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Automotive Antifreezes

UNITED STATES DEPARTMENT OF COMMERCE

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Automotive Antifreezes

Frank L. Howard, Donald B. Brooks, and Ronald E. Streets



National Bureau of Standards Circular 576

Issued July 26, 1956

Supersedes Circular 506

For sale by the Superintendent of Documents, U. S. Government Printing Office

Washington 25, D. C. - Price 15 cents

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Automotive Antifreezes

Frank L. Howard, Donald B. Brooks,¹ and Ronald E. Streets²

This Circular gives information on the pertinent physical properties of various materials used as engine antifreezes and on their water solutions. Factors regarding choice of antifreeze, cooling-system corrosion, and testing of antifreeze solutions are discussed.

1. Properties of an Antifreeze

The function of an antifreeze is to prevent freezing of an engine coolant at low temperatures. In addition, there are several other requirements that should be met before an antifreeze can be considered for use in an automotive engine. These are:

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

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There are no practical substances satisfying all of these requirements. However, the major requirements have been met satisfactorily by properly compounded solutions of the simple alcohols (methyl, ethyl, and isopropyl) and of ethylene glycol. Propylene glycol has also been used as a base for antifreezes, and some of these products are apparently satisfactory. Various other substances that have been tried, such as inorganic salts, sugar, honey, and petroleum fractions, have been found unsatisfactory for one reason or another. Reliable information regarding the service performance of glycerine antifreezes is lacking. An idea of the relative merit of each of the types of antifreeze may be obtained by referring to the table in section 6, in which are listed the various coolant materials and some of their pertinent properties.

2. Types of Antifreezes

2.1. Alcohol Antifreezes

Methyl (wood) alcohol is the most commonly used base for alcohol antifreezes, although small amounts of ethyl (grain) alcohol and isopropyl alcohol are used. 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 9. The boiling points of water and of solutions of antifreezes in water decrease about 2 deg F for each 1,000-foot 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.

Antifreeze solutions of alcohols, when properly inhibited, do not attack radiator hose and may be expected to 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.

At operating temperatures the specific heats of alcohol solutions 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. For protection to lower temperatures, alcohol solutions are less viscous than the corresponding ethylene glycol solutions, 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 may be taken as a danger signal, and the making of any necessary repairs is advisable. Alcohols are volatile and 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].³

³ Figures in brackets indicate the literature references given in the bibliography, section 7.

2.2. Glycol Antifreezes

Ethylene glycol has long been on the market as an automotive anti-freeze 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 9. 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 11, 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. It has recently been demonstrated [191] that this disadvantage of propylene glycol may be overcome by addition of approximately 30 percent of glycerine. The resulting mixture, when added to water, gives solutions of approximately the same freezing points and densities as ethylene glycol solutions, and therefore may be tested with hydrometers calibrated for ethylene glycol solutions.

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 from glycol solution is practically all water, whereas evaporation from alcohol antifreeze solutions results in loss of alcohol, the antifreeze base. In actual service, however, loss by evaporation has been found to be negligible as compared to the overflow loss of liquid from violent boiling [121; 169, p. 34; 170].

Antifreeze solutions composed of ethylene glycol, when properly inhibited, can be expected to protect the cooling system from corrosion for one 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, p. 70 to 72; 170]. From the standpoint of inhibitor service life and corrosion protection, the term "permanent" as applied to antifreezes is a misnomer [188].

Glycol solutions cause water-soaked radiator hose to shrink slightly; hence the hose clamps may need to be tightened when glycol antifreeze is installed, 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 non-flammable at operating temperatures.

Leakage of antifreeze solution into the combustion space or crankcase of an engine can cause serious damage, because the solution is not readily removed by evaporation through the crankcase breather pipe in cold weather. Because of their higher boiling points, glycol solutions are not as readily removed as are alcohol solutions. Neither antifreeze solution nor water is suitable for engine lubrication. When either mixes with engine oil, the subsequent formation of sludge and gum may impair lubrication and cause sticking of valves, hydraulic valve lifters, and piston rings. 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 of coolant into the engine may be replaced [151, p. 26 to 27].

2.3. 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 noncorrosive [10, 11, 12]. As early as 1903 [14], however, the corrosiveness of calcium chloride solutions was established. Efforts directed toward finding a compound that would inhibit this corrosiveness have been entirely unsuccessful.

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 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 may be used for preliminary screening [152, p. 36; 170], but more reliable results may be obtained from tests performed under conditions more closely simulating actual engine operation.

