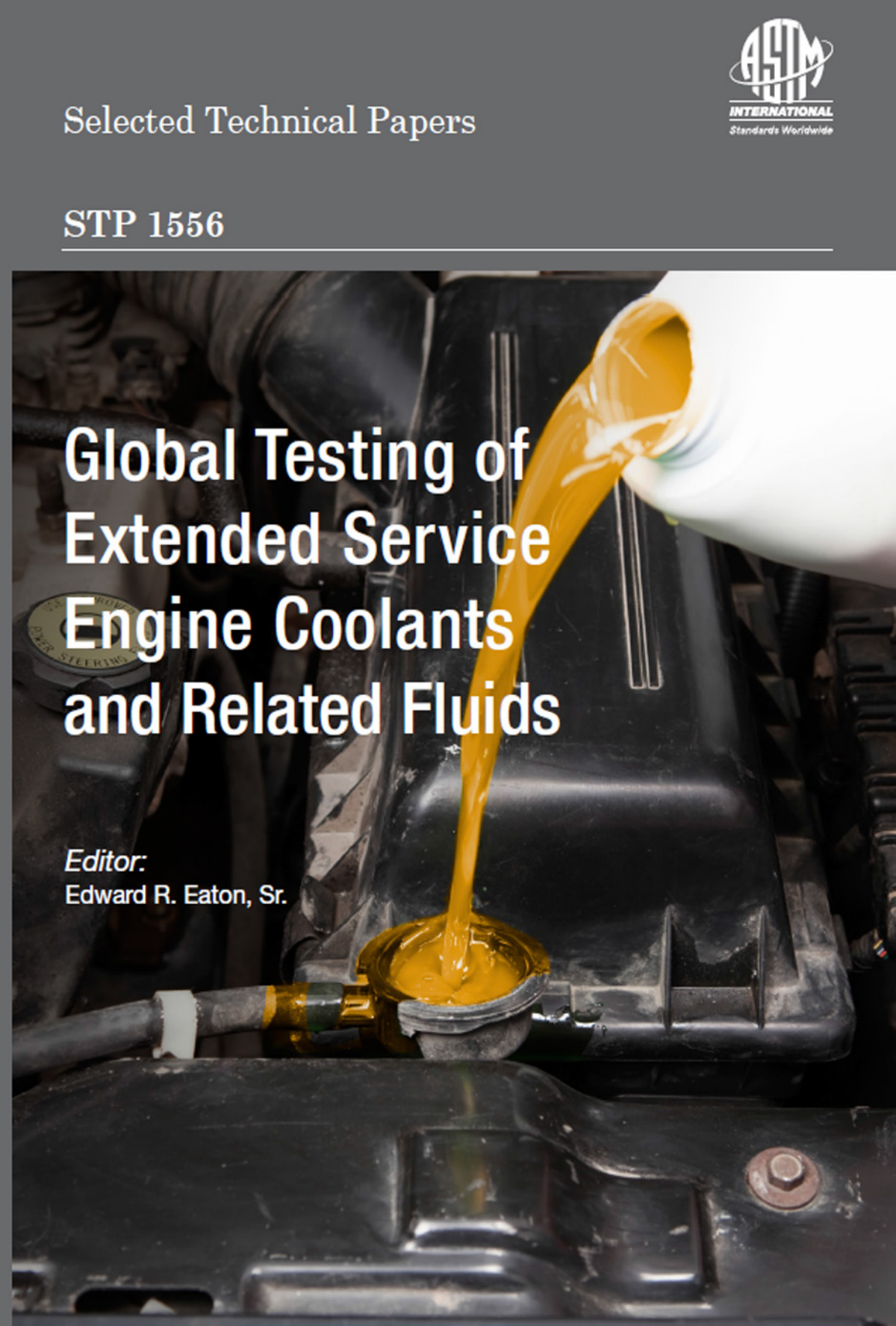


Selected Technical Papers

STP 1556



A close-up photograph of a car engine. A white plastic jug is pouring a bright yellow-orange liquid, likely engine coolant, into the open coolant reservoir. The liquid is captured mid-pour, creating a dynamic stream. The engine components are dark and metallic, with some hoses and wires visible in the background.

Global Testing of Extended Service Engine Coolants and Related Fluids

Editor:
Edward R. Eaton, Sr.



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Foreword

This Compilation of *Selected Technical Papers*, STP1556, *Global Testing of Extended Service Engine Coolants and Related Fluids*, contains peer-reviewed papers that were presented at a symposium held May 23, 2013 in Indianapolis, IN, USA. The symposium was sponsored by ASTM International Committee D15 on Engine Coolants and Related Fluids and Subcommittee D15.21 on Extended Life Coolants.

The Symposium Chairperson and STP Editor is Edward Eaton, Amalgatech, Phoenix, AZ, USA.

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Overview

This volume reports the proceedings of the *Symposium on Global Testing of Extended Service Engine Coolants and Related Fluids* held in May 2013 at the J.W. Marriott in Indianapolis, Indiana. The Symposium demonstrated the dynamic nature of the Engine Coolant industry in the first part of the twenty-first century. The need for constantly improving engine coolant technologies that included alternative freeze-depressing molecules, cooling efficiency, and inhibitor chemistries, was made manifest.

Coolant service intervals that extend to two or three times earlier recommendations are now the norm. Learning how to test chemistries to better predict the behavior of experimental formulations over these extended service intervals is a point of investigation for several of the papers herein.

Other new directions include further extending coolant change intervals and introducing renewable materials as engine coolant components. In particular, the expansion of bio-fuel manufacturing has provided impetus for evaluation of bio co-product glycerin, 1,3 propanetriol and bio propylene glycol as replacements for, or blending agents with, traditional ethylene glycol.

The papers fall roughly into four categories:

There are two papers that review the state-of-the-art in engine coolants. The first is presented by Dr. Bo Yang et al. of Prestone. This paper summarizes the development of extended life coolants over the last two decades. The second paper, presented by Dr. Tom Light at Evens Cooling Systems, reviews developments in non-aqueous coolant technology. The concept of non-aqueous coolant has recently been receiving more interest by researchers seeking solutions to constantly increasing demands on the engine and the engine cooling systems.

Four papers are grouped as “New Coolant Technology” papers because they discuss potential novel or significant revolutionary-level changes to engine coolants. Dr. Gefei Wu et al. present the proposal of bringing nanofluid technology to engine coolants. The research was performed in cooperation with the U.S. Army and offers the possibility of significant cooling efficiency. Chevron researchers offered two papers that discuss improvements to oxidation stability and aluminum passivation. Both behaviors are important to understand if the goal of further extending coolant service intervals is to be accomplished. The fourth paper, presented by Shawn McGlothlin of Orison Marketing, reveals the benefits of replacing ethylene glycol (1,2 ethanediol) with PDO (1,3 propanetriol). Development and testing data are

reported in this paper which documents a move forward for the corn-based PDO renewable-resource freeze depressant.

A second group of four papers discusses possible modifications and/or uses of existing ASTM test method equipment to challenge coolant formulations and better predict and “rank” possible coolant formulations in terms of their ability to protect metals over a 5-year period; as opposed to the shorter terms heretofore considered of interest in the world of 12 to 24 month new car and truck warranties. Researchers at Amalgatech report of prototype variations of commonly used tests, including ASTM D1384 “Standard Test Method for Corrosion Test for Engine Coolants in Glassware”, ASTM D2570 “Standard Test Method for Simulated Service Corrosion Testing of Engine Coolants”, and ASTM D4340 “Standard Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions.” These tests are evaluated with various coolants and the data are presented. Finally, drawing from the compatibility testing requirements published by major original equipment manufacturers, a proposal is put forward for screening research formulas for possible negative corrosion behaviors when mixed with existing chemistries already in use.

Finally, a group of three papers wherein the discoveries of problem behaviors are reported complete the symposium report. The important interaction of some coolants with CAB brazed aluminum heat exchangers is reported by Fred Alverson and Mary Ranger. Elastomer behaviors in newer coolant chemistries are reported by Dan Hertz Jr., Dan Hertz, III, and Harold Cook. Water pump durability, especially when water pumps are replaced in the automotive repair trade, was investigated and interesting conclusions reached by Loring A. Weisenberger and Yahya Hodjat.

Quoting my mentor, teacher, good friend, and predecessor, Roy E. Beal, I am happy to close the overview by concluding that “A successful symposium with good attendance was achieved. Some controversial presentations were made, but were certainly thought-provoking for the future of coolant technology.”

On behalf of ASTM Committee D15 on Engine Coolants and Related Fluids, I express very sincere thanks for the generous donation of time and other valuable resources that made both the symposium and this volume possible. In today’s “leaner and meaner” business environment, and especially in the context of developmental research, the permission given by participating corporations for such commercially valuable information to be made public is extraordinary and exceedingly benevolent. May the contributors and their organizations from the three continents represented find the effort and sacrifice worthwhile and ultimately profitable!

Edward R. Eaton, Sr.

TECHNICAL REVIEWS

STP 1556, 2014 / available online at www.astm.org / doi: 10.1520/STP155620130109

Bo Yang,¹ Aleksei Gershun,¹ and Peter Woyciesjes¹

Development of Extended Life Coolant Technologies—Past, Present, and Future

Reference

Yang, Bo, Gershun, Aleksei, and Woyciesjes, Peter, "Development of Extended Life Coolant Technologies—Past, Present, and Future," *Global Testing of Extended Service Engine Coolants and Related Fluids*, STP 1556, Edward R. Eaton, Ed., pp. 3–38, doi:10.1520/STP155620130109, ASTM International, West Conshohocken, PA 2014.²

ABSTRACT

Since the introduction of liquid coolant as the heat transfer media for internal combustion engines, improvement of the coolant's performance and properties has always been a key developmental priority. The drive for improved fuel economy and the development of lighter, more compact powertrain designs often result in the need for improvement in the performance and properties of the coolant. The adoption of new and more effective manufacturing technologies and design changes to key cooling system components also contributes to the need for these improvements. Recently, the focus has been on improvement to the longevity of the corrosion protection performance of the coolant. This will allow for extended service life which will lessen environmental impact, reduce operating/maintenance cost, and ensuring continuous improvements of system reliability and durability. In this paper, the major technological developments of extended life coolant products for automotive use, since the 1990 s, are reviewed. Laboratory and fleet test data on several different key extended life coolant products will be presented and compared to demonstrate their performance and areas for potential improvement. The development of the next generation of extended life coolant technologies with improved performance and a longer service life will be discussed.

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²ASTM Symposium on *Global Testing of Extended Service Engine Coolants and Related Fluids* on May 23, 2013 in Indianapolis, IN.

Keywords

engine coolant, antifreeze, extended life coolant, conventional coolant, organic acid technology coolant, hybrid silicate–organic acid technology coolant, next generation coolant, fleet testing, corrosion testing, electrochemical testing, glycol degradation, azole depletion, potassium fluoroaluminate flux, aluminum, cooling system corrosion protection

Introduction

The first commercial marketing of ethylene glycol antifreeze for use in automobiles started in 1927 [1,2]. Many advances in automotive engine coolant technology had taken place over the next decades to improve the performance and durability of the coolant. Particularly, between 1949 and 1955, ethylene glycol based coolants were used widely as factory fill coolant replacing methanol based products used by automakers in order to increase coolant temperature to reduce engine sludging and wear [1,2]. However, some (automakers) still used water with corrosion inhibitors during the warm-weather months as their factory fill at their vehicle production plants [2]. This practice was finally changed in 1962 when all three U.S. car companies—Ford Motor Company, General Motors, and Chrysler—began installing a 50 % water and 50 % ethylene glycol antifreeze solution in their new cars, which led to the emergence of antifreeze/coolant as a year-round functional fluid—just as important as engine oil or automatic transmission fluid [1–3]. The change from water based and water-alcohol based coolants to a 50 % water–50 % ethylene glycol engine coolant, together with the many advances in the inhibitor technologies used in the coolants, greatly increased the service life and durability of engine coolants. The technological advances enable the ethylene glycol–water based coolants to provide the engine with the necessary long-lasting boil-over protection in the summer months and freeze-up protection in the winter months, while at the same time meeting other design and application requirements of the modern engine cooling systems [1–3].

The increased use of lighter-weight aluminum components in the engine cooling system in the early 1970s led to the adoption and approval of a silicate based engine coolant containing the unique and patented silicone-silicate copolymer as factory fill coolant by U.S. automakers [1,2]. The then new silicate–silicone coolant technology was found to be particularly effective in protecting engine cooling system components from increased operating temperatures, which resulted from higher-opening temperature thermostats, new exhaust emission controls, trailer hauling, air conditioning, and other design or operation requirements [1,2].

Automotive engine coolants have experienced further advancement since the 1990s, particularly with regard to the corrosion inhibitor formulations used in the coolants. In 1995, General Motors was the first U.S. manufacturer to use organic acid technology coolant as original factory fill coolant [1]. In the late 1990s to early

2000s, Ford and Chrysler changed to use hybrid low silicate–organic acid technology coolants as factory fill and service coolants in their vehicles [1,4,5]. In 2010, Ford Motors started to change its factory fill coolant from hybrid organic acid technology coolants to organic acid technology coolants and had nearly completed the conversion by the second half of 2011 [5,6]. Chrysler switched to an organic acid technology coolant as its factory fill coolant for the 2013 model year vehicles [6]. During the same time period, Japanese automakers started to change their factory fill and service coolants from triethanolamine and phosphate based coolants to initially high phosphate–organic acid technology coolants in the 1990s and then to low phosphate–organic acid technology coolants between 2003 and 2005 [7–9]. European automakers used organic acid technology coolants in some models of their cars in late 1990s to 2008, while during the same time period using various versions of hybrid low silicate–organic acid technology coolants in the rest of their car models [6,10]. Previously, the dominant inhibited coolant used with aluminum component engines in Europe was the BS 3151 Type A coolant containing triethanolamine orthophosphate and sodium MBT [11,12]. Recently, some European automakers have started to use a new hybrid low silicate–organic acid technology coolants that does not contain borate, nitrate, and nitrite as factory fill coolant in some new models of their vehicles [10]. In other areas of the world, automakers typically use coolant formulations selected by their U.S., European, or Japanese joint-venture partners [7,10].

Coolants based on silicone stabilized silicate technology are still being marketed as conventional (or traditional) coolants to meet the protection needs of older vehicles still on the road today [4,5]. Organic acid technology coolants are often used as extended life coolants since they are capable of providing a much longer service life (or maintenance interval) than provided by conventional coolants [13–16]. Hybrid organic acid technology coolants and phosphate containing organic acid technology coolants are also used to provide a longer service life (or maintenance interval) than provided by conventional coolants based on silicone stabilized silicate technology and/or based on silicate-free triethanolamine phosphate technology used in Japan and Europe [4–10,15]. The recommended engine coolant change and service interval for different automakers typically are not the same [4–6]. The recommended change interval for conventional silicate technology coolants are typically between 30 000 and 40 000 miles or 2 to 3 years of service [4,5,8]. The recommended change interval for conventional triethanolamine phosphate technology coolants are typically between 18 000 and 36 000 miles or up to 2 years of service [8]. The recommended initial change interval for hybrid low silicate–organic acid technology coolants by U.S. automakers is typically 100 000 to 105 000 miles or between 5 and 6 years of service [4–6]. The recommended change interval for organic acid technology extended life coolant is typically 150 000 miles or between 5 and 10 years of service [6]. The recommended initial change interval for phosphate–organic acid technology coolants by Japanese automakers is typically 37 000 to 60 000 miles or between 3 and 4 years of services. The corresponding recommended initial change interval for the newer low phosphate–organic acid technology

coolants is typically 100 000 to 125 000 miles or between 7 and 11 years of service [6,10]. Some European luxury car manufacturers do not provide specific recommended change interval for their factory fill coolants. Instead, they generally require periodic check (e.g., every 20 000 to 40 000 miles as stated in the Scheduled Maintenance Intervals) of the corrosion protection and antifreeze rating of the coolant, as well as the level of the coolant in the vehicle and take corrective action based on the results obtained [6,10].

Degradation of anti-corrosion performance has been considered to be the main parameter in setting the coolant maintenance interval and/or service life [7–20]. The ability of organic acid containing coolants to achieve a longer service life than the ones obtained by silicate or amine-phosphate based conventional engine coolants was attributed to the differences in the depletion rates of the key corrosion inhibitors used in the coolants [7–14,16–20]. Particularly, the various aliphatic and aromatic carboxylic acid corrosion inhibitors used in the organic acid containing technology coolants were found to be depleted much slower than silicate and phosphate used in the conventional coolants [7–14,16–20]. In addition, organic acid technology coolant was shown to be able to provide better protection against localized corrosion (such as pitting and crevice corrosion) of aluminum alloys than the ones provided by silicate based conventional coolants [17]. On the other hand, the inorganic corrosion inhibitors, such as silicate and phosphate, are generally considered to be faster acting than the organic acid corrosion inhibitors [6,15]. The potential formation of silicate gel in coolants containing silicate that can reduce flow and heat transfer efficiency in the engine cooling system is a concern even for coolants containing low levels of silicate such as hybrid low silicate–organic acid technology coolants [21–23]. Recent studies show that the interaction between coolant formulations and potassium fluoroaluminate flux residue introduced by the widely adopted new controlled atmosphere brazing (CAB) method to manufacture aluminum automotive heat exchangers can impact coolant corrosion protection performance and may even pose a challenge to heat transfer and coolant flow, as well as to the normal operation of the engine cooling system [21–24]. As such, there is always a need to develop new and better performing engine coolants with a much longer service life than the ones currently available to lessen environmental impact, reduce operating/maintenance cost, and ensuring better system reliability and durability.

In this paper, the key results obtained from a comprehensive investigation using various electrochemical tests, standard ASTM tests (including D1384, D4340, D2809, D2570 [25–28]), CAB aluminum radiator and heater core tube leaching tests, and fleet tests with the main objective to develop new generation of extended life coolants with superior performance are presented and discussed. The aluminum corrosion protection performance of the key classes of commercial coolants currently available as well as the extended life new generation candidate coolants were studied and compared by electrochemical tests under high temperature heat-rejecting conditions. Aluminum radiator and heater core tube leaching tests at room temperature and at elevated temperature were also used to study whether there are compatibility or corrosion issues between the

tested coolant formulations and the heat exchanger manufactured by the controlled atmosphere brazing method. Based on these test results, the most promising candidate fluids were selected and their performance were confirmed by ASTM tests to ensure that they are in compliance with ASTM D3306 specifications and other applicable major automaker OEM coolant performance specifications. The optimum candidate coolant formulations were selected for fleet tests to confirm their performance. Representative current commercial OAT based extended life coolants and a factory fill hybrid low silicate–organic acid coolant were also fleet tested to generate comparison data to demonstrate the superior performance and durability of the extended life new generation coolants developed.

Experimental

SOLUTIONS

The base test solutions used in electrochemical tests and radiator/heater core leaching tests were prepared by mixing commercial available coolants with de-ionized water to yield the desired coolant concentrations used in the tests. Solutions used in ASTM tests were prepared according to the specifications of the latest applicable ASTM standards. Candidate test coolants were prepared from commercial products purchased from local stores. Unless otherwise specified, all test coolant solutions in this study were prepared by mixing the test coolant concentrate with de-ionized water to yield the desired coolant concentrations used in the tests.

ELECTROCHEMICAL TEST PROCEDURES

A piece of sand cast aluminum AA 319 (UNS A03190) cut from a 3.0 L engine block supplied by a major North America car manufacturer was used as the working electrode in electrochemical tests. Other test conditions were the same as described in the previous publications [22–24].

RADIATOR AND HEATER CORE LEACHING TEST PROCEDURES

The test methods used were the same as the ones described in a previous publication [23]. Five different types of radiators and three different types of heater cores from six different models of recently introduced North American light duty vehicles were selected for test. The radiators and heater cores were produced by different manufacturers based in North America, Europe, and Japan. Two radiators have seam welded tubes. The other radiators and heater cores have folded tubes (B-type tubes). As described in a previous publication [23], the leaching tests were done by placing cooling filled radiator tubes and heater core tubes sealed with either bee's wax (for tubes to be tested at room temperature) or a high temperature chemically inert epoxy in the intended test environment at $20 \pm 1^\circ\text{C}$ (i.e., room temperature) or at either $49 \pm 1^\circ\text{C}$ or $90 \pm 1^\circ\text{C}$ oven. The coolant solution in the tubes was sampled after 7, 28, and 56 days of exposure into a clean and chemically inert container and submitted for analysis.

FLEET TESTS

The fleet test data presented in this paper for the experimental extended life new generation coolants were collected from 2010 Ford Crown Victoria in the state of New York. Two experimental extended life new generation coolant formulations were tested. Extended Life New Generation Coolant A was installed in six 2010 Ford Crown Victoria cars operated by Putnam County Sheriff's Office in the spring of 2011. Extended Life New Generation Coolant B was installed in four 2010 Ford Crown Victoria cars operated by Westchester County Parkway Police in the fall of 2011. To provide comparison data, a commercial Organic Acid Technology Coolant A (OAT Coolant A) was also installed in two 2010 Ford Crown Victoria cars operated by Westchester County Parkway Police in the fall of 2011. To provide additional data for comparison, data obtained from three additional police car fleet tests using a factory fill Hybrid Low Silicate–Organic Acid Technology Coolant D in the 2007 Chrysler Dodge Charger, a factory fill Organic Acid Technology Coolant C in the 2009 General Motor Chevrolet Impalas, and the commercial Organic Acid Technology Coolant A in the 2007 Ford Crown Victoria were also presented in this paper. The two factory-fill coolant tests were started in the winter of 2010 using cars operated by Putnam County Sheriff's Office. The 2007 Crown Victoria fleet test was started in the summer of 2008.

The test coolants were installed in the police car cooling system as soon as practical for the fleet test after the new car arrived at the police station. The cooling system was drained, flushed with tap water, flush water was drained, and the cooling system was filled with test coolant concentrate, and the test coolant was diluted to 50 vol. % with police station tap water. For the fleets using factory fill coolants, no flushing or draining of the cooling system were carried out. Startup mileage in the fleet tests ranged from 0 miles to an average of 55 miles for the 2010 Ford Crown Victoria. The test vehicles were maintained according to standard operating procedure. The concentration of the test coolant in the test vehicle was monitored by measuring the refractive index and adjusted, if necessary, to 50 vol. % by adding either tap water or test coolant concentrate. Danbury tap water was used in the Putnam County fleet tests. Police station tap was used in the Westchester County fleet tests. Coolant samples were taken at 5000 mile intervals, except for the first sample, which was taken at 500 miles test mileage. A 60 ml sample was taken each time and it was submitted for analysis as soon as the sample was taken.

Results and Discussions

EFFECT OF DIFFERENT COOLANT CHEMISTRY ON CORROSION PROTECTION PERFORMANCE AT HIGH TEMPERATURE

25 Vol. % Coolant + 100 ppm Chloride

Table 1 shows the electrochemical test results of corrosion protection performance (i.e., surface area average corrosion rates, average anodic current densities, and corrosion potentials for sand cast aluminum AA 319 cut from a 3.0 L engine block at

TABLE 1 3.0L Sand Cast 319 Al Engine Block Corrosion—Modified GM 9066 P Test Results—Heat Rejecting Surface, 25 vol. % coolant + 100 ppm Chloride, 130°C.

Test Coolant ID	OAT A	OAT B	OAT C	OAT D	OAT E	Heavy Duty OAT A	Hybrid, Low Si-OAT A	Hybrid, Low Si-OAT B	Asian Low P-OAT A	Asian Low P-OAT B	Extended Life New Gen. Coolant A	Extended Life New Gen. Coolant B	Extended Life New Gen. Coolant C
LPR CorrRate @ 1h, mpy	10.04	8.67	8.52	9.11	9.16	12.60	6.94	6.43	0.44	0.95	0.44	0.60	0.57
Corrosion Potential @ 1h, V versus AgAgCl, 3 M NaCl	−0.932	−0.852	−0.889	−0.891	−0.893	−0.831	−0.912	−0.977	−0.799	−0.779	−0.883	−0.858	−0.819
LPR CorrRate @ 3h, mpy	9.70	6.54	ND	ND	ND	9.44	6.17	3.61	0.38	0.84	0.27	0.36	0.41
Corrosion Potential @ 3h, V versus AgAgCl, 3 M NaCl	−0.910	−0.811	ND	ND	ND	−0.793	−0.668	−0.901	0.781	−0.766	−0.836	−0.834	−0.830
LPR CorrRate @ 5h, mpy	9.11	5.43	6.76	7.81	7.06	8.20	1.45	1.26	0.37	0.92	0.22	0.40	0.30
Corrosion Potential @ 5h, V versus AgAgCl, 3 M NaCl	−0.902	−0.782	−0.852	−0.851	−0.865	−0.777	−0.664	−0.769	−0.776	−0.753	0.830	−0.819	−0.814
CorrRate_Anodic Tafel Extrapolation @ 5.2h, mpy	12.45	6.50	ND	ND	ND	10.75	0.26	0.95	0.25	0.74	0.13	0.21	0.25
Corrosion Potential @ 5.2 hours, V versus AgAgCl, 3 M NaCl	−0.905	−0.782	ND	ND	ND	−0.790	−0.673	−0.769	−0.781	−0.753	−0.881	−0.831	−0.815

TABLE 1. Continued

Test Coolant ID	OAT A	OAT B	OAT C	OAT D	OAT E	Heavy Duty OAT A	Hybrid, Low Si-OAT A	Hybrid, Low Si-OAT B	Asian Low P-OAT A	Asian Low P-OAT B	Extended Life New Gen. Coolant A	Extended Life New Gen. Coolant B	Extended Life New Gen. Coolant C
Effectiveness of the Test Coolant on Anodic Passivation, @ 5.2 h													
Average of Anodic Current Density, A/cm ² , -0.1 V to 0.9 V/AgAgCl, 3 M NaCl	2.42 E-04	7.57 E-05	ND	ND	ND	8.83 E-05	5.32 E-05	2.59 E-05	4.25 E-05	5.00 E-05	2.71E-05	3.26E-05	2.76E-05
Average of Anodic Current Density, A/cm ² , 0.9 V to 2.0 V/AgAgCl, 3 M NaCl	2.60 E-04	1.51 E-04	ND	ND	ND	2.42 E-04	1.16 E-04	1.98 E-04	7.82 E-04	3.82 E-04	4.31 E-05	6.46 E-05	3.81 E-05
LPR CorrRate @ 6 h, mpy			6.75	7.37	6.64								
Corrosion Potential @ 6 h, V vs. AgAgCl, 3 M NaCl			-0.868	-0.892	-0.863								
LPR CorrRate @ 10 h, mpy			4.67	7.03	6.09								
Corrosion Potential @ 10 h, V versus AgAgCl, 3 M NaCl			-0.830	-0.831	-0.870								

130°C) under heat rejecting surface condition in 25 vol. % coolant + 100 ppm chloride test solutions as a function of exposure time to high temperature using the modified GM 9066 P test method. The effectiveness of the test coolant on AA 319 anodic passivation was indicated by the average values of anodic current density at -0.1 to 0.9 V/AgAgCl, 3 M NaCl, and at 0.9 to 2.0 V/AgAgCl, 3 M NaCl. The anodic polarization curve measurements (see Figs. 1 and 2) show similar results as presented in Table 1.

One can see the following from the results in Table 1 and Figs. 1 and 2:

1. The surface area average corrosion rates determined by linear polarization resistance (i.e., LPR or the Stern–Geary method) as specified in GM 9066 P are generally in agreement with the surface area average corrosion rates determined by Tafel extrapolation of the anodic curve for each test coolant.
2. The surface area average corrosion rate of sand cast AA 319 aluminum alloy tends to decrease with increasing immersion time under the chosen test conditions. During same time period, the corrosion potential of the AA 319 gradually increases with time. They both indicate that the corrosion protection of AA 319 by the tested coolants is improving with immersion time.
3. Among the coolant solutions tested, the five OAT coolants, A, B, C, D, E, and heavy duty OAT Coolant A yielded a similar corrosion rate and they also yielded the highest surface area average corrosion rates in all the tested exposure time periods. In addition, the corrosion rates obtained in the OAT Coolants and the heavy duty OAT Coolant A tend to decrease quite slowly with time. On the other hand, the three Extended Life New Generation Coolants, A, B, C, and Asian Low P-OAT Coolant A yielded the lowest surface area average corrosion rates in all the tested exposure time periods. They were

FIG. 1 Modified GM9066P results: anodic polarization curves, 130°C, 5.2 h in 25 vol. % fresh coolant + 100 ppm chloride, sand cast AA 319, 3.0 L engine block section.

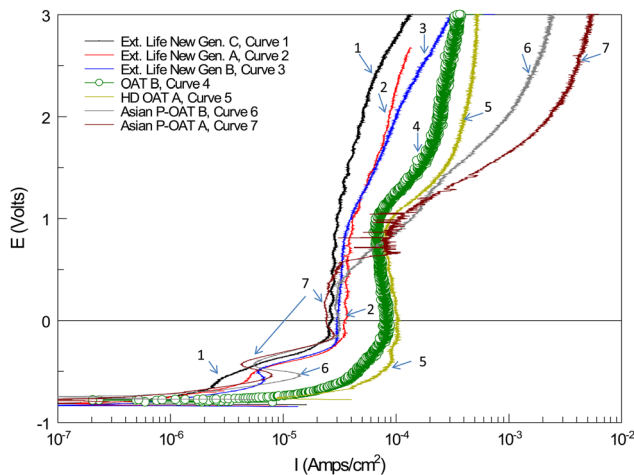
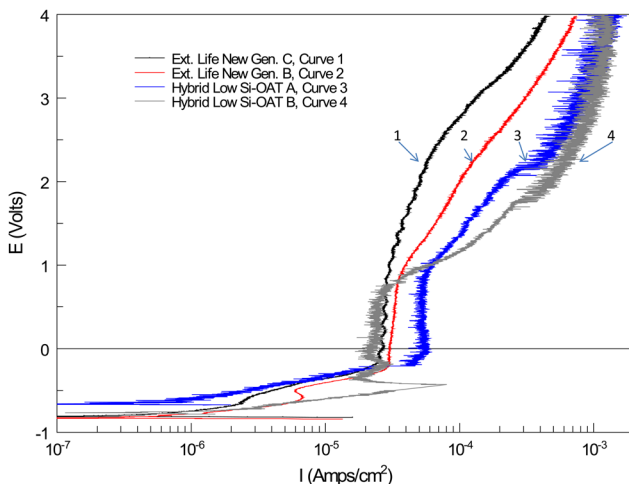


FIG. 2 Modified GM9066P results: anodic polarization curves, 130°C, 5.2 h in 25 vol. % fresh coolant + 100 ppm chloride, sand cast AA 319, 3.0 L engine block section.



typically about 2 % to 8 % of the corresponding corrosion rates observed in the OAT and HD OAT coolants. The corrosion rates observed in the three Extended Life New Generation Coolants and the Asian Low P-OAT coolant A were also quite similar under the chosen test conditions. The two hybrid low Si-OAT coolants A and B also show similar corrosion protection performance. They yielded a surface area average corrosion rate at 1 h at 130°C almost as high as the ones obtained in the OAT coolant solutions. The corrosion rates for the two hybrid low Si-OAT coolant then decreases considerable with time. After 5 h of exposure under the test conditions, the corrosion rates of the two hybrid coolants became much less than the ones observed in the OAT coolant solutions, but they are still higher than the ones observed in the Extended Life New Generation Coolants. The corrosion rates obtained in Asian Low P-OAT coolant B were slightly higher than the corresponding corrosion rates obtained for the three Extended Life New Generation Coolants and the ones for Asian Low P-OAT coolant A. However, they were lower than the ones obtained in other tested coolants.

