ENGINE COOLANT TESTING: STATE OF THE ART

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Committee D-15 on
Engine Coolants
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Foreword

This publication on Engine Coolant Testing: State of the Art contains papers presented at a symposium held 9–11 April 1979 at Atlanta, Georgia. The symposium was sponsored by the American Society for Testing and Materials through its Committee D-15 on Engine Coolants. W. H. Ailor, Reynolds Metals Company, served as symposium chairman and editor of this publication.

Related ASTM Publications

Selection and Use of Engine Coolants and Cooling System Chemicals, STP 120B (1973), $3.00, 04-120200-12

Multicyclinder Test Sequences for Evaluating Engine Oils, STP 315G (1977), 04-315070-12

Single Cylinder Engine Tests for Evaluating the Performance of Crankcase Lubricants, Part I: Caterpillar IG2 Test Method, STP 509A (Part I), 1979, bound, $9.75, 04-509010-12; looseleaf, $12.75, 04-509011-12

Single Cylinder Engine Tests for Evaluating the Performance of Crankcase Lubricants, Part II; Caterpillar IH2 Test Method, STP 509A (Part II), 1979, bound, $9.75, 04-509020-12; looseleaf, $12.75, 04-509021-12

Single Cylinder Engine Tests for Evaluating the Performance of Crankcase Lubricants, Part III: Caterpillar ID2 Test Method, STP 509A (Part III), 1979, bound, $9.75, 04-509030-12; looseleaf, $12.75, 04-509031-12

LP-Gas Engine Fuels, STP 525 (1973), $4.75, 04-525000-12

Low-Temperature Pumpability Characteristics of Engine Oils in Full-Scale Engines, DS 57 (1975), $16.00, 05-057000-12

A Note of Appreciation to Reviewers

This publication is made possible by the authors and, also, the unheralded efforts of the reviewers. This body of technical experts whose dedication, sacrifice of time and effort, and collective wisdom in reviewing the papers must be acknowledged. The quality level of ASTM publications is a direct function of their respected opinions. On behalf of ASTM we acknowledge with appreciation their contribution.

ASTM Committee on Publications

Editorial Staff

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Introduction

A critical component for any internal combustion engine is its coolant system. The combination of dissimilar metal components, including cast iron, brass, zinc, aluminum, solders, etc., operating in a liquid system at increasingly higher temperatures creates potentially severe corrosion and heat transfer problems.

The use of alcohol as an antifreeze for engine coolants has given way to inhibited ethylene glycol solutions in available local supply waters for year-round operation. The diversity of inhibitors available for corrosion and erosion protection has further complicated the coolant picture. Higher flow rates have introduced cavitation and erosion problems as new concerns.

During 9–11 April 1979, ASTM Committee D15 on Engine Coolants sponsored an International Symposium on the State of the Art in Engine Coolant Testing. The sessions were held at the Sheraton-Biltmore Hotel in Atlanta, Ga. The 21 papers presented included both invited papers and offered papers from knowledgeable persons in the automotive and coolant manufacturing fields. Authors came from England, West Germany, Japan, Switzerland and, of course, the United States.

The symposium was designed to present the current thinking of those involved with engine coolant testing and to indicate areas for work to meet new problems. The sessions were of special value to newcomers in the field and served as educational lectures. At the same time, the continuing efforts towards standardization of test methods were reported by members of ASTM Committee D15 on Engine Coolants, based on more than 30 years of committee efforts.

The papers and discussion resulting from this symposium make up this Special Technical Publication. The book should be very useful to engineers, chemists and others concerned with engine and solar heat exchangers and designers, stylists and others whose work involves heat transfer equipment.

All Committee D15's test methods may be found in the current *Annual Book of ASTM Standards* (*Part 30*). In the 1978 edition there were 21 methods.

ASTM STP 120B on *Selection and Use of Engine Coolants and Cooling System Chemicals* (1974) is an updated revision of earlier helpful discussions on engine cooling systems, antifreeze-coolants, installation and service, and cooling system chemicals.

