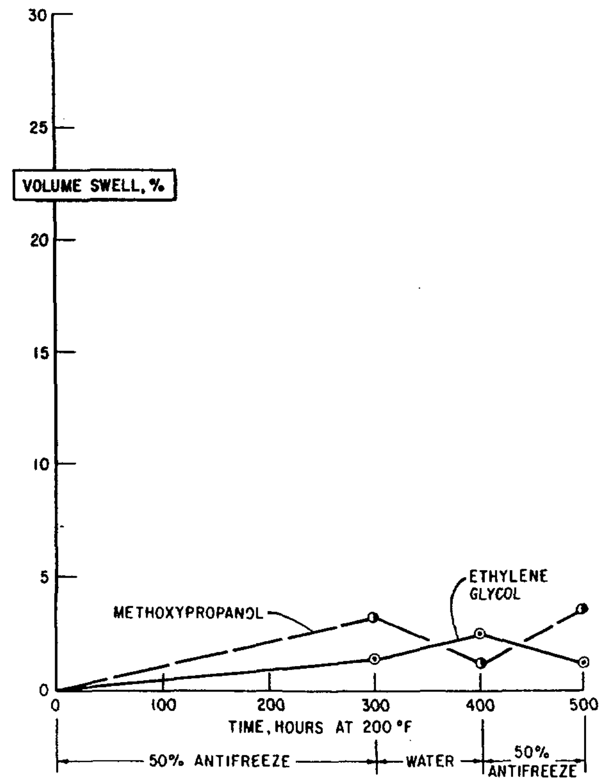

Fig. 5 - Ethylene-propylene (EPT) "O" rings

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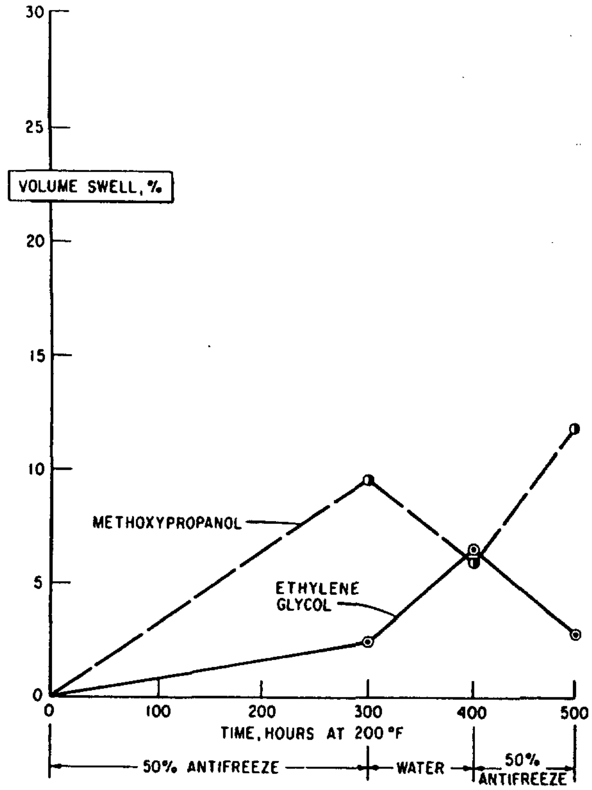