4. Among the coolants tested, the three Extended Life New Generation Coolants showed the best anodic passivation performance and the Extended Life New Generation Coolant C was the best overall. Asian low P-OAT coolant A appeared to show the worst anodic passivation protection performance, especially at high anodic potential. Asian low P-OAT coolant B showed the second worst anodic passivation protection performance. The two OAT coolants tested, i.e., A and B and the two hybrid low Si-OAT coolants, showed similar anodic passivation performance. However, at high anodic potential, the anodic current density for the two hybrid low Si-OAT coolants become slightly

TABLE 2 3.0L Sand Cast 319 Al engine block corrosion—modified GM 9066 P test—heat rejecting surface, no corrosive ion added.

Immersion Time (h)	E-Corr (V/AgAgCl)	Polarization Resistance (Ohm·cm ²)	LPR CorrRate (mpy)	CorrRate_Tafel_Anodic (mpy)	Surface T (°C)
1. 50 vol. % OAT Coolant A, Electrode surface temperature = 136 ± 3°C					
1.5	-0.936	1433	14.97		136
6.5	-0.881	2024	10.60		136
22.0	-0.182	331 260	0.06		22
23.5	-0.950	1657	12.95		136
28.5	-0.856	2246	9.55		136
28.7	-0.857			12.63	136
2. 50 vol. % Extended Life New Generation Coolant B, electrode surface temperature = 136 ± 3°C					
1.5	-0.897	39 463	0.54		136
3.5	-0.885	46 844	0.46		136
6.5	-0.874	59 230	0.36		136
22.0	-0.326	16 262 000	0.0013		22
23.5	-0.834	157 240	0.14		136
25.5	-0.844	112 410	0.19		136
28.5	-0.840	108 100	0.20		136
28.7	-0.840			0.14	136
3. 50 vol. % Extended Life New Generation Coolant C, electrode surface temperature = 136 ± 3°C					
1.5	-0.881	21 646	0.99		136
6.5	-0.856	35 421	0.61		136
22.0	-0.479	6 114 500	0.0035		22
23.5	-0.847	43 945	0.49		136
28.5	-0.836	61 197	0.35		136
28.7	-0.844			0.32	136
4. 50 vol. % Extended Life New Generation Coolant A, Electrode Surface Temperature = 136 ± 3°C					
1.5	-0.904	21 094	1.02		136
3.5	-0.901	21 472	1.00		136
6.5	-0.894	25 358	0.85		136
22.0	-0.370	5 318 300	0.0040		22
23.5	-0.886	41 732	0.51		136
28.5	-0.872	62 379	0.34		136
28.7	-0.872			0.32	136
5. 50 vol. % Extended Life New Generation Coolant A, Post Fleet Test Coolant (PSO 221 EOT coolant, test mileage: 89 068 miles, Engine Test Hours: 3889 h), electrode surface temperature = 136 ± 3°C					
1.5	-0.856	9451	2.27		136
4.0	-0.538	32 473	0.66		136
6.5	-0.518	72 191	0.30		136
22.0	-0.113	4 020 200	0.0053		22

TABLE 2. Continued

Immersion Time (h)	E-Corr (V/AgAgCl)	Polarization Resistance (Ohm*cm ²)	LPR CorrRate (mpy)	CorrRate_Tafel_Anodic (mpy)	Surface T (°C)
23.5	-0.566	84 699	0.25		136
28.5	-0.550	93 541	0.23		136
28.7	-0.560			0.28	136
6. 50 vol. % Extended Life New Generation Coolant A, Post Fleet Test Coolant (PSO 223 EOT coolant, test mileage: 62 225 miles, engine test hours: 2562 h), electrode surface temperature = 136 ± 3°C					
1.5	-0.856	18 963	1.13		136
3.5	-0.580	30 875	0.69		136
6.1	-0.532	83 613	0.26		136
6.8	-0.530	60 299	0.36		136
22.0	-0.112	8 372 300	0.0026		22
23.5	-0.576	164 230	0.13		136
28.5	-0.533	171 950	0.12		136
28.7	-0.610			0.14	136

higher. In addition, the anodic polarization curves for the two hybrid low Si-OAT tends to be most noisy, indicating the passive film may be less stable than the ones in other coolants, such as the ones for OAT coolants and the ones for Extended Life New Generation coolants. Coolants showing good anodic passivation performance in anodic polarization curve measurements tend to indicate that they have better corrosion protection performance against pitting corrosion, crevice corrosion, and galvanic corrosion under the test conditions.

50 Vol. % Coolant With No Added Corrosive Ion

Table 2 shows the electrochemical test results of corrosion protection performance (i.e., surface area average corrosion rates, polarization resistance, and corrosion potentials for sand cast aluminum AA 319 cut from a 3.0 L engine block) under heat rejecting surface and under room temperature conditions in 50 vol. % coolant test solutions as a function of immersion time using the modified GM 9066 P test methods. The tested coolant solutions include the three Extended Life New Coolants A, B, and C, OAT coolant A, and two Putnam county police fleet test End-of-Test (EOT) coolants from two fleet test vehicles, having a test mileage of 89 068 miles (engine test hours: 3889 h) and 62 225 miles (engine test hours: 2562 h). The results in Table 3 and Fig. 3 show that all the fresh Extended Life New Generation Coolants A, B, and C, as well as the two post fleet test Extended Life New Generation Coolant A samples show much better corrosion protection than the one provided by OAT Coolant A. Corrosion rates about 15–50 times lower than the corresponding corrosion rates observed in the presence of OAT Coolant A were obtained in the Extended Life New Generation Coolants, including both fresh

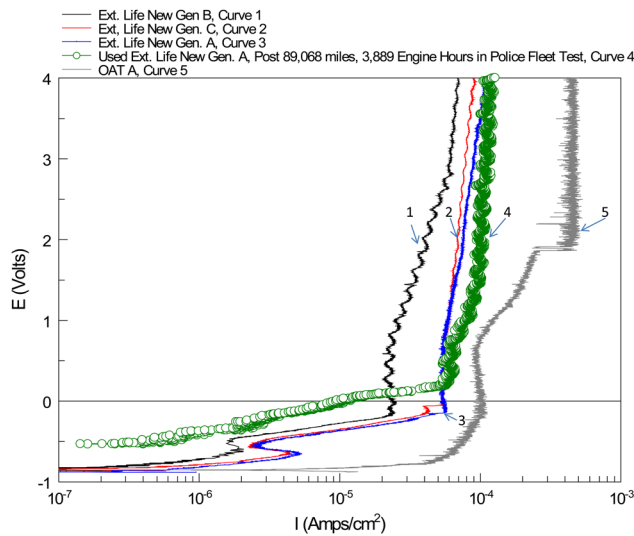
coolants and post fleet test coolant samples with a test mileage as high as 89 068 miles (3889 h of engine test time).

The results shown in [Table 1](#) and [2](#) and [Figs. 1-3](#) clearly suggest that the Extended Life New Generation Coolants A, B, and C provide the fastest, complete, very effective, and extremely durable corrosion protection of the sand cast AA 319 aluminum alloys under the test conditions used. The corrosion protection performance shows

TABLE 3 Radiator and heater core tube leaching test results—solution analysis after one week exposure at room temperature.

	Fresh HOAT Coolant A	Week 1 - 50% HOAT Coolant A		Fresh HOAT Coolant C	Week 1 - 50% HOAT Coolant C		Fresh HOAT Coolant D	Week 1 - 50% HOAT Coolant D			New HOAT Coolant E	Week 1 - 50% HOAT Coolant E		New HOAT Coolant F	Week 1 - 50% HOAT Coolant F
Sample	50% HOAT Coolant A	Radiator 1, Welded Tube	Heater Core 1, B-Type	50% HOAT Coolant C	Radiator 1, Welded Tube	Radiator 2, B-Type	50% HOAT Coolant D	Radiator 1, Welded Tube	Radiator 2, B-Type	Heater Core 1, B-Type	50% HOAT Coolant E	Radiator 1, Welded Tube	Heater Core 2, B-Type	50% HOAT Coolant F	Radiator 1, Welded Tube
Obsevation	Clear, no ppt	Clear, no ppt	Clear, no ppt	Minor ppt	clear, no ppt	Clear, no ppt	clear, no ppt	clear, no ppt	Clear, no ppt	clear, no ppt	Clear, no ppt	Clear, no ppt	Clear, no ppt	Clear, no ppt	Clear, no ppt
pH, As Is	8.45	8.29	8.18	7.58	7.64	7.60	8.02	8.05	7.98	8.01	8.36	8.32	8.33	8.82	8.65
EG, vol%	52	52	52.2	51.4	51.5	51.5	51.0	51.2	51.2	51.3	51.3	51.3	51.7	51	51
Silicon, mg/L	63	57	55	130	122	112	132	122	123	132	120	110	110	150	130
Aluminum, mg/L	ND	3	5	ND	15	38	ND	9	36	4	ND	6	3	ND	14
Potassium, mg/L	440	450	390	4.2	27	91	139	187	191	178	6	58	42	61	100
Fluoride, mg/L	ND	NA	14	ND	9	20	ND	10	27	15	ND	20	12	ND	21
	New OAT Coolant A	Week 1 - 50% OAT Coolant A		New OAT Coolant D	Week 1 - 50% OAT Coolant D		New Asian P-OAT B	Week 1 - 50% Asian P-OAT B			New Asian P-OAT C	Week 1 - 50% Asian P-OAT C			
Sample	50% OAT Coolant A	Radiator 1, Welded Tube	Heater Core 2, B-Type	50% OAT Coolant D	Radiator 1, Welded Tube	Radiator 2, B-Type	Heater Core 1, B-Type	50% Asian P-OAT B	Radiator 1, Welded Tube	Radiator 2, B-Type	Heater Core 1, B-Type	50% Asian P-OAT C	Radiator 1, Welded Tube	Heater Core 1, B-Type	Heater Core 2, B-Type
Obsevation	clear, no ppt	clear, no ppt	Clear, no ppt	clear, no ppt	clear, no ppt	clear, no ppt	clear, no ppt	clear, no ppt	minor ppt	minor ppt	minor ppt	clear, no ppt	clear, no ppt	clear, no ppt	clear, no ppt
pH, As Is	8.6	8.69	8.59	8.44	8.55	8.35	8.34	7.74	7.85	7.76	7.76	8.26	8.3	8.09	8.2
EG, vol%	51.1	52.6	51.6	50.2	50.4	50.5	50.6	50.9	50.9	50.8	51.1	52.3	52.4	52.9	52.5
Silicon, mg/L	ND	ND	ND	7	ND	ND	ND	5	3	2	4	ND	ND	ND	3
Aluminum, mg/L	ND	ND	ND	ND	ND	3	ND	ND	ND	8	6	ND	3	2	2
Potassium, mg/L	4.5	39	43	4700	5170	5110	4860	6670	6930	7100	6920	6100	6500	7000	7000
Fluoride, mg/L	ND	33	12	ND	23	16	5	ND	2	5	2	ND	5	2	4
	Extended Life New Gen. Coolant D	Week 1 - 50% New Ext. Life New Gen. Coolant D	New Extended Life New Gen. Coolant E	Week 1 - 50% Extended Life New Gen. Coolant E	New SIT Coolant	Week 1 - 50% SIT Coolant									
Sample	50% Ext. Life New Gen D	Heater Core 1, B-Type	50% OAT Coolant B	Radiator 1, Welded Tube	Radiator 2, B-Type	Heater Core 2, B-Type	50% SIT Coolant	Radiator 1, Welded Tube	Radiator 2, B-Type	Heater Core 1, B-Type					
Obsevation	Clear, no ppt	Minor ppt	clear, no ppt	clear, no ppt	clear, no ppt	clear, no ppt	Clear, no ppt	Clear, no ppt	Clear, no ppt	minor ppt					
pH, As Is	8.67	8.57	8.22	8.24	8.32	8.23	10.56	10.41	10.41	10.3					
EG, vol%	52.3	52.4	51.4	51.3	51.5	51.6	50.3	50.4	50.6	51.5					
Silicon, mg/L	ND	ND	ND	ND	4	3	300	274	291	302					
Aluminum, mg/L	ND	ND	ND	ND	ND	ND	ND	ND	4	2					
Potassium, mg/L	2	12	5	41	38	31	5	65	42	20					
Fluoride, mg/L	ND	3	ND	9	10	4	ND	50	41	11					

FIG. 3 Modified GM9066P results: 50 vol. % coolant, 136°C, 28.5 h immersion, sand cast AA 319, 3.0 L engine block section.



little detectable degradation even after in fleet test use with a test mileage as high 89 068 miles and engine test hours as high 3889 h. It should be noted that the corrosion rates shown in [Table 1](#) and [2](#) for the Extended Life New Generation Coolants are much less than the corrosion rate limits specified by ASTM [D3306](#) and/or GM6277M for ASTM [D4340](#) tests using either 25 vol. % coolant + 100 ppm Chloride (the D3306 or GM6277M limit is 1 mg/cm²/week or 193 μm/yr or 7.60 mpy maximum) or 50 vol. % coolant with no corrosive ions added (the GM6277M limit is 2 mg/cm²/week or 386 μm/yr or 15.2 mpy maximum). It should be noted that the corrosion rates determined by the modified GM9066P generally decrease with increasing exposure time, in agreement with expectation. The maximum corrosion rate limits listed above for ASTM [D3306](#) or GM6277M are time and surface area average corrosion rates for the specified one week test duration.

RADIATOR AND HEATER CORE TUBE LEACHING TESTS

[Table 3](#) and [4](#) shows the results obtained from analysis of 12 different coolant solutions after being stored inside the sealed radiator and heater core tubes for 7 and 28 days at room temperature (i.e., 20 ± 1°C), respectively. [Tables 5](#) and [6](#) show the results obtained from analysis of 10 different coolant solutions after being stored inside the sealed radiator and heater core tubes for 7, 28, and 56 days in a 49°C oven. [Tables 7](#) and [8](#) show the results obtained from analysis of 14 different coolant solutions after being stored inside the sealed radiator tubes for 7 and 28 days in a 90°C oven. The results indicate the following:

TABLE 4 Radiator and heater core tube leaching test results—solution analysis after four week exposure at room temperature.

	Week 4 - 50v% HOAT Coolant A		Week 4 - 50v% HOAT Coolant C		Week 4 - 50v% HOAT Coolant D				Week 4 - 50v% HOAT Coolant E		Week 4 - 50v% HOAT Coolant F
Sample	Radiator 1, Welded Tube	Heater Core 1, B-Type	Radiator 1, Welded Tube	Radiator 2, B-type	Radiator 1, Welded Tube #1	Radiator 1, Welded Tube #2	Radiator 2, B-type	Heater Core 1, B-Type	Radiator 1, Welded Tube	Heater Core 2, B-Type	Radiator 1, Welded Tube
Observation	Clear, no ppt	Clear, no ppt	Minor ppt	Gelled	Minor ppt	Minor ppt	Gelled	Minor ppt	Clear, no ppt	Clear, no ppt	Clear, no ppt
pH, As Is	8.3	8.14	7.67	7.62	8.07	8.03	7.99	7.96	8.35	8.24	8.61
EG, vol%	51.9	52.3	51.7	51.5	51.6	51.2	51.3	51.6	51.3	52.1	51.1
Silicon, mg/L	48	43	86	52.5	117	115	121	104	100	110	130
Aluminum, mg/L	5	9	21	28	19	23	46	30	4	4	12
Potassium, mg/L	460	400	69	166	204	211	210	183	85	56	130
Fluoride, mg/L	14	16	23	21	18	23	33	24	10	18	37

	Week 4 - 50v% OAT Coolant A		Week 4 - 50v% OAT Coolant D			Week 4 - 50v% Asian P-OAT B			Week 4 - 50v% Asian P-OAT C		
Sample	Radiator 1, Welded Tube	Heater Core 2, B-Type	Radiator 1, Welded Tube	Radiator 2, B-Type	Heater Core 1, B-Type	Radiator 1, Welded Tube	Radiator 2, B-Type	Heater Core 1, B-Type	Radiator 1, Welded Tube	Heater Core 1, B-Type	Heater Core 2, B-Type
Observation	Minor ppt	minor ppt	Minor ppt	Minor ppt	Minor ppt	Moderate amt of ppt	Moderate amt of ppt	Moderate amt of ppt	Small amt of ppt	Small amt of ppt	Minor ppt
pH, As Is	8.65	8.48	8.55	8.33	8.38	7.9	7.8	7.81	8.32	8.27	8.56
EG, vol%	52.6	52.1	50.3	50.8	50.7	51	51	51.2	52.4	53.5	52.9
Silicon, mg/L	ND	ND	ND	2	ND	4	3	4	2	5	7
Aluminum, mg/L	ND	ND	ND	ND	ND	3	7	12	3	8	ND
Potassium, mg/L	70	70	5200	5100	5020	6940	7150	6970	6200	7500	7300
Fluoride, mg/L	29	18	23	17	8	4	7	6	9	3	4

	Week 4 - 50v% New Ext. Life New Gen. Coolant D	Week 4 - 50v% Extended Life New Gen. Coolant E			Week 4 - 50v% SIT Coolant						
Sample	Heater Core 1, B-Type	Radiator 1, Welded Tube	Radiator 2, B-Type	Heater Core 2, B-Type	Radiator 1, Welded Tube #1	Radiator 1, Welded Tube #2	Radiator 2, B-Type	Heater Core 1, B-Type			
Observation	Minor ppt	clear, no ppt	clear, no ppt	clear, no ppt	minor ppt	minor ppt	minor ppt	minor ppt			
pH, As Is	8.6	8.31	8.27	8.22	10.45	10.36	10.25	9.55			
EG, vol%	52.6	51.4	51.4	53.1	50.4	50.4	50.9	53.2			
Silicon, mg/L	4	2	2	6	278	280	285	303			
Aluminum, mg/L	ND	ND	ND	ND	3	2	ND	ND			
Potassium, mg/L	16	59	50	37	55	63	52	26			
Fluoride, mg/L	4	12	13	6	46	54	52	16			

Note: Analytical results for fresh coolant samples are listed in Table 3.

1. Different concentrations of fluoride, aluminum, and potassium ions were detected in different types of coolants under the test conditions after 7 - to 56-day exposure to the interior surfaces of the tubes of the radiators and heater core.
2. Small variations in the measured concentrations of aluminum, potassium, and fluoride ions were detected in duplicated radiator tube 1 (welded tube) test samples after 7 and 28 day exposure at room temperature or at 90°C. It should be noted that the leached coolant samples taken from the heater core tube were the combined samples from four to eight different tube cavities. The leached coolant samples taken from the radiator 2, 4, and 5 (B-type tube) were the combined samples taken from either two or four tube cavities.

TABLE 5 Radiator and heater core tube leaching test results—solution analysis after one week exposure at 120 °F.

	Week 1 - 50v% HOAT Coolant A		Week 1 - 50v% HOAT Coolant C		Fresh OAT Coolant C	Week 1 - 50v% OAT Coolant C			Fresh OAT Coolant E	Week 1 - 50v% OAT Coolant E
Sample	Heater Core 1, B-Type	Heater Core 3, B-Type	Heater Core 1, B-Type	Heater Core 3, B-Type	50v% OAT Coolant C	Radiator 3, Welded Tube	Heater Core 1, B-Type	Heater Core 3, B-Type	50v% OAT Coolant E	Heater Core 1, B-Type
Observation	Minor ppt	Minor ppt	Gelled	Gelled	clear, no ppt	clear, no ppt	clear, no ppt	clear, no ppt	Clear, no ppt	Clear, no ppt
pH, As Is	8.32	7.85	7.54	7.50	8.4	8.3	8.01	8.04	8.31	8.37
EG, vø%	52.2	51.9	52.6	52.4	51.3	51.7	52	51.5	50.8	52.2
Silicon, mg/L	33	29	130	120	ND	ND	ND	ND	ND	ND
Aluminum, mg/L	11	14	43	54	ND	ND	ND	ND	ND	ND
Potassium, mg/L	440	550	51	210	ND	49	19	110	170	210
Fluoride, mg/L	25	23	20	18	ND	16	10	32	ND	10

	Week 1 - 50v% Asian P-OAT B		Fresh Extended Life New Gen. Coolant A	Week 1 - 50v% Ext. Life New Gen. Coolant A	Fresh Extended Life New Gen. Coolant B	Week 1 - 50v% Ext. Life New Gen. Coolant B	Fresh Extended Life New Gen. Coolant F	Week 1 - 50v% Ext. Life New Gen. Coolant F		
Sample	Heater Core 1, B-Type	Heater Core 3, B-Type	50v% Ext. Life New Gen A	Radiator 3, Welded Tube	50v% Ext. Life New Gen B	Heater Core 1, B-Type	50v% Ext. Life New Gen F	Heater Core 1, B-Type		
Observation	minor ppt	minor ppt	Clear, no ppt	Clear, no ppt	Clear, no ppt	Minor ppt	Clear, no ppt	Clear, no ppt		
pH, As Is	7.85	7.82	8.6	8.8	8.2	8.3	8.1	8.1		
EG, vø%	52.2	52.3	51.8	51.8	51.5	51.3	51.1	51.5		
Silicon, mg/L	ND	ND	ND	ND	ND	ND	ND	ND		
Aluminum, mg/L	6	6	ND	ND	ND	ND	ND	ND		
Potassium, mg/L	7800	8000	ND	41	ND	19	ND	22		
Fluoride, mg/L	2	14	ND	10	ND	6	ND	6		

Note: Additional analytical results for fresh coolant samples are listed in Table 3.

3. In some cases, the potassium ion concentration in the post leaching test solution may be lower than the initial potassium ion concentration for coolant containing high potassium ions. This may be due to that the expected error range of the ICP measurement of $\pm 5\%$ of the measured value was far greater than the amount of potassium ions leached from the flux residue in the radiator or heater core tubes. Much higher potassium ion concentrations were detected in the coolant samples at 90°C than the comparable samples at room temperature. Different models of radiator and heater core tubes tend to leach out different concentrations of potassium ions, indicating that the flux loading on the radiator and heater core tubes are not the same for different manufacturers.
4. Fluoride ions were detected in all the coolant samples taken from the radiator and heater core tubes. The highest fluoride concentrations were mostly detected in the Conventional Silicate Technology (SIT) coolant samples at room temperature. The lowest fluoride concentrations were detected in the Extended Life New Generation Coolants D and E, and the Asian P-OAT Coolants B and C at room temperature. The fluoride concentrations detected in the OAT Coolants A and D, and in the five Hybrid Low Si-OAT Coolant A, C, D, E, and F samples at room temperature were similar to each others. At 49°C, the fluoride concentrations detected in the Extended Life New Generation Coolants, A, B, and F, as well as in Asian P-OAT Coolant P and OAT Coolant E appears to be lower than the ones detected in the Hybrid Low Si-OAT Coolants A and C, and in OAT Coolant C after one week of exposure. However, after four weeks of exposure, the differences in fluoride concentration being

TABLE 6 Radiator and heater core tube leaching test results – solution analysis after four or eight week exposure at 120 °F.

	Week 4 - 50v% HOAT Coolant A		Week 4 - 50v% HOAT Coolant C		Week 4 - 50v% HOAT Coolant D	Week 4 - 50v% Asian P-OAT B	
Sample	Heater Core 1, B-type	Heater Core 3, B-type	Heater Core 1, B-type	Heater Core 3, B-type	Heater Core 1, B-Type	Heater Core 1, B-Type	Heater Core 3, B-Type
Observation	Minor ppt	ppt	Gelled	Gelled	ppt	NA	NA
pH, As Is	7.55	NA	7.48	7.50	NA	NA	NA
EG, vol%	52	51.9	52.8	52.4	51.4	52.4	52.2
Silicon, mg/L	29	31	120	140	110	ND	ND
Aluminum, mg/L	21	42	95	160	37	6	6.6
Potassium, mg/L	450	750	56	420	190	7700	7600
Fluoride, mg/L	19	17	24	38	34	5	20

	Week 4 - 50v% OAT Coolant C			Week 4 - 50v% OAT Coolant E	Week 4 - 50v% Ext. Life New Gen. Coolant A	Week 4 - 50v% Ext. Life New Gen. Coolant D
Sample	Radiator 3, Welded Tube	Heater Core 1, B-Type	Heater Core 3, B-Type	Heater Core 1, B-Type	Radiator 3, Welded Tube	Heater Core 1, B-Type
Observation	clear, no ppt	Minor ppt	NA	Clear, no ppt	Minor ppt	Clear, no ppt
pH, As Is	8.6	8.32	NA	NA	8.4	8.43
EG, vol%	52.5	51.5	51.5	53.7	51.9	51.4
Silicon, mg/L	ND	ND	ND	ND	ND	ND
Aluminum, mg/L	ND	ND	ND	ND	ND	ND
Potassium, mg/L	56	27	210	220	49	39
Fluoride, mg/L	23	16	29	18	21	19

	Week 8 - 50v% Ext. Life New Gen. Coolant B	Week 8 - 50v% Ext. Life New Gen. Coolant F
Sample	Heater Core 1, B-Type	Heater Core 1, B-Type
Observation	Minor ppt	Minor ppt
pH, As Is	8.2	8.2
EG, vol%	52.7	54.1
Silicon, mg/L	ND	ND
Aluminum, mg/L	ND	ND
Potassium, mg/L	56	49
Fluoride, mg/L	20	18

Note: Fresh coolant analysis results are listed in Tables 3 or 5.

detected in the post leaching test solution appears to be smaller among the coolants tested. It appears that Hybrid Low Si-OAT Coolant C and D have a slightly higher fluoride concentrations being detected than the ones being detected in other coolants after four weeks of exposure at 49°C. At 90°C, very high fluoride concentrations (e.g., 80 to 118 ppm F) were being detected in the Conventional Silicate Technology (SIT) coolant, Hybrid Low Si-OAT Coolant D, E, and F, as well as in Asian P-OAT Coolant B and C between one to four weeks of testing. Only OAT Coolant A, C, and D, as well as Hybrid low Si-OAT coolant A yielded lower fluoride concentrations in the post leaching test solution samples.

5. The aluminum ion concentrations detected the post leaching test coolant show clear observable trends. In the post leaching test coolant samples of the Extended Life New Generation Coolants A, B, C, D, E, and F, as well as OAT coolants A, C, and E, taken from radiator and heater core tubes, the aluminum

TABLE 7 Radiator and heater core tube leaching test results - solution analysis after one week exposure at 90 °C.

	Week 1 - 50v% HOAT Coolant A				Week 1 - 50v% HOAT Coolant C	Week 1 - 50v% HOAT Coolant D			Week 1 - 50v% HOAT Coolant E	Week 1 - 50v% HOAT Coolant F
Sample	Radiator 1, Welded Tube	Radiator 3, Welded Tube	Radiator 2, B-type	Radiator 4, B-type	Radiator 1, Welded Tube	Radiator 1, Welded Tube	Radiator 2, B-type	Radiator 4, B-type	Radiator 1, Welded Tube	Radiator 1, Welded Tube
Observation	ppt	ppt	lots of ppt	Floating ppt	Large amt of gel	Turbid, white ppt, gel	turbid, lots of white ppt	Turbid, moderate amt of ppt	gel like ppt	gel like ppt
pH, As Is	8.02	7.8	7.93	8.43	8.01	7.9	9.08	9.69	8.78	8.22
EG, vol%	53.7	52.7	52.4	53.9	51.6	51.2	52.5	53.7	51.3	51.1
Silicon, mg/L	29	45	15	4	64	81	4	< 2	35	41
Aluminum, mg/L	< 2	6	29	22	41	7	3	6	25	25
Potassium, mg/L	570	523	960	1200	250	312	819	920	220	230
Fluoride, mg/L	51	40	21	23	44	36	35	82	32	102

	Week 1 - 50v% OAT Coolant A				Week 1 - 50v% OAT Coolant C	Week 1 - 50v% OAT Coolant D	Week 1 - 50v% Asian P-OAT B			
Sample	Radiator 1, Welded Tube	Radiator 2, B-type	Radiator 4, B-type	Radiator 3, Welded Tube	Radiator 1, Welded Tube	Radiator 1, Welded Tube #1	Radiator 1, Welded Tube #2	Radiator 3, Welded Tube	Radiator 2, B-type	Radiator 4, B-type
Observation	Minor ppt	Minor ppt	Minor ppt	Minor ppt	Minor ppt	St. Turbid, wh. Ppt	ppt	minor ppt	ppt	ppt
pH, As Is	8.81	8.12	7.77	7.98	8.49	7.82	7.57	7.8	7.71	7.64
EG, vol%	53.2	51.4	53.8	51.7	51.7	51	52.6	52.6	51.4	52.8
Silicon, mg/L	ND	ND	ND	ND	ND	2	ND	ND	6	4
Aluminum, mg/L	ND	ND	ND	ND	ND	3	4	3	1	2
Potassium, mg/L	220	370	570	300	5300	7600	7000	7710	7520	7500
Fluoride, mg/L	32	21	15	20	41	29	38	25	96	84

	Week 1 - 50v% Asian P-OAT C				Week 1 - 50v% Ext. Life New Gen. Coolant A	Week 1 - 50v% New Ext. Life New Gen. Coolant D	Week 1 - 50v% Extended Life New Gen. Coolant E		Week 1 - 50v% SIT Coolant	
Sample	Radiator 1, Welded Tube	Radiator 3, Welded Tube	Radiator 2, B-type	Radiator 4, B-type	Radiator 3, Welded Tube	Radiator 1, Welded Tube	Radiator 4, B-type	Radiator 1, Welded Tube	Radiator 2, B-type	Radiator 1, Welded Tube
Observation	No ppt	Minor ppt	No ppt	No ppt	Minor ppt	Minor ppt	Minor ppt	clear, no ppt	clear, no ppt	Clear, gel on bottom
pH, As Is	8.22	7.6	8.03	8.05	8.4	8.51	8.16	8.05	8.1	9.71
EG, vol%	52.5	53	53.2	56.5	51.9	54.3	52.5	52.5	55.5	50.3
Silicon, mg/L	ND	4	2	5	ND	ND	5	2	3	130
Aluminum, mg/L	4	2	6	6	ND	ND	ND	ND	ND	ND
Potassium, mg/L	6300	7630	7500	8400	69	170	260	150	120	210
Fluoride, mg/L	44	23	76	95	43	42	93	41	56	83

Note: Fresh coolant analysis results are listed in Tables 3 or 5.