The contributions and efforts of all the members of ASTM Committee D15 on Engine Coolants is appreciated. Many members served in planning the program, chairing the sessions, reviewing the papers, supervising the social functions. Special thanks are due our overseas authors and session chairmen who not only prepared excellent oral and written presentations but helpfully have written answers for many questions raised at the sessions. The support and interest of their organizations and for all participating companies is gratefully acknowledged.

Members of D15's Organizing and Planning Committee included: Norman R. Cooper, Union Carbide Corp.; Donald L. Cramer, Houston Chemical Co.; Joseph C. Gould, E. I. duPont de Nemours; Vincent R. Graytok, Gulf Research and Development Co.; Donald L. Wood, Shell Development Co.; and Charles W. MacKenzie, *Radiator Reporter*.

W. H. Ailor

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L. C. Rowe[1]

Automotive Engine Coolants: A Review of Their Requirements and Methods of Evaluation

REFERENCE: Rowe, L. C., "**Automotive Engine Coolants: A Review of Their Requirements and Methods of Evaluation,**" *Engine Coolant Testing: State of the Art, ASTM STP 705,* W. H. Ailor, Ed., American Society for Testing and Materials, 1980, pp. 3-23.

ABSTRACT: A brief review of early automobiles shows the development of the engine cooling system, and some of the associated problems with these early cars are discussed.

A liquid is commonly used to transfer heat from an operating automobile engine to a radiator where the heat can be dissipated to the air. In order that the liquid perform effectively, it must have the appropriate chemical and physical properties. Of foremost consideration is the capability of the fluid to transfer heat over a wide range of operating conditions. In addition, the fluid must be stable, must not freeze when not in use or boil during or after engine operation, and must not cause or allow excessive corrosion of the parts it contacts.

To determine how well the cooling system is capable of performing its function, it is necessary to perform a variety of tests to evaluate the operational characteristics of component parts, the properties of the coolant fluid and its long-range stability, and the capability of the fluid to minimize corrosion of all materials. Tests range from the shorttime laboratory test to the longer and more comprehensive field test. Operating conditions are often difficult to simulate in the laboratory, and the test tends to be restrictive. Field tests are usually more definitive but can be difficult to control. However, the end result of an effective development program over a number of years has been a cooling system that has provided good durable service.

KEY WORDS: engine coolants, engine cooling system, coolant properties, coolant testing, antifreeze, heat transfer, corrosion

A brief review of our early automobiles provides some insight into the reasons for the need and the development of an effective engine cooling system. There has been continual improvement over the past 75 years in the design of the cooling system and in the quality of the antifreeze coolants. However, many of the same problems that were found with the earlier

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cooling systems still exist today because the motorist is not sufficiently informed or concerned to provide the required maintenance or to use proper engine coolants.

The history of the self-propelled land vehicle is only a little over 200 years, but much has happened during that short period of time. The earliest vehicles could hardly be classed as automobiles, as we know them today, because many of them were merely some form of "land carriage" with a means of propulsion added. These early vehicles were primarily steam operated, and one of the first patents for such a vehicle was granted to Oliver Evans in 1787 in Maryland for a steam wagon that was only able to operate for a short distance at a very slow speed before breaking down [*1*].[2] A commercial practical gasoline engine was produced by Etienne Lenoir in France in 1860 [*1*]. Carl Benz from Germany is given the credit in 1885 for the first road vehicle propelled by an internal combustion engine [*2*]. It was not until 1892 that the Duryea brothers produced the first gasoline engine in the United States [*1,3*]. Following this introduction, the interest in vehicular transportation grew at an increasing rate.

The internal combustion engine required some means for removing the excess heat from the engine because all of it was not transformed into mechanical energy. If the heat was not removed, the engine overheated and soon malfunctioned. Both air and water were used to cool engines in the early part of the 20th century. Air cooling required that the outer surface of the combustion chamber be in direct contact with the surrounding air to remove the heat. The amount of heat that could be removed was limited by the metal surface area that came in contact with the air, so it was not unusual to add a few metal ribs to the surface to increase the contact area [*4*]. Air cooling was more feasible in these early days than in later years because the early low-horsepower engines were small and produced little excess heat. Air cooling was often preferred by the manufacturer of the small, light car because it added less weight than a water-cooling system and was a simple design. In addition, it was not affected by freezing temperatures.

