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Automotive Antifreezes

UNITED STATES DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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Automotive Antifreezes



National Bureau of Standards Circular 506

Issued November 4, 1952

Supersedes Circular 474

Preface

For over 25 years the National Bureau of Standards has issued a leaflet on automotive antifreezes as an expedient means of answering the many letters of inquiry on this subject. This leaflet was revised as new data became available. A discussion is given in the present Circular of the results of extensive tests at the National Bureau of Standards as well as a summation of the work of other investigators. The studies of the Bureau, made largely for various Federal agencies, have included not only simulated and actual service tests of antifreezes but also basic investigations of the physical and chemical properties of antifreeze compounds and of materials currently used in the cooling system itself.

This Circular is intended primarily for the average automobile owner. It should also prove helpful to manufacturers and businessmen interested in entering the field of antifreeze production. Common types of antifreezes are discussed, with a presentation of their properties, and information has been provided on the cooling systems of automobiles. Knowledge of the cooling system is important not only in the choice and proper use of an antifreeze but also in the normal operation of automotive vehicles.

A. V. ASTIN, *Director.*

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Automotive Antifreezes¹

When antifreeze should be installed, what strength should be used, and what kind of antifreeze is best suited to the service involved are discussed. Pertinent physical properties and service performance of the major categories of antifreezes are given. A section treats of how the automobile should be prepared for antifreeze. Simple means for distinguishing the different types of antifreezes and for determining the protection are described. The replacement of antifreeze solution loss and the question of whether antifreeze solutions can be used safely for more than one season is discussed.

I. Cooling Systems and Coolants

1. Engine Cooling Systems

The cooling system of the modern automotive engine is composed essentially of a radiator, radiator hose, circulating pump or pumps, cooling fan, and the passages in the engine block and cylinder head through which the coolant² flows to the various parts of the engine. In addition, most engines have devices designed to control operating temperature and to reduce coolant losses due to overflow from boiling. These accessories include thermostats and special pressure-type radiator caps.

In operation, the final cooling is by means of air flowing through the radiator, which is really a heat exchanging device. However, the engine is referred to as liquid-cooled, because the heat is first transferred from the metal parts of the engine to the circulated coolant.

The path of the coolant is essentially the same in all automotive engines. The coolant is forced by the pump through the engine, passing over the hot areas of the cylinders, valve ports, and the top of the combustion chamber. This liquid, having received heat from the engine, is then passed through the radiator, and the cooled liquid is returned to the circulating pump through the lower radiator hose, thus completing the cycle.

Engine block and cylinder head. The water passages in the engine block and cylinder head form the engine water jacket through which the circulating coolant must pass in order to provide effective cooling of the hot parts of the engine. Narrow passages within this jacket provide cooling around cylinders, valve ports and seats, and over the combustion chamber at the top of the cylinder.

¹During the recent emergency, a short supply of alcohols and glycols caused many substitute materials to appear on the market as antifreezes. The regulatory agencies of the Government called on the National Bureau of Standards to provide technical information about these substitutes, and it was necessary to develop tests by which they could be evaluated. The Bureau does not have authorization, funds, or facilities to test antifreezes for any but Governmental agencies, and the detailed results of individual tests are not made public. Neither does the Bureau recommend or endorse any proprietary product or material.

²A "coolant" is any cooling liquid, e. g., water, antifreeze, or other liquid.

These passages are designed to control the circulation of the coolant in a definite manner. Thus any restriction, such as may be produced by rust or the deposition of minerals from hard water, will seriously interfere with proper cooling and may lead to local temperatures so high that damage to the metal parts may result.

The joint between the cylinder head and the block is made tight by means of a special gasket having suitable holes that allow proper flow of the coolant. Since this gasket must withstand the pressure produced in the combustion chamber during the power-producing explosions, it is imperative that it be properly installed and kept completely leak-proof at all times. Liquid coolant leaking into the combustion spaces or exhaust gases being forced into the coolant surrounding the cylinders may lead to serious trouble during subsequent operation.

Radiator. The radiator serves as a heat exchanger in which the heat transferred to the coolant in passing through the engine is dissipated into the surrounding atmosphere. Although the details of construction of radiators vary somewhat, a radiator consists essentially of the top tank, the core, and the bottom tank, with the top tank providing a means of distributing the coolant over the core and the bottom tank serving as a collector of the coolant and a sump for the deposition of sediment.

The top and bottom tanks are usually brass and are soldered to the core. In order to obtain the maximum transfer of heat, the core is composed of a large number of small vertical passages alternating with air spaces between them. These are formed from thin-walled tubing or sheet of brass or copper. The effective area for heat transfer is further increased by closely spaced strips of thin sheet copper soldered to the outside of the vertical passages. The purpose of this construction is to provide the largest possible ratio of area to volume consistent with the required rates of coolant flow through the inside of the core and air flow around the outside.

Circulating pump. The centrifugal circulating pump usually has a cast-iron housing and impeller; although aluminum alloys are sometimes used. As the pump is driven from the outside, it must be provided with a suitable seal around the pump shaft to prevent coolant losses. Under some conditions of operation, the pump may circulate coolant at the rate of 6,000 gallons per hour or more. The importance of maintaining a clear, unrestricted cooling system is thus evident.

Thermostat. The thermostat in the cooling system is essentially an automatic valve, opening when hot and closing when cold. It serves to prevent unnecessary coolant flow in a cold engine, thereby decreasing warm-up time and wear, and to maintain an engine coolant temperature such as to provide the most efficient operation. The thermostat is generally placed in the cylinder-head water-outlet housing so that coolant coming from the engine must pass through the thermostat before entering the radiator.

Under light loads or in cold weather, a cooling system without a thermostat will provide more cooling than is desirable. Over-cooling will result in poor fuel economy, crank case oil sludging and an increase in engine wear and may cause a decrease in power.

Pressure-type radiator cap. This device, used on most modern vehicles, differs considerably from the ordinary type of cap. It is composed of two spring-loaded valves, the pressure and vacuum

valves, both of which are normally closed. The pressure valve seals the cooling system by seating against a flange in the radiator filler neck and prevents overflow losses during normal operation. By maintaining a small pressure in the cooling system, usually 4 to 8 pounds per square inch, it also raises the boiling point of the coolant and reduces the likelihood of coolant losses from overflow of the more volatile antifreezes. It also prevents loss of coolant from splashing or sloshing out of the top reservoir of the radiator.

The vacuum valve opens when the pressure in the cooling system falls below the outside air pressure as the engine cools down. Its function is to prevent the collapse of radiator hose and other thin-walled members by bleeding in air when the internal pressure is below atmospheric. As soon as the inside and outside pressures become approximately equal, the valve closes.

2. Properties of an Ideal Antifreeze

As the name implies, the function of an antifreeze is to prevent partial or complete solidification of an engine coolant when low temperatures prevail. In addition to functioning satisfactorily as an engine coolant, there are several other requirements that must be met before an antifreeze can be considered for use in an automotive engine.

An ideal antifreeze should have the following properties:

MAJOR REQUIREMENTS:

1. It should prevent freezing of the coolant at the lowest temperature to which the equipment will be exposed.
2. It must not attack any of the materials of the cooling system under operating conditions.
3. It must be chemically stable under conditions encountered in engine operation. Decomposition products of an unstable antifreeze may be corrosive.
4. It should be a poor conductor of electricity to retard galvanic corrosion, and the material itself or any residue it may leave on evaporation should not cause ignition failure.
5. The viscosity (resistance to flow) should not be so high as to interfere with engine cooling at any operating temperature.
6. The specific heat and heat conductivity of the solutions should be as high as possible, in order to prevent large temperature gradients in the cylinder wall.
7. It should not foam when small amounts of air leak into the system. Foaming causes loss of antifreeze through the overflow tube.

MINOR REQUIREMENTS:

1. The material should be readily available at a reasonable price.
2. It should not materially lower the boiling point of water.
3. It should have a reasonably low coefficient of expansion to reduce overflow losses.
4. The antifreeze should be nontoxic and nonflammable.
5. It should not produce an unpleasant odor.

There are no practical substances satisfying all the requirements for an ideal antifreeze. However, the major requirements have been met

satisfactorily by properly treated solutions of the simple alcohols (methyl, ethyl, and isopropyl) and of ethylene glycol. Quite recently, propylene glycol-base antifreezes have been marketed, and some of these are apparently satisfactory. Various other substances that have been tried, such as inorganic salts, sugar, honey, and petroleum fractions, have shown over the years that for one reason or another they are not satisfactory. Reliable information regarding the service performance of glycerine antifreezes is lacking, because it has been a number of years since glycerine was generally used for this purpose. An idea of the relative merit of each of the types of antifreeze may be obtained by referring to the table on page 26, in which are listed the various coolant materials and some of their pertinent properties.

3. How to Distinguish the Different Types of Antifreeze Bases

Although determining the basic component of an antifreeze is a simple matter in the laboratory, the layman cannot be expected to have either the knowledge or equipment necessary to conduct a chemical analysis. Nevertheless, there are certain simple checks that will serve to distinguish the various antifreeze bases. If a gallon of unmixed antifreeze is carefully measured out and weighed, the following approximate weights, exclusive of container, will help to identify the material:

- Methyl alcohol (methanol)—7 pounds.
- Ethyl alcohol (ethanol)—7 pounds.
- Isopropyl alcohol (isopropanol)—7 pounds.
- Ethylene glycol—9½ pounds.
- Propylene glycol—9 pounds.
- Glycerine—10½ pounds.
- Salt-base—9½ to 10½ pounds.
- Petroleum-base—6½ to 7 pounds.