Note: Fresh coolant analysis results are listed in Tables 3 or 5.

ion concentrations were below the detection limit (i.e., 2 mg/L) at room temperature after 7, 28, or 56 days exposure at room temperature, at 49°C and at 90°C. For OAT coolant D, only one sample (one week with radiator 2, B-type at room temperature) among the tested conditions yielded an aluminum ion concentration just above the detection limit. Similarly, aluminum ion concentrations in the post leaching test coolant samples taken from the radiator and heater core tubes using the Conventional Silicate Technology Coolant (SIT) were either below or just above the detection limits at room temperature or at 90°C. On the other hand, high (e.g., > 20 mg/L) to very high (e.g., 40–170 mg/L) aluminum ions concentrations were detected in the post leaching coolant samples taken from radiator and heater core tubes using the Hybrid Low Si-OAT Coolants A, C, D, E, and F. In the absence of significant reduction of silicate concentration in the post test coolant and/or formation of a large amount of precipitate, the aluminum ions concentration being detected tends to

TABLE 8 Radiator and heater core tube leaching test results—Solution analysis after four week exposure at 90 °C.

	Week 4 - 50% HOAT Coolant A				Week 4 - 50% HOAT Coolant C		Week 4 - 50% HOAT Coolant D				Week 4 - 50% HOAT Coolant E	Week 4 - 50% HOAT Coolant F
Sample	Radiator 1, Welded Tube	Radiator 3, Welded Tube	Radiator 2, B-type	Radiator 4, B-type	Radiator 1, Welded Tube #1	Radiator 1, Welded Tube #2	Radiator 1, Welded Tube #1	Radiator 1, Welded Tube #2	Radiator 2, B-type	Radiator 4, B-type	Radiator 1, Welded Tube	Radiator 1, Welded Tube
Observation	ppt	ppt	lots of white ppt	White ppt	loose ppt	ppt	White ppt, gel	Lots of ppt	Turbid, White ppt	White ppt	Lots of ppt	Lots of white ppt
pH, As Is	7.95	8	9.24	8.97	9.32	10.1	9.92	7.89	9.83	9.91	11.62	10.39
EG, vol%	54.1	56	57.6	60.4	51.8	52.7	52.1	51	56.2	58.4	54	53.5
Silicon, mg/L	16	43	< 2	< 2	3.5	2	3	47	3	ND	7	3
Aluminum, mg/L	4	8	5	2	11	12	4	20	3	6	170	8
Potassium, mg/L	620	516	1300	1500	180	250	343	280	787	1200	270	420
Fluoride, mg/L	35	32	48	33	12	40	29	30	29	47	79	47

	Week 4 - 50% OAT Coolant A			Week 4 - 50% OAT Coolant C	Week 4 - 50% OAT Coolant D	Week 4 - 50% Asian P-OAT B				Week 4 - 50% Asian P-OAT C			
Sample	Radiator 1, Welded Tube	Radiator 2, B-type	Radiator 4, B-type	Radiator 3, Welded Tube	Radiator 1, Welded Tube	Radiator 1, Welded Tube	Radiator 3, Welded Tube	Radiator 2, B-type	Radiator 4, B-type	Radiator 1, Welded Tube	Radiator 3, Welded Tube	Radiator 2, B-type	Radiator 4, B-type
Observation	Minor ppt	Minor ppt	Minor ppt	Minor ppt	Minor ppt	minor ppt	minor ppt	minor ppt	minor ppt	Minor ppt	Minor ppt	Small amt. of ppt	Minor ppt
pH, As Is	9.41	8.04	8.17	9.29	9.24	7.97	7.6	7.82	7.64	8.33	7.8	8.1	8.11
EG, vol%	57.1	56.1	52.7	52.9	51.1	64.1	53.8	58.1	58.6	60.6	54.1	53.4	55.5
Silicon, mg/L	ND	ND	ND	ND	ND	2	4	8	7	ND	2	3	7
Aluminum, mg/L	ND	ND	ND	ND	ND	5	4	1	ND	5	3	5	5
Potassium, mg/L	270	490	750	290	5100	8910	8040	7900	9100	7500	7680	7900	7900
Fluoride, mg/L	29	20	44	19	11	43	36	87	84	65	40	104	118

	Week 4 - 50% Ext. Life New Gen. Coolant A	Week 4 - 50% Ext. Life New Gen. Coolant B	Week 4 - 50% New Ext. Life New Gen. Coolant D		Week 4 - 50% Extended Life New Gen. Coolant E			Week 4 - 50% SIT Coolant
Sample	Radiator 3, Welded Tube	Radiator 5, B-type	Radiator 1, Welded Tube	Radiator 4, B-type	Radiator 1, Welded Tube #1	Radiator 1, Welded Tube #2	Radiator 2, B-type	Radiator 1, Welded Tube
Observation	Minor ppt	Clear, no ppt	Minor ppt	Minor ppt	clear, no ppt	clear, no ppt	Very minor ppt	ppt
pH, As Is	8.3	8	8.24	8.3	8.18	8.2	8.02	10.02
EG, vol%	52.2	57.7	58.9	63.3	51.4	51.5	57.2	68.7
Silicon, mg/L	ND	4.58	ND	11	ND	3	3	130
Aluminum, mg/L	ND	ND	ND	ND	ND	ND	ND	ND
Potassium, mg/L	95	131	210	310	120	130	130	170
Fluoride, mg/L	61	NA	66	100	32	30	38	104

Note: Fresh coolant analysis results are listed in Tables 3 or 5.

increase with increasing test temperature and/or increasing exposure time. Aluminum ion concentrations much higher than the detection limits were also being detected in most of the post leaching test coolant samples taken from the radiator and heater core tubes containing the Asian Low P-OAT Coolants B and C, although the aluminum ion concentrations being detected were typically lower than the ones being observed in the comparable test conditions using the Hybrid Low Si-OAT coolants. It should be noted that visual

examination with or without the aid of an optical microscope (up to 200× magnifications) of an opened and water washed radiator one tube after 28 days of exposure in Asian Low P-OAT Coolant at room temperature revealed sign of widely distributed localized corrosion attack on the whole length of the radiator tube.

6. At 90°C or at lower temperatures after four weeks of leaching tests, significant reduction of silicate concentrations in comparison with the ones in fresh coolants are often observed in the post leaching test coolant samples using the Hybrid Low Si-OAT Coolants A, C, D, E, and F. In many samples taken from radiator or heater core tubes tested at 90°C, little or no silicate were detected in the post leaching test coolant samples using the Hybrid Low Si-OAT Coolants.
7. Gel formation, precipitate, and turbid coolant were observed in some of the leaching test conditions, as shown in [Tables 4, 5, 6, 7, and 8](#), especially in the tests using Hybrid Low Si-OAT Coolants A, C, D, E, and F, as well as the ones using Asian Low P-OAT Coolant B. Depending on the extent of the problem, gel and precipitate formation in an engine coolant could lead to potential enhanced corrosion (e.g., under-deposit or crevice corrosion), reduction of heat transfer and flow restriction in slow flow areas or location of the engine cooling system and may pose challenge to the normal operation of the cooling system.

As reported in a previous study [\[23\]](#), after one week of exposure in the radiator tubes, the corrosivity of the post leaching test Hybrid Low Si-OAT coolant sample toward AA 319 cast aluminum can be increased by up to 100 times in comparison to the ones observed in the fresh coolant. Visual inspection of several of the opened post leaching test radiator and heater core tubes using Hybrid Low Si-OAT Coolants after four weeks of testing indicate that significant corrosion had indeed occurred in the interior of the tubes during the leaching tests.

ASTM TEST RESULTS

ASTM D1384 Tests

[Table 9](#) shows the ASTM [D1384](#) [\[25\]](#) test results for Extended Life New Generation Coolants A, B, and C, as well as an End-of-Test fleet test coolant using Extended Life New Generation Coolant A after a test mileage of 89 068 miles (engine test hours: 3889 h). [Table 10](#) shows the long term ASTM [D1384](#) test results for an OAT Coolant and a conventional silicate technology coolant where the post test solutions were reused for 12 times after the initial test, and a new coupon bundle was installed after each repeated test. One can see that all the three Extended Life New Coolants A, B, C, the OAT coolant, and the conventional silicate technology coolant meet the coupon weight loss requirements of ASTM [D3306](#), GM6277M, and Ford WSS-M97B44-D (both the GM and Ford specifications are for OAT based extended life coolant specifications) for corrosion protection of all the metals specified. In contrast to the conventional silicate technology coolant, the corrosion protection performance of the OAT coolant and the Extended Life New Generation Coolant A

TABLE 9 ASTM D1384 [25] test results.

Fluid	Coupon Weight Loss Results - mg/coupon							Modine	Diluent	Fluid Test Hours
	Conc.	Copper	ASTM	Brass	C. Steel	Cast Fe	Cast Al			
Extended Life New Generation Coolant A	33 vol. %	0.2	0.1	2.0	−0.1	−2.1	0.8	37.6	ASTM	336
Extended Life New Generation Coolant B	33 vol. %	0.7	−0.5	1.9	−0.3	−0.5	−2.2	67.9	ASTM	336
Extended Life New Generation Coolant B	50 vol. %	0.6	−0.4	2.7	−0.1	−2.4	−1.9	71.6	DI H2O	336
Extended Life New Generation Coolant C	33 vol. %	0.1	−0.3	1.4	−0.4	−0.7	−1.8	86.0	ASTM	336
PSO221EOT, Ext. Life New Gen. Coolant A, post 89 069 test miles/3889 test h	33 vol. %	−0.4	−0.8	2.2	−1	−2.8	−1.4	44.1	ASTM	336
PSO221EOT, Ext. Life New Gen. Coolant A, post 89 069 test miles/3889 test h	50 vol. %	1.9	0.4	4.9	−0.9	−2.8	−3.1	111.8	None	336
ASTM D3306 Limits, max.	33 vol. %	10	30	10	10	10	30	None	ASTM	336
GM6277M Limits, max.	33 vol. % or 50 vol. %	10	20	10	10	10	20	None	ASTM or DI H2O	336
Ford WSS-M97B44-D Limits, max.	33 vol. %	10	10	10	10	10	10	Report	ASTM	336

TABLE 10 Long term ASATM D1384 [25] test results.

Fluid	Conc.	Diluent	Coupon Set	Cumulative Fluid Test Hours	Modine	Coupon Weight Loss Results - mg/coupon					Cast Al	Cumulative Fluid Test Duration
						Copper	ASTM	Brass	C. Steel	Cast Fe		
OAT coolant	33 %	ASTM Corr. H2O	1	336	149.0	0.1	-0.1	0.4	-0.6	-1.2	1.0	2 weeks
	A		2	672	78.6	1.1	-0.5	1.4	-0.4	-0.6	-2.3	4 weeks
	B		3	1008	71.9	0.1	0.8	0.6	-0.2	-0.9	-1.3	6 weeks
	C		4	1344	27.4	0.1	0.1	0.5	-0.3	-3.1	-1.7	8 weeks
	D		5	1680	27.4	0.8	0.0	0.4	0.0	-1.8	-4.0	10 weeks
	E		6	2016	13.2	0.3	1.8	-0.9	0.3	-0.9	-2.4	12 weeks
	F		7	2352	23.1	0.3	-1.1	-0.2	-0.5	-2.0	-3.3	14 weeks
	G		8	2688	20.6	0.4	0.6	0.1	-0.1	-2.2	-3.4	16 weeks
	H		9	3024	17.5	0.0	-0.8	-0.6	-0.2	-1.8	-3.0	18 weeks
	I		10	3360	9.5	-0.6	-0.2	-0.2	-0.6	-2.7	-3.3	20 weeks
	J		11	3696	19.0	-0.1	-0.1	-0.8	-0.5	-1.7	-3.4	22 weeks
	K		12	4032	42.4	0.5	0.5	-0.2	-0.3	-3.1	-2.2	24 weeks
	L		13	4368	23.6	0.4	0.3	-0.1	-0.4	-2.7	-2.6	26 weeks
Conventional Silicate Coolant	33 %	ASTM Corr. H2O	1	336	86.7	1.0	0.0	1.1	-0.1	3.3	-2.0	2 weeks
	A		2	672	44.8	0.6	-0.9	1.9	-0.9	3.0	-2.0	4 weeks
	B		3	1008	49.0	1.1	-0.1	3.9	0.3	7.7	-1.0	6 weeks
	C		4	1344	100.9	1.0	0.1	5.6	0.0	2.6	-0.6	8 weeks
	D		5	1680	82.4	1.5	0.3	6.1	-0.2	24.5	-0.9	10 weeks
	E		6	2016	111.3	0.8	3.6	9.8	0.6	4.9	0.1	12 weeks
	F		7	2352	138.6	0.5	6.8	11.3	0.1	3.8	-0.1	14 weeks

TABLE 10. Continued

Fluid	Conc.	Diluent	Coupon Set	Cumulative Fluid Test Hours	Modine	Coupon Weight Loss Results - mg/coupon					Cast Al	Cumulative Fluid Test Duration
						Copper	ASTM	Brass	C. Steel	Cast Fe		
	G		8	2688	146.8	1.2	8.9	9.5	0.0	27.7	-0.2	16 weeks
	H		9	3024	137.1	1.3	22.2	11.6	0.1	115.3	-0.4	18 weeks
	I		10	3360	105.9	1.5	16.1	11.5	0.1	82.3	-0.2	20 weeks
	J		11	3696	200.9	22.9	113.5	11.6	0.5	249.3	-0.4	22 weeks
	K		12	4032	267.3	44.6	104.8	9.1	0.7	365.3	-0.2	24 weeks
	L		13	4368	321.0	40.9	145.9	3.6	4.6	559.5	1.1	26 weeks

did not degrade with test time. For the conventional silicate technology coolant, corrosion protection degradation in a repeated D1384 test can be observed after 1344 h of the repeated test. While the OAT coolant show no degradation of corrosion protection up to 4368 h of repeated D1384 tests. For the Extended Life New Generation Coolant A, no corrosion performance degradation can be detected in ASTM D1384 test after 89 068 miles (engine test hours of 3889 h) of the fleet test. Hence, the D1384 results shown in Tables 9 and 10 indicate that both the OAT Coolant and Extended Life New Generation Coolant A can provided extended life corrosion protection, much better than the ones provided by the conventional silicate technology coolant tested.

ASTM D4340 Tests

Table 11 shows the ASTM D4340 [26] test results for Extended Life New Generation Coolants A, B, and C, as well as an End-of-Test fleet test coolant using Extended Life New Generation Coolant A after a test mileage of 89 068 miles (engine test hours: 3889 h). One can see that all of the three Extended Life New Coolants A, B, C, as well as the End-of-Test fleet test Extended Life New Generation Coolant A, meet the coupon weight loss requirements of ASTM D3306, GM6277M, and Ford WSS-M97B44-D (both the GM and Ford specifications are for OAT based extended life coolant specifications) for corrosion protection of all the metals specified. It should be noted that the post D4340 test aluminum (AA 319) samples has shiny metallic color and show no sign of corrosion or discoloration.

ASTM D2809 and D2570 Tests

Repeated internal and external independent laboratory ASTM D2809 [27] and D2570 [28] tests show that the Extended Life New Generation Coolants A, B, and C meet the requirements specified by ASTM D3306. The typical pump ratings

TABLE 11 ASTM D4340 [26] results.

Fluid	Conc.	Sand Cast 319 Al Corrosion Rate		Chloride Conc.
		Water Cleaned	Acid Cleaned	
Extended Life New Generation Coolant A	25 vol. %	−0.7	0.0	100 ppm
Extended Life New Generation Coolant B	25 vol. %	−0.3	0.1	100 ppm
Extended Life New Generation Coolant B	50 vol. %	−0.6	0.0	DI H2O
Extended Life New Generation Coolant C	25 vol. %	−0.2	0.2	100 ppm
Extended life New Gen. Coolant A, EOT, post 89 069 test miles/3889 test h	50 vol. %	0.0	0.0	DI H2O
ASTM D3306 Limits, max.	25 vol. %		1	100 ppm
Ford WSS-M97B44-D Limits, max.	25 vol. %	0.5	0.5	100 ppm
GM6277M Limits, max.	25 vol. %	0.3	1	100 ppm
GM6277M Limits, max.	50 vol. %	1	2	DI H2O

obtained in the 100 h standard D2809 and the 300 h D2809 tests modified to satisfy Ford and Chrysler specifications are 10 for the three Extended Life New Generation Coolants A, B, and C. Inspection of the post D2809 pumps show that no corrosion or erosion is present, there is no metal loss, and there is no change from original casting configuration.

FLEET TEST RESULTS

Glycol Acid Degradation as a Function of Coolant Chemistry

During use of the vehicle, ethylene glycol and other glycols in engine coolants can degrade to generate acidic degradation products, such as glycolic acid, formic acid, and acetic acid for ethylene glycol based coolants [29–32]. The generation of acidic glycol degradation products will gradually reduce the pH of the engine coolant and can eventually lead to a substantial increase of metal corrosion rate in the engine cooling system. Hence, monitoring the level of these acids is critical in determining the durability and the service life of the engine coolant [8,32]. Figure 4 shows the total glycol degradation acid concentration (i.e., sum of glycolic acid, formic acid, and acetate acid concentration in the coolant) as a function of test mileage for the 2010 Crown Victoria using the Extended Life New Generation Coolant B and the OAT Coolant A for the six test vehicles monitored in the WCP police fleet test.

Figure 5 shows the total glycol degradation acid concentration (i.e., sum of glycolic acid, formic acid, and acetate acid concentration in the coolant) as a function of test mileage for the six 2010 Ford Crown Victorias using the Extended Life New Generation Coolant A as the test coolant. Figure 6 shows total glycol degradation acid concentration as a function of test mileage for three 2007 Ford Crown Victorias using the OAT Coolant A as the test coolant. Figure 7 shows total glycol degradation acid concentration as a function of test mileage for six 2009 GM Chevrolet Impalas using factory fill OAT Coolant C as the test coolant. Figure 8 shows total glycol degradation acid concentration as a function of test mileage for four 2007 Chrysler Chargers using factory fill Hybrid Low Si-OAT Coolant E as the test coolant. Based on the results shown in Figs. 4–8, one can reach the following conclusions:

1. The two Extended Life New Generation Coolants A and B generated the least amount of glycol degradation acids as a function of test mileage. The total glycol degradation acid concentrations generated by the Extended Life New Generation Coolant A and B were roughly 1/3 to 1/4 of the amount generated by OAT Coolant A under comparable test mileage conditions. The highest total glycol degradation concentrations generated were less than 600 mg/L for test mileage as high as ~90 000 miles.
2. The factory fill Hybrid Low Si-OAT Coolant E generated the highest amount of total glycol degradation acid concentrations. Close to 3000 mg/L was generated for test mileage as low as ~40 000 miles. The two OAT Coolants A and C fleet tested also generated lower concentrations of the total glycol degradation acids than the ones observed in the factory fill Hybrid Low Si-OAT coolant E

FIG. 4 Total glycol degradation acid concentration as a function test mileage—Extended Life New Generation Coolant B versus OAT Coolant A in 2010 Crown Victoria WCP fleet test.

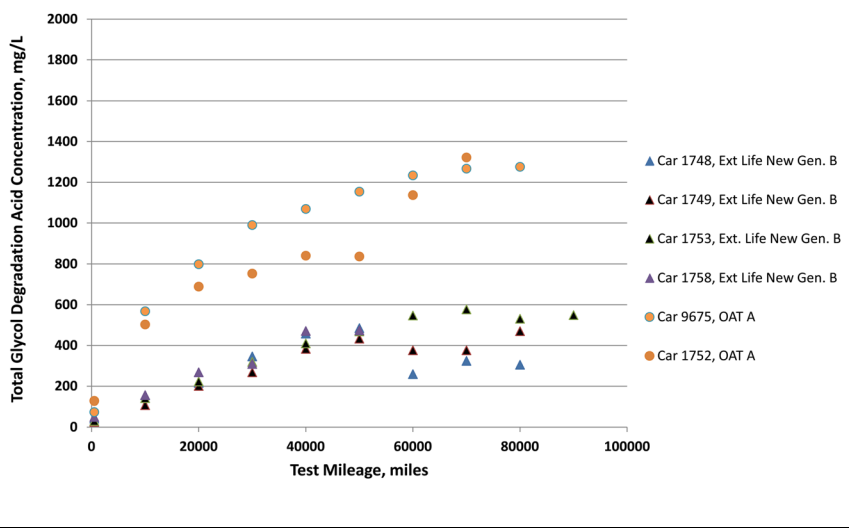


FIG. 5 Total glycol degradation acid concentration as a function test mileage—Extended Life New Generation Coolant A in 2010 Crown Victoria PSO fleet test.

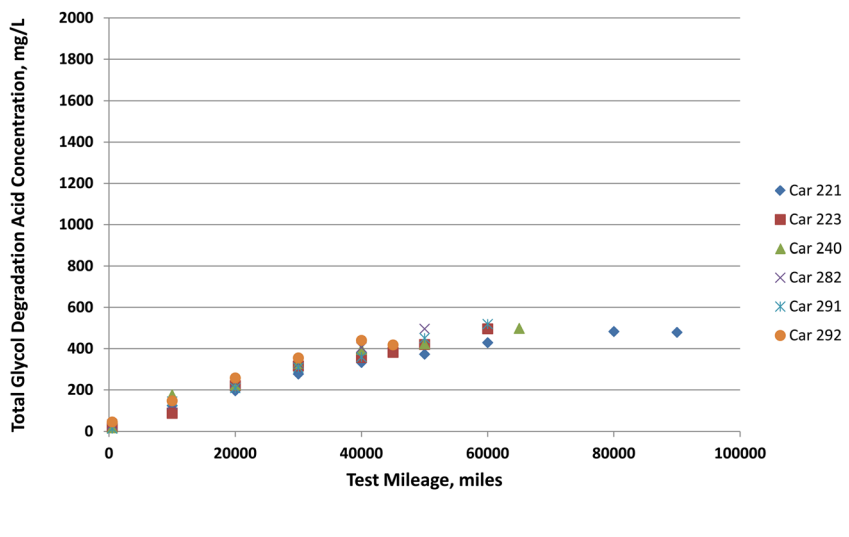


FIG. 6 Total glycol degradation acid concentration as a function test mileage—OAT Coolant A in 2007 Ford Crown Victoria WCP fleet test.

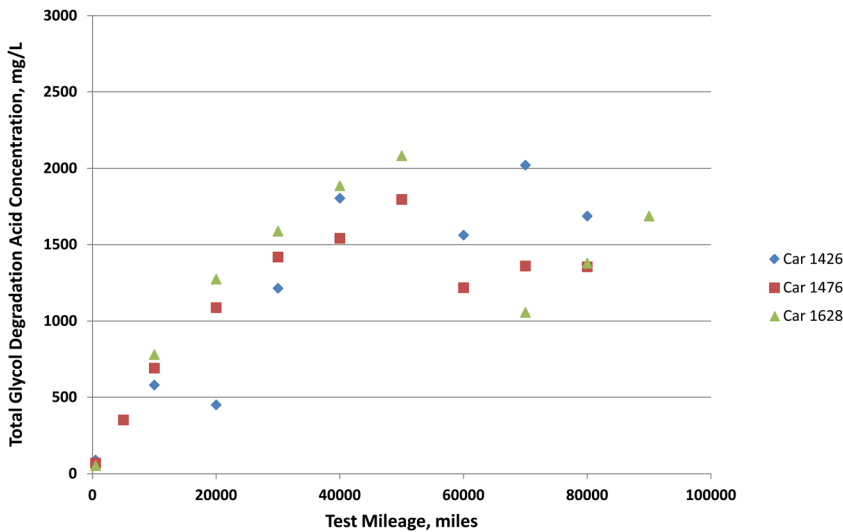


FIG. 7 Total glycol degradation acid concentration as a function test —Factory fill OAT Coolant C in 2009 GM Chevrolet Impalas PSO fleet test.

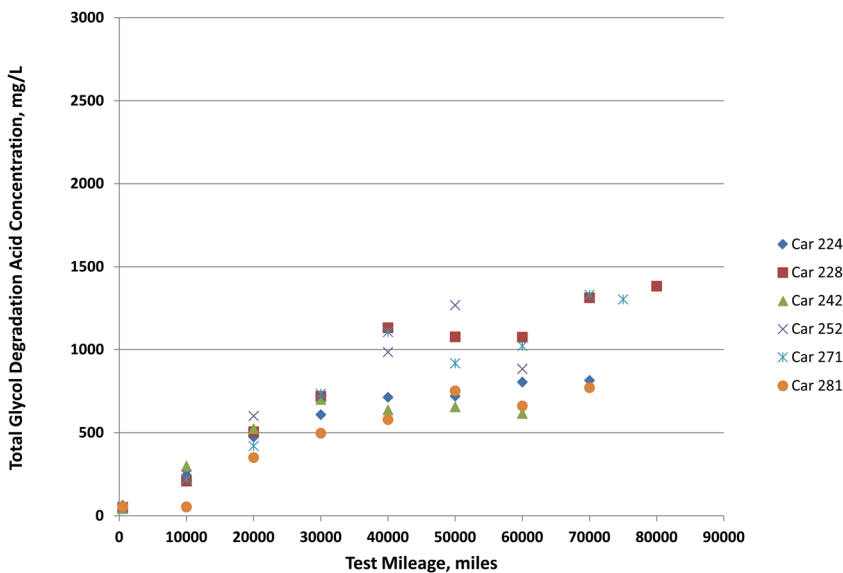
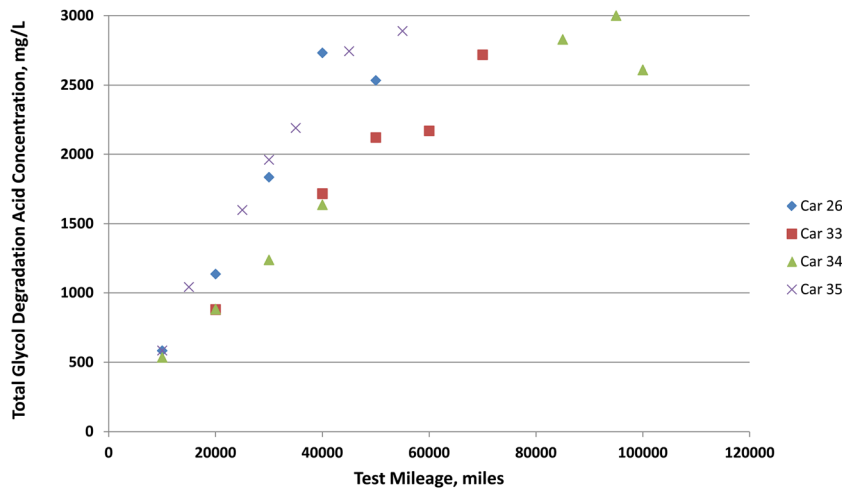


FIG. 8 Total glycol degradation acid concentration as a function test mileage—Factory fill Hybrid Low Si-OAT Coolant E in 2007 Chrysler Charger PSO fleet test.



fleet test. The total glycol degradation acid concentrations generated by the OAT Coolants were typically 1/2 or less than the ones generated by the HOAT coolant. It should be noted that the concentration of the total glycol degradation acids versus test mileage results obtained in the OAT coolant fleet tests of the current study agreed well with the results reported earlier in literature for a different OAT coolant using different test vehicles [31].

3. The total glycol degradation acid concentration generally increased rapidly initially with increasing test mileage. They typically reach a plateau after ~40 000 miles of the fleet tests. Afterwards, the acid concentration seemed to increase slowly with increasing test mileage.

Fleet Test Coolant pH Versus Coolant Chemistry

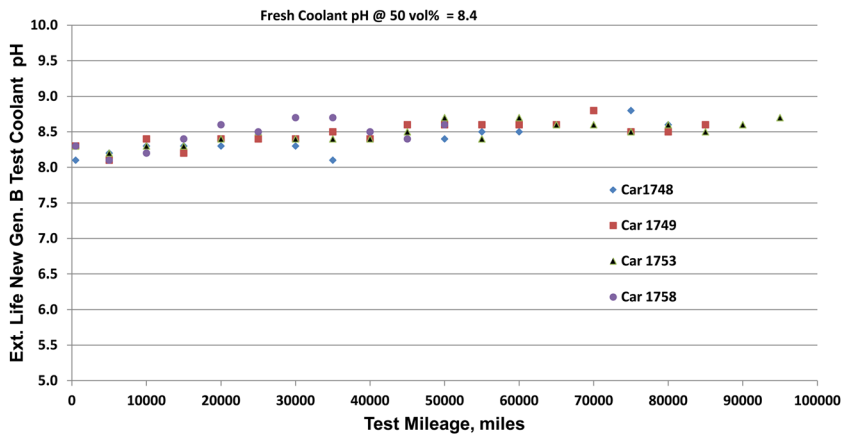
Figures 9, 10, and 11 show the fleet test coolant pH as a function of test mileage for Extended Life Next Generation Coolant B, factory fill OAT Coolant C and factory fill Hybrid Low Si-OAT E.

The results shown in Figs. 9, 10, and 11 indicate the following:

1. Test coolant pH in the fleet test using Extended Life Next Generation Coolant B show little variation with increasing test mileage, up to ~95 000 miles.
2. The test coolant pH in both the OAT Coolant C and Hybrid Low Si-OAT Coolant E tends to decrease with increasing test mileage. The Hybrid Low Si-OAT Coolant pH decreased the most with increasing test mileage, dropping as low to as 6.7 during the fleet test.

To help prevent corrosion of the metal components in the engine cooling systems, it is critical to maintain the coolant pH to the optimal levels. Excessive change

FIG. 9 Police fleet results: Test Coolant pH versus test mileage for Extended Life New Generation Coolant B.



of coolant pH during vehicle use can negatively impact the corrosion protection performance of the coolant and in some cases can result in instability of the coolant formulation in use and can lead to precipitate formation in the cooling systems, which could potentially lead to flow restriction and loss of heat transfer efficiency.

FIG. 10 Police fleet results: Test Coolant pH versus test mileage for factory fill OAT Coolant C. The fresh test coolant pH is 8.6.