Fig. 6 - Butyl heater hose section

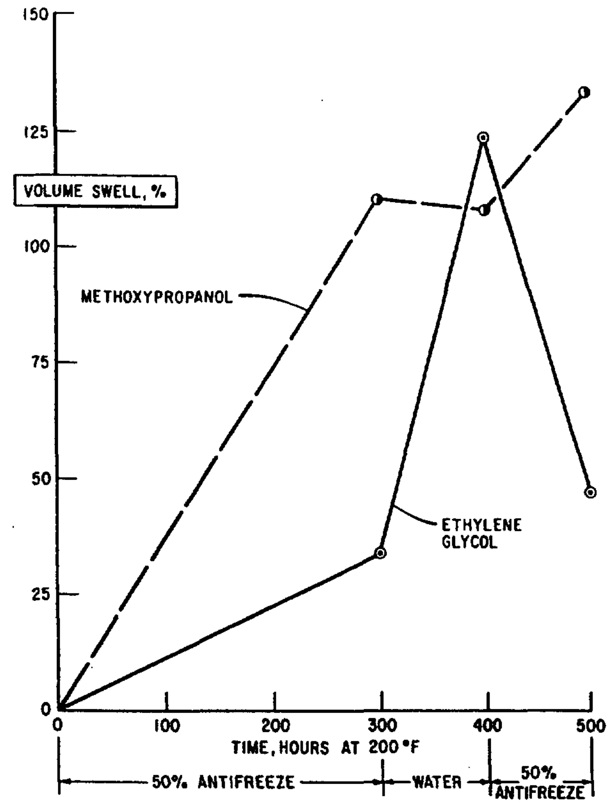

Fig. 8 - Section of heater hose made of Hypalon

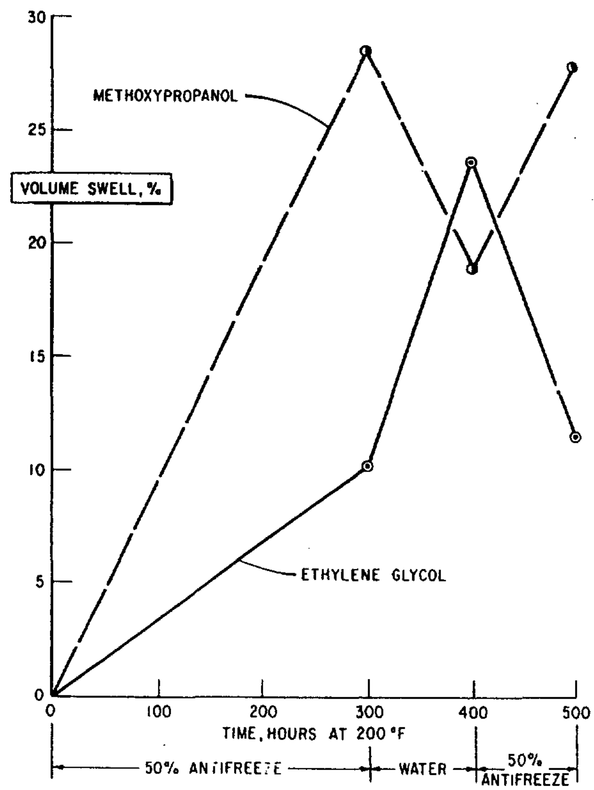

Fig. 7 - Neoprene heater hose section

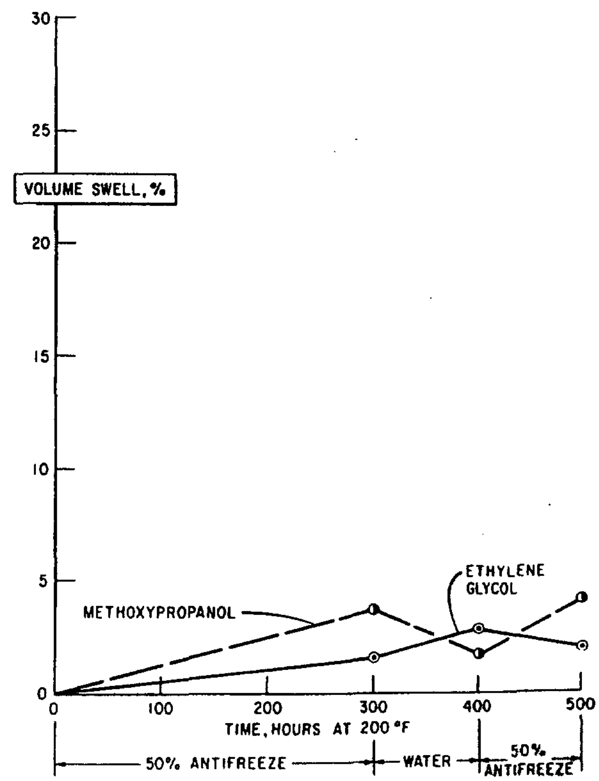

Fig. 9 - EPT heater hose section

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(EPT), buna-S, buna-N, and relaim stock. The data obtained from these tests are shown in Figs. 6-12.

It should be emphasized that all the materials tested with the cycling pattern of coolant were commercially available materials, representative of what is being used today in all types of heavy-duty equipment.