The Bureau has found that laboratory engine, or simulated engine, tests are sufficient to demonstrate the corrosive action of the salt-base antifreezes tested thus far.

Pictures of some of the damages that have resulted in tests of salt-base antifreezes are shown, figures 1 to 4. 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.

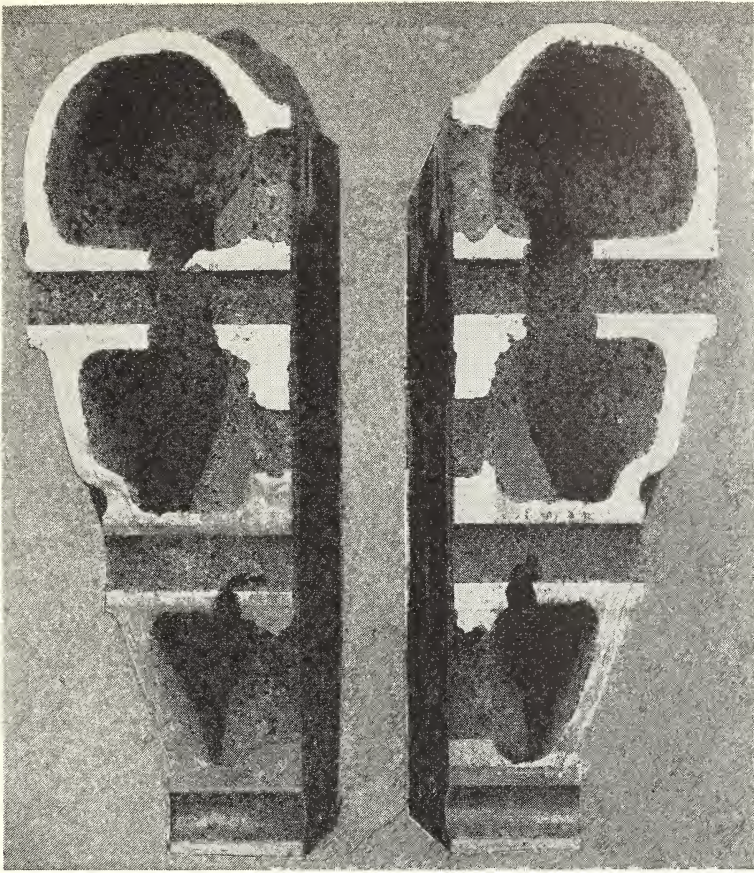


FIGURE 1. *Corrosion of an aluminum cylinder head by magnesium-chloride antifreeze.*

After the test was completed, 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.

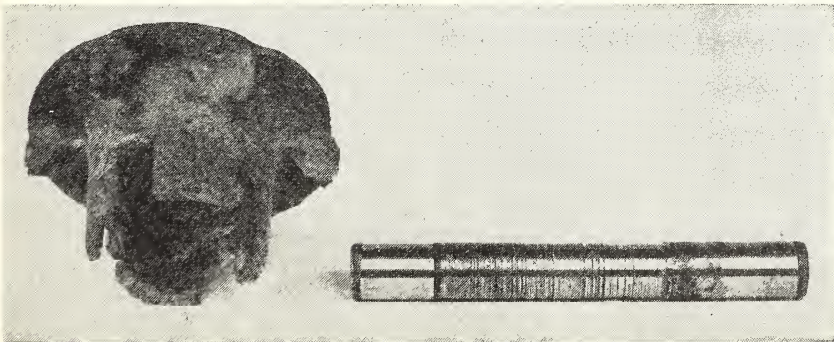


FIGURE 2. *Water-pump impeller and shaft after 853-hour operation on magnesium-chloride antifreeze.*

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.