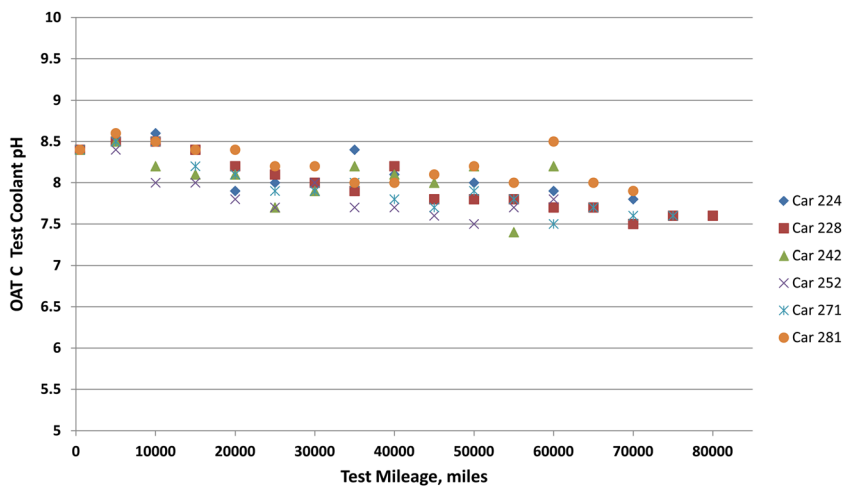
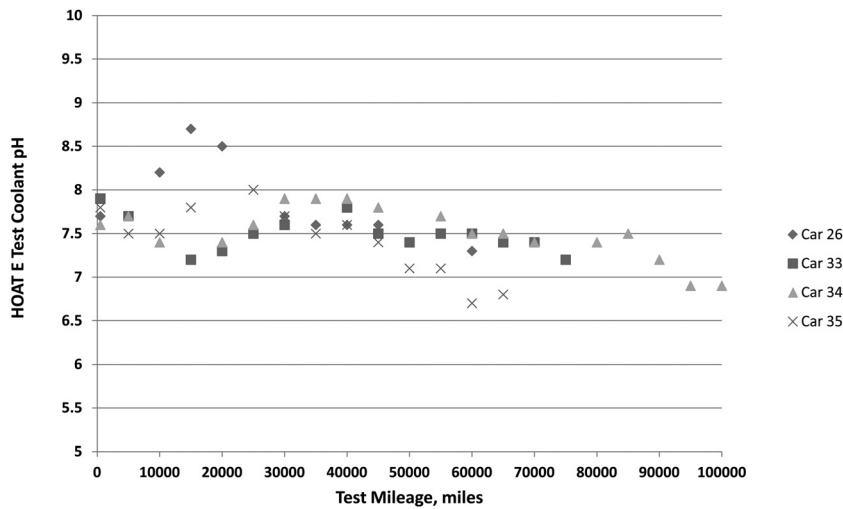


FIG. 11 Police fleet results: Test Coolant pH versus test mileage for factory fill Hybrid Low Si-OAT Coolant E. Fresh test coolant pH is 8.3.



Inhibitor Residual Concentrations Versus Fleet Test Mileage

The average % azole remained in the test coolant as a function of test mileage for the Extended Life New Generation Coolant B and OAT Coolant A obtained from the 2010 WCP Crown Victoria police fleet test is shown in Fig. 12. The average % azole remained in the test coolant as a function of test mileage for the factory fill Hybrid Low Si-OAT Coolant E obtained from the PSO police fleet test is shown in Fig. 13.

One can see from comparing the results in Figs. 12 and 13 that among the three test coolants tested, the azole concentration depleted the fastest in the HOAT coolant E, dropping to ~19 % remaining after 95 000 miles. The azole concentration in the OAT Coolant A also decrease much faster than the Extended Life New Generation Coolant B under comparable test conditions, dropping to at or below 50 % of the initial fresh coolant concentration after 70 000–80 000 miles of the test. In comparison, greater 75 % of initial azole concentration remained in the test where the Extended Life New Generation Coolant B was used at between 70 000–80 000 miles of fleet test. In addition, other corrosion inhibitor components in the Extended Life new Generation Coolant B remained largely unchanged during the fleet test, as shown in Fig. 14 for one of the key corrosion inhibitors in the coolant.

It should be noted that the azole concentration depletion results obtained in the fleet tests of the current study for OAT coolants were in general agreement with the results reported earlier by other researchers for different OAT coolants using different test vehicles [15,16,18,20].

FIG. 12 Average % azole concentration remained in the test coolant in comparison to initial azole concentration as a function of fleet test mileage—Extended Life New Generation Coolant B versus OAT Coolant A.

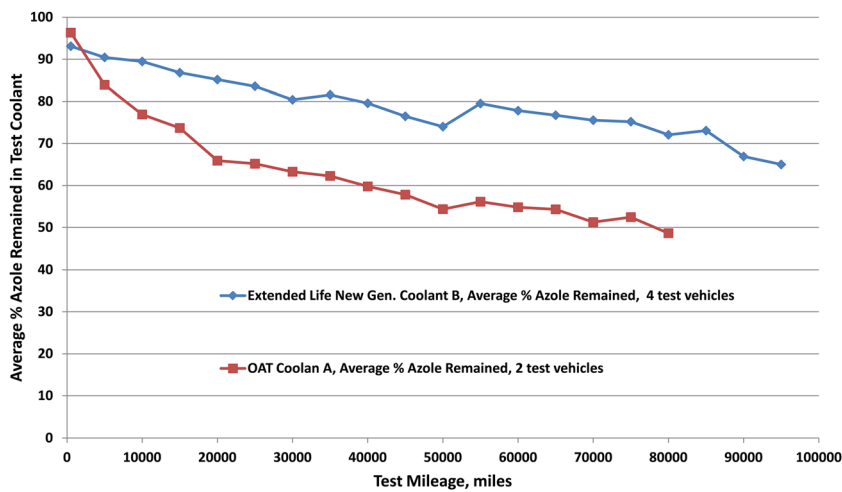
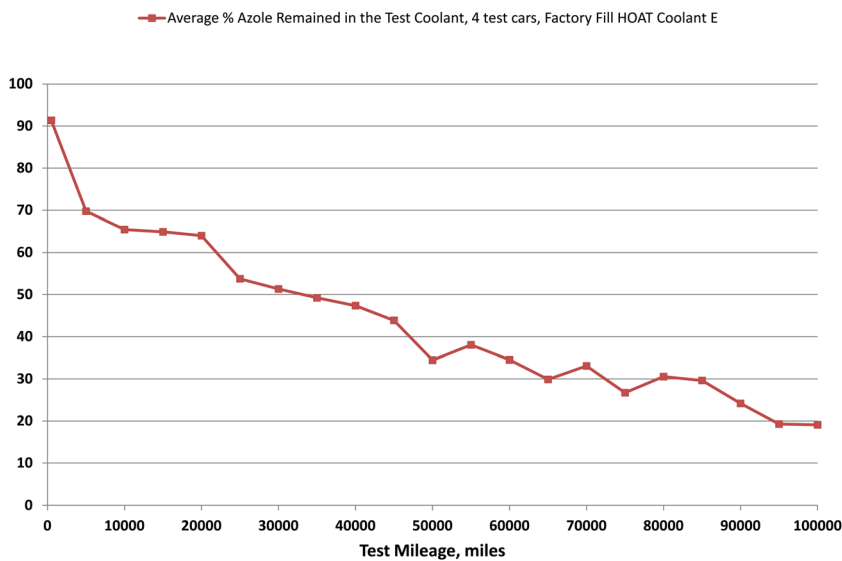


FIG. 13 Average % azole concentration remained in the test coolant in comparison to initial azole concentration as a function of fleet test mileage for factory fill Hybrid Low Si-OAT Coolant E in PSO police fleet test.



Corrosion Product Ion Concentrations Versus Fleet Test Mileage

The aluminum ion concentrations measured in the test coolant as a function of the test mileage for the Extended Life New Generation Coolant B, OAT Coolant A obtained from the 2010 WCP Crown Victoria police fleet test is shown in Fig. 15, and for the factory fill Hybrid Low Si-OAT Coolant E in the PSO police fleet test in Fig. 16. One can see that the aluminum ion concentration detected in Extended Life New Generation Coolant B and the OAT Coolant A remained low during the fleet test, with test mileage up to 95 000 miles. The small aluminum ion concentrations detected in both coolants were generally not much higher than the detectable limits. Inspection of the key cooling system components (including radiator and water pump) of test vehicle (car 1748) at around 52 371 miles indicate that, indeed, no corrosion had occurred on the inspected components. The surfaces of the components were like-new conditions, with no sign of any corrosion or degradation. The aluminum ion concentrations detected in the factory fill Hybrid Low Si-OAT Coolant E were considerably higher than detected in the Extended Life New Generation Coolant B and OAT Coolant A. In particular, the aluminum ion concentration detected in Car 35 appeared to be increasing quickly with increasing test mileage after 55 000 miles. It appeared to indicate that active corrosion was occurring in the test vehicle and the test coolant was quite close to end of its protective service life.

FIG. 14 Average % corrosion inhibitor residual concentration as a function of fleet test mileage for Extended Life New Generation Coolant B in the 2010 WCP Crown Victoria fleet test.

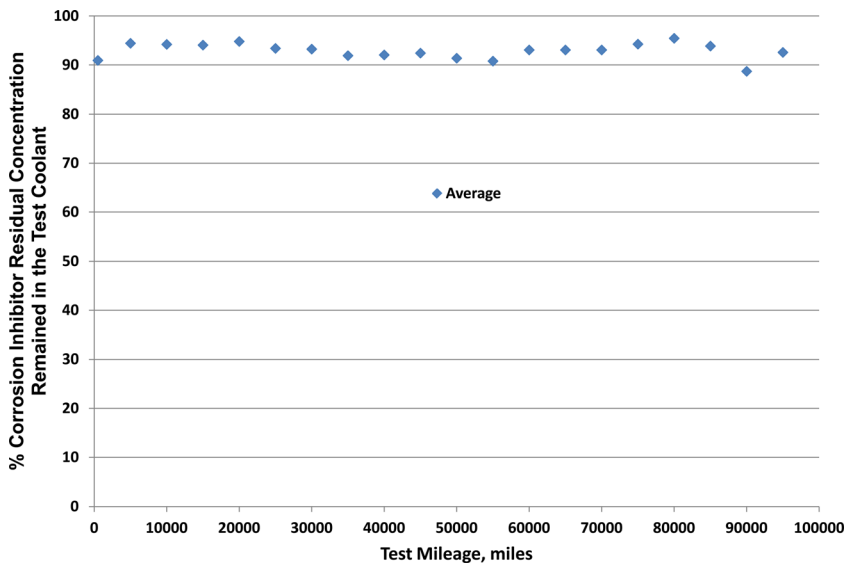


FIG. 15 Aluminum ion concentration in the test coolants as a function of test mileage—Extended Life New Generation Coolant B versus OAT Coolant A.

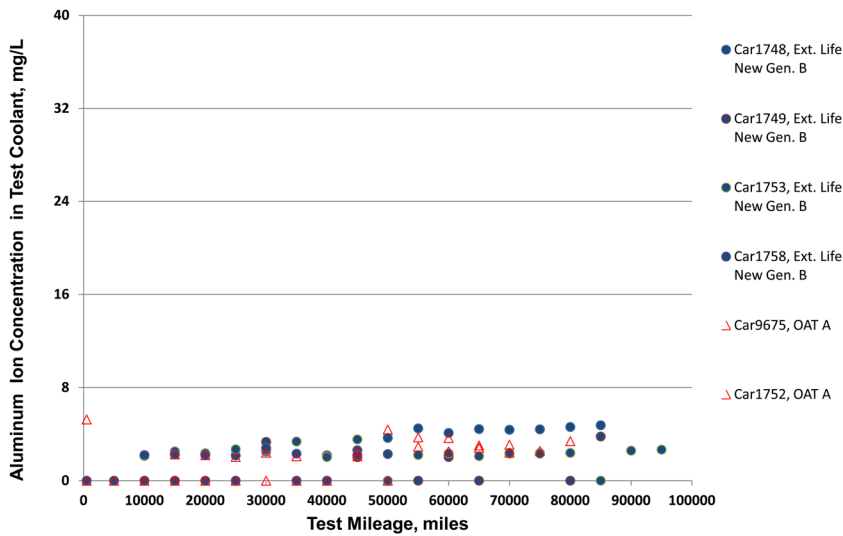
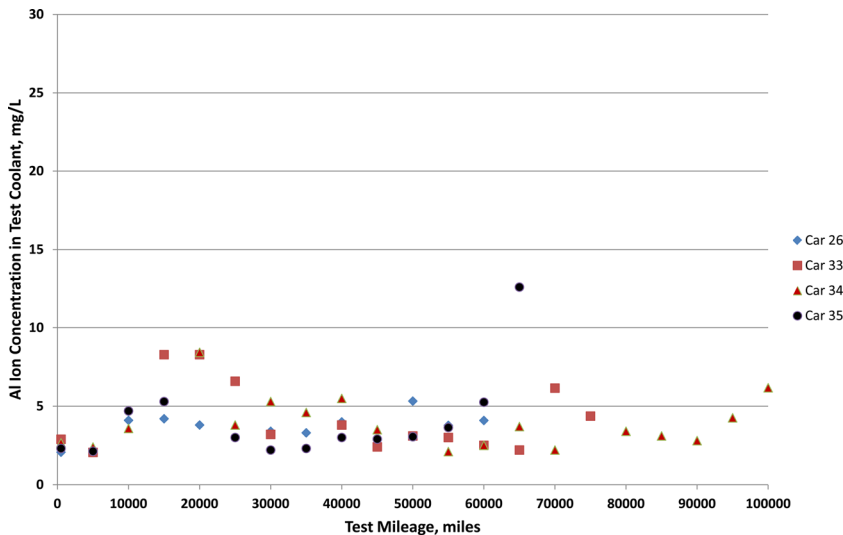


FIG. 16 Aluminum ion concentration in the test coolant as a function of test mileage—Factory fill Hybrid Low Si-OAT Coolant E.



It should be noted that other corrosion product ion concentrations such as copper and iron in the police fleets tested remained low during the tests. No cooling system related problems were noted in the fleet test vehicles using the Extended Life New Generation Coolant A and B. In addition, no cooling system related problems were noted in the fleet test vehicles using the OAT Coolants A and C.

Conclusions

Extended life new generation coolants with improved performance were developed and lab and fleet tested. In comparison with the extended life coolants available commercially, the extended life new generation coolants were shown to offer the following advantages:

- Provide quick, complete, highly effective, and extremely durable corrosion protection to all metals used in prevalent engine cooling systems.
- Highly compatible with CAB aluminum heat exchangers. Provide better corrosion protection to aluminum surfaces with CAB flux residues than other coolants, such as Hybrid Si-OAT and Asian Low P-OAT Coolants.
- Showed low inhibitor depletion rates, stable pH, and low glycol degradation rate over the service life of the coolant.
- Even the end-of-test coolants (test mileage: 89 069 miles, engine test hours: 3889 h) provide quick, complete, highly effective, and extremely durable corrosion protection to all metals used in the engine cooling systems.

ACKNOWLEDGMENTS

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Jonathan Thomas Light¹

Non-Aqueous Coolant Perspectives

Reference

Light, Jonathan Thomas, "Non-Aqueous Coolant Perspectives," *Global Testing of Extended Service Engine Coolants and Related Fluids*, STP 1556, Edward R. Eaton, Ed., pp. 39–53, doi:10.1520/STP155620130068, ASTM International, West Conshohocken, PA 2014.²

ABSTRACT

The discussion of non-aqueous (aka anhydrous or waterless) engine coolants begins with the acknowledgment of the superiority of liquid-state water as a medium of heat transfer. Even when the water is cut 50 % with the addition of a freezing point depressant, the resulting heat capacity and thermal conductivity parameters dominate in comparison to those figures for any practical non-aqueous fluid. The challenge for water-based coolant, however, is keeping it in its liquid state at all times under the high heat density conditions of modern engines and their EGR coolers. As water-based coolants are operated close to their boiling points, water vapor from localized boiling is not always surrounded by liquid coolant cold enough to condense it. Consequences of vapor accumulation are discussed. Non-aqueous coolants have atmospheric boiling points that are far hotter than the temperatures at which they are used. Localized boiling can still produce vapor but it condenses immediately into colder surrounding liquid coolant, avoiding the accumulation and pocketing of vapor. Just as the users of water-based engine coolants need the assurance of ASTM Standards with regard to functionality and corrosion protection, so do users of non-aqueous coolants. Additionally, the opening up of the use of new chemical compositions for coolants, offered by non-aqueous possibilities, require that coolant candidates conform to viscosity, thermal conductivity, and flash point limits. This paper discusses the development of standards and

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specifications for non-aqueous coolants, including the use of existing tests that may be used without changes, the modification of existing tests (making them become new tests), and tests that are entirely new.

Keywords

non-aqueous, waterless, anhydrous, engine coolant

Introduction

Liquid water has excellent engine coolant attributes. [Table 1](#) compares water’s heat capacity, thermal conductivity, and dynamic viscosity to the similar attributes of a collection of other fluids. Water is best by a wide margin in these categories. Taken together, with the fact that water is nearly free, it is no wonder that water, with glycol and anti-corrosion additives has, for nearly 100 years, been the first choice for cooling internal combustion engines.

Advantages of Water as an Engine Coolant Constituent

The ASTM has established standards and specifications for engine coolants that are water in combination with ethylene glycol, propylene glycol, or glycerin for freezing point depression, and inhibitors to control corrosion. Water generally occupies about 50 % of the coolant. There are no specifications for heat capacity, thermal

TABLE 1 Attributes of water compared to other fluids.

Fluid	Specific Heat Capacity J/kg · K @ 20°C	Density kg/m ³ @ 20°C	Volumetric Heat Capacity kJ/m ³ · K @ 20°C	Thermal Conductivity W/m · K @ 20°C	Dynamic Viscosity mPa · s @ 20°C
Water	4187	998	4179	0.60	1
Glycerin	2430	1261	3064	0.29	1200
50 % Glycerin and 50 % water ^a	3230	1128	3643	0.42	6
Ethylene glycol	2428	1113	2707	0.26	21
50 % E glycol and 50 % water ^a	3310	1066	3528	0.39	3.5
1,2-Propanediol	2470	1036	2559	0.21	56
1,3-Propanediol	2219	1060	2337	0.22	52
Diethylene glycol	2303	1118	2575	0.20	36
Ethylene glycol monobutyl ether	2380	900	2142	0.16	2.9
SAE 10 motor oil	1820	857	1560	0.15	79

^aPercentages by weight, parameters from Ref. [1].

conductivity, or viscosity for these blends because a 50 % blend of water with a polyhydric alcohol gives excellent heat transfer as well as a very acceptable viscosity.

Consider the case of ethylene glycol, the most common freezing point depressant, and its effect on the thermal conductivity of water in a 50/50 mixture. At 100°C (see [Table 2](#)), water, by itself, has a thermal conductivity of 0.67 W/m · K. A 50/50 mixture of water and ethylene glycol (“50/50 EGW”) has a thermal conductivity of 0.42 W/m · K. The thermal conductivity of the heat transfer fluid is reduced 37 %, yet the difference in cooling system performance is barely perceptible.

An Engine Cooled by a Radiator is “Air Side Limited”

A coolant pump draws coolant from the radiator and pushes it through the engine and back through the radiator. A fan blows air through the radiator. The coolant absorbs heat from the hot engine metal and gives up heat to the metal in the radiator. The most difficult heat transfer is from the metal of the radiator to the ambient air because the thermal conductivity of the air is so small (0.032 W/m · K). The difference in thermal conductivity between water (0.67 W/m · K) and 50/50 EGW (0.42 W/m · K) has little effect on system temperatures because of the limitation placed on the system by the thermal conductivity of air. That is the meaning of the term “air side limited” as applied to an engine cooling system that has a radiator.

At 100°C, a typical non-aqueous coolant would have a thermal conductivity of 0.26 W/m · K. The further 25 % reduction from the thermal conductivity of water *does* have a perceptible effect on the coolant temperature, but it is small. A fully loaded cooling system using a typical non-aqueous coolant, the thermostat being wide open and the bypass closed, will exhibit a coolant temperature that is about 5.5 C (10°F) warmer than the system with 50/50 EGW.

TABLE 2 Thermal conductivity of cooling system metals, coolants, and gases.

Material	Temp.	Thermal Conductivity W/m · K
Cast iron	100°C	50
Aluminum	100°C	200
Water, liquid phase	100°C	0.67
Water, vapor phase	100°C	0.024
50% E glycol/50% water (by mass)	100°C	0.42
Non-Aqueous coolant	100°C	0.26
Air	100°C	0.032

Regarding Viscosity, Water-Based Coolants Have the Advantage

From [Table 1](#), observe that the viscosity of 50/50 EGW is 83 % less than ethylene glycol. The viscosity reduction seen with 50/50 glycerin is an amazing 99.5 % versus neat glycerin. Viscosities of polyhydric alcohol coolants that are 50 % water are so low that the ASTM water-based coolant specifications [2] do not include a maximum viscosity limitation. In contrast, the non-aqueous coolant specifications under development within the ASTM will definitely include an upper limit on viscosity.

When one considers that water has the highest specific heat capacity, the greatest thermal conductivity, the lowest viscosity, and a latent heat of vaporization (2257 kJ/kg) that towers above all other practical liquids, one might question why there would be an attraction for an engine coolant that did not contain water. The simplest answer to that question is that when a water-based coolant boils, water vapor is produced at the hottest locations in the cooling system and liquid coolant is displaced from those hottest locations. The problem centers on the difficulty of keeping water in its liquid state and the difficulty of condensing water vapor.

Do Water-Based Fluids Really have the Advantage With Regard to the Latent Heat of Vaporization?

Nucleate boiling by a heat source in a pool of water conducts heat from the heated element to the pool very efficiently. The small amount of vapor at the interface breaks away into the liquid and condenses. The conversion from liquid to vapor absorbs heat based upon the mass of the liquid vaporized and the latent heat of vaporization of the fluid. The heat is given up to the liquid in the pool when the vapor condenses. The question is, “are pool conditions maintained in a cylinder head?”

A typical cylinder head contains many confined passages that are connected in parallel. As the coolant flows through the cylinder head, some routes offer less flow resistance than other routes. At locations where vapor is being produced, the pressure increases due to the production of that vapor. The increase in pressure increases the flow resistance and decreases coolant flow at that location. Nucleate boiling cannot be sustained without the “pool” to condense into. Under certain conditions, the local volume fills with vapor, causing an uncontrolled temperature rise of the adjacent metal.

Consider the consequences of boiling that takes place in a cylinder head coolant jacket and compare the difference between water and a high molecular mass organic with regard to the vapor. Water (see [Table 3](#)) has the greatest latent heat of vaporization of any practical substance. A single gram vaporized removes 2257 J. In contrast, it would take 2.63 g of ethylene glycol vaporized or 2.56 g of propylene glycol vaporized to remove the same amount of heat.

TABLE 3 Heats of vaporization and volumes of vapor produced per heat absorbed.

	Molecular Mass g	Latent Heat of Vaporization kJ/kg	Molar Heat of Vaporization kJ/mole	Vol of Vapor Produced per kJ Absorbed mole/kJ	Pct Vol Vapor Produced per kJ Compared to Water
Water	18.02	2257	40.7	0.0246	–
Ethylene glycol	62.07	857	53.2	0.0188	–23.5 %
Propylene glycol	76.09	880	67	0.0149	–39.3 %

However, the real problem is the amount of vapor produced, not the amount of liquid involved in the evaporation. It is the vapor that insulates between hot metal and liquid coolant and is the cause of the hot spots in the cylinder head. One must therefore look at the molar heat of vaporization to see what is happening on the vapor side.

All gases at STP occupy 22.4 L. The figures for the molar heats of vaporization indicate that, for the same amount of heat removed, ethylene glycol and propylene glycol would produce volumes of vapor that would be 23 % less and 39 % less, respectively, as compared to water.

A mixture of glycol and water has a somewhat elevated boiling point from water alone. It is important to note, however, that when 50/50 EGW is boiled, of the vapor produced, nearly 100 % of the glycol portion immediately condenses, leaving behind nearly pure water vapor. The water vapor cannot condense except at a temperature that is colder than the boiling point of water for the pressure of the system (a temperature that is lower than the boiling point of the glycol-water coolant), an environment that frequently does not exist near the location where the water vapor is being produced.

Cooling systems using water-based coolants are operated near the boiling point of water for the pressure of the system. In contrast, a non-aqueous coolant has a boiling point above 177°C (350°F) and an operating temperature very much colder than its boiling point. Any locally-produced vapor condenses immediately into the surrounding coolant.

What Water Vapor Does in an Engine Cooling System

Water vapor in a cooling system always occupies a volume that displaces a like volume of liquid coolant from the location of the water vapor. The hottest parts of the cylinder head are the likeliest locations for localized boiling of coolant and water vapor creation. If the nearby surrounding liquid coolant is hotter than the boiling point of water at the local pressure, the vapor will remain at that location, forming an insulating barrier between the hot cylinder head metal and the liquid coolant. How good is the insulation? Water vapor has just 4 % of the thermal conductivity

of a liquid coolant that is half water. With water vapor present and its attendant poor thermal conductivity, less heat is conducted from the hot metal, the metal temperature rises, and a “hot spot” forms. A cylinder head hot spot in any engine stresses the metal, possibly causing the head to warp or crack. In a spark-ignition engine, the hot spot can be a site for pre-ignition and detonation.

Pump cavitation is a possibility whenever water-based coolant is operated too close to its boiling point. The reduced pressure at the “eye” of the coolant pump can be low enough to cause the coolant to boil and make water vapor at that location. The ability of the pump to function is compromised when there is water vapor in the eye of the pump. The coolant flow will diminish and may stop altogether. An interruption in coolant flow causes a sharp increase in coolant temperature and widespread boiling.

Operation of water-based engine coolant near its boiling point creates the condition for *cavitation erosion of cylinder liners* in heavy duty engines. Each piston oscillates within its cylinder liner, vibrating the liner at the frequency of the piston movement. Locations of the liner that move away from the liquid, form low pressure areas where the coolant boils and water vapor forms. On the other half of the vibration cycle, those locations move toward the liquid, causing an increase in pressure, and the vapor condenses. The cycles repeatedly scrub these sites making them vulnerable to cavitation and erosion.

Afterboil is caused by water-based coolant that is at a temperature near its boiling point in an engine that has been stressed by running hard and then shut down. Heat stored in the cylinder head continues to dissipate into the coolant in the head cooling jacket. Boiling and water vapor occur when the coolant temperature exceeds the boiling point of the coolant for the pressure of the system. Afterboil can be a cause of a *mysterious loss of coolant* from a non-leaking cooling system that has a pressurized expansion tank. Water vapor from the after-boiling displaces liquid coolant in the cylinder head, forcing the pressure high enough to open the pressure relief valve at the cap on the expansion tank. Coolant is pushed out of the expansion tank, sometimes as a liquid onto the ground and sometimes as a mist or spray.

As water expands in volume more than a thousand times when it is converted to steam, not much liquid water needs to be vaporized to create a significant vapor pocket in an engine. [Table 4](#) is a computation of the amount of vaporized water it would take to reach the relief pressure of a typical 101 kPa (1 bar) expansion tank cap for a cooling system on a heavy duty engine at sea level.

In the example of [Table 4](#), it is shown that the vaporization of just 1.42 g of water is enough to increase the system pressure to 101 kPa (gauge) and open the relief valve. The volume of vapor in the engine coolant jacket would be 0.88 L.

The EGR cooler, an exhaust to coolant heat exchanger for controlling NOX emissions, is another site within a heavy duty cooling system where water-based coolant is likely to boil. The reason is that the coolant is near its boiling point

TABLE 4 Computation of mass of vaporized water needed to open a typical expansion tank cap.

Assumptions		
Volume of the cooling system:	40 L	
The average temperature of the coolant cold:	20°C	
The average temperature of the coolant hot:	80°C	
The volume of the air space in the expansion tank cold:	5 L	
The absolute pressure in the expansion tank cold:	101 kPa	
The expansion of 50/50 EGW per degree C:	0.06732 %	
Computations		
Volume of coolant expansion by heating from 20°C to 80°C:	$(80-20) \times 0.0006732 \times 40 = 1.62 \text{ L}$	(1)
Remaining volume of air in expansion tank at 80°C:	$(5-1.62) = 3.38 \text{ L}$	(2)
Absolute pressure in expansion tank by Boyles Law:	$101 \times (5/3.38) = 149.4 \text{ kPa}$	(3)
Volume of vapor needed to reach 202 kPa absolute:	$(5/2)-1.62 = 0.88 \text{ L}$	(4)
Mol fraction needed to make 0.88 L vapor at 202 kPa absolute:	$2 \times (0.88/22.4) = 0.0786 \text{ mol}$	(5)
Water (mol mass = 18 g) needed for vapor to make 202 kPa absolute:	$(0.0786 \times 18) = 1.42 \text{ g}$	(6)

Note: It only takes 1.42 g water, vaporized, to open the 101 kPa (14.7 psig) cap on the expansion tank. The volume occupied by the vapor to build enough pressure to open the cap is 0.88 L.

already and then subjected to exhaust gas temperatures above 550°C (1022°F). The boiling releases water vapor inside the EGR coolers that insulates and causes high temperature excursions, resulting in cracks and premature failure of the EGR cooler. High boiling point non-aqueous coolants are able to absorb the heat without making vapor, keeping the EGR cooler full of liquid coolant at all times.

Efforts to Address the Problems of Water Vapor and “Overheating” in Heavy Duty Engines

Large radiator fans, that draw between 18 and 56 kW (25 to 75 hp), depending on RPM, are used to hold coolant temperatures low enough to prevent the boiling of coolant. Most of these fans are driven by the engine through an on-off fan clutch. The activation temperature of the clutch is below the boiling point of the water for the pressure of the system. The power drain of the fan is significant. A heavily loaded truck climbing a mountain generally needs a lower gear when the fan turns “on.” The energy need for a fan that is sufficient to maintain coolant temperatures low enough to keep water-based coolant functioning, negatively impacts fuel economy.