FIELD FAILURE PATTERNS

Tests by leading hose, seal, and engine manufacturers as well as customer experience have shown no significant differences in the service life of commonly used nonmetallic materials whether methoxypropanol or glycol-based antifreeze is used. The data presented in Figs. 2-12, however, suggest that seals are more likely to fail at the time of replacement of water with glycol or replacement of methoxypropanol with water. That is, if the hose or seal is nearing the end of its useful life, the sudden "shock" caused by changing the coolant may cause failure to occur at the time of changing the coolant.

Limited field data tends to confirm that most seal failures occur when switching to glycol from water or to water from methoxypropanol. That is, in the fall if glycol antifreeze is used and in the spring if methoxypropanol is used. Fig. 13 shows a typical distribution of seal failures when glycol antifreeze is used. Also shown on Fig. 13 is the distribution of seal failures for one over-the-road carrier using Dowtherm 209 coolant (methoxypropanol base). The peaks occurred soon after the coolant was changed to or from water.

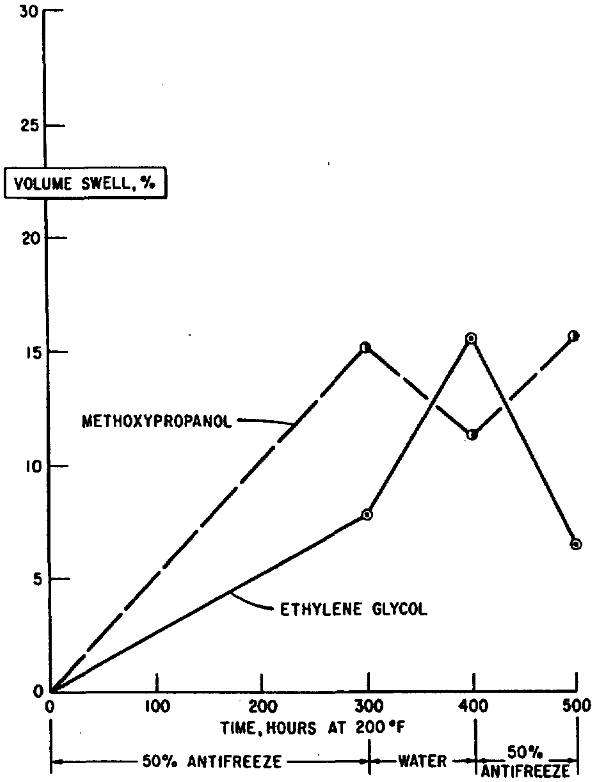

Fig. 10 - Buna-S heater hose section

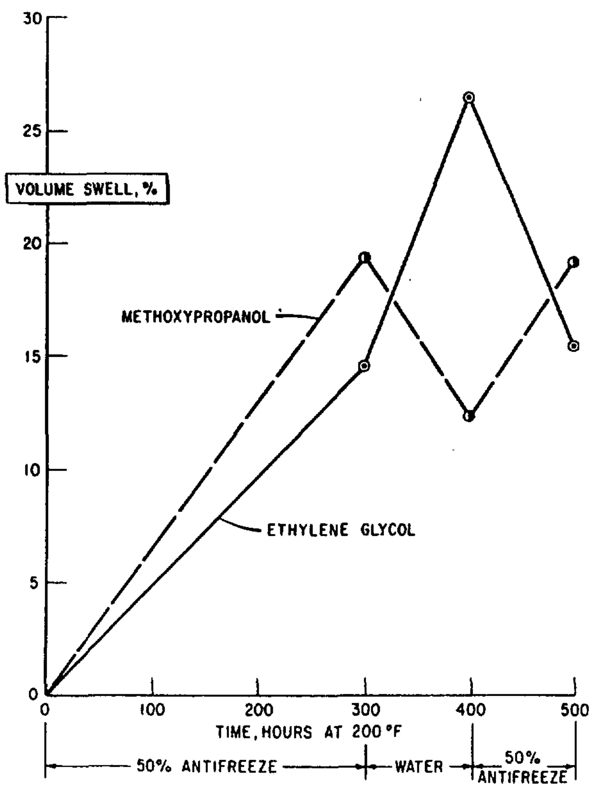

Fig. 11 - Buna-N heater hose section

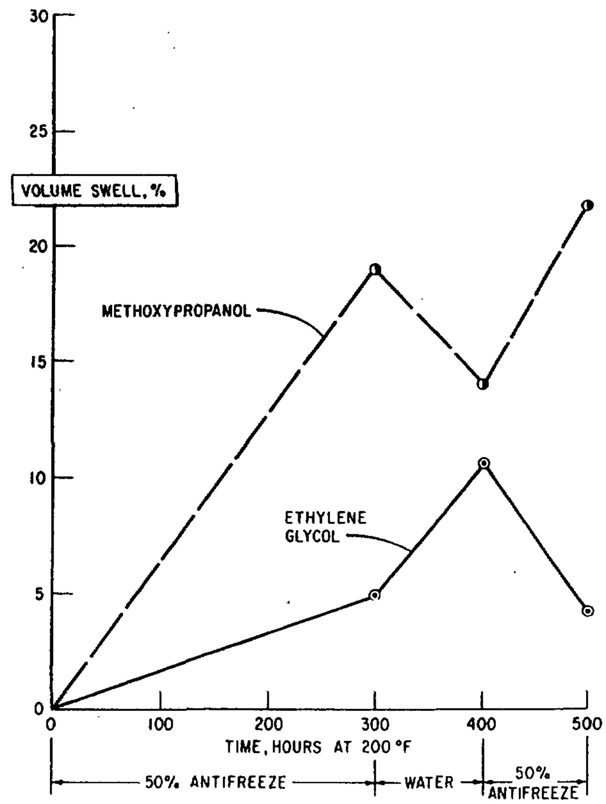

Fig. 12 - Reclaim heater hose section

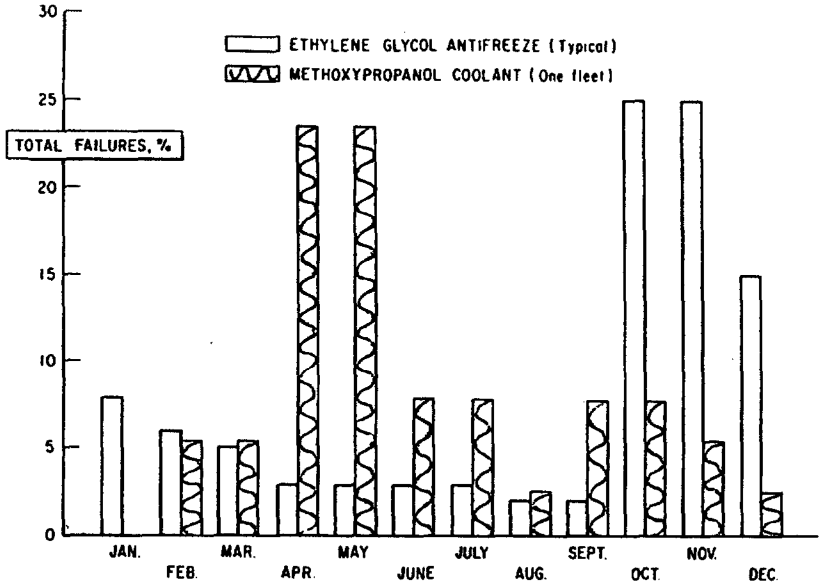

Fig. 13 - Typical seal failure pattern