Petroleum coolants can be distinguished readily by the fact that they will not mix with water. A further check may be made by dipping a small rag in the material, then attempting to ignite it with a match (keep at a safe distance from any open containers). If the material burns with a clean bluish flame it is an alcohol, and if the flame is yellow and smoky it is petroleum-base. If the material is not readily ignited, evaporate a small amount to dryness. A salt-base antifreeze will leave a heavy deposit. If little or no deposit is left on evaporation of an antifreeze weighing 10½ pounds per gallon, it probably is glycerine. Salt-base antifreezes are occasionally sold as dry crystals, for the customer to prepare the solution.

4. The Choice of Antifreeze and Its Use

When the supply situation itself is not a compelling factor, the type of antifreeze to be used is determined by the expected service and by local climate. An important source of guidance is the "owner's manual" provided by automobile manufacturers, for this tends to take into account the specific requirements of a particular automobile system.

For average passenger car service, it is possible to use antifreeze of either low boiling point (alcohol) or of high boiling point (glycol). For heavier duty, prolonged idling, or operation at high altitudes, a high-boiling antifreeze is usually considered preferable, although low-boiling antifreezes have been used successfully [121; 151, page 36; and 169, pages 27 to 31].³

As shown by figure 1, the boiling points of solutions of the so-called volatile-type antifreezes drop with increasing protection against low temperatures. In addition, the boiling points of water and of these solutions decrease nearly 2 deg F for each thousand feet of altitude. The bellows-type thermostat, which is commonly used, compensates very well for the effect of altitude on boiling point by opening at a lower temperature at higher altitudes. Metallic-expansion types, however, open at a fixed temperature, and thus do not compensate for altitude. If the temperature of any portion of the coolant reaches its boiling point either while the engine is operating or after it is stopped, overflow loss of the solution may occur. The possibility of

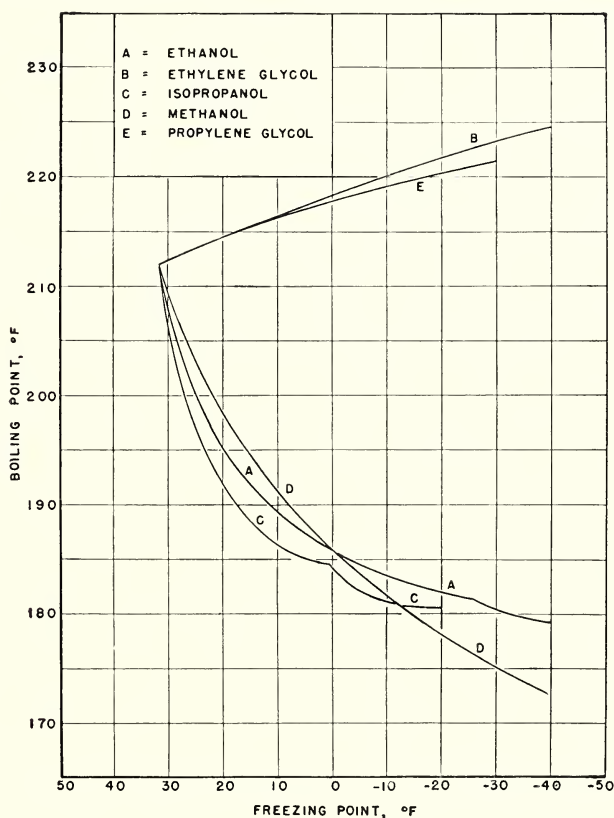


FIGURE 1. Variation of boiling points of antifreeze solutions with freezing-point protection.

The boiling-point temperatures on this chart decrease nearly 2 deg F for each 1,000-feet elevation above sea level.

³ Figures in brackets refer to the literature references given in section IV.

some part of the coolant reaching its boiling point is greater the lower the temperature at which it boils.

Having selected the type of antifreeze to use, it is then necessary to determine when it shall be added and how much to use. Antifreeze should be used in the car between the first killing frost in the autumn and the last one in the spring. The dates of killing frosts vary by as much as a month from year to year. To be safe, antifreeze should be placed in the car not later than the earliest recorded date of killing frost in the locality and left in until after the latest date. These dates usually can be obtained from the nearest U. S. Weather Bureau office, or the frost warnings of the local weather forecast may be used as a guide. The supply situation, however, may make it desirable to purchase antifreeze well before the season for its use begins.

The strength of the antifreeze solution to be used will depend on the lowest temperature to which the car will be exposed. A car parked outdoors overnight represents the worst condition. The antifreeze solution in this case should be sufficient to protect the car at as low an air temperature as is expected to occur. In a car standing over certain surfaces the car temperature may be several degrees below air temperature on a clear night. The engine coolant will not usually fall much below air temperature, because the heat capacity of engine and antifreeze affords some protection, and because the lowest air temperature usually lasts only an hour or two.

The "freezing point" of an antifreeze solution is defined as the temperature at which the first ice crystals form. Unlike water, antifreeze solutions do not become solid at their freezing points. The antifreeze solution must be cooled several degrees below its freezing point before ice crystals make the liquid difficult to circulate [140]. This compensating factor means that the lowest air temperature is a good value to use in determining the antifreeze protection needed.

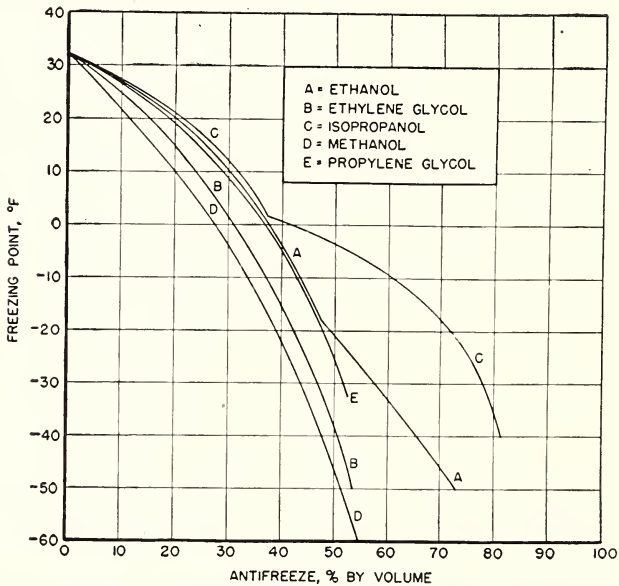


FIGURE 2. Relation of concentration to freezing point for antifreeze solutions.

As a general practice, enough antifreeze should be added to protect against the average annual minimum. With only this strength of antifreeze, the solution should be tested if an unusually cold spell is forecasted, and more antifreeze added if needed. If none is available, other measures (covering hood and radiator with several blankets, covering entire vehicle with tarpaulin, draining coolant, or putting vehicle in garage) may be taken to help furnish the needed protection. It should be remembered that covering the radiator of vehicle merely retards the rate of heat loss. If the car is protected to 10 deg F below the average low temperature, the chances of trouble are almost certainly eliminated, for a temperature that low is a rare occurrence.

A table giving the concentration required to protect to various temperatures is usually furnished with packaged antifreezes. Freezing points of the different basic components used in antifreezes are given in figures 2 and 3. The concentrations given in figure 2 and the specific gravities in figure 3 are for water solutions of the pure base compounds. Since some commercial antifreezes contain small amounts of water, slightly higher volume concentrations than shown in figure 2 may be required. Antifreezes also contain corrosion inhibitors and other additives to make them function properly as cooling liquids. These affect freezing point slightly and specific gravity to greater degree. Thus if a protection table is furnished with the antifreeze, it should be used in preference to either of the figures.

Protection to a temperature lower than is likely to occur may be regarded as insurance against damage by freezing. If low-boiling antifreezes are used, however, excessive protection is undesirable, because the lowering of the boiling point (fig. 1) may result in loss of solution by overflow from boiling [169, page 28].

Figure 4, which is adapted from information published by the U. S. Weather Bureau [172], shows the *average* annual minimum tempera-

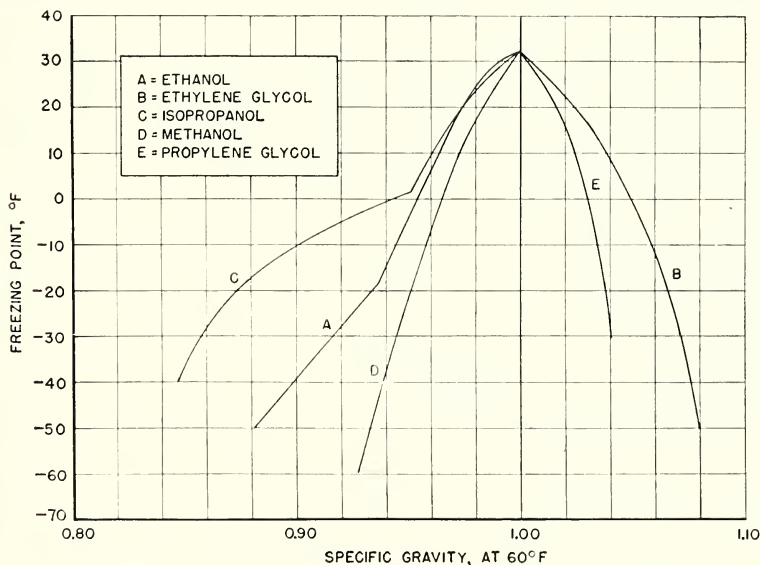


FIGURE 3. Relation of specific gravity to freezing point for antifreeze solutions.