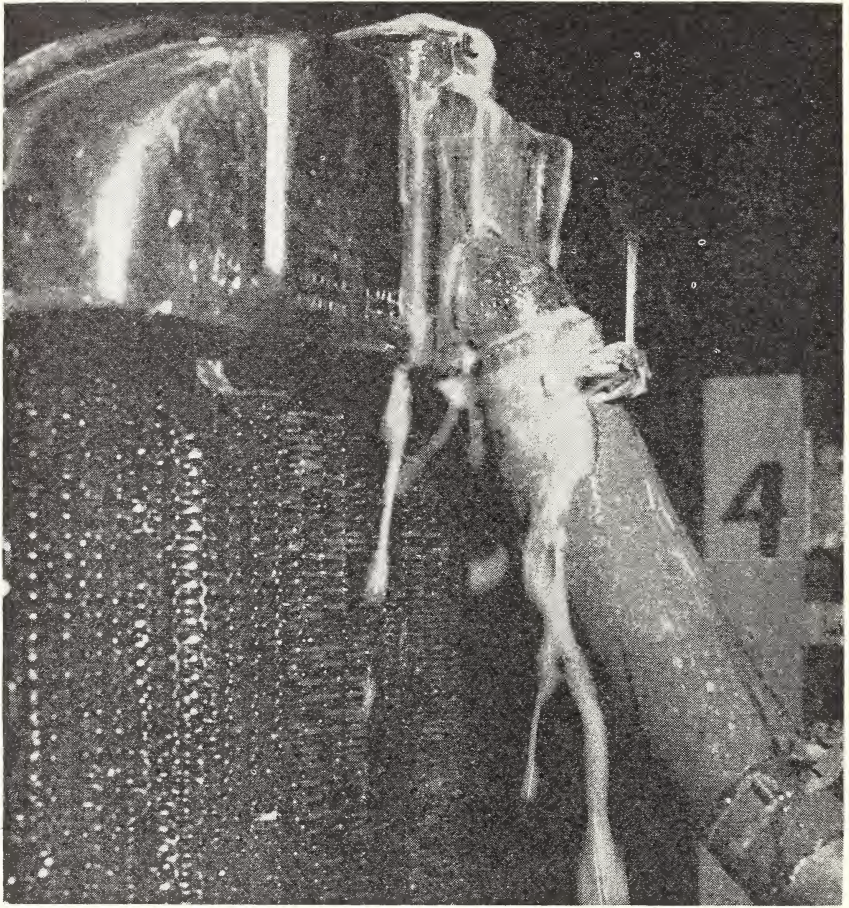


FIGURE 3. *Antifreeze foaming out the top of radiator in simulated service test.*

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.

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. With the salt-base antifreezes that have been tested, corrosion around the water passages is heavy, as shown in figure 1. The metal portions of the cylinder-head gasket are likewise subject to corrosion. Thus, through its own action, a corrosive 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 tested and found to be corrosive. Considerable effort was expended during World War II 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 disadvantage 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].

In summary, engine and laboratory tests of salt-base antifreezes have shown that all of those tested, whether inhibited or uninhibited, have been found to have injurious effects on the cooling and ignition systems of automotive engines [152, p. 34; 169, p. 36]. Such solutions cause serious corrosion of the cylinder block, water pump, radiator, and especially any aluminum parts such as cylinder 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 damage to the internal parts of the engine. As erosion of the water pump impeller shaft occurs, the solution may be sprayed over the outside of the engine as well. Salt solutions are good conductors of electricity and may thus short-circuit the ignition system. Often this trouble can be cured only by complete replacement of the parts involved.

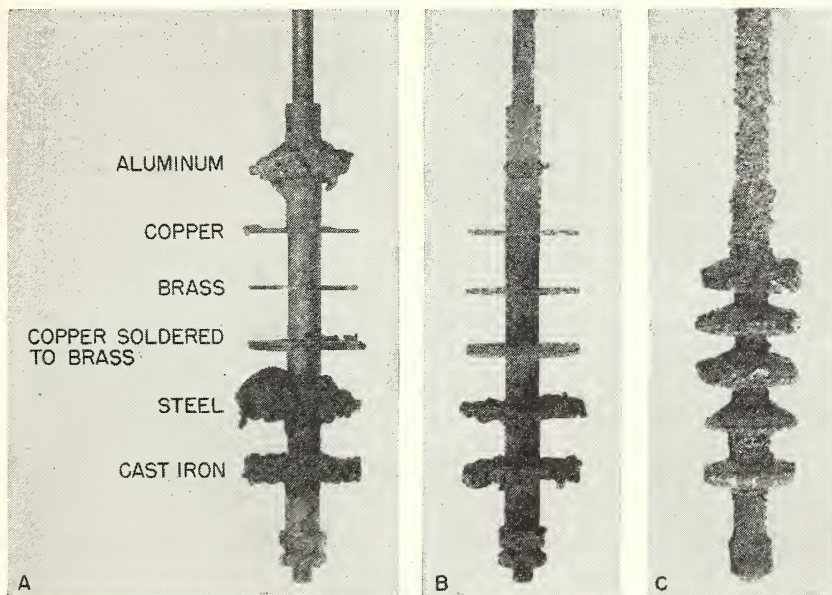


FIGURE 4. Results of test of magnesium-chloride antifreeze in simulated service unit, showing condition of metal test specimens after exposures for the times indicated.