If use of the fan cannot prevent the coolant temperature from climbing past approximately 107°C (225°F), the engine is programmed to undergo

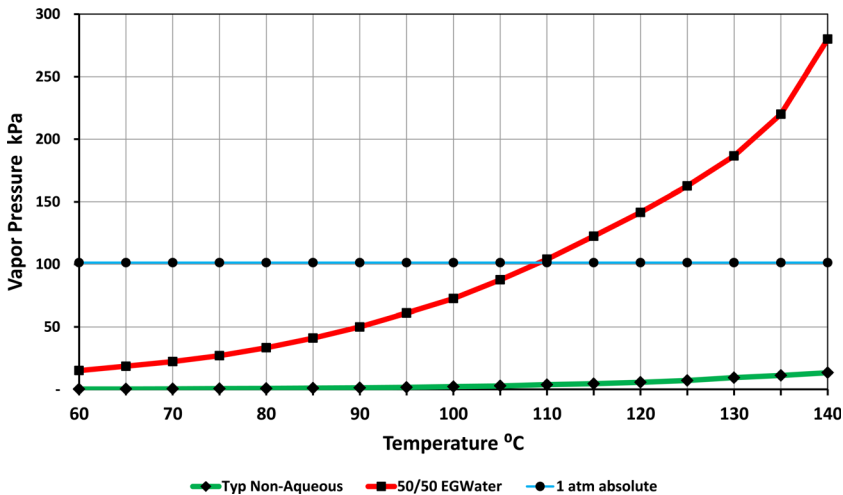
derating or to automatically shut down. Automatic shut-down frequently means a long delay before the engine can be re-started. Such delays, common when ambient temperatures are high, prevent efficient use of equipment and manpower.

How Non-Aqueous Engine Coolant Addresses Issues Relating to Cooling System Water Vapor and “Overheating”

Non-aqueous coolants do not contain water and they have boiling points considerably hotter than the temperatures at which they are operated. The huge separation between operating temperature and boiling point means that any locally generated vapor immediately condenses into nearby liquid that is much colder than the coolant’s boiling point. With no vapor to contend with, the following benefits become available:

1. There is no displacement of liquid coolant by vapor.
2. There is no vapor to insulate hot areas of the cylinder head from liquid coolant.
3. In spark ignition engines, the spark is at a more efficient setting because less knock is sensed.
4. The coolant pump does not cavitate because no amount of reduced pressure at the eye can make the coolant boil.
5. Cavitation erosion of cylinder liners is minimized because the low pressure instants from vibration are not low enough in pressure to make the coolant boil. There is no vapor made and no vapor to condense during the high pressure instants, sharply reducing any surface scrubbing.
6. There is no afterboil because the coolant in the cylinder head is much colder than its boiling point and acts as a heat sink with the capability to absorb all residual cylinder head heat without boiling.
7. If the cooling system has no leaks, there will be no need to replace lost coolant because the only pressure at the expansion tank will be from the expansion of the liquid coolant from being heated. There is no component of vapor in the system causing a pressure increase.
8. The life of the EGR cooler is extended because the entire cooling system, including the EGR cooler, is filled with liquid coolant and absent of water vapor. The waterless coolant is able to absorb the heat from the exhaust gases without boiling because the operating temperature of the coolant is much colder than its 177°C (350°F) boiling point.
9. **Figure 1** shows that the vapor pressure of a typical non-aqueous coolant is very low in comparison with 50/50 EGW. A cooling system will pressurize somewhat from the expansion due to the heated fluid but there is no pressure vector from the presence of vapor in the cooling system. Hose life is extended because hoses do not undergo the significantly higher pressures of a water-based system.

FIG. 1 Comparison of vapor pressures; typical non-aqueous coolant vs. 50% ethylene glycol/50% water coolant.



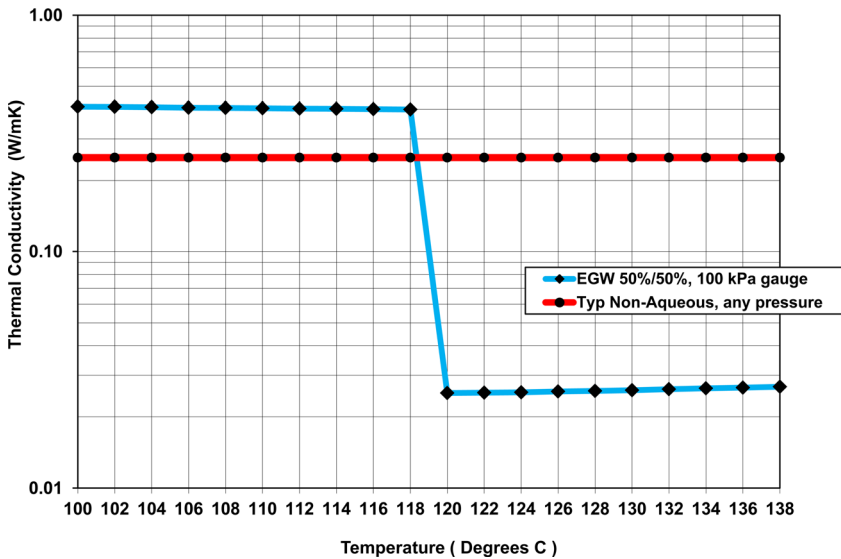
Heavy Duty Diesel Engines, in the Absence of Water Vapor, Can Tolerate Higher Coolant Temperatures

Figure 2 is a comparison of the thermal conductivities of a typical non-aqueous coolant and of 50/50 EGW. The water-based coolant has a superior thermal conductivity but only when water vapor is not present, i.e., at temperatures that are below the boiling point of water for the pressure of the system. The non-aqueous coolant maintains its thermal conductivity at all temperatures but the water-based coolant loses its ability to conduct heat away from hot metal at the locations where boiling takes place. Engines can safely tolerate higher coolant temperatures because hot engine metal is never insulated from liquid coolant by vapor.

Running a heavy duty diesel engine at elevated temperatures, enabled by the use of non-aqueous engine coolant has been shown to reduce fuel consumption. A 3 % reduction in fuel consumption was proved by SAE Type II testing at Auburn University by using higher temperature thermostats in conjunction with non-aqueous engine coolant.

Fuel is also saved when the radiator sees a higher coolant temperature, enabled by a non-aqueous coolant. The radiator becomes more efficient at dissipating heat because the temperature difference between the radiator and the ambient air increases. The cooling system becomes slightly less air-side limited, meaning that the same amount of heat can be removed with less fan-on time. The fan still draws between 25 and 75 hp but, if it turns on at 110°C (230°F) instead of 99°C (210°F),

FIG. 2 Thermal conductivity of the liquid and vapor phases of water-based coolant vs. a typical non-aqueous coolant (the vapor phase of water-based coolant has almost no thermal conductivity).



the fan-on time will be reduced considerably, saving fuel and adding to the truck’s usable power on hills.

Heavy equipment used in high ambient temperature and/or high altitude environments is frequently inefficient to use because of shut-down devices that actuate for coolant temperatures as low as 102°C (215°F). The shut-down temperature is chosen at a level where the coolant in the cylinder head still has some capacity to absorb heat after shut-down, without massive boiling. Generally there is a time delay required before re-starting can commence. Machine time and labor are wasted and the prospect for more shut-downs remains. With non-aqueous coolant in the cooling system, there is no need for easily-reached shut-down temperatures. The shut-down temperature can be raised because there is no vapor competing with the liquid coolant. The coolant temperature is so much colder than the boiling point of the coolant that in the event of an abrupt shut-down, all of the remaining heat in the cylinder head can dissipate into coolant in the cylinder head without causing the boiling of coolant. The engine can be re-started at any time, including immediately.

Spark-Ignition Engines and Taming Engine Knock

The computer for a modern spark-ignition engine continuously adjusts the spark advance to optimize performance and fuel economy by employing a knock sensor

input. When no knock is sensed, the computer advances the spark until threshold knock is sensed. When incipient knock is sensed, the computer retards the spark, automatically adjusting the engine from a more efficient setting to one that will protect the engine from detonation. The engine loses performance and fuel economy whenever the engine settings shift toward the “protection mode.” By avoiding vapor in the cooling system, through the use of a non-aqueous coolant, the prevalence of knock is reduced and the engine spends more of its time operating under conditions of more-advanced spark, offering better performance and improved fuel economy.

ASTM Standards for Non-Aqueous Engine Coolants

The requirements for non-aqueous coolants are necessarily more complex from those for water-based coolants because, by making water the non-ingredient, the door is open to a huge universe of chemicals from which to choose. Consequently, there are a number of standards and specifications that are necessary for non-aqueous coolants that have not been needed for aqueous coolants. The work of ASTM Subcommittee D15.22 Non-Aqueous Coolants is to set these standards and specifications. In discussing this effort, it is useful to describe the tests and limits needed for non-aqueous coolants in context with existing specifications for aqueous coolants, i.e., the specifications of ASTM [D3306](#) [2].

The following physical and chemical requirements are essential for achieving the operational benefits of a non-aqueous coolant:

1. *The minimum thermal conductivity* of a non-aqueous coolant should exceed $0.250 \text{ W/m} \cdot \text{K}$ at 90°C (194°F). It is earlier argued in this paper that the air side limitation decreases the performance difference between, say, water and 50/50 EGW. Thermal conductivity does, however, become an issue if it is too low. Organic compounds that have low thermal conductivities and, when combined into a non-aqueous coolant, test below $0.250 \text{ W/m} \cdot \text{K}$, are not suitable. Thermal conductivity is not specified by D3306.
2. *The volumetric heat capacity* is the measure of how much heat can be absorbed in a given volume of coolant per degree K. A minimum of $2500 \text{ kJ/m}^3 \cdot \text{K}$ at 90°C (194°F) is appropriate. The D15.22 subcommittee, through Work Item WK34987, is in the process of developing a “Standard Test Method for Thermal Conductivity, Diffusivity and Volumetric Heat Capacity of Engine Coolants and Related Fluids by Transient Hot Wire Liquid Thermal Conductivity Method.” The related equipment can generate both the thermal conductivity and the volumetric heat capacity in a single test. Specific heat capacity can be derived by dividing the volumetric heat capacity by the density at the test temperature. Volumetric heat capacity is not specified by D3306.
3. *An upper limit on dynamic viscosity at low temperature* is needed so that the non-aqueous coolant is pumpable at temperatures that are unusually cold but

reachable at inhabited regions of the world. The dynamic viscosity of a non-aqueous coolant at -40°C (-40°F) should not exceed $2.7\text{ Pa}\cdot\text{s}$. It is understood that a centrifugal engine coolant pump is inefficient when pumping a fluid that has a viscosity of $2.7\text{ Pa}\cdot\text{s}$; however, (1) only a small coolant flow is needed at -40°C and (2), the viscosity of a non-aqueous coolant drops sharply once it warms. ASTM D2983 [3] will be the specified test method. Passing the low temperature, dynamic viscosity test obviates the need for either a freezing point test or a pour point test. The dynamic viscosity at low temperature is not specified by D3306.

4. *Establishing a lower limit on the flash point* for a non-aqueous coolant is appropriate, given that possible ingredients might have low flash points. The flash point should be at least 118°C (245°F) as tested by ASTM D93 [4]. Flash point is not specified by D3306 [1].
5. *A boiling point high enough* to provide considerable separation between the operating temperature of the coolant and the boiling point of the coolant. The large separation is needed to enable the condensation of coolant vapor close to the location where it is created. The elimination of vapor keeps liquid coolant in contact with the hot metals in a cylinder head or EGR cooler. Coincident with a high boiling point are low vapor pressures at all operating temperatures. The coolant will not be pressurized by a vapor component. The only pressure in a closed expansion tank comes from heat-expanded liquid squeezing the air that lies between the coolant level and the top of the expansion tank. An acceptable boiling point is 177°C (350°F). ASTM D1120 [5] will be the specified test method. D3306 specifies a minimum boiling point of 163°C (for ethylene glycol concentrates) and 152°C for propylene glycol concentrates.
6. *An upper limit on the water content* of a non-aqueous coolant is desirable as water is an undesirable contaminant in a non-aqueous engine coolant because of its volatility as compared to the primary ingredients. Volatile non-aqueous ingredients are also undesirable as vapor from them would likely not condense. The minimum boiling point of 177°C addresses the overall volatile content but the water portion should separately be held to 0.75 % or less of the non-aqueous coolant, tested by ASTM D1123 [6]. D3306 specifies a maximum water content of 5 % for concentrates.
7. The *pH* for a non-aqueous coolant will be limited to a range of 7.5 to 11, the same as D3306. The measurement is taken after a 50 % by volume dilution with deionized water, in accordance with ASTM D1287 [7].
8. *The ash content* of a non-aqueous coolant will be limited to a maximum of 5 %, the same as D3306 for concentrates, and determined by ASTM D1119 [8].
9. *The chloride content* of a non-aqueous coolant will be limited to a maximum of $25\text{ }\mu\text{g/g}$, the same as D3306, as determined by ASTM D3634 [9] or ASTM D5827 [10].
10. *The reserve alkalinity* of a non-aqueous coolant will be as agreed upon between the supplier and customer, the same as D3306, as determined by ASTM D1121 [11].

11. *The effect on automotive finish* of a non-aqueous coolant must be “no effect,” the same as [D3306](#), as determined by ASTM [D1882](#) [12].
12. Given the wide diversity of possible non-aqueous engine coolants, a density range is not expected to be specified.

A non-aqueous engine coolant must also pass the following performance requirements:

1. *A new corrosion in glassware test* for non-aqueous engine coolants patterned on ASTM [D1384](#) [13], is underway by Subcommittee D15.22. The test method will be modified, wherein the amount of corrosive water added will be considerably less than the 67 vol. % used for water-based coolant. One could argue that the test should be conducted without the addition of any water. Suggestions to do exactly that were met with complaints that the coolant would not be “stressed” enough if no water were added. Although a user of a non-aqueous engine coolant would attempt to keep the coolant as water-free as possible, the test will be conducted with water well in excess of the amount of water as might be in a typical installation. Operationally, running a “non-aqueous” coolant with excessive water would negate most of the benefits of the no vapor, low pressure environment. The test, with excessive water, however, would reveal the ability of a non-aqueous coolant to tolerate water without causing corrosion issues. Although specifications for non-aqueous coolants are not yet developed, it is likely that specific values for maximum coupon weight loss will be the same as ASTM [D3306](#) [1] (in [D3306](#), the maximum weight losses for copper, solder, brass, steel, cast iron, and aluminum are 10, 30, 10, 10, 10, and 30 mg, respectively.) As of this writing, the Work Item for the new standard, *Standard Test Method for Corrosion of Non-Aqueous Engine Coolants in Glassware*, is underway.
2. *A new simulated service test* for non-aqueous engine coolants patterned on ASTM [D2570](#) [14], is planned for development by Subcommittee D15.22. The test solution in ASTM [D2570](#) is 56 % by volume corrosive water. The non-aqueous test method will specify a much smaller percentage of corrosive water. Although specifications for non-aqueous coolants are not yet developed, it is likely that the specific values for coupon weight loss will be the same as [D3306](#). The maximum weight losses for copper, solder, brass, steel, cast iron and aluminum are 20, 60, 20, 20, 20, and 60 mg, respectively, for [D3306](#).
3. *A new heat rejecting surface corrosion test* for non-aqueous engine coolants patterned on ASTM [D4340](#) [15] is underway. In [D4340](#), the test solution is 75 % by volume sodium chloride water, the operating temperature is 135°C (275°F), and the operating pressure is 193 kPa (28 psig). It is expected that the non-aqueous test method will contain a much smaller percentage of corrosive water and will likely be run at a temperature higher than 135°C and probably with an applied pressure very much lower than 193 kPa. Although specifications for non-aqueous coolants are not yet developed, it is likely that in evaluation of the test results, the expected specific value for the coupon weight loss will be 1.0 mg/cm²/week, the same as [D3306](#).

4. *Foaming tendencies* of non-aqueous coolants will be tested according to ASTM D7840 [16] and the results must not exceed these specific values: volume = 150 ml max and break time = 5 s max.
5. A new *cavitation erosion test* for non-aqueous coolants patterned on ASTM D2809 [17] is planned for development by Subcommittee D15.22. The test solution in D2809 is 83 % by volume corrosive water and the operating pressure is set at 103 kPa (15 psig). The non-aqueous test method will contain far less corrosive water, and will operate at a pressure reduced from 103 kPa. Although specifications for non-aqueous coolants are not yet developed, it is likely that the rating for pitting, cavitation, and erosion of the water pump will be the same or greater than the minimum of 8 as required by D3306 for the D2809 test.

All new ASTM Standard Test Methods under the jurisdiction of D15 require approval by ballot under D15. The actual standards may differ from the expectations expressed herein. The setting of the actual specifications for non-aqueous engine coolants will require approval by D15 balloting as well.

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NEW ENGINE COOLANT TECHNOLOGY

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Integration of Nano-Fluids into Commercial Antifreeze Concentrates With ASTM D15 Corrosion Testing

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ABSTRACT

Originally, five candidates of nano-material were chosen for making stable nano-dispersions. Nano-graphite particles remain a practical choice for nano-fluids thermal application after taking divergent performance attributes into full account: significant thermal conductivity increases, minimal viscosity increase, low density for better dispersion stability, and relatively low cost, among others. Three different types of commercial antifreeze coolants were chosen for the integration with graphite nano-fluids. Without corrosion inhibitors, our nano-coolants typically fail both ASTM D15 engine coolant corrosion tests. Yet, heating up and adding in electrolytes are two common ways to destroy a nano-particle dispersion. After making adjustments in particle loading, choosing an effective

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dispersant, and establishing proper dispersant levels, one nano-graphite coolant made from commercial nano-source passed both engine coolant corrosion tests plus the CID AA-52624 A compatibility and storage stability tests. Compared with the base fluid, the nano-graphite coolant’s thermal conductivity has more than a 25 % increase at 2 vol. % particle loading, which is a significant enhancement.

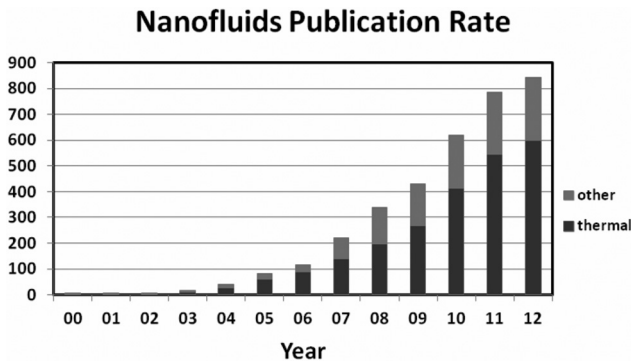
Keywords

graphite, alumina, nano-fluids, thermal conductivity, ASTM D15 corrosion tests

Introduction

Inclusion of high thermal conductivity particles into fluid to enhance the thermal properties of the finished fluids had been tried as early as the 19th century [1]. However, before ultra-fine particles were available it had never been successful because of rapid particle settling and potential clogging in application. After nano-technology emerged, the idea of dispersing nano-particles into fluids to form nano-fluids with unique properties has inspired broad interests of research in multiple domains in the first decade of 21st century. The most attractive performance enhancement of nano-fluids has been the anomalous thermal conductivity increase observed [2–6]. Carbon nano-tube dispersions once made a sensation with up to 300 % thermal conductivity increases. However; at the same time, the viscosity increased by thousands of % [7]. As a result, researchers mostly looked at nano-metal and metal oxide particles Using “nano-fluids” as the “topic” to perform a Sci-Finder literature search, more than 3650 papers have been published so far (see Fig. 1). The publication surge of recent years is largely a result of worldwide interest in the topic because thermal management is always of great importance in many

FIG. 1 Nano-fluids publication rate since the year 2000.



industries. Refining the search with “thermal,” around 2500 papers are available. About two-thirds of them deal with thermal conductivity or heat transfer. However, there has not been any paper reporting the ASTM automotive coolant corrosion tests on nano-fluids. The purpose of this paper is to achieve a stable nano-dispersion that has significantly better thermal conductivity and passes the ASTM D15 corrosion tests, and the CID AA-52624 A compatibility and storage stability tests.

Thermal conductivity (k) is just one factor that contributes to the heat-transfer coefficient (h). Special heat capacity (C_p), density (ρ), and viscosity (η) can also play a role in impacting the heat transfer efficiency. For example, under turbulent flow conditions, per Dittus-Boelter correlation [8] (where Nu = Nusselt number, $Nu = hD/k$; Re = Reynolds number, $Re = DU\rho/\eta$; Pr = Prandtl number, $Pr = C_p\eta/k$; U = the flow rate, D = the pipe diameter):

$$Nu = 0.023 Re^{0.8} Pr^{0.33}$$

We can estimate the heat-transfer coefficient by the following equation:

$$h = 0.023 \left(\rho^{0.8} U^{0.8} C_p^{0.33} k^{0.67} \right) / (D^{0.2} \eta^{0.47})$$

Therefore, whereas thermal conductivity, density and special heat capacity positively affect the heat-transfer coefficient, the viscosity has a negative impact. So, for a nano-coolant to have the best heat-transfer effect, theoretically it must have higher thermal conductivity, higher heat capacity, higher density, and lower viscosity. In reality, water has the highest heat capacity among common solids and liquids, so it is not practical for nano-fluids to have a higher heat capacity in an aqueous system. Because most solids have higher density than water and glycol, it is possible for nano-fluids to have higher density than water–glycol solution. However, density is dependent on particle loading, and high-density particles would incline to settle down much faster than lighter ones. To make a stable dispersion, lighter particles are more desirable. Besides, under the same mass percentage, lighter particles give a higher volume fraction, which contributes more to thermal conductivity increase. With nano-particles dispersed in a liquid, the viscosity always gets inevitably higher because of the surface interaction of particles and liquid molecules. The more and the finer the particles are, the higher the viscosity. Thus, it is not practical for nano-fluids to have lower viscosity either. Accordingly, this nano-fluid research has focused on increasing thermal conductivity while minimizing viscosity increase.

The general trend is that nano-particles with inherently higher thermal conductivity will produce nano-fluids with higher thermal conductivity. Metals and carbon material, such as diamond and nano-tubes, have the highest thermal conductivity. However, they are also much more expensive and most metals have high density. Besides, nano-metal particles have oxidation stability issues and nano-tubes involve

health concerns [9]. There is also difficulty in making stable dispersions of nano-metal particles and carbon nano-tubes. Metals and carbon nano-tubes with graphitic surfaces have free electrons and so are highly polarizable, which leads to the largest forces of attraction between the particles [10]. Thus, aggregation will be hard to control and viscosity increase is inevitable. So metals and carbon nano-tubes are excluded from our scope.

Originally five candidates were chosen: aluminum oxide (alumina), copper oxide, graphite, silicon carbide, and diamond. These choices were made upon aforementioned reasoning and other considerations like commercial availability and literature popularity. They are summarized in Table 1.

Our first approach was focused on solving the practical nano-fluids application barricade: stability. We employed a centrifugation method to accelerate the evaluation of the dispersion stability. After making stable nano-dispersions, properties of thermal conductivity and viscosity were measured and evaluated to determine the next-step candidates for corrosion tests. Eventually, graphite particles were identified as a practical choice after taking divergent performance attributes into account: significant thermal conductivity increases, minimal viscosity increase, low density for better dispersion stability, and relatively low cost, among others.

It is still challenging for nano-fluids to perform well in ASTM D15 engine coolant corrosion tests D1384 [11] and D4340 [12]. First, both tests are under high temperatures (around 200 °F). Second, commercial antifreeze concentrates contain up to 5 % electrolytes [13]. Yet, heating up and adding in electrolytes are two common ways to destroy a nano-particle dispersion. Without corrosion inhibitors, our nano-coolants typically fail both tests. Three different types of commercial antifreeze coolants were chosen for the integration of nano-fluids. After making adjustments in particle loading, choosing an effective dispersant, and establishing proper dispersant levels, one nano-graphite coolant was made from a commercially available graphite source that can pass ASTM engine coolant corrosion tests plus the CID AA-52624 A compatibility and storage stability tests. Compared with the base fluid, this nano-graphite coolant’s thermal conductivity has more than a 25 % increase at 2 vol. % particle loading, which is a significant enhancement.

TABLE 1 A summary of properties and situations of five candidate materials.

Materials	Thermal Conductivity <i>k</i> (W/mK)	Density <i>d</i> (g/cm ³)	Dispersability	Commercial Availability	Literature Popularity
Diamond	2300	3.5	Low	Low	Low
Graphite	1000 (<i>x</i> plane) 5.5 (<i>y</i> plane)	2.1	Medium	Medium	Low
Silicon carbide	110	3.22	Medium	Medium	Medium
Alumina	30	3.97	High	High	High
Copper oxide	18	6.31	High	High	High

Experimental

THERMAL CONDUCTIVITY MEASUREMENT

A KD2 Pro-Thermal Property Analyzer by Decagon Devices was used to measure the thermal conductivity (k). It employed the transient hot wire technique and has an accuracy of $\pm 5\%$ when the thermal conductivity is from 0.2 to 2 W/mK. A vial of glycerin provided by the manufacturer was used to do daily checks to make sure the data is within $\pm 5\%$.

VISCOSITY MEASUREMENT

Because nano-fluids are mostly murky and sometimes stain, no automated viscometer was used. Instead, a manual reverse-flow type kinematic viscometer by Cannon Instrument Company was used with the ASTM D445 [14] standard. The viscosity tubes were cleaned by ultrasonic cleaner after every use to remove any particle residue from the inside the tube wall.

OTHER MEASUREMENTS

pH value was measured by a pH ISE meter from Denver Instrument. The freezing point was measured by Phase Technology's 70 XAF Cloud, Pour and Freeze Point Lab Analyzer, or a portable digital refractometer from MISCO.

CENTRIFUGE AND BOIL-UP TESTS

These two tests were in-house empirical tests. The centrifuge test was used to quickly evaluate the dispersion stability. After 50 min under 2000 rpm centrifuging, an unstable dispersion would have a clear top fluid, which indicates failure. Otherwise, the bottom sediments were collected, washed, dried, and weighed. The sediment rate depends on particle sizes. Empirically, if less than 20 % of the particles settle under aforementioned centrifuge conditions, the dispersion is deemed stable and has the potential of a practical application. The boil-up test was used to see whether dispersions can survive heating. The nano-fluid was boiled with boileezers under reflux for 5 h, if agglomeration or gel up was observed, the test was regarded as a failure. Please note that both ASTM D15 corrosion tests are under high temperatures.

CID A-A-52624 A COMPATIBILITY AND STORAGE STABILITY TESTS

These two tests were published by U.S. Army Tank–Automotive and Armaments Command.

ASTM D15 CORROSION TESTS

ASTM D1384 Corrosion Test for Engine Coolants in Glassware and ASTM D4340 Corrosion Test of Cast Aluminum Alloys in Engine Coolants under Heat-Rejecting Conditions were performed in Ashland Engine Lab, Ashland, KY.

NANO-MATERIALS

Alumina: 10 nm, 20–30 nm, and 40–80 nm powers were purchased from Nano-Amor and 45 nm 50 mass % in water dispersion concentrate form Alfa Aesar

(Nano Dur, 1121 W, made by Nanophase). Sasol provided free powder samples Dispa X-0 (110 nm), X-30 (275 nm), 25F4 (108 nm), T25N4 (242 nm).

Copper oxide: was purchased from NanoAmor as powders (30–50 nm) and Alfa Aesar (made by Nanophase) as dispersion concentrate (NanoArc U1121W, 30 nm, 50 mass % in water).

Silicon carbide: Saint-Gobain provided free nano-slurry samples (300 nm, 360 nm, 13 mass % in water). 80 nm powders were purchased from NanoAmor.

Diamond: 6-nm nano-diamond powder samples were purchased from NanoAmor.

Graphite: nano-graphite powders were purchased from NanoAmor (400 nm) and GrafTech (GS-4 E, 2000 nm), dispersion concentrate (in paste form) was purchased from Ladd Research (made by Acheson Colloid under brand name of Aquadag E with an average particle size of 750 nm).

DISPERSANTS

Solsperse 20000 and Solsperse 27000 were provided free from Lubrizol Company. Both are polyether type and further detailed properties are proprietary. Dispersant T was provided free from Evonic Company; it is a polyglycol type dispersant and its specifics are also proprietary.

BLENDING AND MILLING

For sample sizes smaller than 100 ml, a Fisher Scientific Model 550 Sonic Disembrator was used in making nano-dispersions with a typical operation time of 2 min. For sample sizes larger than 1 l, a horizontal 2 l Laboratory Mill from Engineered Mills, Inc (Eiger) was used to make even dispersion with a milling time of 10 min under 1000 rpm milling speed.

Results and Discussion

MAKING STABLE NANO-FLUIDS IN ETHYLENE GLYCOL/WATER SOLUTION

The first stage evaluation was focused on dispersion stability and thermal conductivity increase (which was expected to be 20 % or higher). Only when a nano-dispersion is stable and has significant increase in thermal conductivity, it can be regarded as acceptable for further evaluation. The first stage evaluation was not tried with commercial antifreeze concentrate. Instead, pure ethylene glycol (EG) was used. Commercial antifreeze concentrate has up to 5 mass % electrolytes that have a severely detrimental impact on dispersion effect. For example, when replacing pure EG with commercial antifreeze concentrate, the otherwise stable dispersions turned into paste. The centrifuge test was used to evaluate the dispersion stability. Except for diamond, each of the other four candidates had at least one stable dispersion in EG/water (1 + 1) volume/volume solution (Please note, for practical purpose, the EG to D.I. water ration in this paper is always (1 + 1) by volume

TABLE 2 Description of five stable nano-dispersion in EG/water.

Material Supplier	Specific Description	Dispersion in EG/water		Nano-Dispersion
		Mass (%)	Vol. %	
EG/water (1 + 1) volume	Base line	–	–	Base line
Alumina, Sasol Dispal X-0	113 nm, powder	20	5	A
Alumina, NanoDur 1121 W	45 nm, 50% in water	32.3	8	B
CuO, NanoArc U1121W	30 nm, 50% in water	32.3	4.8	C
SiC, Saint-Gobain	300 nm, 13% in water	6	1.9	D
Graphite, Aquadag E	750 nm, 22% in water	7.5	3.5	E

and will be simplified as EG/water). Their thermal conductivity (k) and viscosity performance at 75 °F were summarized in [Tables 2](#) and [3](#).

Please note that sonication and adding proper dispersant are typical ways to make stable nano-dispersions. Dispersants play very important role in making most effective dispersion which will be seen in this paper. The above five stable dispersions could be accomplished without using extra dispersants because the suppliers already incorporated proper dispersants into their products (concentrations or powders). In [Tables 2](#) and [3](#), only two nano-dispersions, alumina (Sasol) and graphite (Acheson) have higher than 20 % thermal conductivity increase but the viscosities increased way higher. For nano-alumina dispersions, much higher particle loading were needed to have higher than 20 % thermal conductivity increase. Based on these first-stage screening experiments, nano-alumina and graphite were chosen to study further.