It should be made clear that both cases described by Fig. 13 are extreme and the average user of either type of antifreeze does not experience this severe seasonal failure rate. However, whenever seasonality of seal failures occurs, it imposes an additional burden on the equipment operator due to loss of availability of many units at one time. Whenever seasonality is severe, it appears to be coincident with:

1. A large number of units with a similar high mileage (and hence seals which are nearing the end of their normal life span).

2. A sudden change from antifreeze/coolant to plain water or vice-versa.

Some operators have found that year-around use of methoxypropanol coolant helps to reduce the seasonality of seal failures. Others simply allow the concentration to decrease slowly by the addition of water as make-up once the danger of freezing is past. Likewise, year-around use of glycol antifreeze should minimize the seasonal pattern of seal failures, and result in a more uniform rate of leakage throughout the year.

SUMMARY AND CONCLUSIONS

1. Different types of elastomers are affected differently by different types of coolant. The general effect can often be estimated by an examination of various chemical and thermodynamic properties of both the elastomer and coolant.

2. Changing the composition of the coolant in contact with a given elastomer causes corresponding changes in the volume of the elastomer.

3. Limited field data indicate that seasonal failure of hoses and seals may be due to a sudden change in the composition of the coolant.

4. From the data presented, it may be reasonably concluded that seasonal failure of nonmetallic components of the cooling system can be minimized by avoiding sudden changes in the composition of the coolant.

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