In water-cooled engines, water passed through a jacket surrounding the combustion chamber, absorbed the heat, and transmitted it to a radiator where it could be dissipated to the air. One of the distinct advantages to the water-cooled system is that the surface area of the radiator can be made many times greater than that of the engine block, permitting a more rapid transfer of heat to the air. Two systems were used to circulate the water; namely, natural circulation and forced circulation with a pump. In natural circulation, a water tank was placed above the engine. The water passed by gravity from the bottom of the tank through a radiator and into the bottom of the engine water jacket where it was heated [*5*]. The hot

[2] The italic numbers in brackets refer to the list of references appended to this paper.

water rose to the top of the jacket and then back into the tank again. This system was fraught with difficulties and had many limitations. Other means were needed to improve cooling and to facilitate circulation of the water, and the best and most frequently used method was forced circulation with a pump, usually a rotary, centrifugal pump.

There were early concerns about the location of the engine, whether it should be placed in the front, rear, or under the middle of the vehicle. The cooling system was destined to play a significant role in this selection, as indicated by one author's comments after a reliability race in 1902 from New York to Boston. The author stated that "troubles with the cooling system are shown to have exceeded those due to faulty ignition and fuel feed as causes for delay" [*6*]. The author went on to speculate that some of the troubles could be traced to the long piping necessary to take the cooling water from the engine in the rear of the car to the radiator at the front. It was suggested that a compact cooling system with the radiator and engine both at the front reduced the opportunity for leaks and the formation of deposits to clog the system. As the cars grew heavier, the distribution of weight became of concern, and there was less objection to a better distribution of weight by placing the engine over the front axle. The importance of a reliable, more efficient cooling system continued to take on greater significance, and the trend to water-cooled systems increased.

The automobile was such a completely new experience to people in these early days that the owners could hardly be expected to be concerned with the cooling system when they tended to neglect other basic procedures that were necessary for dependable vehicle operation. They were chided because they forgot to recharge the acetylene generator that supplied gas lamps or neglected to tighten the brake bands [*7*]. Even running out of gas was attributed to carelessness because the owner forgot to remove the filling cap "to sound with a lead pencil, bit of string, wire, or clean stick to determine the quantity remaining in the tank" [*7*]. The cooling system received little owner concern because loss of coolant would be noted by boiling liquid before the cylinders became overheated. However, the same writer suggested drawing off some old water and filling the system with fresh water before a trip to avoid the necessity of "bothering some roadside resident for water and the loan of a bucket" [*7*].

This simplistic approach was not endured for long. The automobile had provided the people with a new degree of freedom. They could now travel longer routes and explore lesser traveled areas, and they demanded more reliability. As the popularity of the automobile grew, it was no longer regarded as a warm weather vehicle but one that could be used any time of the year. It became necessary to use a substance that would not freeze by itself or that would lower the freezing point of water when mixed with it. Many people were satisfied to add any substance to water as long as it depressed the freezing point, but there were those that warned against the use of certain materials. Salts, such as calcium or sodium chloride, were known to be destructive to metal and were not recommended. Glycerin that was not chemically pure was said to attack both metal and rubber components, and it rapidly degraded and had to be replaced, adding to the expense of its use.

The obvious concern for freezing of the coolant is indicated in a letter to the editor of *The Automobile* in 1904. A substitute for water is suggested in this extraction from the letter. "I have just made a test of an antifreeze article .... It is no less than an inexpensive lubricating oil .... I put this clear (no water) in a 4-cylinder Toledo car ... and it cooled every bit as much as water ... and it will not freeze" [*8*]. Regardless of this individual's experience, there never has been a trend to the use of lubricating oils for cooling.