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.

2.4. Petroleum "Antifreezes" or Coolants

The materials 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 the volume of the cooling system. 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 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 may flash into steam, causing the coolant to overflow.

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 little or no aromatics or olefins. These remarks therefore apply also to less highly refined products.

Petroleum coolants attack ordinary (natural or reclaimed rubber) radiator hose (see fig. 5) and also hose made from some kinds of synthetic rubber [152, p. 34; 169, p. 36]. However, the better grades



FIGURE 5. *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 service, during the life of this hose.

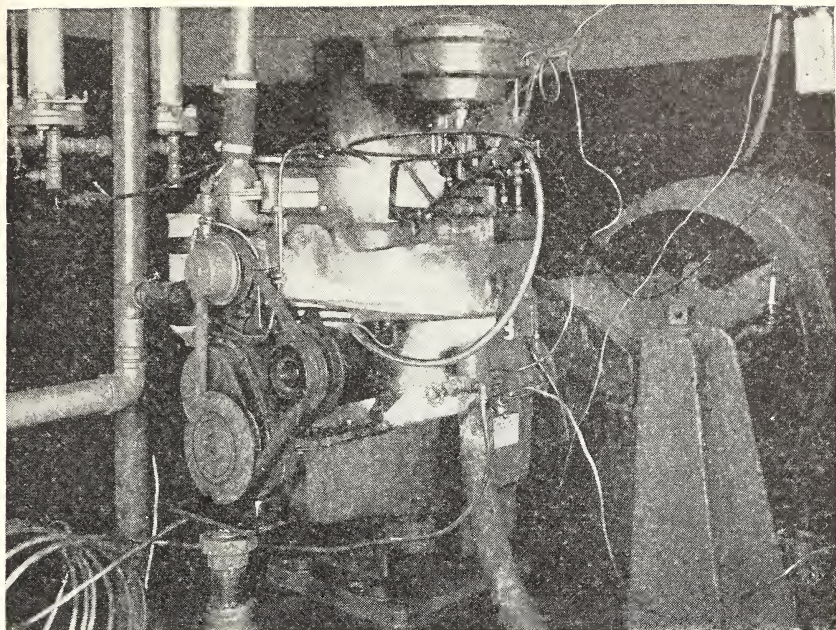


FIGURE 6. *Spontaneous ignition of petroleum antifreeze on engine exhaust manifold.*

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. 5) 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.

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.

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 hot exhaust manifold may serve as a source of ignition. Figure 6 shows the fire that resulted under these engine conditions when two teaspoonfuls of petroleum coolant were poured on the engine exhaust manifold. 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 a disadvantage in mild weather and especially in an occasional warm spell. Figure 7 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 (with an aqueous coolant) 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 9. Boiling of the coolant usually becomes obvious to the driver, by sight or odor, before it is too late. 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

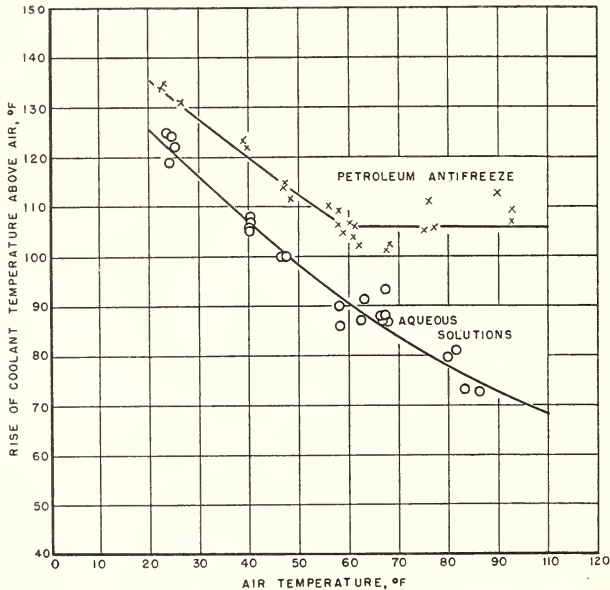


FIGURE 7. Comparative operating temperatures with petroleum and with aqueous coolants.

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.

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.

Neither petroleum coolants nor salt antifreezes are new. Oils or kerosine have been used for a half century, but to a limited extent only. In a cooling 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.