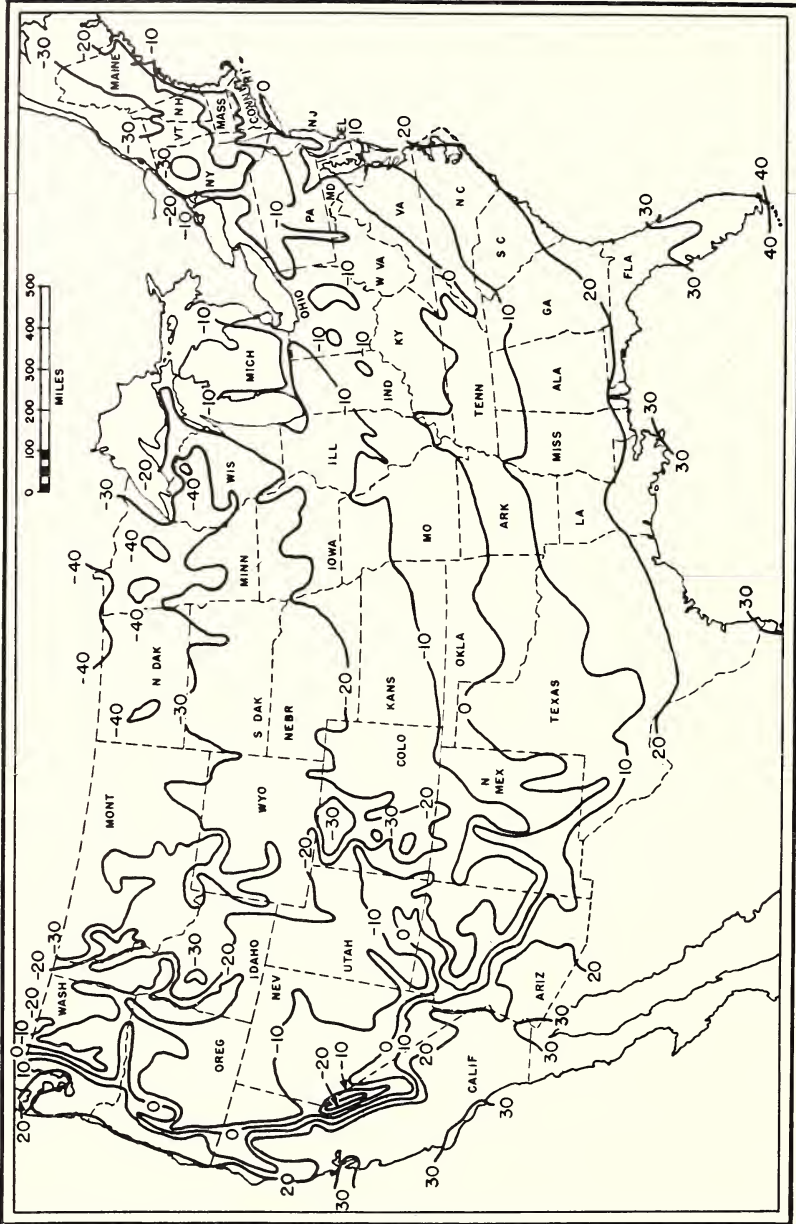


FIGURE 4. Average annual minimum temperature. On the average, lower temperatures occur about every other year. Once in about 29 years, temperatures 10 deg F below average minimum are experienced. Temperature averages are adapted from a U. S. Weather Bureau map.

ture for points within the continental United States. About every 2 years the lowest temperature will be below that given in figure 4. Once in about 20 years, the lowest temperature will be as much as 10 deg F below the average low. In a map, such as figure 4, conditions for all localities cannot be adequately shown. The average low temperature in certain areas, particularly in mountainous regions, will not agree with the values shown in figure 4. In any case where local records do not agree with figure 4, the value from the records should be used. Figure 4 is believed to be fairly accurate for localities below 1,500-foot elevation above sea level, with some local exceptions in New England.

II. Types of Antifreezes

1. Alcohol Antifreezes

The alcohols commonly used as bases for antifreezes are methyl (wood) alcohol, ethyl (grain) alcohol, and isopropyl alcohol. The technical names of these compounds are methanol, ethanol, and isopropanol, respectively.

The boiling points of alcohol antifreeze solutions are below that of water, the difference increasing with the concentration of alcohol, or the protection, as shown in figure 1. The boiling points of water and of solutions of antifreezes in water decrease about 2 deg F for each thousand feet increase in altitude. Hence, in high, cold localities, and in heavy duty service, a greater danger exists of overflow loss resulting from boiling if these antifreezes are used. Keeping the cooling system clean and free from rust, and using a corrosion inhibitor in the cooling water during the summer will reduce the likelihood of antifreeze loss by boiling. Alcohol antifreezes are sometimes used in high-altitude locations in normal passenger-car service, and should give no trouble in properly maintained cars. However, high-boiling antifreezes are preferred for this type of service.

Antifreeze solutions of alcohols, when properly inhibited, do not attack radiator hose and should protect the cooling system from corrosion for at least one winter's use in properly maintained vehicles. Such solutions, when installed in reasonably clean cooling systems, are generally free from sediment, rust, or discoloration when drained in the spring.

In concentrations up to about 25 percent by volume, the specific heats of methyl alcohol solutions are somewhat higher than that of water, thus facilitating engine cooling [124]. Conversely, at temperatures near freezing, the specific heats are somewhat lower than that of water, hence the solutions will warm up more quickly. At operating temperatures, however, the specific heats do not differ greatly from that of water. The viscosities of ethyl alcohol solutions are slightly higher than that of water, and for equal protection, are higher than those of ethylene glycol solutions for freezing protection to temperatures not lower than -30° F. Alcohol solutions for protection to lower temperatures are less viscous, but the difference in viscosity between alcohol and ethylene glycol solutions at any winter temperature normally encountered is of no practical consequence.

In a properly maintained vehicle, with no loose hose connections or leaks, neither flammability nor toxicity of alcohol antifreezes is

a problem. However, in a car equipped with a hot-water heater and using alcohol antifreeze, any indication of leakage from the heater should be promptly investigated, and any necessary repairs should be made immediately. Alcohols are volatile and would vaporize readily from the heater surface. Breathing alcohol vapors in concentrations that could occur in this way can cause loss of coordination and lead indirectly to serious results. The vapors of methanol are more toxic than are those of the other alcohols [82, 87, 93].

2. Glycol Antifreezes

Ethylene glycol has long been on the market as an automotive antifreeze compound. More recently, propylene glycol has been marketed for this purpose. The boiling points of solutions of both glycols are above that of water and increase with concentration of the glycol, or the protection, as shown in figure 1. Because the glycols boil at higher temperatures than water, they are termed high-boiling antifreezes. Of these two glycols, ethylene glycol is more efficient as a freezing-point depressant, and it is easier to measure "protection" of its solutions with a hydrometer. As can be seen in figure 3, the specific gravity-freezing point curve for propylene glycol is very steep at gravities greater than 1.02. This makes an accurate reading of its protection very difficult with a hydrometer.

Although glycol antifreeze solutions will operate at higher engine temperatures without boiling, liquid may be lost through the overflow pipe, when such solutions boil violently, in the same manner that alcohol solution or water would be lost. Any evaporation of glycol solution is practically all water, whereas evaporation of alcohol antifreeze solutions results in loss of alcohol, the antifreeze base. In actual service, however, the loss by evaporation of either ethylene glycol or alcohol has been found to be negligible as compared to the overflow loss of liquid from violent boiling [121; 169, page 34; 170].

Antifreeze solutions composed of ethylene glycol, when properly inhibited, should protect the cooling system from corrosion for a winter's driving season, in properly maintained vehicles. As in the case of alcohol antifreezes, the inhibitors may be weakened and depleted by hard or extended driving or through lack of proper vehicle maintenance. The service life of inhibitors is shortened by such conditions as high driving mileage, high engine speeds and heavy loads, air leaks into the solution (around water-pump drive shaft, for example), combustion gas leakage into the coolant through a loose cylinder-head joint, rust deposits in the system, localized hot spots in the engine, and added contamination such as that from radiator cleaners that have not been thoroughly flushed out after use [169, pages 70 to 72; 170]. From the standpoint of inhibitor service life and corrosion protection, the term "permanent" as applied to antifreezes is a misnomer.

Glycol solutions cause water-soaked radiator hose to shrink slightly; hence the hose clamps should be tightened when installing glycol antifreeze, and again after a few days' use. The specific heats of ethylene glycol solutions are lower than that of water, at temperatures near freezing, and the viscosities are higher. Hence such solutions warm up somewhat more rapidly. Glycol solutions are nonflammable at operating temperatures.

Leakage of antifreeze solution into the combustion space or crankcase of an engine can cause serious damage, especially in cold weather when the solution is not removed as readily as during warm weather. Because of their higher boiling points, glycol solutions are not as readily removed as are alcohol solutions. Neither antifreeze solutions nor water is suitable for engine lubrication. When either mixes with engine oil, the subsequent formation of sludge and gum may cause lubrication failure, sticking valves and piston rings, and serious damage if driving is continued. Leakage of coolant into the engine can be avoided by having the cylinder-head joint checked regularly to make sure that the gasket is in good condition and that the cylinder-head bolts are tightened in accordance with the engine manufacturer's recommendations. Cracked or porous castings that might permit leakage into the engine should be replaced [151, pages 26 to 27].

Tests by the Bureau have shown that properly inhibited antifreeze solutions of alcohols or ethylene glycol do not cause corrosion in a season's use if used as directed in a properly maintained engine. It should be noted that such solutions consequently will not get into the engine cylinders by any corrosive action of their own.

3. Salt-Base Antifreezes

The low cost of salt antifreezes such as calcium, magnesium, or sodium chlorides, and their effectiveness in lowering the freezing point of water have made these compounds appear attractive as automotive antifreezes for the past half century. Some early experimenters erroneously believed that chemically pure compounds would be non-corrosive [10, 11, 12]. As early as 1903 [14], however, the corrosiveness of pure, or even of alkaline calcium chloride solutions was established. Efforts directed toward finding a compound that would inhibit this corrosiveness have been entirely unsuccessful.