The motorist turned next to the use of wood (methyl) alcohol for freezing protection because it was cheaper than grain (ethyl) alcohol which was taxed at $2.10 per proof gallon [*9*]. The tax was removed from ethyl alcohol in 1907 because it was being used increasingly for industrial purposes. Ethyl alcohol proponents claimed the following advantages over methyl alcohol: (*a*) lower freezing point (only true for pure alcohol—a 50 percent solution has a higher freezing point), (*b*) higher boiling point, (*c*) cheaper because less of it was needed, and (*d*) more uniform because it contained no solids and required no filtering, and (*e*) less destructive to parts of the cooling system [*9*]. The growing need for alcohol is indicated in this statement regarding availability: "If the plans of the United States Department of Agriculture are consummated, denatured alcohol will, within the next few years, be manufactured by every farmer in the country from his waste material" [*9*]. Although this claim was never fulfilled, it is interesting that similar claims are being suggested today in regard to the use of alcohol as a gasoline substitute.

There has been continued improvement in cooling system design and in the quality of coolant materials. Much of the credit for these improvements belongs to organizations such as ASTM, the Society of Automotive Engineers (SAE), The Chemical Specialties Manufacturing Association (CSMA), and similar organizations in other countries. Information bulletins, standards, and specifications have been written to give guidance in the selection and use of coolant materials. ASTM Committee D15 on Engine Coolants deserves much of the credit for these standards. This committee was formed in 1947 as the Engine Antifreeze Committee with the following scope:

> The study of engine antifreezes, including terminology, identification and classification, methods of sampling and testing of engine antifreeze and cooling system corrosion inhibitors; interpretation and significance of tests; and the preparation of specifications.

This was quite an assignment, but over 20 methods, practices, or specifications have been written and continually revised over the intervening years, and these standards are used throughout the world. Committee members have contributed additional information and knowledge on the subject through published papers, reports, and seminars. Even the name of the committee was changed to "Engine Coolants" in 1972 in recognition of a greater concern for the entire coolant rather than just its antifreeze aspect. This continued activity has resulted in fairly well defined parameters for an engine coolant.

Requirements of an Engine Coolant

The requirements of the coolant must be directed to fulfilling the objective of transferring heat from the engine to the radiator for dissipation. Many of the desired characteristics and requirements of an engine coolant are listed in Table 1.

No single material can satisfy all these requirements for an engine coolant, so some concessions must be made. The first requirement, high specific heat and good thermal conductivity, is basic to the function of the coolant to transfer heat from one site to another. Water with a specific heat of one is the best material available for this purpose. It meets many of the other desired requirements, but it fails to meet three very essential categories; specifically, freezing, boiling, and corrosivity. These shortcomings of water were mentioned in the brief review of the early automobiles, and it is interesting that even today there are still automobile owners who disregard the requirements of a good coolant and use either water alone as a coolant or highly diluted ethylene glycol antifreeze.

To overcome the deficiencies of water, it was necessary to find a substitute for it or to mix it with other materials to improve its characteristics. The choice of materials has usually been divided among (*a*) salts, (*b*) alcohols, (*c*) petroleum products, and (*d*) polyhydroxy alcohols (glycerol and glycols). Unfortunately, these materials may satisfy those requirements that water cannot, but they may be less acceptable in other areas.

Salts have never been satisfactory because it requires a high concentration

TABLE 1—*Characteristics and requirements of an engine coolant.*

High specific heat and good thermal conductivity
Fluidity within the temperature range of use
Low freezing point
High boiling point
Noncorrosive to metals; minimum degradation of nonmetals
Chemical stability over the temperature range and conditions of use
Nonfoaming
Low flammability; high flash point
Reasonable compatibility with other coolants or oil
Low toxicity; no unpleasant odor
Reasonable cost; available in large quantities

of salt for freezing protection. These solutions are highly corrosive, and it is difficult to inhibit corrosion through the addition of small quantities of chemicals. In addition, radiator-tube blockage may be enhanced through salt recrystallization in tubes. If a salt solution should leak into the engine compartment, its high conductivity may contribute to a shortcircuit in the electrical system.

Alcohols have many satisfactory characteristics, and alcohol-water mixtures were used successfully as engine coolants for many years. They fail to meet present-day requirements for a high boiling coolant that will allow higher operating temperatures. The flash point and flammability of alcohols are not as satisfactory as that of other materials. The corrosion inhibitor systems in alcohol antifreeze coolants were not completely satisfactory in the past, but it is presumed that they could have been improved with further research if the justification had developed.