NANO-ALUMINA DISPERSION IN EG/WATER

The Sasol Diapal X-0 nano-alumina powder is engineered to be readily dispersed in aqueous system. It has a needle like shape. [Table 4](#) shows summary of study of particle loading effects on thermal conductivity and viscosity. It can be seen that thermal conductivity increases lineally with the particle loading, whereas viscosity increases

TABLE 3 Thermal conductivity (k) and viscosity at 75°F of above stable nano-dispersion.

Nano-dispersion	k (W/mK)	k (Increase/%)	Viscosity (cSt)	Viscosity (Increase/%)
Base line	0.399	–	3.55	–
A	0.493	28	18.83	430
B	0.459	19	9.85	177
C	0.447	16	13.22	272
D	0.435	13	4.36	23
E	0.583	47	467	13 055

TABLE 4 Alumina loading effect on *k* and viscosity of nano-dispersion in EG/water at 75°F.

Alumina Loading		<i>k</i> (W/mK)	<i>k</i> (Increase/%)	Viscosity (cSt)	Viscosity (Increase/%)
Mass (%)	Vol. %				
0	0	0.385	–	3.55	–
10	2.5	0.433	12	9.17	158
20	5	0.487	26	19.98	463
30	7.5	0.553	44	102.64	2790

exponentially. [Table 5](#) shows the effects of using extra dispersant to reduce the viscosity increase.

Taking both thermal conductivity and viscosity increases into account, the one with bold letters in [Table 5](#) was chosen to do the centrifuge test, boil-up test, CID A-A-52624 A storage stability test, CID A-A-52624 A compatibility test, ASTM [D1384](#) corrosion test, and ASTM [D4340](#) corrosion test. It passed the first three tests but the other three tests failed by gelling-up when it was mixed with test reference fluids. The reason for gel-up is likely because of the *pH* value change during dilution by the test reference fluids, which exceeded the iso-electric point. The *pH* value of this nano-alumina in water glycol solution was around 4.5 and nano-alumina particles with absorbed protons repel each other; thus maintaining suspension in the dispersion. Once the *pH* value is higher than its iso-electric point the nano-alumina dispersion just gels up.

The nano-dispersion B in [Tables 2](#) and [3](#) (made from NanoDur 1121 W) had close to 20 % increase in thermal conductivity. It is very different from dispersion A because it passed the centrifuge test, CID A-A-52624 A storage stability test, and CID A-A-52624 A compatibility test. However it failed the boil-up test badly: it turned into dreggy form after being cooled. This is mostly because of its high

TABLE 5 Dispersant effect on *k* and viscosity of nano-alumina dispersion in EG/water at 75 °F.

Alumina (mass %/vol. %)	Dispersant (mass %)	<i>k</i> (W/mK)	<i>k</i> (Increase/%)	Viscosity (cSt)	Viscosity (Increase/%)
20/5	0.5	0.487	26	19.77	457
20/5	1	0.486	26	17.68	398
20/5	2	0.486	26	17.56	394
20/5	3	0.486	26	17.34	388
10/2.5	0	0.433	12	9.17	158
10/2.5	0.5	0.433	12	8.11	128
30/7.5	0	0.553	44	102.64	2790
30/7.5	1	0.549	44	72.23	1935

Note: Alumina is Sasol Dispal X-0; dispersant is Solsperse 20000.

TABLE 6 Graphite loading effect on k and viscosity of nano-dispersion in EG/water at 75 °F.

Graphite Loading		k (W/mK)	k (Increase/%)	Viscosity (cSt)	Viscosity (Increase/%)
Mass (%)	Vol. %				
0	0	0.385	–	3.55	–
2.5	1.2	0.439	14	5.11	44
5	2.3	0.509	32	46.94	1222
7.5	3.5	0.583	51	467	13 055
10	4.6	0.642	67	Paste	

particle loading of 32.3 mass %. In addition, its viscosity reduction effort was not successful. Because its viscosity increase (177 %) was almost 10 times the thermal conductivity enhancement, there was no need to run the two corrosion tests. Overall, the nano-alumina dispersions have a very mediocre thermal conductivity enhancement performance if viscosity increase has to be minimized. Thus, further work would be focused on nano-graphite dispersions.

NANO-GRAPHITE DISPERSIONS IN EG/WATER

From [Tables 2](#) and [3](#), the most promising candidate is the nano-graphite dispersion. It has a much higher thermal conductivity increase under the equivalent particle loadings. The loading and dispersant effects on nano-graphite (Acheson Aquadag E) are summarized in [Tables 6](#) and [7](#).

Here it was observed that an effective dispersant could play a very important role in reducing the viscosity. In addition, once the dispersion became more

TABLE 7 Dispersant effect on k and viscosity of nano-graphite dispersion in EG/water at 75 °F.

Graphite (mass %/vol. %)	Dispersant (mass %)	k (W/mK)	k (Increase/%)	Viscosity (cSt)	Viscosity (Increase/%)
5/2.3	0	0.509	32	46.94	1222
5/2.3	1	0.507	32	9.3	162
5/2.3	2	0.493	28	7.08	99
5/2.3	3	0.483	25	6.67	87
5/2.3	4	0.483	25	6.34	79
2.5/1.2	0	0.439	14	5.11	44
2.5/1.2	1.5	0.421	9	4.86	37
7.5/3.5	0	0.583	51	467	13 055
7.5/3.5	3	0.565	47	13.6	283
3.8/1.8	1.5	0.469	22	6.57	85
10/4.6	0	0.642	67	Gel	
10/4.6	3	0.628	63	46.18	1200

Note: The graphite is Acheson Aquadag E; the dispersant is Solsperse 27000.

effective the thermal conductivity enhancement was compromised, which reflects the clustering mechanism in nano-fluids thermal conductivity increase. The formula with bold letters in [Table 7](#) was chosen to do the same six tests. It just passed the centrifuge test and the CID A-A-52624-A storage stability test. However, both corrosion tests failed so badly that the tests had to be aborted because of too much agglomeration. Now it was thought that if a nano-dispersion did not fare well in the boil-up test, it might not perform well during the corrosion tests. By reducing the graphite loading the formulae with bold letters in [Table 8](#) passed the boil-up test. Then the two corrosion tests could be finished, bur the results were still failure. This failure was not unusual because there were no corrosion inhibitors in the nano-fluids. The next experiments would replace the EG with commercial anti-freeze products.

NANO-GRAPHITE DISPERSIONS IN COMMERCIAL ANTIFREEZE ZEREX/WATER

Three commercial antifreeze concentrates were chosen:

Zerex G-05: Phosphate free, long-life hybrid formulation, mostly used for passenger cars.

Zerex 618: Fully formulated with organic acid, mostly used for heavy-duty diesel engines.

Zerex Dex-Cool: Phosphate and silicate free, organic acid technology, mostly used for GM and Asian vehicles.

Here, the pure EG was replaced with Zerex antifreeze concentrates. In the finished formula Zerex to D.I. water ratio is also (1 + 1) by volume and will be also simplified as Zerex/water. The boil-up test results along with thermal conductivity (*k*) and viscosity data at 75 °F are summarized in [Table 9](#).

The formulae with bold letters is in above [Table 9](#), which passed boil-up tests were sent for the two corrosion tests. The results along with other test results are summarized in [Table 10](#). The Zerex 618 based nano-coolant was successful in passing both corrosion tests. But it failed the CID A-A-62624-A storage stability and compatibility tests. The next effort was to find a more effective dispersant.

TABLE 8 Boil-up test result for reformulated nano-graphite dispersion in EG/water.

Graphite (mass %/vol. %)	Dispersant (mass %)	<i>k</i> (W/mK)	<i>k</i> (Increase/%)	Viscosity (cSt)	Viscosity (Increase/%)	Boil-up Test
7.5/3.5	3	0.565	47	13.6	283	Failed
4.4/2.1	0	0.499	30	6.55	75	Failed
4.4/2.1	1	0.495	29	5.82	56	Failed
4.4/2.1	2	0.490	27	6.20	67	Passed

Note: The graphite is Acheson Aquadag E; the dispersant is Solsperse 27000.

TABLE 9 Boil-up test result for nano-graphite dispersion in Zerex/water.

Graphite (mass %/vol. %)	Dispersant (mass %)	<i>k</i> (W/mK)	<i>k</i> (Increase/%)	Viscosity (cSt)	Viscosity (increase/%)	Boil-up Test
Zerex G-05 based nano-fluids						
0	0	0.392	–	3.96	–	–
4.4/2.1	0	Gel	–	Gel	–	–
4.3/2.1	2	0.513	31	13.4	238	F
4.2/2.0	4	0.503	28	10.17	157	F
4.1/2.0	6	0.485	24	9.67	144	P
Zerex 618 based nano-fluids						
0	0	0.392	–	3.76	–	–
4.4/2.1	0	Gel	–	Gel	–	–
4.3/2.1	2	0.504	29	20.1	434	F
4.2/2.0	4	0.501	28	10.07	168	F
4.1/2.0	6	0.480	22	9.82	161	P
Zerex Dex-Cool based nano-fluids						
0	0	0.389	–	3.67	–	–
4.4/2.1	0	Gel	–	Gel	–	–
4.3/2.1	2	0.508	31	11.56	215	F
4.2/2.0	4	0.499	28	8.24	124	P
4.1/2.0	6	0.476	22	7.17	95	P

Note: The graphite is Acheson Aquadag E; the dispersant is Solsperse 27000.

NANO-GRAPHITE DISPERSIONS WITH NEW DISPERSANT IN COMMERCIAL ANTIFREEZE ZEREX/WATER

After the new dispersant, Dispersant T (trade secret), had been identified, not only Zerex 618 based formula passed all the tests, the Zerex G-05 based formula also passed all tests, whereas the Zerex Dex-Cool based formula only failed the Aluminum in the ASTM D1384 corrosion test (see Tables 11 and 12). The pictures of end-of-test (EOT) coupon assembly can be reviewed in Fig. 2, where the Zerex 618 based

TABLE 10 Test results for nano-graphite dispersion in EG/water and Zerex/water.

Medium Base	Graphite (mass %/vol. %)	Dispersant (mass %)	Boil-up Test	Centrifuge (out/%)	Storage Stability	Compatibility Test	D1384 Test	D4340 Test
EG	4.4/2.1	2	P	1.3	P	F	F ^a	F
G-05	4.1.2.0	6	P	12.7	F	F	F ^b	P
618	4.1/2.0	6	P	15.8	F	F	P	P
Dex-Cool	4.2/2.0	4	P	14.9	F	F	F ^c	P

Note: the graphite is Acheson Aquadag E; the dispersant is Solsperse 27000.

^aFailed in iron, steel, brass, and solder; passed on aluminum and copper.

^bFailed in iron only.

^cFailed in iron only.

TABLE 11 Boil-up test result for nano-graphite dispersion with Dispersant T in Zerex/water.

Medium Base	Graphite (mass %/vol. %)	Dispersant (mass %)	<i>k</i> (W/mK)	<i>k</i> (Increase/%)	Viscosity (cSt)	Viscosity (Increase/%)	Boil-up Test
G-05	4.2/2.0	5	0.488	25	6.89	74	P
618	4.2/2.0	5	0.489	25	6.91	84	P
Dex-Cool	4.2/2.0	4	0.488	25	6.20	69	P

Note: The graphite is Acheson Aquadag E; the dispersant is Dispersant T (trade secret).

TABLE 12 Test results for nano-graphite dispersion with Dispersant T in Zerex/water.

Medium Base	Graphite (mass %/vol. %)	Dispersant (mass %)	Boil-up Test	Centrifuge (out/%)	Storage Stability	Compatibility Test	D1384 Test	D4340 Test
G-05	4.2/2.0	5	P	13.8	P	P	P	P
618	4.2/2.0	5	P	14.2	P	P	P	P
Dex-Cool	4.2/2.0	4	P	14.1	P	P	F ^a	P

Note: The graphite is Acheson Aquadag E; the dispersant is Dispersant T (trade secret).

^aFailed in aluminum only.

nano-coolant had hardly left any deposit on the coupons. [Figure 3](#) shows images of EOT specimens of ASTM D 4340 corrosion test, where bigger particles had settled down over time. All EOT coupons and specimens were washable with water though. Based on the observation of EOT coupon assembly, Zerex 618 was preferred to Zerex G-05.

FIG. 2 The end-of-test coupon assembly of corrosion test D1384 for nano-graphite (Acheson Aquadag E) in Zerex G-05/water (left) and Zerex 618/water (right).

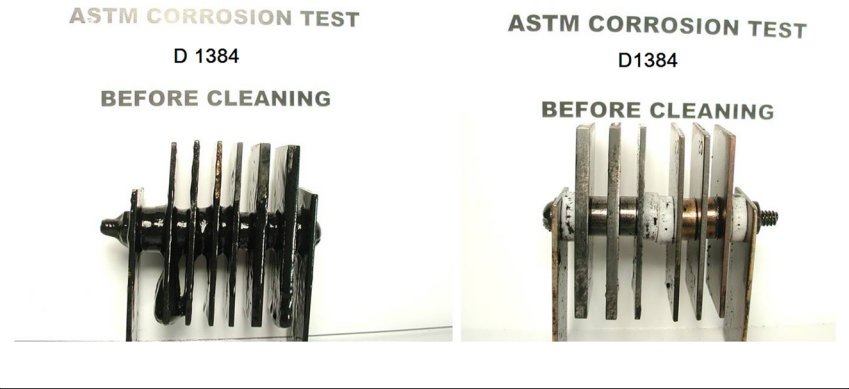
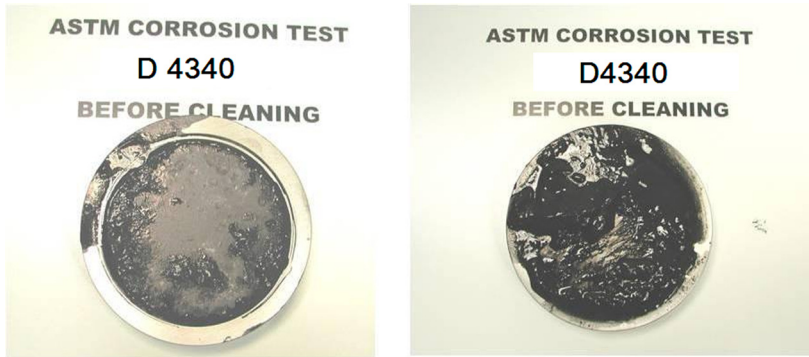


FIG. 3 The end-of-test specimen of corrosion test D4340 for nano-graphite (Acheson Aquadag E) in Zerex G-05/water (left) and Zerex 618/water (right).



Conclusions

Although nano-alumina dispersions have been the most popular research subject in the nano-fluid domain [15], this paper has demonstrated that properly engineered nano-graphite dispersions can be of much more practical application. This is especially true taking divergent performance attributes into account: significant thermal conductivity increases, minimal viscosity increase, low density for better dispersion stability, and relatively low cost, among others. An in-house centrifuge test was used to evaluate the nano-dispersion stability and a boil-up test was explored to serve as a screening test to see whether a nano-dispersion would survive high temperatures in engine coolant corrosion tests. Without corrosion inhibitors, the nano-coolants failed the corrosion tests. Without an effective dispersant, the nano-graphite coolant could not pass the CID AA-52624 A compatibility and storage stability tests. After making adjustments in particle loading, identifying an effective dispersant, and establishing proper dispersant levels, one commercial nano-graphite concentrate was successfully integrated into commercial antifreeze Zerex 618. It passed both engine coolant corrosion tests ASTM D1384 and ASTM D4340 plus the CID AA-52624 A compatibility and storage stability tests. Compared with the base coolant, the nano-graphite coolant has more than a 25 % increase in thermal conductivity at 2 vol. % particle loading, which is an anomalous enhancement.

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Carboxylate Based Coolant With Superior Oxidation Stability

Reference

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ABSTRACT

Modern engine coolants have advanced significantly in the last decades. This advancement focused mostly on the selection of more performing and robust additive technologies. Nevertheless, the majority of coolants still in use today use the same base fluid as 60 years ago, namely a mixture of water and monoethylene glycol (MEG). MEG is a vicinal alcohol and thus relatively susceptible to oxidation. The oxidation of MEG results in the formation of short chain acids such as formic and glycolic acid, which lower the *pH* of the coolant, increase corrosiveness and reduce additive stability. Increased power output in the modern engine, sometimes combined with accidental or design related air intake may result in such severe MEG oxidation that optimal coolant performance becomes jeopardized. This paper presents data on the oxidation stability of a fully formulated carboxylate salt based engine coolant. The base fluid is comprised out of an aqueous solution of potassium propionate. Corrosion inhibition is provided by the addition of an optimized additive package. The data is compared with that generated on two long-life monoethylene glycol based engine coolants. The new coolant looks virtually indifferent to oxidation, despite the extreme testing circumstances. No significant acidification occurred resulting in a highly stable *pH* and little or no discoloration of the liquid. Additive concentrations were hardly affected. The corrosion protection effectiveness remained excellent, resulting in very low soluble iron concentrations and no deposit formation.

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Keywords

coolant, oxidation stability, monoethylene glycol, potassium propionate, carboxylate

Introduction

Modern engine development has been a continuous journey towards higher efficiencies, lower emissions, and improved fuel economics [1,2]. This has resulted in more powerful engines, increased thermal stresses on the cooling system components, and the engine coolants used. Changing operational conditions include higher coolant temperature and cooling system pressures, a higher heat flux towards the coolant, reduced cooling system dimensioning, and less effective deaeration. All of these factors have the potential to increase the oxidation and degradation rate of coolants, reduce additive stability, increase the risk of coolant system corrosion, and shorten the life expectancy of a coolant.

Monoethylene glycol (MEG), Ethane-1,2-diol (IUPAC), has since long been the predominant choice of base fluid for coolants use in internal combustion engines. Quality MEG based coolants offer balanced performance properties such as being an effective heat transfer medium, freezing and boiling protection, acceptable flammability, and toxicity as well as effective corrosion protection [3]. MEG ($\text{HO-CH}_2\text{-CH}_2\text{-OH}$), as well as other glycols and alcohols, is, however, susceptible to oxidative degradation at higher temperature in the presence of oxygen [4]. The oxidation of MEG results in the formation of glycolic acid ($\text{HO-CH}_2\text{-COOH}$) and formic acid (HCOOH). Several authors have shown that the oxidation stability of MEG based coolant is influenced by different parameters, such as additive technology, metal induced catalysis, pressure, and test duration. The most important parameters, however, appear to be temperature and the availability of air [5–7].

Potassium propionate ($\text{CH}_3\text{-CH}_2\text{-COOK}$) is a highly soluble carboxylate salt. In solution, it can serve as an alternative base fluid for engine coolants. Corrosion inhibitors, including OAT (Organic Additive Technology), can be dissolved in the potassium propionate solution to provide corrosion protection [8,9]. Contrary to MEG and primary and vicinal alcohols in general, the propionate anion does not contain a hydroxyl functional group (-OH) group that can be easily oxidized [10].

In the following work, we compare the oxidative stability of an inhibited potassium propionate solution (Coolant A), with that of two monoethylene glycol based engine coolants (Coolant B and Coolant C). For this purpose, the coolants were subjected to high temperatures alternated with intermediate contact to ambient air at low temperature. Acidification was determined by pH and reserve alkalinity measurements. Additive stability was compared by coolant analysis, as well as the corrosion protective properties of the exposed coolants.

Experimental

HIGH TEMPERATURE OXIDATION TEST

All coolants tested had an identical freezing point of -37°C as determined according ASTM Standard Test Method for Freezing Point of Aqueous Engine Coolants (D1177-12) [11]. The high temperature oxidative resistance of the coolants was tested by heating the coolants to a high temperature (175°C , liquid temperature) in a pressure resisting stainless steel container. The container had a total volume of 1100 mL and filled with 750 mL test liquid. The heat was transmitted to the liquid by a mantle using electrical resistance heating. The coolants were exposed to 10 temperature cycles each with a total duration of 24 h. An individual cycle consistent out of 1 h heating to 175°C , 18 h steady-state at 175°C , and a 5 h cool down period. During the final 1.5 h of the cool down period, the liquid was exposed to ambient air. In our laboratory, the first cycle started at 1 PM. The container was sealed and the heating was switched on. The coolant liquid reached 175°C within 1 h, electrical power output was then controlled so a steady-state temperature of 175°C could be maintained. The morning (8 AM) of the next working day, the heating was switched off and the coolant was allowed to cool down to 40°C . At 11.30 AM, the container was opened and free access to the ambient air of the laboratory was allowed until 1 PM. The cycle was repeated 10 times. The high temperature oxidation test was performed with a without the presence of a cast iron ring (SAE grade G2500, 2.6 dm^2 surface) submerged in the test liquid. In Fig. 1, a picture of the test setup is shown.

FIG. 1 Picture of the high temperature oxidation test setup.



ANALYSIS OF TEST SOLUTIONS

The pH of the coolants was measured according to ASTM D1287-11 [12]. The amount of anionic, inorganic corrosion inhibitors (for example: nitrite), and glycol degradation products (glycolate and formate) were determined with ion chromatography (IC) according to test method ASTM D5827-09 [13]. Other inorganic corrosion inhibitors (for example: molybdate) and iron ions (present in the test solutions as corrosion product) were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The amount of organic corrosion inhibitors was determined with high pressure liquid chromatography (HPLC). Buffer capacity degradation of the engine coolant was expressed as the decrease in reserve alkalinity of the coolant as measured according to ASTM D1121-11 [14]. The amount of deposit formed was determined by transferring the sample to a glass cone after the high temperature oxidation test and allowing it to settle for 24 h. The amount of deposit was expressed to the nearest 0.1 mL.

SELECTION OF COOLANT FORMULATIONS

Coolant A, which uses an aqueous potassium propionate solution as base fluid, contains organic corrosion inhibitors and a small amount of molybdate. For the test program, two commercially available MEG based engine coolants (Coolant B and C), were selected. These claim to meet heavy-duty requirements like ASTM D4985-10 [15] or ASTM D6210-10 [16], or both. Coolant B is an OAT-coolant. Coolant C contains predominantly inorganic corrosion inhibitors. Coolant A and B contain aliphatic organic acid salts. Coolant C includes various inorganic inhibitors and additionally 2-mercaptobenzoathiazole. All three additive technologies are combined with azoles for copper and brass protection. The selected coolants and compositional information are listed in Table 1.

Results and Discussion

PH, ACIDIFICATION, AND BUFFER CAPACITY DEGRADATION

Figure 2 shows the evolution of the pH of tested coolant solutions as a function of the number of cycles in the high temperature oxidation test. Table 2 shows the amount of glycolate, formate, and sulphate formed as well as the measured buffer capacity degradation after 5 and 10 cycles in the high temperature oxidation test. Strong pH decreases were observed with both Coolant B and C (Fig. 2). These pH decreases became larger with an increasing number of cycles in the high temperature oxidation test. The pH of Coolant A only showed a small initial decrease after the first cycle, but subsequently remained very stable. The presence of the cast iron surface had only a minor effect on the pH of the tested coolant solutions. Both MEG based coolants (Coolant B and C) contained an important amount of glycolate and formate after 5 and 10 cycles, respectively. These amounts were higher after 10 cycles than after 5 cycles, but little affected by the presence of cast iron. Coolant C contained a higher amount of glycol degradation products than Coolant B, both

TABLE 1 Coolant inhibitor formulations.

Inhibitor	Coolant ^a		
	A	B	C
Aliphatic acid A	X		
Aliphatic acid B	X		
Aliphatic acid C		X	
Aliphatic acid D		X	
Triazole	X	X	X
Na-2-MBTZ ^b			X
MoO ₄ ²⁻	X		X
NO ₂ ⁻			X
NO ₃ ⁻			X
SiO ₃ ²⁻			X
B ₄ O ₇ ²⁻			X

^aX indicates the presence of this inhibitor by analysis.

^bSodium-2-mercaptobenzothiazole.

after 5 and 10 cycles; additionally, Coolant C also contained sulphate after the test. No such degradation products were found in Coolant A. The observed buffer capacity degradation was limited in Coolant A and very similar after 5 and 10 cycles. In the MEG based coolants, the buffer capacity degradation was stronger and higher after 10 than after 5 cycles. Coolant C showed the severest buffer capacity degradation.

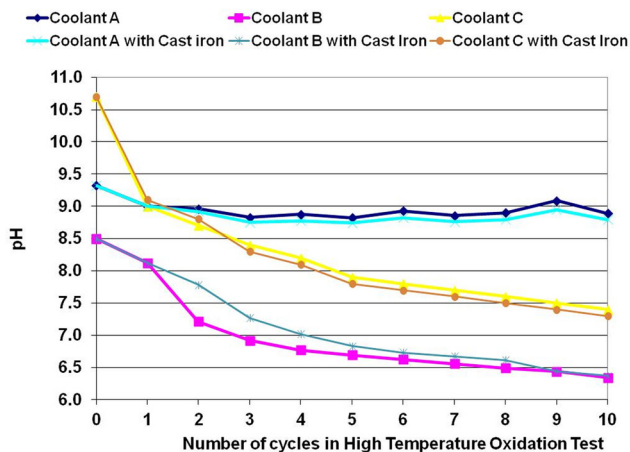
FIG. 2 Evolution of the pH of Coolant A, B, and C as a function of the number of cycles in the high temperature oxidation test.

TABLE 2 Buffer capacity degradation, glycolate-, formate- and sulphate concentrations, after 5 and 10 cycles in the high temperature oxidation degradation test.

Coolant, 5 cycles	Buffer Capacity Degradation, ml 0.100 N HCl ^b	Glycolate, ppm	Formate, ppm	Sulphate, ppm
A	0.3	ND ^a	ND	ND
B	2.2	770	130	ND
C	3.8	1520	270	310
A + Cast Iron	0.4	ND	ND	ND
B + Cast Iron	1.9	790	120	ND
C + Cast Iron	4.0	1630	280	358
Coolant, 10 cycles				
A	0.3	ND	ND	ND
B	3.6	1760	310	ND
C	7.7	3070	980	492
A + Cast Iron	0.3	ND	ND	ND
B + Cast Iron	2.1	1960	290	ND
C + Cast Iron	8.1	3370	990	508

^aND: not detected.

^b20 mL sample.

VISUAL APPEARANCE, DEPOSIT FORMATION, AND ADDITIVE STABILITY

Table 3 reports the visual appearance of the tested coolants and the amount of deposit formed after 10 cycles. **Figure 3** shows the visual appearance of Coolant A and B after 10 cycles in the presence of a cast iron ring. **Table 4** reports the percentage of corrosion inhibitors remaining in the test liquids after 5 and 10 cycles in the high temperature oxidation test. While all coolants were clear, transparent liquids before the test, the visual appearance of Coolant B and C changed dramatically in the sense that opaque, black liquids were obtained after the test. Coolant A, which was colorless before test, remained transparent and became yellowish. It is thought that the yellow discoloration is due to the thermal degradation of some of the triazole present in the formula. This shift in visual appearance was independent of the presence of the cast iron ring. Only a slight amount of deposit accumulated in Coolant A after 10 cycles. In the presence of cast iron, Coolant B, but especially Coolant C, yielded a higher amount of deposit after the test. Additive stability was highly variable between the coolants tested. Coolant A, showed only a significant decrease in the amount of triazole, while the concentration of both aliphatic acids as well as molybdate remained unaltered. In Coolant B, triazole depletion was higher than in Coolant A and a decrease in the concentration of one of the aliphatic acids was observed. In Coolant C, additive stability was most severely affected, with nitrite and sodium-2-mercaptobenzothiazole concentrations dropping below 5 % of their initial concentration after 5 and 10 cycles, respectively. Unlike Coolant A,

TABLE 3 Visual appearance of the test liquid and amount of deposit after high temperature oxidation test.

Coolant	Visual Appearance	Deposit, mL
A	Yellowish	< 0.5
B	Black	3.5
C	Black	2.5
A + Cast Iron	Yellowish	< 0.5
B + Cast Iron	Black	3.5
C + Cast Iron	Black	40

molybdate levels in Coolant C also showed an important depletion. In Coolant C, opposite to all other inhibitors, an increase in the nitrate levels was observed. This increase is thought to be associated with the depletion of nitrite.

CAST IRON CORROSION PROTECTION

To validate the effectiveness of the coolants to protect cast iron during the high temperature oxidation test, the iron levels in the liquids were determined after 5 and 10 cycles. Results are shown in [Table 5](#). For all coolants, no iron could be detected without the presence of a cast iron ring in the stainless steel container. In the presence of a cast iron ring, this remained the case for Coolant A. However,

FIG. 3 Visual appearance of Coolant A and Coolant B after the high temperature oxidation test in the presence of a cast iron ring (left Coolant A / right Coolant B).



TABLE 4 Percentage of corrosion inhibitors remaining in the test liquids after 5 and 10 cycles in the high temperature oxidation test.

Coolant	Percentage of Corrosion Inhibitor Remaining in Coolant, 5 cycles					
	a. Organic Inhibitors					
	OAT-Inhib A	OAT-Inhib B	OAT-Inhib C	OAT-Inhib D	Triazole	Na-2-MBTZ
A	100	100	NA ^a	NA	79	NA
B	NA	NA	100	87	72	NA
C	NA	NA	NA	NA	78	49
A + Cast Iron	100	100	NA	NA	77	NA
B + Cast Iron	NA	NA	100	83	70	NA
C + Cast Iron	NA	NA	NA	NA	78	34
Coolant	b. Inorganic Inhibitors					
	MoO ₄ ²⁻	NO ₂ ⁻	NO ₃ ⁻	SiO ₃ ²⁻	B ₄ O ₇ ²⁻	PO ₄ ³⁻
A	100	NA	NA	NA	NA	NA
B	NA	NA	NA	NA	NA	NA
C	47	<5	133	60	90	NA
A + Cast Iron	100	NA	NA	NA	NA	NA
B + Cast Iron	NA	NA	NA	NA	NA	NA
C + Cast Iron	47	< 5	129	39	90	NA
Coolant	Percentage of Corrosion Inhibitor Remaining in Coolant, 10 cycles					
	a. Organic Inhibitors					
	OAT-Inhib A	OAT-Inhib B	OAT-Inhib C	OAT-Inhib D	Triazole	Na-2-MBTZ
A	100	100	NA	NA	69	NA
B	NA	NA	100	75	58	NA
C	NA	NA	NA	NA	57	< 5
A + Cast Iron	100	100	NA	NA	71	NA
B + Cast Iron	NA	NA	100	73	62	NA
C + Cast Iron	NA	NA	NA	NA	47	< 5
Coolant	b. Inorganic Inhibitors					
	MoO ₄ ²⁻	NO ₂ ⁻	NO ₃ ⁻	SiO ₃ ²⁻	B ₄ O ₇ ²⁻	PO ₄ ³⁻
A	100	NA	NA	NA	NA	NA
B	NA	NA	NA	NA	NA	NA
C	46	<5	128	38	89	NA
A + Cast Iron	100	NA	NA	NA	NA	NA
B + Cast Iron	NA	NA	NA	NA	NA	NA
C + Cast Iron	46	<5	121	36	89	NA

^aNA: not applicable.