In 1927, D. B. Keyes [67] made the following statement:

Calcium chloride was for many years the popular antifreeze compound, possibly because it not only depressed the freezing point of water to a marked degree, but it also stayed in the system and was not lost by evaporation. It was cheap, easily obtained, and there was an adequate supply. Its real fault, however, was that, in common with all chloride salt solutions, it will corrode common metals. Where two metals join and a couple action is possible, this corrosion is extremely vigorous. It was thought for a time that the addition of chromates, such as sodium chromate, would prevent this corrosion by rendering the material passive. This addition of chromate helped materially in some cases but fell down in others, notably when parts were made of aluminum. Magnesium chloride was found to be even more corrosive than calcium chloride. Not only was trouble experienced with corrosion, but when leaks occurred a fine salt spray would appear and have a tendency to short circuit spark plugs and ignition wires. There was also a tendency for the salts to crystallize out and clog pumps and cut down the heat transfer in the radiator.

It is generally conceded today that calcium chloride and other salts are unsatisfactory as antifreeze compounds.

In 1945, Darrin [159] wrote, "No concentration of chromate or other inhibitor has been found capable of inhibiting the corrosion of iron or steel in contact with brass in a calcium chloride antifreeze at temperatures simulating an automobile cooling system (160° F)."

A large number of tests of various salt antifreeze solutions have been made. Even compounds like sodium or potassium acetate or tartrate, whose water solutions are alkaline, have been found to be excessively corrosive. In all cases that have come to our attention, wherever the

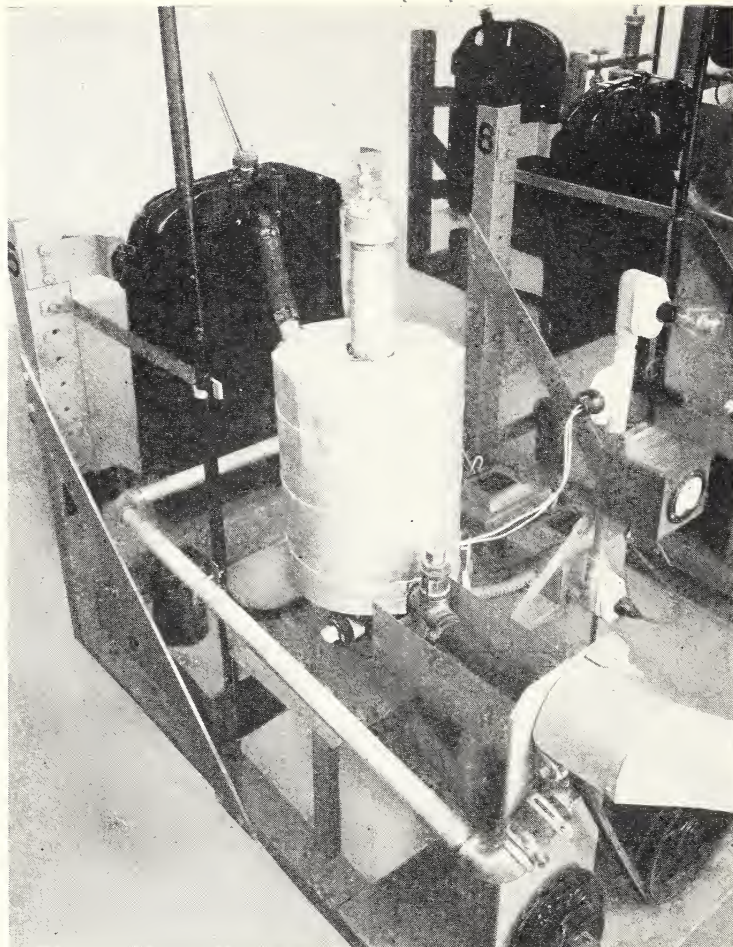


FIGURE 5. Apparatus developed by National Bureau of Standards for simulating engine tests of antifreezes.

Radiator, water pump (under shield at right), and hose connections are standard automotive parts. Tank in center simulates engine and is heated by electric hot plate.

test has been made by competent technical personnel, such antifreezes have been found to be too corrosive for automotive use. A common mistake is that of believing that a salt-base antifreeze can be tested satisfactorily by heating it in a beaker, with metal specimens immersed therein, and noting the corrosion of the specimens. Such tests are worthless except for preliminary screening [152, page 36; 170]. Thus, if a solution corrodes metals in such a test, no further testing is warranted. If it does not corrode metals, further testing may be justified. Even if the metals are in electrical contact and air is bubbled into the hot solution, absence of corrosion does *not* mean the antifreeze is safe for use in automobiles.

Leading engineers in the antifreeze field contend that no test short of actual service is satisfactory for deciding, for example, between two kinds of inhibitors for a glycol antifreeze. The Bureau has not had

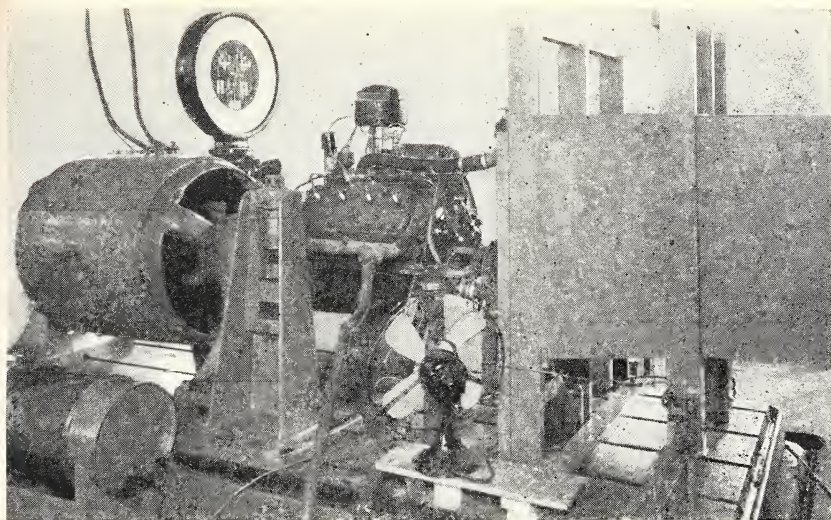


FIGURE 6. *Engine test of antifreeze.*

Radiators are within box structure at right, which houses fans blowing air through radiators, at a rate equalling effect of car speed on the road. Two separate cooling systems, one for each bank of four cylinders, are used on this V-8 engine. One cylinder head of aluminum and one of cast iron were used in this test to find effects of antifreeze in each case. Electric dynamometer at left absorbs engine power, making it possible to duplicate road operation.

this problem but has found that laboratory engine or simulated engine tests are sufficient to demonstrate most vividly the corrosive action of the salt-base antifreezes tested thus far. The simulated service test apparatus used by the National Bureau of Standards is shown in figure 5. The results obtained on radiators and metal test specimens in this simulated test have been correlated with results of engine tests, made on equipment such as is illustrated in figure 6. It is possible to state with certainty that antifreezes that give trouble in this simulated test will also give trouble in use. However, passing this test does not guarantee that the antifreeze in question will perform satisfactorily in service.

Pictures of some of the damages that have resulted in tests of salt-base antifreezes are shown, figures 7 to 14. It can be seen that radiators and water pumps are ruined, as are cylinder heads or other parts made of aluminum. Even more serious is the invisible damage—the formation of a layer of corrosion products on the surface of all cast iron in the cooling system. Within this layer corrosion will continue, even though the salt antifreeze is removed. This corrosion layer reduces cooling of engine parts, such as the exhaust valve seats. Under some operating conditions, heat cracks will then result, ruining the cylinder block at least.

In discussing the glycol antifreezes it was noted that if the glycol is used in accordance with directions and if the engine is properly maintained, the glycol will not get into the engine cylinders or crankcase. Such is not the case with the salt-base antifreezes that have been tested. As shown in figures 7, 8, and 13, corrosion around the water passages is heavy. The metal portions of the cylinder-head gasket are likewise subject to corrosion. Thus, through its own action, the



FIGURE 7. *Aluminum cylinder head after 734-hour operation on magnesium-chloride antifreeze.*

Note hole eaten through head (upper right), and heavy corrosion around water passages. For general appearance of a new cylinder head, see figure 8.