Petroleum products, such as oil or kerosene, have had limited use as a substitute for water mixtures. The heat transfer characteristics are not satisfactory, and engines tend to run hotter than when water mixtures are used. Petroleum-base coolants, if used, would be restricted to mild temperatures and moderate driving conditions where little stress is placed on the engine. There is a tendency for these materials to be more flammable than desired, and they are subject to ignition under certain conditions. Some products may attack polymeric materials in the cooling system. Finally, the engine may be damaged from overheating because the high boiling point of these products does not provide the warning by boilover that water-base materials do.

A water solution of glycerol should be a satisfactory engine coolant under most conditions if properly inhibited. Corrosion was the principal problem in its early use because inhibitors were not used. However, glycerol is not as good a freezing point depressant as the other polyhydroxy alcohols. The most satisfactory product in this category has been ethylene glycol, which often has small percentages of diethylene glycol or propylene glycol mixed with it. Although ethylene glycol does not meet all the requirements of a coolant, it provides a fairly good overall balance. It has a specific heat of about 60 percent that of water, but a 50:50 mixture of ethylene glycol and water raises this to about 80 percent. In addition, a 50 percent solution has a 7°C (15°F) higher boiling point than water alone, and this provides a definite advantage. It has been demonstrated that a car at idle at an ambient temperature of 38°C (100°F) that contains a 50 percent mixture of ethylene glycol and water can be operated 40 percent longer than when water alone is used before boiling occurs [*10*]. Thus, some of the disadvantage of the lower specific heat is offset by the higher boiling point. To meet other engine coolant requirements, small quantities of chemicals are added to the ethylene glycol concentrate: (*a*) inhibitors to prevent metal corrosion, (*b*) alkaline substances to provide a buffering action against acids, (*c*) an antifoam agent to reduce foaming tendencies, (*d*) a dye to provide identity, and (*e*) a small amount of water to dissolve certain chemicals and to provide stability. It is quite evident that the ethylene glycol coolant concentrate is a carefully formulated product. A basic outline of the composition of such a product is shown in Table 2.

ASTM Reference Coolant (D 3585-77) is a typical example of a formulated product. Certain physical and chemical properties of a product must be checked to ensure that the product meets the specific requirements of the cooling system. Standard test methods have been developed by ASTM Committee D15 for this purpose. A list of these methods is shown in Table 3 with a reference to the specific function of each method. There is no ASTM standard for the complete chemical analysis of an antifreeze coolant, but published procedures are available from other sources [*11,12*].

Many of these standard methods are used for quality control to ensure that a product falls within certain specified limits or to determine whether a product meets engineering specifications that may include composition or physical characteristics. Some methods may be used in test programs to

TABLE 2—*Basic composition of ethylene glycol coolant concentrate.*

Composition	Concentration, %
Ethylene glycol	80 min
Other glycols	15 max
Multi-inhibitor system	
Buffer or neutralizer	~5
Foam suppressor	
Dye	
Water	

TABLE 3—*Standard ASTM test methods to determine physical and chemical properties of an engine coolant concentrate.*

Numerical Designation	Title
D 1119-65	Ash Content of Engine Antifreezes, Antirusts, and Coolants
D 1120-72	Boiling Point of Engine Coolants
D 1121-72	Reserve Alkalinity of Engine Antifreeze, Antirusts, and Coolants
D 1122-58	Specific Gravity of Engine Antifreezes by the Hydrometer
D 1123-73	Water in Engine Coolant Concentrate by the Iodine Reagent Method
D 1177-65	Freezing Point of Aqueous Engine Coolant Solution
D 1287-78	pH of Engine Antifreezes, Antirusts, and Coolants
D 1881-73	Foaming Tendencies of Engine Coolants in Glassware
D 1882-66	Effect of Cooling System Chemical Solutions on Organic Finishes for Automotive Vehicles
D 3634-77	Trace Chloride Ion in Engine Antifreezes/Coolants in the Presence of Mercaptobenzothiazole