TABLE 5 Iron in solution after 5 and 10 cycles in the high temperature oxidation test.

	Fe, ppm	Fe, ppm
Coolant	5 cycles	10 cycles
A	< 1	< 1
B	< 1	< 1
C	< 1	< 1
A + Cast Iron	< 1	< 1
B + Cast Iron	1	2
C + Cast Iron	1	13

soluble iron was found in both Coolant B and C after 10 cycles. The amount of iron in Coolant C was 6.5 time higher than in Coolant B.

Conclusion

Test results confirm the hypothesis that a coolant using an aqueous solution of potassium propionate as base fluid can offer excellent oxidative stability at high temperatures. The oxidation resistant base fluid led to high pH —stability, limited discoloration, and the formation of only a limited amount of deposit. The behavior is in-line with the relative high oxidation resistance of carboxylates versus alcohols and glycols known from organic chemistry literature.

The results also showed that the observed pH stability is not due to a superior buffer capacity in comparison with the two reference MEG based coolants as the degradation of buffer capacity was significantly less to that in the two MEG based coolants.

Furthermore, the oxidation resistant carboxylate matrix provided a highly stable environment for the selected corrosion inhibitors. With the exception of triazole, no inhibitor depletion occurred despite the severe test conditions. Contrary to one of the aliphatic acid in the comparative example (Coolant B) and molybdate in the comparative example (Coolant C), neither the aliphatic acids, nor the molybdate in the potassium propionate based coolant showed a measurable depletion rate.

The high oxidation resistant potassium propionate matrix, in combinations with the highly stable additive package resulted in an effective corrosion protection of cast iron, despite the high temperatures and the repeated access of oxygen during the test procedure.

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Improved Aluminum Passivation for Heavy-Duty Coolants

Reference

Claeys, Sandra, Lievens, Serge, De Kimpe, Jurgen, and Van de Ven, Paul, "Improved Aluminum Passivation for Heavy-Duty Coolants," *Global Testing of Extended Service Engine Coolants and Related Fluids*, STP 1556, Edward R. Eaton, Ed., pp. 81–95, doi:10.1520/STP155620130066, ASTM International, West Conshohocken, PA 2014.²

ABSTRACT

To improve the energy efficiency of combustion engines, lightweight materials are being used in modern vehicle designs. As a consequence, aluminum is increasingly being selected as an additional metallurgy in cooling systems including heat-exchanger applications. Different brazing techniques can be used to assemble heater core components during construction of aluminum heat exchangers. Controlled atmosphere brazing (CAB), using potassium aluminum fluoride flux material is increasingly being used. Field reports, together with laboratory investigations, have confirmed that flux residues are partly soluble in coolant formulations and the findings indicate that the dissolved substances can interact with coolant additives, resulting in a loss of performance. Depending on the coolant chemistry, field experiences range from simple color changes from pH shifts to overheating, because of additive instabilities or even corrosion damage. Others have studied interactions of flux residues with coolants using different methods; this paper uses an alternative test method to evaluate the effects of CAB brazed aluminum heat exchanger materials to correlate with field observations. Parameters monitored for the study included changes in the physical chemical properties, additive stability and corrosion-protection performance of the test fluids. The study focused on heavy-duty coolants with different additive technologies, including nitrite-containing and nitrite-free

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formulations. The results clearly demonstrate that the field observations, mainly originating from the interactions with reactive aluminum surfaces, can be simulated using this test method. A novel additive chemistry has been developed and was added to the different coolant formulations, enabling a reduction or even elimination of the typical field observations. The adapted chemistry not only resulted in a more stable pH, but also reduces the consumption of corrosion inhibitors including nitrites and silicates. As a result, these coolant formulations are more robust and the concentration of coolant additives, to obtain the appropriate metal protection levels, are maintained.

Keywords

coolant, aluminum, controlled atmosphere brazing, flux, heat exchangers, radiators, nitrites, silicates, heavy-duty, passivation

Introduction

The use of aluminum as an alternative for ferrous and copper alloys is increasing in modern heavy-duty engine applications. An important reason for this change is the light weight characteristic of aluminum, which can significantly improve fuel economy and helps satisfy more stringent environmental emission regulations. Combined with acceptable strength, stiffness, and heat-transfer properties, aluminum alloys gained prominence in the manufacturing of cooling-system components, including heat exchangers [1].

Different brazing techniques have been developed to join the various parts of aluminum heat exchangers [2–14]. Since the early 1980s, controlled atmosphere brazing (CAB) using NOCOLOK Flux,³ developed by Alcan International, has been the preferred method for producing aluminum heat exchangers [7–13]. In this process, the bulk aluminum metal is joined using a low melting aluminum–silicon filler metal and potassium aluminum fluoride flux with a general formula $K_{1-3}AlF_{4-6}$ [7,8]. The brazing takes places at temperatures around 600°C in a dry, inert-gas atmosphere. At this temperature, the flux on the aluminum alloys melts and becomes reactive. The flux removes the aluminum-oxide layer naturally present on the aluminum-alloy surface without reacting with the underlying pure metal, allowing the filler aluminum material to diffuse into the bulk material. Subsequently, a cooling cycle enables the metal alloys to solidify and to fuse. The benefits of the CAB brazing process are a successful removal of the aluminum-oxide layer during the brazing process, the ability to work at atmospheric pressure and the use of the non-corrosive NOCOLOK Flux; thus avoiding the need for post-brazing treatment [7,13].

In the last decade, field reports, together with laboratory investigations, confirmed that remaining flux residues on the aluminum surface are partly soluble in

³ NOCOLOK Flux is a registered trademark of Solvay Fluor GmbH, Germany.

coolant formulations and can interact with coolant additives leading to a loss of performance [15–21]. Depending on the coolant chemistry, this resulted in different field observations ranging from coolant color changes and high aluminum and fluoride concentrations, from *pH* shifts to overheating because of instabilities and heat-exchanger blockage or corrosion damage [19–21]. As a reaction to these observations, coolant and heat-exchanger manufacturers together with the flux producers and vehicle manufacturers acknowledged the importance and further studied these phenomena. Laboratory tests indicated that fluorides are released in the coolant after being exposed to CAB brazed aluminum materials, resulting in reduced corrosion-protection performance of the coolant additive package [16,18]. Some studies focused on the influence of coolant corrosion inhibitor technologies on flux solubility, the effects of CAB brazed aluminum on coolants *pH*, additive stability and corrosion-protection performance [15,19,21], whereas others elaborated on the influence of flux composition and flux loading of CAB brazed aluminum surfaces [17,18].

This paper reports the results of a study looking into the effects of CAB brazed aluminum heat-exchanger material on commercially available heavy-duty coolant formulations with different additive chemistries, including nitrite-containing and nitrite-free technologies. An alternative test method that allows the simulation of field observations is also discussed. Parameters evaluated are the changes in the physical–chemical properties, the additive stability and the corrosion-protection performance of the tested coolants. The work further illustrates that the addition of novel additive chemistry to different coolant formulations can reduce or even eliminate performance losses caused by interaction with CAB brazed aluminum surfaces. The results clearly demonstrate that the proposed additive package is able to increase the *pH* stability and to reduce the consumption of corrosion inhibitors, such as silicates and nitrites, and have no negative impact on the general corrosion-protection performance. These formulated coolants exhibit an increased additive stability resulting in more robust coolant formulations.

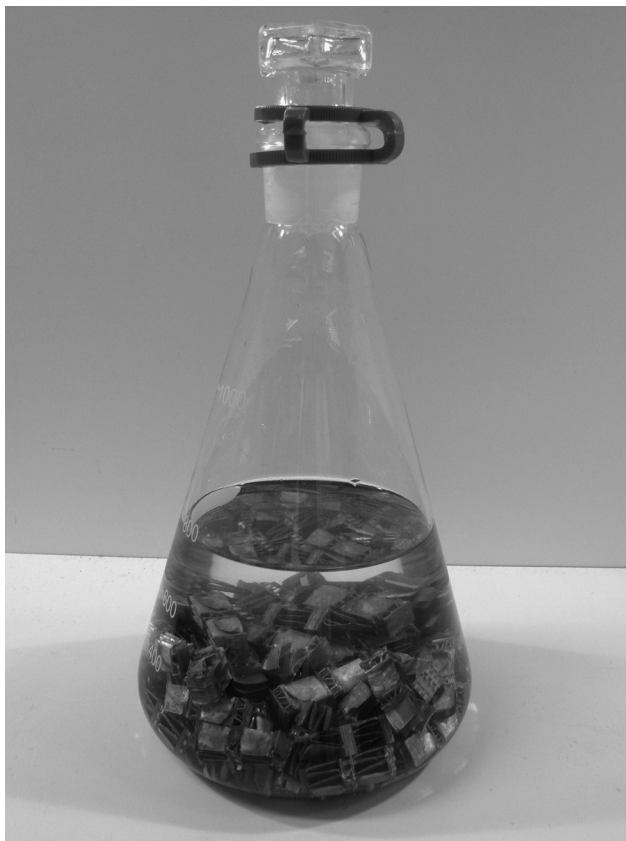
Experimental

CAB BRAZED ALUMINUM RADIATOR CUBE IMMERSION TEST

CAB Brazed Aluminum Cubes

A CAB brazed aluminum radiator, with an aluminum alloy AA3103 core and aluminum filler alloy AA4045 using potassium aluminum fluoride flux for the brazing process, was selected for coolant testing. This radiator was selected because it has been shown to influence the coolant performance both in the field and in laboratory testing. Some of the reported coolant changes included significant *pH* shifts and fast consumption of corrosion inhibitors like nitrites and silicates. For consistent testing purposes, a commercial radiator was cut into cubes with approximate dimensions 30 mm × 10 mm × 10 mm.

FIG. 1 Picture of the CAB brazed aluminum radiator cube immersion test setup.



CAB Brazed Aluminum Radiator Cube Immersion Test

The test solutions were prepared by mixing commercially available coolants with deionized water to yield a coolant concentration of 50 % (vol./vol.). In a 1-l flask, 76 of these cubes were immersed in 700 ml of test solution, after which the flasks were sealed and put in an oven at a temperature of 100°C for 10 days. During the test no agitation of the coolant occurred. In [Fig. 1](#), a picture of the test setup is shown. After treatment, the coolants were filtered to remove the cubes and deposits.

Analysis of Test Solutions

pH of the coolants was measured according to ASTM [D1287-11](#) [[22](#)]. The amount of anionic, inorganic corrosion inhibitors (for example, nitrites, nitrates, and phosphates), presence of contaminants, like fluorides originating from the flux residue, and glycol degradation acids were determined with ion chromatography (IC) according to test method ASTM [D5827-09](#) [[23](#)]. Other inorganic corrosion

inhibitors (for example, molybdates, silicates, and borates) and aluminum ions (present in the test solutions from the dissolved flux residue or as corrosion products) were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The amount of organic corrosion inhibitors was determined with high-performance liquid chromatography (HPLC). Ammonia formation in the nitrite-containing coolant solutions was determined with the HACH Pocket Colorimeter II,⁴ with the LANGE Cuvette Test LCK 303.⁵

CORROSION-PROTECTION PERFORMANCE TESTING OF COOLANT FORMULATIONS

The effectiveness of coolants to provide corrosion protection was tested according ASTM D4340-10 (corrosion protection of aluminum under heat-transfer conditions) [24] and ASTM D1384-05 (glassware corrosion test) [25]. For the fresh coolants the tests were run as prescribed. The ASTM D4340 procedure was adapted for the fluids after exposure to the CAB brazed aluminum radiator cube immersion test. After the immersion test, the coolants were filtered and the 50 % (vol./vol.) coolant solutions were further diluted with corrosive water (containing sodium chloride (NaCl)) to obtain a 25 % (vol./vol.) coolant solution with 100 ppm of chloride ions. The coolant concentration after immersion test and after dilution for corrosion testing was controlled by determination of the freezing point of the diluted coolants with refractometer according ASTM D3321-12 [26].

SELECTION OF COOLANT FORMULATIONS

For the test program, commercially available ethylene-glycol-based engine coolants, recommended for heavy-duty applications, were selected. All products claim to meet heavy-duty requirements like ASTM D4985-10 [27] or ASTM D6210-10 [28], or both. Using the coolant classification presented by Lievens and Garcia-Juan [21], one OAT-coolant, two hybrid, and two lobrid coolants were evaluated. The selected coolants and compositional information are listed in Table 1. All of these additive technologies are combined with azoles for copper and brass protection. Coolant A contains only organic corrosion inhibitors. Coolant B additionally includes low amounts of mineral inhibitors: a combination of nitrites and molybdates, and is, therefore, considered a lobrid. The use of nitrites and molybdates are widespread in the United States in heavy-duty applications for the protection of the engine's ferrous wet sleeve liners against cavitation-induced corrosion. Its use is recommended by truck and fleet owners, the Technology and Maintenance Council through the Recommended Practice TMC RP329 [29] and is mentioned in the standard specification ASTM D6210-10 [28]. The organic corrosion inhibitors in coolants A and B are a combination of aliphatic monocarboxylic and dibasic acids. In coolant C and D organic acid corrosion inhibitors are combined with a silicate additive package.

⁴ HACH Pocket Colorimeter II is a trademark from the HACH Company.

⁵ LANGE Cuvette Test LCK 303 is available at HACH LANGE GmbH, Germany.

TABLE 1 Coolant-inhibitor formulations.

Inhibitor	Coolant ^a				
	OAT	Lobrid		Hybrid	
		(NM) ^b	(Si) ^b	(Si) ^b	(P) ^b
A	B	C	D	E	
Monoacid	X	X			
Dibasic acid	X	X	X		
Aromatic acid				X	X
SiO ₃ ²⁻			X	X	
NO ₃ ⁻				X	X
B ₄ O ₇ ²⁻				X	
PO ₄ ³⁻					X
Triazole	X	X	X	X	X
MoO ₄ ²⁻		X			
NO ₂ ⁻		X		X	

^aX indicates the presence of this inhibitor by analysis.

^bInorganic inhibitor present in the coolant: NM, nitrite-molybdate; Si, silicate; P, phosphate.

Lobrid coolant C is a combination of aliphatic dibasic acid technology and a low amount of a silicate additive package. Hybrid coolant D contains aromatic monocarboxylic acids and is characterized by the presence of a significant amount of inorganic corrosion inhibitors such as silicates, borates, nitrates, and nitrites. Coolant E, also a hybrid, consisting of aromatic monocarboxylic acids and a significant amount of inorganic phosphates and nitrates.

PLANNING OF EXPERIMENTS

The coolants were each run in the CAB brazed aluminum radiator cube immersion test to evaluate the effect of CAB brazed aluminum (CAB Al) on pH stability, additive consumption, ammonia formation, and corrosion protection as determined in the ASTM D4340-10 test [24]. The CAB exposed coolants were then tested as recovered and with the inclusion of a novel additive chemistry package to study the effect of new components on the CAB Al surface and coolant performance. The same type and amount of new additives were evaluated in all the coolants of this study. The novel additive package was however not further optimized for each of the tested coolants. To exclude any possible effect of temperature exposure of the CAB Al immersion test, a blank determination was also included where the fluids were subjected to the same test conditions but without the presence of the actual CAB brazed material. The corrosion protection of the coolants, post-CAB Al immersion test, were compared with the performance of the fresh coolants in the ASTM D4340-10 test. At the end, the no-harm effect of the novel additive

technology on the general corrosion-protection behavior of these commercial coolants was checked using the ASTM D1384-05 glassware corrosion test [25].

Results and Discussion

EFFECT OF CAB BRAZED ALUMINUM ON THE PHYSICAL-CHEMICAL PROPERTIES OF COOLANTS—INFLUENCE OF NOVEL ADDITIVES

Tables 2, 3, and 4 show the results from the analysis of the tested coolant solutions in the CAB brazed aluminum radiator cube immersion test. Different pH change behavior was observed depending on the coolant additive technology that was used (Table 2). An important pH decrease was observed with OAT-coolant A and silicate-lobrid C in presence of CAB Al, a significant pH increase was measured for nitrite-molybdate-lobrid coolant B. The strong pH reductions with coolant A and C, not observed in the test without CAB Al, is probably the result of flux residue dissolving from the aluminum cubes into the coolants. The strong pH increase observed with coolant B resulted from the high nitrite consumption (Table 3) and the corresponding ammonia formation (Table 4), which only occurred when CAB brazed material was present. These changes in the coolant could be the result of an interaction of nitrite with a reactive aluminum surface. The presence of borate and phosphate buffers in the hybrid coolants D and E explains the high pH stability observed under those conditions. The addition of the novel additive technology resulted in a more stable pH behavior for different coolant formulations (Table 2).

TABLE 2 pH determination of coolants in the CAB brazed aluminum radiator cube immersion test and in the test without CAB Al material.

Coolant	With CAB Al pH			Without CAB Al pH ^a		
	Pre-Test	Post-Test	Δ^b	Pre-Test	Post-Test	Δ^b
A	8.6	7.7	−0.9	8.5	8.6	0.1
B	8.6	9.2	0.6	8.5	8.5	0.0
C	8.6	7.8	−0.8	8.5	8.1	−0.4
D	7.6	7.5	−0.1	7.6	7.6	0.0
E	7.9	7.9	0.0	8.0	8.0	0.0
Coolant + novel additives						
A + additives	8.6	8.3	−0.3	ND	ND	ND
B + additives	8.5	8.1	−0.4	ND	ND	ND
C + additives	8.6	7.9	−0.7	ND	ND	ND
D + additives	7.6	7.5	−0.1	ND	ND	ND
E + additives	8.0	7.7	−0.3	ND	ND	ND

Note: CAB Al cubes immersed in 50 % (vol./vol.) coolant dilution in deionized water, heated to 100°C for 10 days.

^aND, not determined.

^bpH variation of coolant post-test.

TABLE 3 Coolant additive concentration determined in the CAB brazed aluminum radiator cube immersion test and in the test without CAB Al material.

Coolant	Percentage Corrosion Inhibitor Remaining in Coolant Post-Test (%) ^a							
	OAT-Inhibitor	Cu-Inhibitor	MoO ₄ ²⁻	NO ₂ ⁻	NO ₃ ⁻	SiO ₃ ²⁻	B ₄ O ₇ ²⁻	PO ₄ ³⁻
With CAB Al								
A	100	100	NA	NA	NA	NA	NA	NA
B	100	98	97	32	NA	NA	NA	NA
C	100	100	NA	NA	NA	59	NA	NA
D	100	100	NA	93	100	81	100	NA
E	100	94	NA	NA	100	NA	NA	80
Without CAB Al								
A	ND	ND	NA	NA	NA	NA	NA	NA
B	ND	ND	100	90	NA	NA	NA	NA
C	ND	ND	NA	NA	NA	98	NA	NA
D	ND	ND	NA	91	100	100	100	NA
E	ND	ND	NA	NA	100	NA	NA	74
With CAB Al								
A + additives	100	100	NA	NA	NA	NA	NA	NA
B + additives	100	98	100	86	NA	NA	NA	NA
C + additives	100	96	NA	NA	NA	90	NA	NA
D + additives	100	96	NA	91	100	85	100	NA
E + additives	100	94	NA	NA	100	NA	NA	80

Note: CAB Al cubes immersed in 50 % (vol./vol.) coolant dilution in deionized water, heated to 100°C for 10 days.

^aND, not determined; NA, not applicable.

Results show that the previous *pH* decrease with coolant A was significantly reduced in presence of these additives. Coolant B no longer showed an important *pH* increase, instead a limited *pH* decrease was measured. For coolants C, D, and E the effect of the addition of the novel additives on *pH* was almost negligible. The change in *pH* behavior for coolant A and B could be explained by the fast aluminum passivation properties of the novel additive chemistry. The reaction for coolant A was a more stable *pH* and for coolant B, an inhibition of the nitrite–aluminum interaction, which explains the much lower nitrite consumption (Table 3) and corresponding reduction in ammonia formation (Table 4).

An important change in nitrite concentration was observed after coolant B was subjected to the CAB Al test. As discussed, this consumption was likely because of the interaction between nitrite and the activated aluminum surface. The molybdate concentration in coolant B remained almost unchanged. Next to the important *pH* reduction, lobrid C showed significantly higher silicate consumption (41 %) (Table 3). Silicate consumption (19 %) in coolant D is much lower than with silicate-lobrid coolant C. The borate, nitrate, and nitrite content remained relatively

TABLE 4 Coolant contaminations determined in the CAB brazed aluminum radiator cube immersion test.

Coolant	Concentration Contaminants Determined in 50 % (vol./vol.) Coolant Dilutions Post-Test, mg/kg ^a				
	Al	Fluorides	NH ₃	Glycolates	Formates
With CAB Al					
A	<1	19	NA	5	12
B	3	56	78	50	10
C	7	38	NA	<1	<1
D	1	42	6	45	9
E	<1	34	NA	<1	<1
With CAB Al					
A + additives	ND	52	NA	ND	ND
B + additives	ND	43	34	ND	ND
C + additives	ND	31	NA	ND	ND
D + additives	ND	44	4	ND	ND
E + additives	ND	50	NA	ND	ND

Note: CAB Al cubes immersed in 50 % (vol./vol.) coolant dilution in deionized water, heated to 100°C for 10 days.

^aND, not determined; NA, not applicable.

stable (Table 3). The more stable nitrite concentration in comparison with Coolant B indicates that the nitrite reaction and corresponding pH increase in presence of CAB Al varies depending on the coolant additive technology. The phosphate reduction (20 %), measured in coolant E cannot be attributed to the effect of the CAB Al, as a similar reduction was observed when cubes were not present. None of the organic acid inhibited coolants exhibited a reduction in the corrosion inhibition packages. The addition of the novel additive package had a significant effect on the inhibitor depletion rates in the CAB Al immersion test. Not only did it eliminate the nitrite consumption observed with coolant B, but also reduced silicate consumption for coolant C (Table 3), and is an indication of the enhancing aluminum passivation properties of these new additives.

Contaminants resulting from coolants exposed to CAB brazed aluminum material were aluminum, fluorides, and the glycol degradation acids, glycolic and formic acid (Table 4). For nitrite-containing coolants, ammonia was also detected. Measurement of fluoride concentrations allowed the evaluation of coolant technology on the solubility of the flux residue, the only fluoride source under these test conditions. Although only low fluoride levels were measured in all coolants, the lowest amount is found in OAT-coolant A and somewhat higher values in the lobrid and hybrid technologies. The results of the fluoride analysis show that the novel inhibitor package had no significant influence on the release of fluorides in the coolant liquids. Aluminum, originating from flux residue or aluminum corrosion, was

found in coolant B, C, and D. Ammonia formation was observed in the nitrite-containing coolants B and D, with the highest amount in coolant B being in line with the strong *pH* increase and nitrite reduction observed with this coolant technology. The formation of glycol degradation acids (glycolic and formic acids) in all coolants remained very limited under these test conditions and, as such, cannot be the explanation for the important *pH* decreases measured for coolants A and C.

Some of the physical-chemical property changes in the evaluated coolants can be attributed to the effect of the CAB brazed aluminum cubes. These changes, including the strong nitrite depletion reaction and *pH* increase with nitrite-containing coolants, the important consumption of silicate in some formulations and the presence of fluorides and aluminum in coolant solutions, were also observed in light-duty and heavy-duty vehicles where CAB brazed aluminum heat exchangers have been used [19–21]. This demonstrates that the described test method is able to simulate the field observations.

EFFECT OF CAB BRAZED ALUMINUM ON THE ALUMINUM CORROSION-PROTECTION PROPERTIES OF COOLANTS—INFLUENCE OF NOVEL ADDITIVES

The coolant corrosion-protection levels after the CAB brazed aluminum radiator cube immersion test, with and without the use of the new additive chemistry, is reported in Figs. 2 and 3. Figure 2 shows the aluminum corrosion rates obtained with the different fresh coolant technologies in the ASTM D4340 [24] corrosion

FIG. 2 Test results of coolants in corrosion testing according to ASTM D4340-10 [24] on fresh coolants A–E and post-CAB brazed aluminum radiator cube immersion test (on 25 % vol./vol. coolant dilutions with 100 ppm chloride ions).

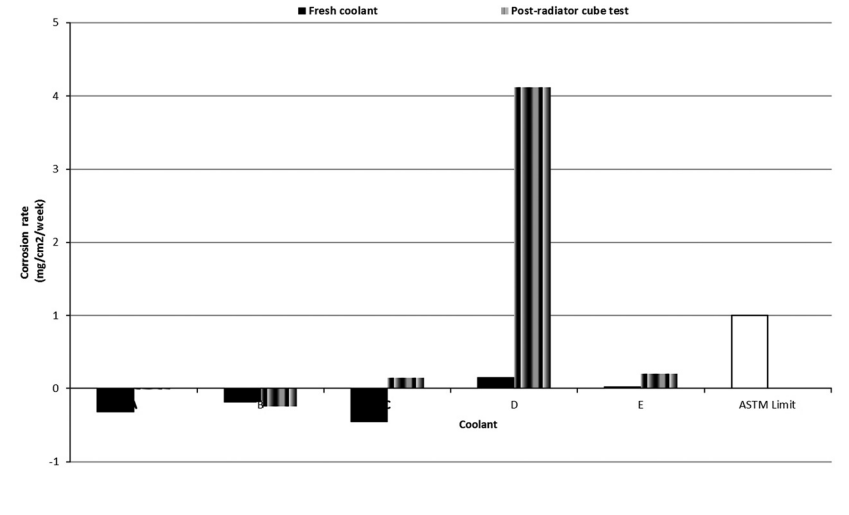
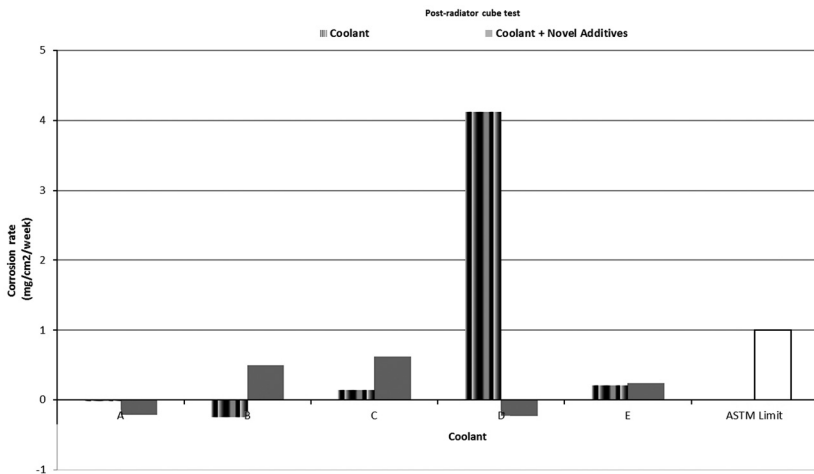


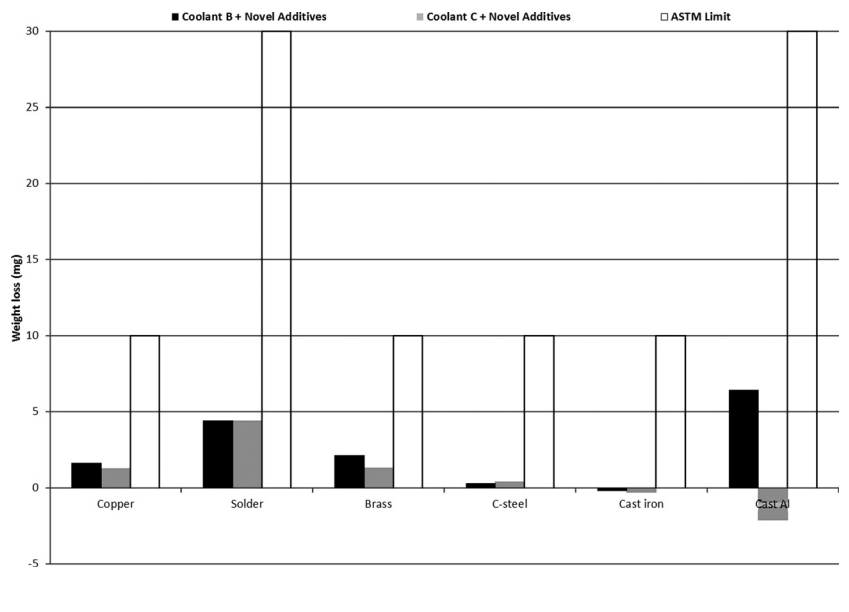
FIG. 3 Test results of coolants in corrosion testing according ASTM D4340-10 [24] on coolants A-E and on coolants A-E with addition of novel additives post-CAB brazed aluminum radiator cube immersion test.



test and a comparison with the results of coolants post-radiator cube immersion test. Results show that effective corrosion-protection performance is obtained with the fresh coolants A-E, meeting the corrosion rate limit put forward in the standard specification ASTM D3306-11 (maximum $1 \text{ mg/cm}^2/\text{week}$) [30]. After the radiator cube immersion test, only the hybrid coolant D showed a significant reduction in corrosion-protection performance, with a corrosion rate much higher than $1 \text{ mg/cm}^2/\text{week}$. In the other coolants, the change in corrosion-protection performance was limited. The results indicate that despite the high pH stability of coolant D (Table 2) and reasonably stable additive concentrations post-radiator cube immersion test (Table 3); the stability and corrosion-protection performance of the additive technology was strongly influenced. Although coolant A was undergoing a larger change in pH and coolants B and C showed a more significant reduction in nitrite and silicate concentration after being in contact with CAB brazed aluminum, the corrosion-protection performance of these coolants toward aluminum remained much more stable.

Figure 3 shows a comparison of the results obtained in this corrosion test on coolants A-E and of the coolants with the novel additive technology, both after being treated in the radiator cube immersion test. The results show that the corrosion-protection properties for coolant D, with the novel additive technology, which showed an important drop in corrosion-protection performance post-immersion test for the sample without the novel additive technology, were maintained at the level of the fresh coolant. This effect is likely caused by the extra

FIG. 4 Test results of fresh coolant B and coolant C with addition of novel additives in the glassware corrosion test according ASTM D1384-05 [25].



aluminum passivation properties of the adapted chemistry. Whereas almost no effect of the new additives toward corrosion protection was observed with coolant A and E, somewhat higher corrosion rates were obtained with coolant B and C however still within the ASTM specification limit according ASTM D3306-11 [30]. This change in performance can be explained by the potential minor destabilization of the existing additive packages in coolants B and C under the applied test conditions caused by addition of the new additives. Further optimization of the additive package would be required to minimize this effect.