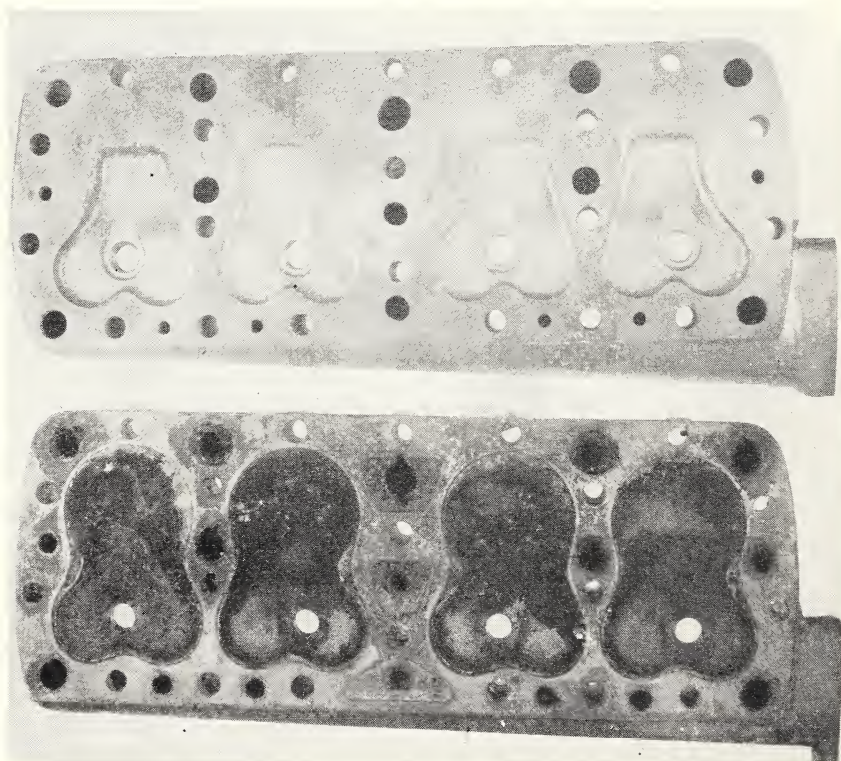


FIGURE 8. *Aluminum cylinder head after 295-hour operation on calcium-chloride antifreeze.*

A hole about $\frac{1}{4}$ inch in diameter, but not visible in this picture, was eaten through this cylinder head by the antifreeze. Note new cylinder head (top) for comparison. The shapes of the cylinders are outlined in the lower head by carbon deposit.

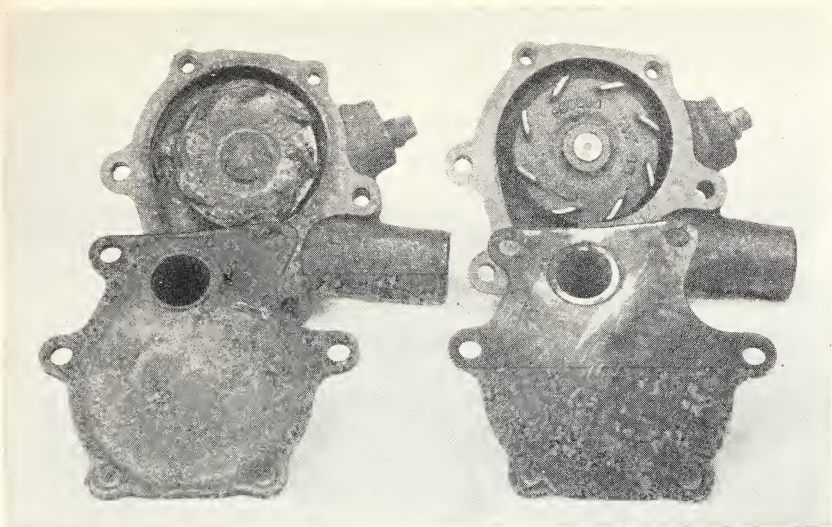


FIGURE 9. *Water pump after 353-hour operation on calcium-chloride antifreeze.*

New pump is shown at right. At this time radiator failed by numerous leaks. See also figure 11.

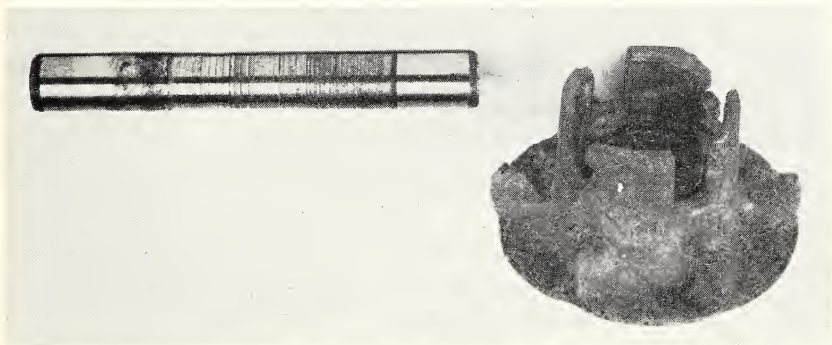


FIGURE 10. *Water-pump impeller and shaft after 853-hour operation on magnesium chloride antifreeze.*

Note great erosion of impeller blades and excessive wear of impeller shaft caused by corrosive action of antifreeze. Similar pumps were operated twice as long on glycol antifreezes without apparent effect on pump.

salt-base antifreeze may reach the interior of the engine, where the extent of damage will depend only on the length of time before its presence is detected.

All the tests illustrated herein have been made on calcium or magnesium chlorides, but other salts, including tartrates and acetates have been found to be unsatisfactory as automotive antifreezes. Considerable effort was expended during the war by foreign governments to develop a satisfactory salt antifreeze to replace the scarce alcohols and glycols. Despite the trained talent devoted to this work, it was not successful. Even if the drawbacks of corrosion and electrical conductivity of salt-base antifreezes were overcome, a remaining serious hazard is that of crystals of hydrated salts depositing in the

small passages of the radiator under some conditions. If such crystals form, it is nearly impossible to remove them. On the other hand, alcohol and glycol antifreezes, when cooled below the initial freezing point, form slush which readily liquefies on being warmed [140].

Salt-base antifreezes are sometimes erroneously advertised as "glycol-base" or "glycerine-base". Several samples of these products have been analyzed at the National Bureau of Standards, and only minor amounts of glycol or glycerine were found to be present.

In summary, engine and laboratory tests of salt-base antifreezes have shown that so-called inhibited, as well as uninhibited, solutions of such materials have highly injurious effects on the cooling and ignition systems of automotive engines [152, page 34; 169, page 36]. Such solutions cause serious corrosion of the cylinder block, water pump, radiator, and especially of any aluminum parts such as cylinder

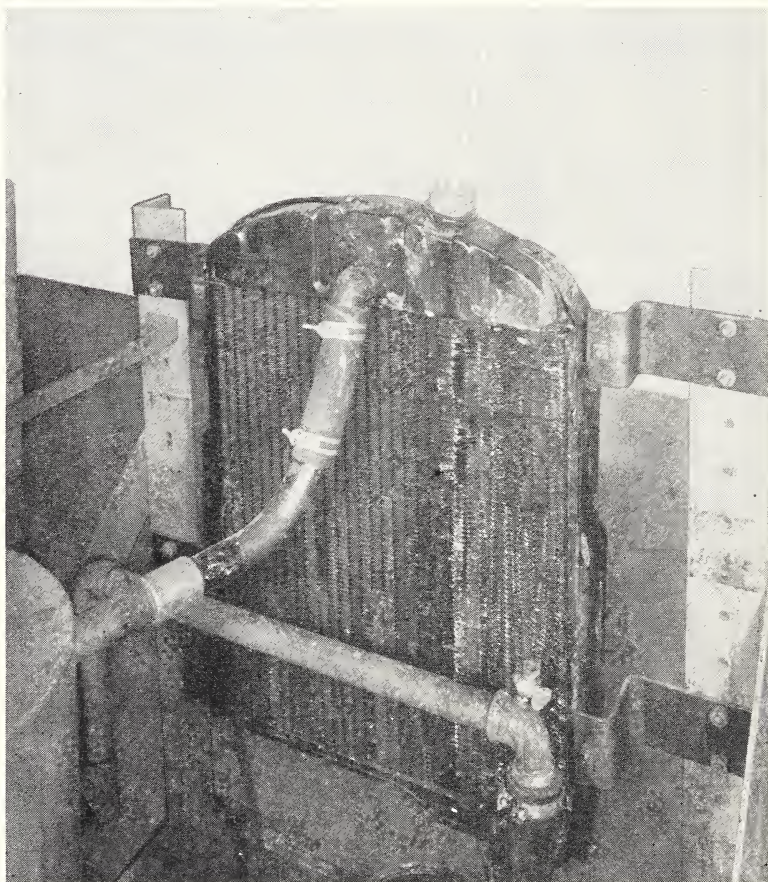


FIGURE 11. *Radiator of simulated service test unit after 882-hour operation on calcium-chloride antifreeze.*

Small corrosion leaks frequently seal themselves during operation, and reopen when radiator cools. This unit was operated with severe leaks for 300 hours. Test stopped when radiator drain cock corroded so badly that it dropped off radiator, emptying the cooling system. Streaks at top were caused by foaming, which often occurs after corrosion begins.

heads. The corrosion products resulting from use of these solutions will accumulate and cause partial or complete stoppage of water passages in the radiator, with consequent overheating and boiling. Being corrosive, these solutions may get into the engine cylinders by corroding the cylinder head or gasket and cause great damage or even completely ruin the engine. As rapid erosion of the water pump impeller shaft occurs, the solution is sprayed over the outside of the engine as well. Salt solutions are good conductors of electricity and thus short circuit the ignition system. Often this trouble can be cured only by complete replacement of the parts involved.