2.5. Miscellaneous Antifreezes

Earlier publications of the Bureau [35, 43, Letter Circular 28] mentioned such other antifreeze compounds as honey, sugar, glycerine, and trimethylene glycol. Honey and sugars are unsatisfactory because they are poor freezing-point depressants, and unstable to heat, and their solutions are too viscous. Trimethylene glycol is not available in commercial quantities. As 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 previously, this result does not prove that such solutions will be free from corrosive effects in actual service.

Diacetone alcohol has been found to be unsuitable as an antifreeze. It is unstable to heat and has a small freezing-point depression. Other compounds, such as butylene glycol, 2-methylpentanediol (hexylene glycol), diethylene glycol, and triethylene glycol likewise are not efficient antifreeze materials. This is because their relatively higher molecular weights make them less effective in lowering the freezing point of water. An exception to this rule is the *levo* form of 2,3-butanediol, a 50-percent solution of which freezes at -22° F.

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

3. Antifreezes in Relation to Performance Requirements

The type of antifreeze to be used is determined by the expected service and by local climate. A 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, antifreezes of either low boiling point (alcohol) or high boiling point (glycol) types may be used. 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, p. 36; and 169, p. 27 to 31].

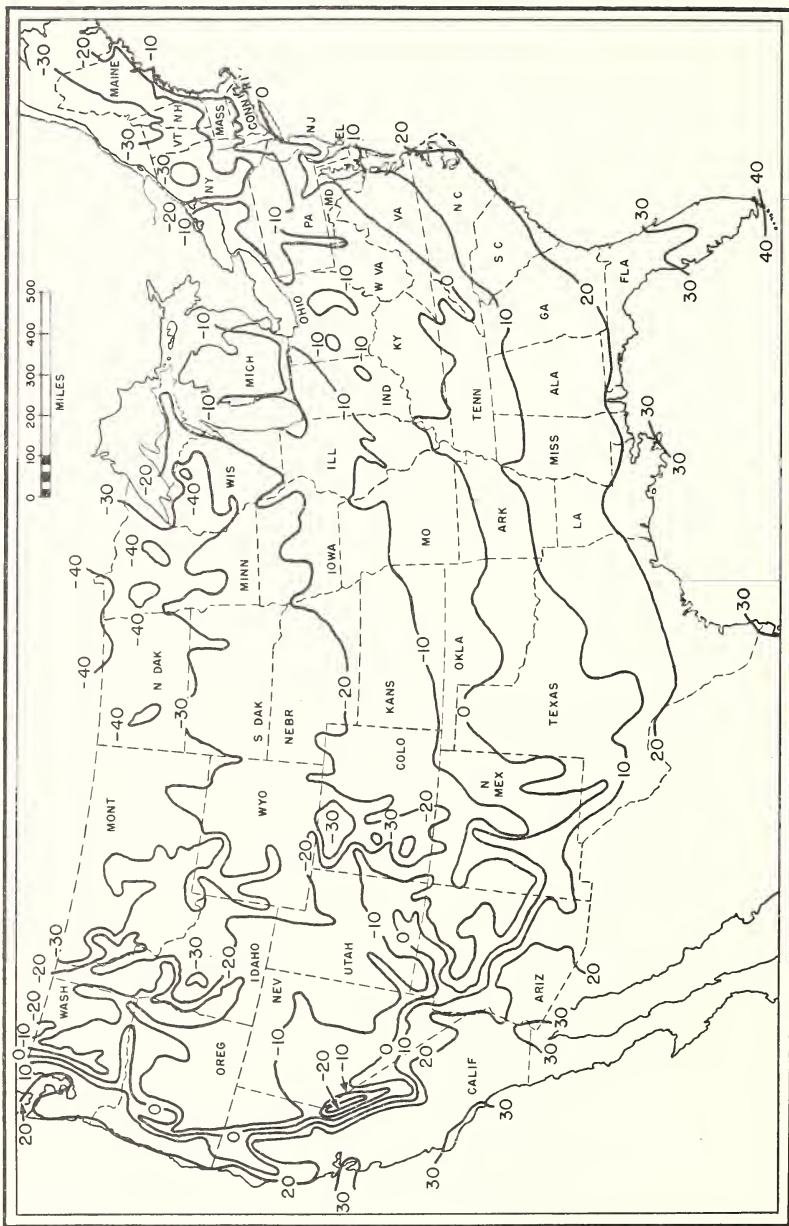


FIGURE 8. Average annual minimum temperature. On the average, lower temperatures occur about every other year. Once in about 20 years, temperatures 10 deg F below average minimum are experienced. Temperature averages are adapted from a U. S. Weather Bureau map.