4. Petroleum "Antifreezes" or Coolants

The compounds previously discussed are all used in water solution. The amount of antifreeze compound employed consequently depended on the protection required, and in most cases was not over half. Petroleum-base antifreezes, or more properly, petroleum coolants, however, are quite like kerosine in properties and do not mix with water. It is necessary to drain the entire cooling system completely and to

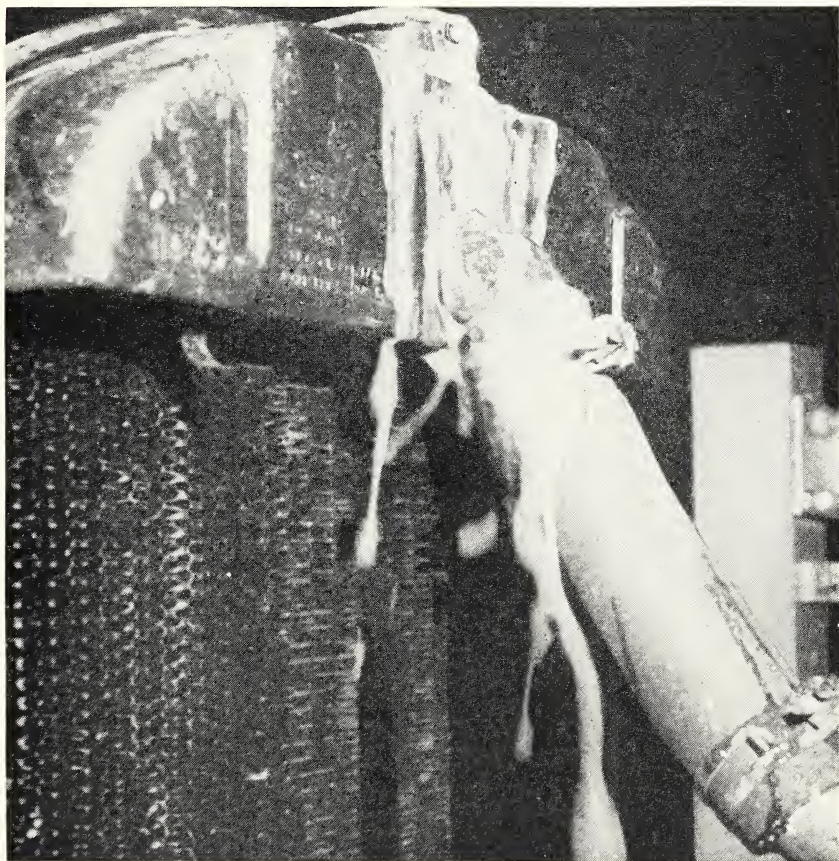


FIGURE 12. *Antifreeze foaming out the top of radiator in simulated service test.*

This material, a calcium-chloride antifreeze, corroded the radiator so badly that several air leaks formed. Air entering the system through these leaks caused the foaming.

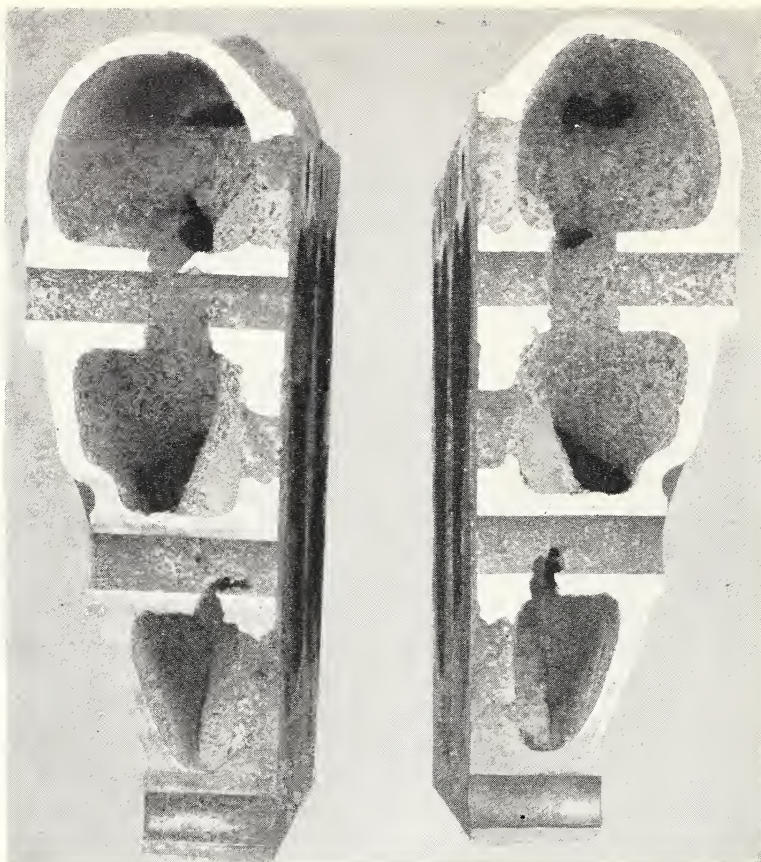


FIGURE 13. *Corrosion of an aluminum cylinder head by magnesium-chloride antifreeze.*

After the test was completed, using the apparatus shown in figure 6, the cylinder head was cut in half, as shown. Notice the extreme corrosion of the water passage, particularly the area around the lower head bolt passage.

refill with the antifreeze compound, regardless of the protection needed. The amount of petroleum coolant needed will therefore be several times that of the water-soluble antifreeze compounds.

Suitably refined petroleum coolants freeze at very low temperatures and are not corrosive to the cooling system metals. Therefore, leakage of properly installed petroleum coolants into the engine should not occur as a result of corrosion. Such leakage would be unlikely to cause extensive engine damage. However, unless great care is taken to dry the cooling system or unless the petroleum coolant contains compounds that will absorb, hold, and inhibit the remaining water, corrosion may occur. Also, if the coolant temperature exceeds the boiling point of water, as often occurs in prolonged idling, the water left in the system will flash into steam, causing the coolant to overflow. For this reason some petroleum coolants contain compounds intended to absorb the water. In this case leakage into the crankcase may result in engine damage.

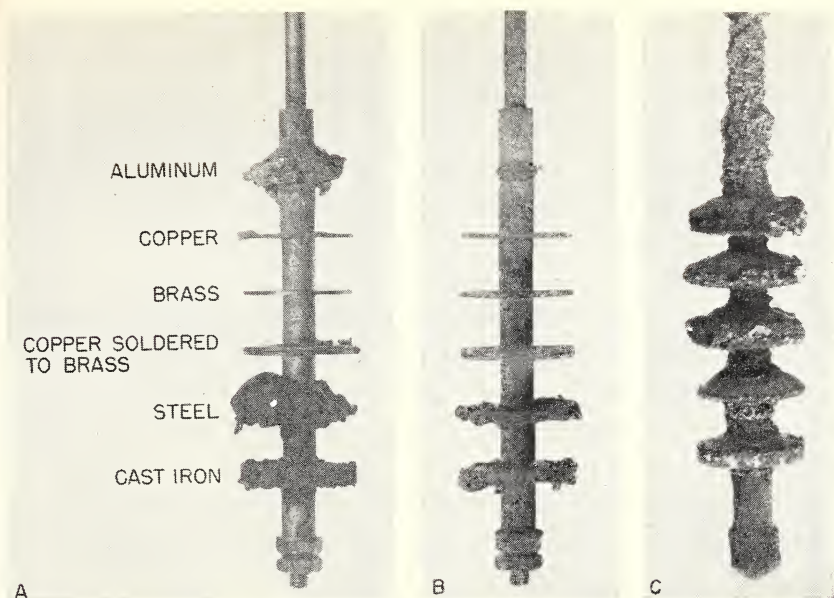


FIGURE 14. Results of test of magnesium-chloride antifreeze in simulated service unit (fig. 5), showing condition of metal test specimens after exposures for the times indicated.

A. After 33-hour operation; B. after 93-hour operation; C. after 537-hour operation. In A, note that brass is the only specimen not showing corrosion; in B, the aluminum is gone; in C, all specimens and the brass suspension rod show corrosion.

Petroleum coolants have certain properties that render them unsuitable in present cars. All succeeding remarks apply to, and all tests were made on, petroleum coolants that were highly refined, of high flash point, narrow boiling range, and that contained no aromatics or olefins. These remarks therefore apply with equal or greater emphasis to less highly refined products.

Petroleum coolants attack ordinary (natural or reclaimed rubber) radiator hose and also hose made from some kinds of synthetic rubber [152, page 34; 169, page 36]. However, the better grades of ordinary hose, having several layers of fabric, in some cases are reported to have been used for a full season with petroleum coolant without failure. Some other types of synthetic rubber are not seriously affected by petroleum products. The availability of oil-resistant synthetic hose would, of course, obviate the above objections to the use of petroleum coolants. Information currently available indicates that oil-resistant radiator hose is being used to a very limited extent, if at all, on original equipment and that such hose is quite difficult to obtain as replacement.

In the course of an official test on an automobile, operating in personal service chiefly in the city of Washington for 5 months during the winter of 1947-48, with petroleum coolant, the automobile hose had to be replaced three times. The first hose (factory production for the car) lasted 47 days (1,325 miles) and failed by splitting. This hose had previously been used with water and with alcohol antifreeze. The second hose (stock replacement molded hose for this car) lasted 63 days (1,675 miles) and failed by splitting. The third hose, similar

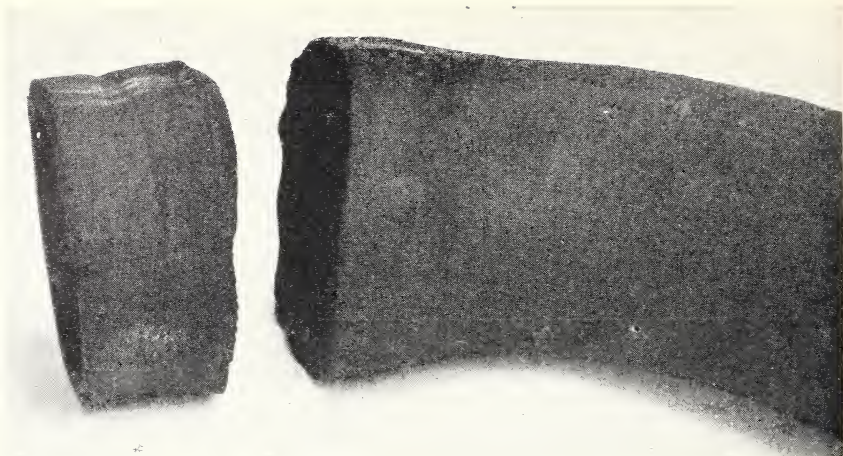


FIGURE 15. *Automotive radiator hose after 7 days' use with petroleum antifreeze.*

Car was operated 230 miles at speeds not over 30 mph in city, in normal personal service, during the life of this hose.