3.1. Minimum Temperatures in the Continental United States

Antifreeze is needed 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. 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 strength of the antifreeze solution to be used should be sufficient to protect the car at as low an air temperature as is expected to occur.

Figure 8, which is adapted from information published by the U. S. Weather Bureau [172], shows the average annual minimum temperature for points within the continental United States. About every 2 years the lowest temperature will be below that given in the figure. 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 8, 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 any case where local records do not agree with figure 8, the value from the records is preferred. Figure 8 is believed to be fairly accurate for localities less than 1,000 feet above sea level, with some local exceptions in New England.

3.2. Relation of Composition to Freezing Point

As shown by figure 9, the boiling points of alcohol solutions are lowered and those of the glycols are raised with increasing protection against low temperatures. The boiling points of all the coolant solutions, including water, decrease about 2 deg F for each 1,000 feet of altitude. The bellows-type thermostat compensates for the effect of altitude by operating at lower temperatures at higher altitudes. This type of thermostat is also affected by changes in pressure in a cooling system using a pressure-type radiator cap. That is, the opening temperature is raised the same number of degrees that the boiling point of the coolant is raised by increased pressure. On the other hand, bimetallic or solid-expansion types of thermostats open at a fixed temperature, independent of the altitude or pressure in the system. Thus use of a pressure type radiator cap with bimetallic or solid-expansion thermostats increases the temperature differential between boiling point of the coolant and the operating temperature of the engine. If the temperature of any portion of the coolant reaches its boiling point either while the engine is operating, or after it has stopped, overflow loss of the solution may occur. Thus the advantage of using a low-range thermostat with the higher concentrations of alcohols is also apparent from figure 9.

The boiling-point temperatures on this chart decrease nearly 2 deg F for each 1,000 feet above sea level. The data apply to water solutions of the antifreeze base materials; the curves may be shifted upwards slightly by the presence of inhibitors in commercial antifreezes. They are also raised about 3 deg for every pound of pressure in the system when pressure caps are used.

The freezing point of an antifreeze solution ⁴ is defined as the temperature at which the first ice crystals form. An antifreeze solution may be cooled somewhat below its freezing point before ice crystals

⁴ For a theoretical discussion of the freezing point behavior of antifreeze base materials see reference [190].

make the liquid difficult to circulate [140]. This compensating factor increases with the strength of the antifreeze and gives an additional margin of safety if the expected lowest air temperature is used in determining the antifreeze protection needed.

A table giving the concentration required to protect to various temperatures is usually furnished with antifreezes. Freezing points of the water solutions of antifreeze base materials are given as a function of their concentrations in figure 10, and of their specific gravities in figure 11. As some commercial antifreezes contain small amounts of water, slightly higher volume concentrations than those shown in figure 10 may be required. Most commercial antifreezes also contain corrosion inhibitors and other additives to make them function properly as cooling liquids. These affect the freezing point slightly and the specific gravity to a greater extent. Thus if a protection table is furnished with the antifreeze, it may be used in preference to either of the figures given here.

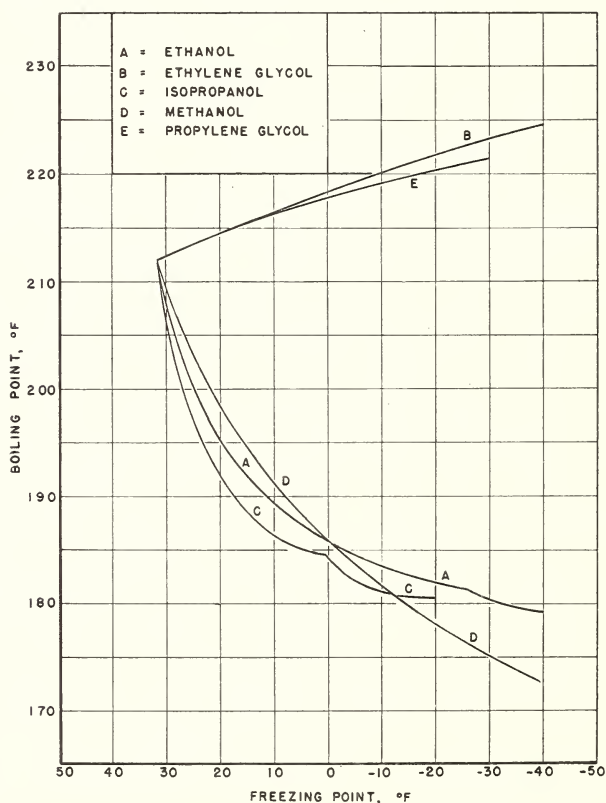


FIGURE 9. Variation of boiling points of antifreeze solutions with freezing-point protection.

The boiling-point temperatures on this chart decrease nearly 2 deg F for each 1,000 feet above sea level. The data apply to water solutions of the antifreeze base materials; the curves may be shifted upwards slightly by the presence of inhibitors in commercial antifreezes. They are also raised about 3 deg for every pound of pressure in the system when pressure caps are used.

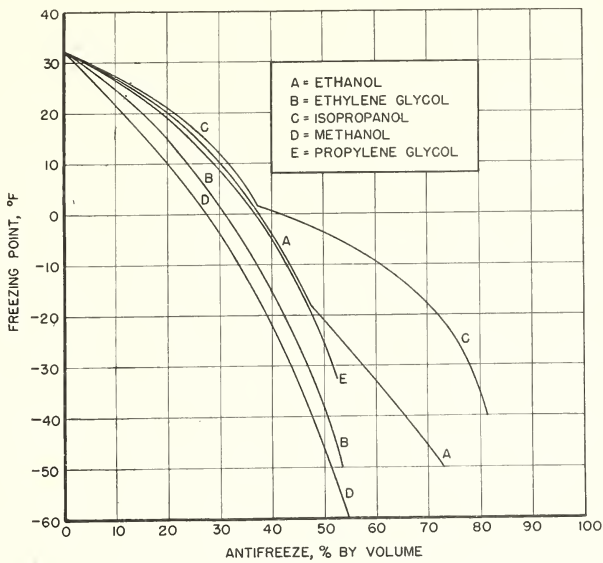


FIGURE 10. Relation of concentration to freezing point for solutions of antifreeze base materials.

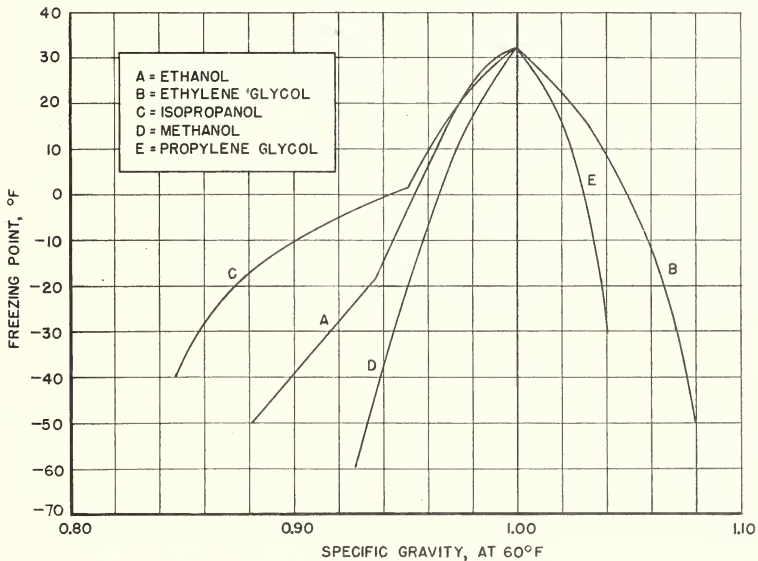


FIGURE 11. Relation of specific gravity to freezing point for solutions of antifreeze base materials.

Protection to a temperature lower than is likely to occur may be regarded as added insurance against damage by freezing. If low-boiling antifreezes are used, however, excessive protection is undesirable, because the lowering of the boiling point (fig. 9) may result in loss of solution by overflow from boiling [169, p. 28] or, to a lesser extent, by evaporation.

3.3. 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, methyl alcohol—can be determined with satisfactory accuracy. If a simple hydrometer-type tester without thermometer or correction chart is used, significant 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 is heated to engine operating temperature and tested in a simple hydrometer graduated for methyl alcohol, antifreeze protection to 7° F is 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 ethylene glycol and 1 gallon of propylene glycol—the protection can no longer be determined satisfactorily by hydrometer. As can be seen from figure 11, 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 sample with a thermometer inserted in it. If the sample is frozen, allow it to warm, stirring it with the thermometer, and note the temperature at which complete melting occurs. If the sample is not frozen, protection at least to the temperature shown by the thermometer is assured.