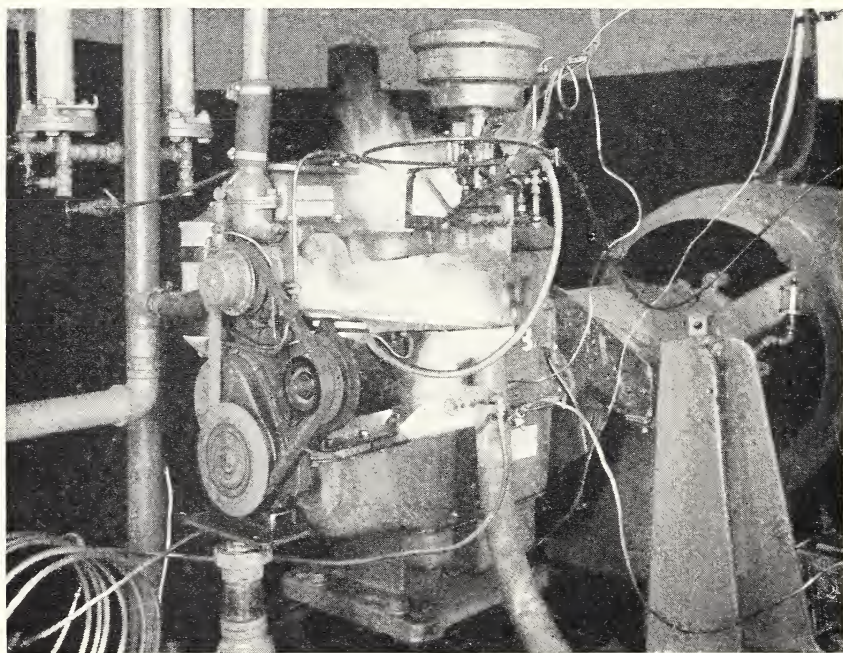


FIGURE 16. *Spontaneous ignition of petroleum antifreeze on engine exhaust manifold.*

Two teaspoonfuls of petroleum antifreeze were spilled on manifold while engine was operating at half load and two-thirds rated speed. Equivalent car condition is climbing a slight grade at 40 mph. If hose (fig. 15) split so that antifreeze was sprayed on manifold—as can happen in many cars—a disastrous fire would ensue. Alcohol and glycol antifreezes did not ignite under the same test conditions.

to the second but obtained from other stock, lasted 7 days (230 miles) and failed in a clean break, as shown in figure 15. The fourth hose, same origin as the third, had weakened but had not failed when the test was terminated after this hose had been in service for 18 days and 412 miles.

The simple loss of radiator hose and part or all of the antifreeze, however, does not constitute all of the damage that may result. At engine operating temperatures, all petroleum coolants that have been tested are flammable. Should a source of ignition, such as a static spark from the fan belt, be present, a leak may result in a fire. If the engine is operating under load, such as climbing a moderate grade at 40 miles per hour, the exhaust manifold will serve as a source of ignition. Figure 16 shows the fire that resulted under these engine conditions when two teaspoonfuls of petroleum coolant were poured on the engine exhaust manifold.

When antifreezes composed of methyl or ethyl alcohol were poured on the exhaust manifold of the engine under the same conditions that caused the petroleum coolant to ignite, ignition did not occur. Ignition also did not occur, under the same conditions, when an equal amount of motor gasoline was poured on the exhaust manifold. Any spark, or a leak allowing passage of exhaust flames, however, would have ignited either the alcohol antifreeze or the gasoline. The fire hazard of petroleum coolants is greater than that of alcohol coolants mainly because the chances of the petroleum solutions reaching the exhaust manifold are greater as a result of hose deterioration. From an operating point of view this likelihood is probably of greater significance than the fact that burning petroleum coolants generate five to six times as much heat as ethyl alcohol antifreeze solution protecting to 0° F, in addition to the fact that fires from petroleum coolants are also more difficult to quench.

Petroleum coolants have less heat capacity than other types, hence the engine itself runs hotter. Although this may not be a drawback in extremely cold weather or under light driving conditions, it is disadvantageous in mild weather and especially in the occasional warm spell. Figure 17 shows the comparative coolant temperatures when the same car was operated on petroleum and on aqueous coolants. In these tests it was found that the internal engine temperatures were higher with petroleum than with aqueous coolant at the same coolant temperature. Concurrent tests also showed that the octane number requirement of the automobile was increased about 7.5 units when a petroleum coolant was used. This means that a car that did not knock on regular gasoline might be expected to knock considerably on premium gasoline if a petroleum coolant were used.

In the event of cooling trouble, an engine can overheat only to the boiling point of the coolant as long as there is sufficient coolant in the system to maintain circulation. With alcohol or glycol, the boiling temperature is not far from that of water, 212° F, as shown in figure 1. Boiling of the coolant usually becomes obvious to the driver, by sight or odor, before it is too late. Highly refined petroleum coolants, however, boil in the range 400° to 500° F. These temperatures are above the melting point of the solder used in the radiator, and before they are reached in the engine the bearings would burn out or piston seizure would occur. Thus aqueous antifreezes afford some protection against overheating, which is not available with petroleum coolants.

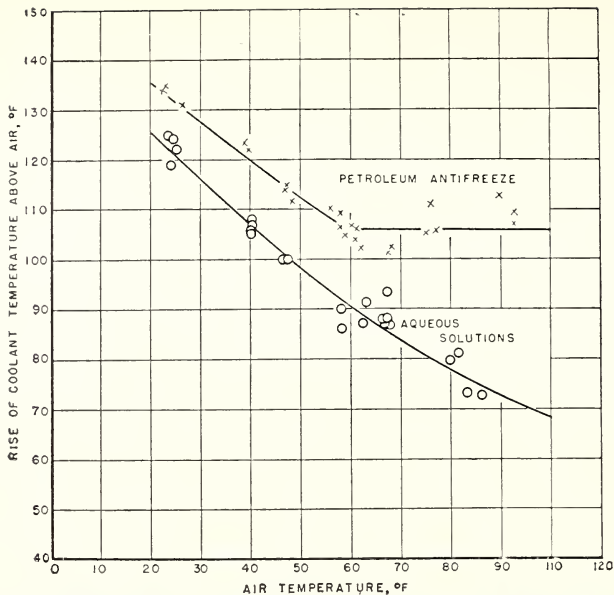


FIGURE 17. *Comparative operating temperatures with petroleum and with aqueous coolants.*

Points on the lower line were obtained with alcohol antifreeze in most cases, with water in some cases. Note break in upper line, indicating that thermostat was wide open, and could no longer control coolant temperature. Tests made in a 1946 automobile, the two types of antifreeze being tested on the same day under identical test conditions.

Neither petroleum coolants nor salt antifreezes are new. Oils or kerosene have been used for a half century, but to a limited extent only. In a coolant system designed for its use, preferably closed and all-metal, a petroleum coolant might be used to considerable advantage if protected against overheating. The complete absence of corrosion, making heat transfer always like that in a new car, would be worth much. In present cars, however, such coolants are considered to be unsafe.

5. Miscellaneous Antifreezes

Earlier publications of the Bureau [35, 43, Letter Circular 28]⁴ mentioned such other antifreeze compounds as honey, sugar, glycerine, and trimethylene glycol. Honey and sugars are unsatisfactory because they are poor freezing point depressants, are unstable to heat, and their solutions are too viscous. Trimethylene glycol is not available in commercial quantities. Glycerine solutions have been found to be corrosive in actual service, but since it has been many years since glycerine has been used to any extent as an automotive antifreeze, no current service performance data on later inhibitor formulations are available. In a recent simulated service test no serious corrosion was experienced with an inhibited [117a] glycerine solution. However, as pointed out on page 7, this result does not indicate that such solutions will be free from corrosive effects in actual service.

⁴ Letter Circular LC28, issued December 9, 1921, revised November 15, 1924, and December 1, 1925, is out of print, and is superseded by this Circular.

Diacetone alcohol has been found to be unsuitable as an antifreeze. It is unstable to heat, is corrosive, and has a small freezing-point depression. Other compounds, such as butylene glycol, 2-methylpen-
nediol (hexylene glycol), diethylene glycol, and triethylene glycol likewise are not efficient antifreeze materials. This is because their relatively high molecular weights make them less effective in lowering the freezing point of water.

Antifreezes comprising mixtures of glycols have been marketed. If improperly compounded, use of such materials introduces an uncertainty in measuring "protection" by a hydrometer, because the concentration-density relation is different for each mixture.

In general, although an antifreeze costs little in comparison with a car, the wrong kind of antifreeze can cause great damage to the car. If antifreeze cannot be obtained, it is possible to operate in mild climates when the temperature is above freezing by filling the radiator with warm water, and draining it whenever the car is to be exposed to freezing temperatures. The water used should, of course, contain a rust inhibitor.