Devices for the direct determination of the freezing temperature of an antifreeze have been described [186, 187]. With these devices, reliable results may be obtained even if the composition of the antifreeze is unknown. With these devices, the sample withdrawn from the radiator is frozen by “dry ice” or expansion of liquid carbon dioxide. A thermometer inserted in the sample gives an indication of the temperature at which the sample froze.

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 methods 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 solu-

tion or various oxidizing agents. An example is the formation of rust on iron by the combination of the metal with water and oxygen.

Electrolytic corrosion is the result of action between dissimilar metals joined together in contact with a solution that conducts electricity by means of ionized particles. 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. Salt solutions are excellent conductors of electricity, and hence are very unsatisfactory antifreezes because they promote 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 particles, such as rust or sand. Because 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. Erosion can also occur from bubbles of air or other gases dispersed in the liquid.

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 antifreezes 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 necessarily 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.

5. Depletion of Corrosion Inhibitors

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 may 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 several causes, including exhaust gas leaking into the cooling system. This gas, containing oxides of carbon, sulfur, and nitrogen, may react with some inhibitors, destroying their effectiveness. Small amounts of air leaking into the system hasten corrosion and may cause "gas erosion." The effects of air are much greater if the liquid level is allowed to fall low enough to cause entrainment of air 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, may also cause depletion of inhibitors. The antifreeze base material itself is subject to decomposition, with the formation of organic acids

and aldehydes, which may react with the inhibitors. It is not feasible to predict the time when these factors will lead to corrosion in the cooling system of a given automobile because of the various extent of each. It is certain, however, that corrosion products such as rust will eventually form if the solution is used beyond its useful life. Once corrosion begins it will proceed at an increased rate, as pointed out in reference [170]. The same article gives data from a series of tests to determine inhibitor life. In 2 to 50 percent of the tests, the inhibitors were completely exhausted at 10,000 miles, depending on the formula being tested. In a recent survey of used antifreeze [187] it was reported that 20 percent of cars showed "high acidity and rust or deposits" in the cooling system at the end of the first year's use and "in the two to three year group . . . about 68% of the cars showed rust or deposits in the radiator." A chemical analysis of a used antifreeze may tell how much inhibitor remains, but will not predict how long it will last.

A filling of fresh antifreeze may usually remain good for one winter. Antifreeze left in the cooling system during the summer will be expected to deteriorate more rapidly under summer driving conditions.

Some kinds of water are very corrosive [152, p. 29; 169, p. 64]. Where the water is excessively hard or contains much dissolved mineral matter, soft water (rain or distilled water) may be used in preparing antifreeze solution, and also used in the summer, together with a corrosion inhibitor in the cooling system [169, p. 36 to 37]. Even distilled water is more corrosive to aluminum than Washington tap water, while the tap water is more corrosive to ferrous metals. Where inhibited water or antifreeze solution is drained for engine repairs, it can, of course, be saved for reuse if it is clean and rust-free.

6. Properties of Coolant Materials

Material	Density	Water soluble	Effect on boiling point of water	Corrosiveness when inhibited	Electrical conductor	Specific heat	Viscosity as used at low temperatures	Flammable ^a
	<i>lb/gal</i>							
Water.....	8.35	-----	-----	Negligible...	No ^b	High.....	Low.....	No
Methyl alcohol.	6.6	Yes	Lowers.....do.....	No	Medium.....do.....	Yes
Ethyl alcohol.	6.8	Yesdo.....do.....	Nodo.....do.....	Yes
Isopropyl alcohol.	6.5	Yesdo.....do.....	Nodo.....do.....	Yes
Ethylene glycol.	9.3	Yes	Raises.....do.....	Nodo.....do.....	No
Propylene glycol.	8.7	Yesdo.....do ^e	Nodo.....do.....	No
Glycerine.....	10.5	Yesdo.....	Moderate ^c	Nodo.....	Medium.....	No
Salts.....	9.5 to 10.5	Yesdo.....	Heavy.....	Yesdo.....	Low.....	No
Petroleum.....	6.5 to 7.0	No	(High-boiling coolant.)	None ^d	No	Low.....do.....	Yes

^a No attempt is made here to denote the degree of flammability. See section 2.4.

^b Applies to pure water.

^c 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.

^d 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.

7. Bibliography

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7.1. 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.

METHYL ALCOHOL

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