III. Proper Use of an Antifreeze

1. Preparation of Car for Antifreeze⁵

Although leaks should never be tolerated, they are often overlooked in the summer, as the replacement even of rust inhibited water is not costly. However, all such leaks should be repaired before antifreeze is put in the car. The cylinder head joint of the engine should be serviced to prevent leakage of antifreeze into the engine [157; 169, pages 51 to 52]. Radiator hose, if in bad condition, should be replaced, hose clamps tightened, and thermostats examined. A thermostat that does not open at the proper temperature can cause loss of antifreeze through boiling; one which does not close properly can impair engine performance in other ways. A competent mechanic should make the examination of this device [169, pages 55 to 56, 98 to 99]. If a test shows that the thermostat does not open within 10° F of the rated opening temperature (usually marked on device and generally ranging from 140° to 160° F in the models for different engines), it should be replaced. This test can be made by suspending the thermostat in a pan of water (thermostat must not touch heated surface of pan) heating, stirring, and noting the temperature at which the thermostat opens. If the engine water jacket and radiator are clogged with rust, boiling and loss of antifreeze may occur during or immediately following operation. In such cases a thorough cleaning is needed. Such cleaning should be done by a competent garage, in accordance with best maintenance practices [169].

Much can be done toward reducing or eliminating cooling system corrosion by using only suitable, properly inhibited antifreezes and by adding corrosion (rust) inhibitor to the water when the antifreeze is drained in the spring [169, page 37]. With the generally higher speed, higher temperature, and resultant greater aeration of the coolant in the summer season, corrosion will occur at a greater rate unless the coolant water is treated with rust inhibitor.

⁵ Reference [169], Maintenance of automotive engine cooling systems. Society of Automotive Engineers, Inc., 29 West 39th Street, New York 18, N. Y., \$2, is an excellent manual for both professionals and amateurs who are interested in maintenance of automotive vehicles.

Some kinds of tap, well, and surface-waters are very corrosive [152, page 29, 169, page 64]. Where the water is hard or contains much dissolved mineral matter, soft water (rain or distilled water) should be used in preparing antifreeze solution, and in the summer it should be used together with corrosion inhibitor in the cooling system [169, pages 36 to 37]. If during the summer season the cooling water is lost by leak, drainage, or boiling, the replacement water should also be soft and should be inhibited. Where inhibited water or antifreeze solution is drained for engine repairs, it can, of course, be saved for reuse if clean and rust-free.

2. Testing of Antifreeze Solutions

The commonly used antifreeze tester is a hydrometer equipped with a thermometer and correction chart. When this instrument is used with proper care, the antifreeze protection of a solution containing only one base—for example, ethyl alcohol—can be determined accurately. If a simple hydrometer-type tester without thermometer or correction chart is used, accurate readings are possible only at one temperature, usually 60° F. The explanation for this is that a hydrometer measures density. The density of liquids changes with temperature. For example, if water containing no antifreeze but heated to engine operating temperature were tested in a simple hydrometer graduated for methyl alcohol, antifreeze protection to +7° F would be indicated, although the water would actually freeze at +32° F. This incorrect indication results entirely from the change of density of water between 60° F and engine operating temperature.

If different antifreezes are mixed—for example, 1 gallon of ethyl alcohol and 1 gallon of methyl, as may be necessary because of scarcity—the protection can no longer be determined accurately by hydrometer. As can be seen from figure 3, this applies with much greater emphasis if an alcohol and a glycol are mixed. In such a case, the mixture may be tested by refrigerating a sealed sample together with a thermometer. If sample is frozen, allow it to warm, stirring with thermometer, and note temperature at which complete melting occurs. If sample is not frozen, protection at least to temperature shown by thermometer is assured. (If this test is performed in a food refrigerator, care should be taken to see that antifreeze does not get on any food. If a glass container is used, place it in a bowl large enough to retain the sample if the glass container cracks.)

3. Replacement and Reuse of Antifreeze

When coolant has been lost by leakage or boiling, it must be replaced at once to prevent overheating and further loss. As coolant losses from evaporation are usually small in comparison with those that result from leakage or overflow [121], replacement may be made by adding an antifreeze solution of strength equal to that originally prepared if no hydrometer is immediately available. The antifreeze protection should be checked periodically by a suitable hydrometer, particularly after any addition of solution.

There are many factors to be considered regarding using antifreeze solutions more than one season. During use, antifreeze is subjected to several conditions that cause it to change its properties. Inhibitors

are depleted by exhaust gas leaking into the cooling system. This gas, containing oxides of carbon, sulfur and nitrogen, reacts with some inhibitors, destroying their effectiveness. It is also thought that it decomposes the antifreeze material itself. Frequently, small amounts of air leak into the system, which causes lowering of inhibitor effectiveness. This effect is much greater if the level of coolant is allowed to fall low enough to cause air entrainment as the coolant is pumped into the top of the radiator. Localized "hot spots" in the engine, such as the area around exhaust valve heads, also cause decomposition of antifreeze.

In order to maintain maximum protection against corrosion, drain the antifreeze solution after one winter's use or earlier if it becomes rusty in a cooling system that was reasonably clean when the fresh antifreeze was installed.

Under some conditions it is possible to use a solution for more than one season without harm; the service life is dependent on the condition of the car and severity of service. However, it is continually depleted by use, and will eventually reach a corrosive condition. Chemical analysis of the used antifreeze solution is much more expensive than new antifreeze, and will not necessarily determine how much longer the old solution will remain rust-free. In view of the comparative cost of antifreeze and of even so minor a replacement part as a water pump or radiator, it is certainly cheaper in the long run to use new solutions each year. Under no circumstances should antifreeze solution remain in the cooling system during the summer, as its deterioration will be much more rapid under summer driving conditions.

4. Cooling-System Corrosion

At various points in this Circular, the corrosiveness of various compounds has been mentioned without further discussion as to the mechanism of corrosion. As used here, *corrosion* is a rather general term and includes the over-all removal of metal, regardless of the method involved. Corrosion in the engine-cooling system may be divided into three categories: chemical corrosion, electrolytic corrosion, and erosion.

Chemical corrosion is the result of direct chemical reaction between the various metals in the cooling system and the components of the coolant. This may be produced by the presence of acids in the solution or various oxidizing agents. An example is the formation of rust on iron by the combination of water and oxygen in the air.

Electrolytic corrosion is the result of action between dissimilar metals joined together, or it may occur in a single piece of metal in which there are existing potential differences due to heterogeneity of composition, or to cold-working, riveting, or welding. This type of corrosion necessarily depends on the presence of a solution which is electrolytic, that is, which conduct electricity by means of ionized particles. Salt solutions are excellent conductors of electricity, and hence are very unsatisfactory antifreezes because of electrolytic corrosion. The action of electrolytic corrosion is identical with that in the ordinary dry cell in which an electric current is caused to flow by conversion of a metal into a salt.

Erosion is the result of a mechanical abrasion produced by abrasive particles, such as rust or sand. Since the circulating coolant must move at relatively high velocities through the various parts of the engine, any particles of rust or other solids in the coolant exert an abrasive effect as they pass over the metal surfaces. It should be pointed out that erosion depends on the products of corrosion, for with a perfectly clean coolant there will be no appreciable erosive wear.

The corrosive effects of the various antifreeze base materials are lessened by addition of suitable inhibitors. Much research has been performed by the major producers of antifreeze materials on development of satisfactory inhibitors, and many patents have been issued on inhibitor formulations. Usually the quantity of inhibitor added is quite small, about 1 to 3 percent.

Inhibitors may be organic or inorganic compounds, or a mixture of the two. Generally a specific inhibitor formulation is most effective when used with the base material for which it was developed, and is not well suited for other base materials. The National Bureau of Standards has not conducted any research specifically for inhibitor evaluation, and has not made a study of the inhibitor formulations of commercial antifreezes.

In conclusion, the importance of preventing corrosion at all times should be stressed. Much can be done toward reducing corrosion during the large part of the year when antifreeze is not used. As mentioned before, pure water in the cooling system will cause considerable rusting, and in some localities the water supply may be especially corrosive due to various salts. When the antifreeze is removed in the spring, the cooling system should be thoroughly flushed to remove all rust, first using a commercial cleaning compound if considerable rust is present in the antifreeze drainings. Following this, the cooling system should be filled with water containing a corrosion inhibitor. Prepared inhibitors suitable for this purpose can be obtained at most service stations and automotive accessory stores. By following this simple procedure each year, it is possible to maintain the cooling system in nearly new condition for years.

5. Properties of Coolant Materials

Material	Water soluble	Effect on boiling point of water	Corrosiveness when inhibited	Electrical conductor	Specific heat	Viscosity as used at low temperatures	Flammable ^a
Water			Negligible	No	High	Low	No.
Methyl alcohol	Yes	Lowers	do.	do.	Medium	do.	Yes.
Ethyl alcohol	Yes	do.	do.	do.	do.	do.	Do.
Isopropyl alcohol	Yes	do.	do.	do.	do.	do.	Do.
Ethylene glycol	Yes	Raises	do.	do.	do.	do.	No.
Propylene glycol	Yes	do.	do ^b	do.	do.	do.	Do.
Glycerine	Yes	do.	Moderate ^b	do.	do.	Medium	Do.
Salts	Yes	do.	Heavy	Yes	do.	Low	Do.
Petroleum	No	(High-boiling coolant.)	None ^c	No.	Low	do.	Yes.

^a No attempt is made here to denote the degree of flammability. See section II 4.

^b Insufficient service performance information precludes definite statements regarding corrosiveness. There are indications that satisfactory antifreezes can be made from these compounds by proper inhibition against corrosion.

^c Unless radiator and heater hoses are disconnected and cooling system is completely dried before petroleum, coolant is installed, corrosion from the remaining water may occur.

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1. Index to Bibliography

This index has been prepared to assist the reader who is interested in specific aspects of the antifreeze and coolant problem. The index is by no means inclusive, as the context of the articles was derived from abstracts in nearly half of the cases. An article listing some of the physical properties of methanol may, for example, be indexed only under "Antifreezes in general, physical properties," if methanol was not mentioned in the abstract. No attempt has been made to include determinations of the properties of antifreeze components other than those made in connection with the use of the materials as antifreezes.

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WASHINGTON, September 30, 1952