NONE-HARM EFFECT OF THE ADDITION OF THE NOVEL ADDITIVE PACKAGE

To validate the none-harm effect of the novel additive package on the coolants general corrosion-protection behavior, the selected coolants, with the new additives were also validated in the corrosion test according to ASTM D1384-05 [25]. This approach ensures that the novel additive package has no negative effect on the corrosion protection of the multiple metals used in the glassware test. Coolant B and C, showing significant changes in physical-chemical properties post-radiator immersion test, were selected for testing. Figure 4 shows the weight losses of the different metal coupons obtained after ASTM D1384 glassware corrosion test with fresh coolants B and C with the novel additives. Also included in the graph are the ASTM D3306-11 limits [30]. The results indicate that coolants B and C with

adapted additive package meet the ASTM D3306 limits and are able to provide efficient corrosion protection.

Conclusion

Test results confirm that the flux residue remaining on aluminum radiators from the brazing process are partly soluble in different coolant additive technologies and formulations and can result in changes in coolant properties and function.

Analysis of the coolant samples indicated that CAB brazed aluminum materials are able to influence the pH and stability of the coolant additives. Under the applied conditions, corrosion inhibitors like nitrites and silicates were the most susceptible to consumption, but the size of this effect largely depended on the combined additive package rather than on the presence of a single inhibitor. The described test method was able to simulate some of the coolants physical–chemical property changes that have been observed in the field. Further it was illustrated that the addition of novel additive chemistry, to some coolant technologies, was able to improve the pH stability in presence of CAB brazed aluminum material, being most pronounced for OAT-coolant A and the nitrite-molybdate-lobrid coolant B. The novel additive chemistry also reduced the consumption of inorganic corrosion inhibitors like nitrites and silicate. The results show that the new additives are a potential solution for these issues observed in the field.

Testing of the effect of CAB brazed aluminum material on the corrosion-protection performance of different coolant technologies toward aluminum, indicated that CAB brazed aluminum can influence the corrosion-protection behavior of coolants. The study also illustrated that despite the important changes in physical–chemical properties of some of the coolants, the aluminum corrosion protection was retained. The study has shown that the addition of novel additives to coolants can enhance additive stability and improves corrosion-protection properties that were affected by the CAB brazing process.

This work focused on the effects of CAB brazed aluminum on the corrosion-protection performance of coolants toward aluminum. Initial none-harm experiments on the novel additive chemistry showed no antagonistic effect toward the different metallic materials used in cooling systems. Further investigations in the future could provide more in depth information about the effect toward other metallurgies.

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Shawn McGlothlin¹

Development of Glycerin (1,2,3-propanetriol)-based Antifreeze With Advanced Nitrite-Free Carboxylate Inhibitors for Light-, Medium-, and Heavy-Duty Engine Cooling Systems

Reference

McGlothlin, Shawn, "Development of Glycerin (1,2,3-propanetriol)-based Antifreeze With Advanced Nitrite-Free Carboxylate Inhibitors for Light-, Medium-, and Heavy-Duty Engine Cooling Systems," *Global Testing of Extended Service Engine Coolants and Related Fluids*, STP 1556, Edward R. Eaton, Ed., pp. 96-118, doi:10.1520/STP155620130065, ASTM International, West Conshohocken, PA 2014.²

ABSTRACT

In 1997 a need was identified for environmentally preferred products to be used in government, military, and commercial transportation companies. By 2007 technologies had been developed that enabled the cost-effective expansion of glycerin-based products to industrial heating and cooling (HVAC) applications, allowing the attractive environmental properties of aqueous glycerin solutions to be realized in HVAC applications. While researching and developing the HVAC market, engineers were surprised to find a dearth of standards, including automotive standards, against which to evaluate glycerin-based antifreeze. In the absence of specifications for glycerin-containing fluids, ASTM D6210 was selected as the benchmark because of its diverse selection of material compatibility and performance requirements. Prototype aqueous glycerin coolant chemistry was tested and found to conform to the performance and material compatibility requirements of ASTM D6210. A similar specification that describes the physical properties of glycerin was developed by ASTM Committee

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D15 on Engine Coolants and Related Fluids and published in 2011 as ASTM D7715. Laboratory testing followed, with successful vehicle fleet testing conducted over a two-year period. This paper documents the development of an extended-life carboxylate-inhibited glycerin-based engine coolant/antifreeze formulation and the glycerin specifications now published as ASTM D7714 and ASTM D7715. It further discusses the advantages of glycerin as opposed to the more conventional molecules ethylene glycol (1,2-ethanediol) and propylene glycol (1,2-propanediol).

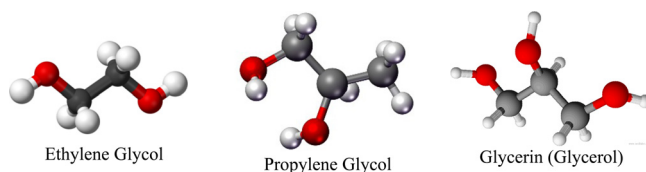
Keywords

glycerin, glycerol, engine coolant, antifreeze, extended service, heavy-duty, organic acid technology, OAT, carboxylate

Introduction

This paper documents the development of an extended-life carboxylate-inhibited glycerin-based engine coolant/antifreeze formulation and the glycerin specifications now published as ASTM D7714 [1] and ASTM D7715 [2]. It further discusses the advantages of glycerin as opposed to the more conventional molecules ethylene glycol (1,2-ethanediol) and propylene glycol (1,2-propanediol) [3] (Fig. 1).

FIG. 1 Chemical structures of ethylene glycol, propylene glycol, and glycerin.



Discussion

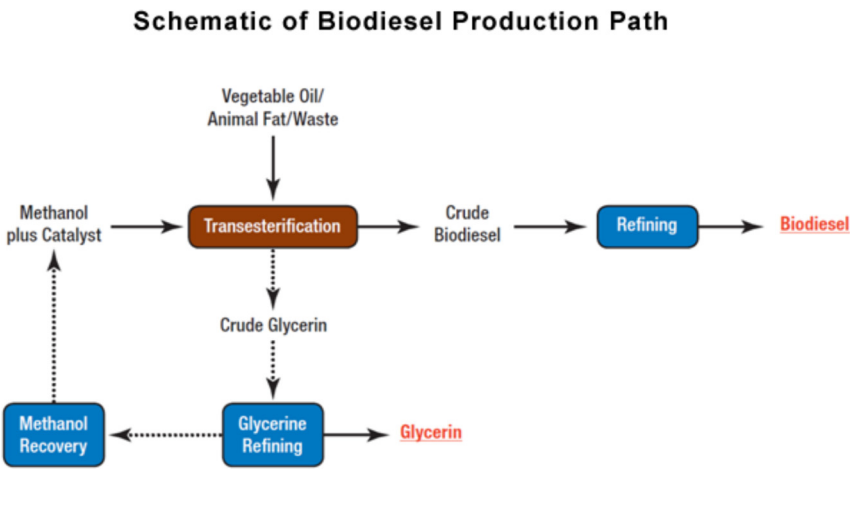
Since the close of the 20th century, government, military, and commercial transportation companies have sought “environmentally friendly” products to be used in automotive operations. By 2007 technologies had been developed that enabled the cost-effective expansion of glycerin-based products to industrial heating and cooling (HVAC) applications. Aqueous glycerin solution has attractive environmental properties for HVAC applications. While researching and developing the HVAC technology, engineers were surprised to find a dearth of standards, including automotive standards, against which to evaluate glycerin-based coolants. In the absence of specifications for glycerin-containing fluids, ASTM D6210 [4] was selected as the benchmark because of its fairly comprehensive and well-accepted protocol for testing material compatibility and performance requirements. Prototype corrosion-

inhibited aqueous glycerin coolant was tested and found to conform to the performance and material compatibility requirements of ASTM D6210. Subsequently, a similar specification that described the physical properties of glycerin and translated the ASTM D6210 specification for glycerin-based coolants was approved by ASTM Committee D15 on Engine Coolants and Related Fluids and published in 2011 as ASTM D7715 [2]. Laboratory testing was followed by successful vehicle fleet testing over a two-year period.

BACKGROUND

Biodiesel is produced from vegetable oils, yellow grease, and tallow. The production process converts oils and fats into chemicals called long-chain monoalkyl esters, or biodiesel. These chemicals are also referred to as fatty acid methyl esters, and the process is referred to as transesterification (Fig. 2). Roughly speaking, 100 lb of oil or fat are reacted with 10 lb of a short-chain alcohol (usually methanol) in the presence of a catalyst (usually sodium hydroxide [NaOH] or potassium hydroxide [KOH]) to form 100 lb of biodiesel and 10 lb of glycerin. The U.S. biodiesel industry reached a key milestone by producing more than 1×10^9 gal of fuel in 2011, according to year-end numbers released by the U.S. Environmental Protection Agency (EPA) in January 2012. The total volume of nearly 1.1×10^9 gal is a record for the industry and exceeded the target of 800 million gal required under the EPA’s Renewable Fuel Standard. The previous record for biodiesel production was about 690×10^6 gal in 2008 [5,6] (Fig. 2).

FIG. 2 Schematic of biodiesel production.



Orison was established in 1997 to offer environmentally friendly chemical alternatives to government, military, and industrial users. One of the avenues pursued

led to the development of glycerin-based antifreeze solutions as glycol replacements. These products have been successfully marketed to several industries, including the aircraft industry and the U.S. Air Force. By 2007 environmental restrictions and the development of new organic corrosion-inhibitor technologies had created an opportunity for Orison to expand its glycerin-based products into industrial HVAC applications.

Because the potential applications were so varied, Orison needed to incorporate a corrosion-inhibitor technology that provided broad material compatibility; corrosion protection for ferrous, cupric, and aluminum alloys; and extended service intervals and that would serve satisfactorily in virtually any application from static pressure testing to heavy-duty spark-ignited or compression engines. To minimize the environmental impact, Orison also disqualified some commonly used inorganic additives, including nitrites, nitrates, phosphates, and silicates.

At present, the target market is customers willing to pay a small premium to minimize environmental concerns and/or impact. These customers include industrial HVAC engineering contractors, government installations, and automotive fleet operations. Combining water, glycerin, and an organic extended-service inhibitor package allays environmental concerns by reducing maintenance requirements and dramatically extending the useful service life of the fluid. Further, glycerin-based fluids are not subject to the petroleum-market price instability that affects glycols, so glycerin is also a cost-effective replacement for ready-to-use glycol-containing fluids. Finally, compared to conventionally inhibited ethylene-glycol-containing coolants, organic-inhibited glycerin-containing coolants are dramatically less toxic. In fact, glycerin is listed by the U.S. Food and Drug Administration as “generally regarded as safe” as a food additive [7].

The next step was to find and test the fluid according to the current heat transfer standards. When we started researching standards for heat transfer fluids, we were surprised to find absolutely nothing; there were apparently no widely accepted standards by which we could evaluate a glycerin-based fluid. The problem with the industrial heat transfer systems is the diversity, even within specific uses. Over the past 75 years, company engineers have either designed the entire system in-house or tailor-made a system incorporating pieces or parts from various sources. Because many of the systems are of the “invented here” type, the materials used are not uniform across the various applications. Therefore, it was necessary to be able to test compatibility and protection on many different materials.

In the absence of specifications for glycerin-containing and/or heat transfer fluids, ASTM D6210 [4] was selected as the benchmark because of its diverse selection of material compatibility and performance requirements. It was concluded that the harshest environment for a glycerin-based fluid would possibly be in an engine-related setup. Although ASTM D6210 is a specification for glycol-based fluids, it offers a diverse selection of material compatibility and well-defined performance requirements.

In 2009 glycerin coolant was tested according to ASTM D6210. The fluid originally tested was closer to a 60 % glycerin blend and had a freeze point of -42°F

and a boiling point of 231°F. The results were even better than expected, showing good compatibility, excellent corrosion and scale protection, and a score of 10 on a pump rating. Based on the analytical success, the next goal was to secure a private fleet to participate in a “real world” fleet test.

The fleet test began in February 2010 and concluded in April 2012. It included five units: four heavy-duty trucks (one was a control) in the Chicago area and one light- to medium-duty truck in Texas. Engines represented were Cummins and Mack. We included the light/medium-duty vehicle, which was a Cummins 5.7 HEMI, because it offered the following:

- (1) a location with vastly different weather conditions,
- (2) smaller cooling system components (i.e., the pump), and
- (3) spark ignition.

None of the test vehicles were new. The least amount of miles was on the medium-duty truck, with just over 53 000, compared to 343 000 for the heavy-duty vehicles.

Our fleet test parameters were structured to make the testing process as easy as possible for the fleet operator. They broke down into three simple instructions:

- (1) flush the cooling system of each vehicle and refill with glycerin coolant,
- (2) top off with glycerin coolant only—no other products at all go into the system, and
- (3) samples of the fluids are to be taken as close to quarterly as possible.

By the end of the test, one truck had accumulated over 200 000 miles, and the other three glycerin coolant test units had driven between 50 000 and 70 000 miles. There were no problems experienced; in fact, the most difficult thing was getting the samples on a timely basis from the fleet operator.

The original fluid was designed to be a *pH*-neutral (approximately 7.0) product, and we started our fleet test prior to the adoption of 7.5 as a minimum *pH* in ASTM D7714 and ASTM D7715. (This *pH* was selected to conform to existing ASTM specifications for glycol-based fluids. In the future, as more experience is accumulated, a lower *pH* may be permissible for glycerin-based fluids.) Therefore, the beginning average *pH* value of the fleet test, 7.21, is lower than the fluid subsequently tested for compliance with ASTM D7714 and ASTM D7715. Researchers expected that the *pH* would drop; the question was, “How far?” Further, they sought to learn whether the inhibitor package would provide the required protection at the lower *pH* levels. The final *pH* values resulted in a fleet average of 6.36. The *pH* drop happened fairly quickly; all the vehicles were showing a *pH* of approximately 6.5 by the third month, after which time the levels stabilized.

The data on the age and wear indicators remained fairly constant with the exception of the notable increases in formate and glycolate. Other than that, only iron had any noteworthy increase in its average (Table 1).

The test averages for azoles and carboxylates present a stable picture. Records document reductions in benzoate and 2-ethylhexanoic acid concentrations (Table 2). (Note that in this formulation, 2-ethylhexanoic acid was used as a *pH* buffer, not as a primary corrosion inhibitor.)

TABLE 1 Age and wear indicators.

	Fleet Average	
	Before	After
Aluminum, $\mu\text{g/g}$	0.0	2.6
Calcium, $\mu\text{g/g}$	7.6	9.0
Chloride, mg/l	22	25
Copper, $\mu\text{g/g}$	0.9	0.1
Formate, mg/l	0.0	498
Glycolate, mg/l	203	805
Iron, $\mu\text{g/g}$	0.0	9.1
Magnesium, mg/l	3.0	3.4
Lead, $\mu\text{g/g}$	0.0	0.4
Sulfate, $\mu\text{g/g}$	11.0	0.4
Zinc, $\mu\text{g/g}$	0.1	0.5

TABLE 2 Inhibitor behavior.

	Fleet Average	
	Before, mg/l	After, mg/l
Tolyltriazole	482	368
Benzoate	168	68
2-ethylhexanoic acid	2976	1691
Sebacic acid	537	376
Pimelic acid	849	1079
Suberic acid	202	280
Azelaic acid	716	430
Dodecanedioic acid	2976	2938

In 2011, ASTM [D15](#) Committee on Engine Coolants and Related Fluids published ASTM [D7715](#) [2]. This specification mirrors ASTM [D6210](#) [4] in compatibility and corrosion-inhibition performance requirements but reflects the physical properties of glycerin rather than glycols. The glycerin coolant completed re-testing according to ASTM [D7715](#) in January 2012.

The glycerin coolant tested is a ready-to-use blend of <60 % glycerin with a polycarboxylate inhibitor package at 4.0 %. [Table 2](#) shows typical concentrations of the commonly analyzed organics.

QUALIFICATION OF GLYCERIN COOLANT ACCORDING TO ASTM [D7714](#) AND ASTM [D7715](#) ENGINE COOLANT SPECIFICATIONS

The glycerin coolant has been subjected to standard ASTM testing twice. The first prototype coolant passed all of the performance tests but fell outside of the accepted

physical properties, as it was tested before the adoption of ASTM D7714 and ASTM D7715. After ASTM Committee D15 on Engine Coolants and Related Fluids published ASTM D7714 and ASTM D7715, the formulation was adjusted to comply with the physical characteristic requirements and re-tested. The results of the second test are reported here.

Review of the Testing Protocols

ASTM D7715 covers the requirements for fully formulated glycerin-based coolants for cooling systems of heavy-duty engines. ASTM D7714 covers the requirements for glycerin-based coolants for cooling systems of light- and medium-duty engines and is a prerequisite to ASTM D7715. These data represent all of the tests performed to evaluate the performance of the candidate with regard to the published requirements. When concentrates are used at concentrations of 40 % to 60 % glycol by volume in water of suitable quality or when prediluted glycol-based engine coolants (50 vol. % minimum) are used without further dilution, they will function effectively during both winter and summer to provide protection against corrosion, cavitation, freezing, and boiling when they conform to these specifications.

This specification is intended to cover the requirements for engine coolants prepared from virgin or recycled glycerin. The coolants governed by this specification are categorized as follows:

- V-FF glycerin (1,2,3-propanetriol) base concentrate
- VI-FF glycerin (1,2,3-propanetriol) prediluted (50 vol. %)

Coolant concentrates adhering to this specification do not require any addition of supplemental coolant additive (SCA) until the first maintenance interval, when a maintenance dose of SCA may be required with some coolant formulations to continue protection in certain heavy-duty engine cooling systems, particularly those of the wet cylinder liner-in-block design. (Note: The coolant reported herein does not require the use of conventionally formulated SCA.) The coolant concentrate mixed with water or the prediluted coolant, when maintained in accordance with the engine and coolant manufacturers' recommendations and those on the product label, shall be suitable for use in a properly maintained cooling system in normal service for a minimum of two years.

The coolant concentrate or prediluted coolant additionally shall provide protection in operating engines against cavitation corrosion (also termed liner pitting) and against scaling of internal engine hot surfaces. Hot surfaces typically are within the engine head, head spacer, upper cylinder liner, or liquid-cooled exhaust manifold.

Laboratory data or in-service experience demonstrating a positive influence on reducing cavitation corrosion in an operating engine is required. In-service qualification tests may consist of single- or multiple-cylinder engine tests. At the discretion of the engine or vehicle manufacturer, such testing may be conducted in "loose engines" or in engines fully integrated into an application, such as a vehicle, a powerboat, or a stationary power source. At least one such test has been developed. Several chemical compositions have been tested extensively by producers and users

and found to satisfactorily minimize cylinder liner cavitation in actual test engines. Coolants with either of the following two compositions are regarded as meeting the liner protection requirements of ASTM D7715 without the need for engine testing:

1. a minimum concentration of nitrite (as NO_2^-) of 1200 ppm in 50 vol. % prediluted coolant, or
2. a minimum combined concentration of nitrite (as NO_2^-) plus molybdate (as MoO_4^{2-}) of 780 ppm in 50 vol. % prediluted coolant. At least 300 ppm each of NO_2^- and MoO_4^{2-} must be present.

The above concentrations are doubled for coolant concentrates.

Under this specification, both concentrated and prediluted coolants must be formulated to minimize hot surface scaling deposits. Certain additives (polyacrylate and other types) minimize the deposition of calcium and magnesium compounds on heat rejecting surfaces. No specific chemical requirements for hot surface scaling and deposit resistance have been established at this time. A test procedure is under development and will be incorporated into the specification when ASTM approves a procedure. This report includes a report of antiscaling performance per the Cummins test method published in Cummins Coolant Specification 14603 [8]. This is the test method that is under consideration for adoption as an ASTM test method.

ASTM D7714 and ASTM D7715 include requirements for physical and chemical tests [1,2] (Tables 3 and 4 [22]).

TABLE 3 ASTM D7714 [1] physical and chemical tests.

Property	Glycerin, Concentrate	Glycerin, Prediluted	Test Method Used
Relative density, 15.5/15.5°C (60/60°F)	1.249–1.265	1.130 min.	ASTM D1122 [9]
Relative density, 25/25°C (77/77°F)	1.252–1.262	1.127 min.	ASTM D5931 [10]
Freezing point, °C (°F)	–27.0 (–16.6) max. 50 % in de-ionized water	–27.0 (–16.6) max. as supplied	ASTM D1177 [11], ASTM D6660 [12]
Boiling point, °C (°F) ^a	106°C (223°F) min.	106°C (223°F) min.	ASTM D1120 [13]
Ash content, mass %	5 max.	2.5 max.	ASTM D1119 [14]
pH, 50 vol. % in de-ionized water (undiluted)	7.5–11.0	7.5–11.0	ASTM D1287 [15]
Chloride, µg/g	25 max.	25 max.	ASTM D3634 [16], ASTM D5827 [17]
Water, mass %	5 max.	N/A	ASTM D1123 [18]
Reserve alkalinity, ml ^b	Report	Report	ASTM D1121 [19]
Effect on automotive finish	No effect	No effect	ASTM D1882 [20]

^aSome precipitate may be observed at the end of the test. This is not a cause for rejection.

^bValue as agreed upon between customer and supplier.

TABLE 4 ASTM D7714 [1] physical chemical tests.

Test Number and Description	Test Result
ASTM D1122 [9], relative density (aka specific gravity)	1.1637
ASTM D1177 [11], freeze point, °C (°F)	−39.4 (−39.0)
50 % with 50 % de-ionized water v/v	
ASTM D1120 [13], boiling point, °C (°F)	110 (230)
As received	
ASTM D1120 [13], boiling point, °C (°F)	N/A
50 % with 50 % de-ionized water v/v	
ASTM D1882 [20], auto finish effect	No effect
ASTM D1119 [14], ash content, mass %	0.5
ASTM D1287 [15], pH, 50 vol. % in distilled water	8.08
ASTM D3634 [16], chloride, µg/g	7
ASTM D1123 [18], water, mass %	37.4
ASTM D1121 [19], reserve alkalinity, ml	2.4
ASTM D1881 [21], foaming tendencies	65-ml volume
	1.6-s break time

ASTM D2809: CAVITATION CORROSION AND EROSION-CORROSION CHARACTERISTICS OF ALUMINUM PUMPS WITH ENGINE COOLANTS

ASTM D2809 [23] consists of pumping an aqueous coolant solution at 113°C (235°F) through a pressurized 103-kPa (15-psig) simulated automotive coolant system. An aluminum automotive water pump, driven at 4600 r/min by an electric motor, is used to pump the solution and serves as the object specimen in evaluation of the cavitation erosion-corrosion effect of the coolant under test. The pump is examined to determine the extent of cavitation erosion-corrosion damage and is rated according to the system given in Table 5.

This test method can be used to distinguish between coolants that contribute to cavitation corrosion and erosion corrosion of aluminum automotive water pumps and those that do not. It is not intended that a particular rating number determined from this test will be equivalent to a certain number of miles in a vehicle test; however, limited correlation between bench and field service tests has been observed with single-phase coolants. A field test under severe operating conditions should be conducted as the final test if the actual effect of the coolant on cavitation corrosion and erosion corrosion is to be appraised. It is also possible, with proper control of the test variables, to determine the effects of pump design, materials of construction, and pump operating conditions on cavitation.

TABLE 5 ASTM D2809 rating system [23].

10	No corrosion or erosion present. No metal loss. No change from original casting configuration. Staining permitted.
9	Minimal corrosion or erosion. Some rounding of sharp corners or light smoothing (or both) or polishing of working surfaces.
8	Light corrosion or erosion may be generalized on working surfaces. Dimensional change not to exceed 0.4 mm (0.016 in.).
7	Corrosion or erosion with dimensional change not to exceed 0.8 mm (0.031 in.). Random pitting to 0.8 mm permitted.
6	Corrosion or erosion with dimensional change not to exceed 0.8 mm. Depressions, grooves, clusters of pits, or scalloping (or more than one of these) within 0.8-mm dimensional change limit permitted.
5	Corrosion or erosion with dimensional change not to exceed 1.6 mm (0.063 in.). Small localized areas of metal removal in high-impingement regions or random pits to 1.6 mm permitted.
4	Corrosion or erosion with dimensional change not to exceed 1.6 mm. Small localized areas of metal removal in high-impingement regions, clusters of pits within 1.6 mm dimensional change. Random pits to 2.4 mm (332 in.) permitted.
3	Corrosion or erosion with dimensional change not to exceed 2.4 mm (0.094 in.). Depressions, grooves, clusters of pits, or scalloping (or more than one of these) permitted.
2	Corrosion or erosion with any dimensional change over 2.4 mm but short of pump case failure.
1	Pump case leaking due to corrosion or erosion.

ASTM D2809 Test Results

Tables 6 and 7 and Figs. 3 through 6 show the results of the test.

TABLE 6 Pump rating.

Pump Rating	Solution pH
8	Start: 7.62; end: 6.83
Light corrosion or erosion is generalized on working surfaces. Dimensional change does not exceed 0.4 mm (164 in.).	

Note: ASTM D7715 requires a pump rating of 8 or higher on a scale of 10 [2].

TABLE 7 Measurements.

	Area Number					
	1	2	3	4	5	6
1	0.08	0.08	0.05	0.08	0.07	0.12
2	0.08	0.08	0.06	0.08	0.07	0.13
3	0.09	0.08	0.06	0.10	0.08	0.12
Average	0.08	0.08	0.06	0.09	0.07	0.12

FIG. 3 ASTM D2809
pump (cover).

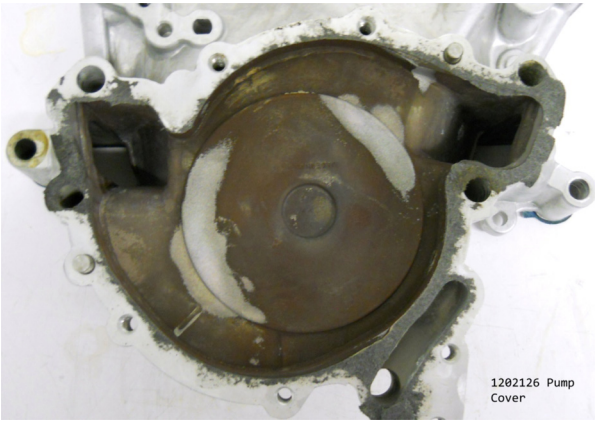


FIG. 4 ASTM D2809
pump (full).

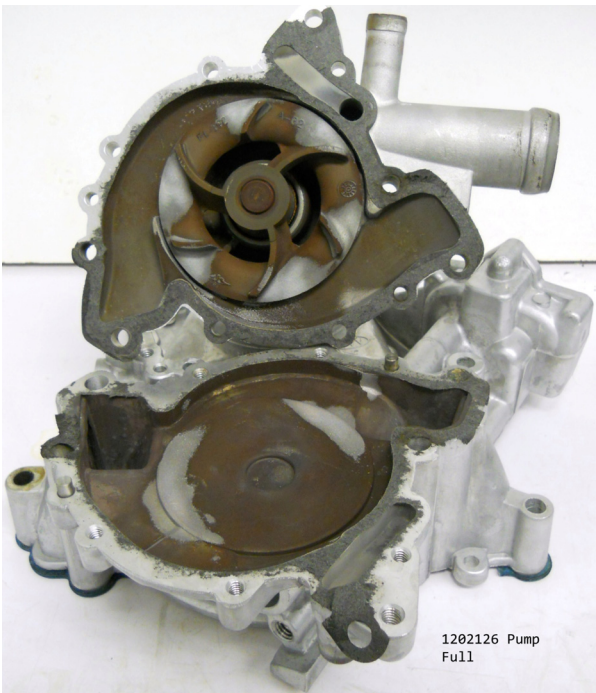


FIG. 5 ASTM D2809
pump (right).

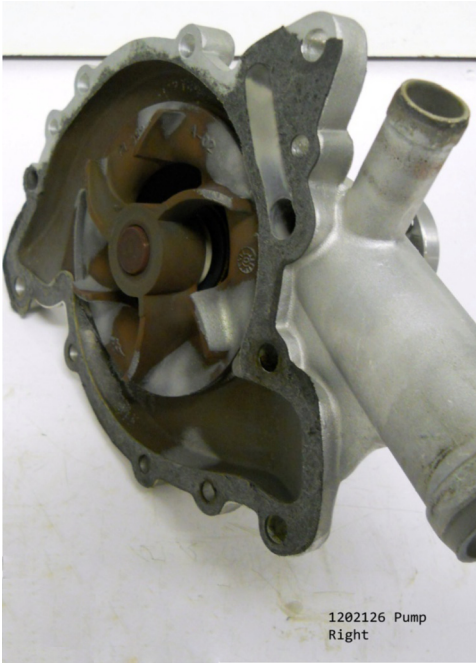
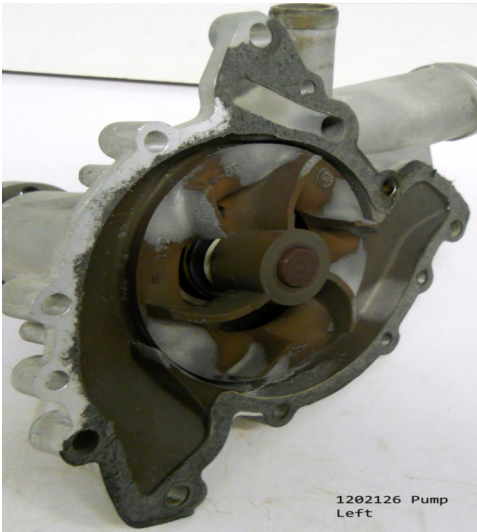


FIG. 6 ASTM D2809
pump (left).



ASTM D4340: CORROSION OF CAST ALUMINUM ALLOYS IN ENGINE COOLANTS UNDER HEAT-REJECTING CONDITIONS

This test method covers a laboratory screening procedure for evaluating the effectiveness of engine coolants in combating the corrosion of aluminum casting alloys under heat-transfer conditions that may be present in aluminum cylinder head engines [24].

In this test method, a heat flux is established through a cast aluminum alloy typical of those used for engine cylinder heads while the alloy is exposed to an engine coolant under a pressure of 193 kPa (28 psi). The temperature of the aluminum specimen is maintained at 135°C (275°F), and the test is continued for 1 week (168 h). The effectiveness of the coolant in preventing corrosion of the aluminum under heat-transfer conditions (hereinafter referred to as heat-transfer corrosion) is evaluated on the basis of the weight change of the test specimen. Table 8 shows the results of this test.

TABLE 8 ASTM D4340 [24] test results.

	Run 1	Run 2	Average
Weight loss, mg/cm ² /week	0.21	0.07	0.14
pH after	8.52	8.51	

Notes: ASTM places the maximum corrosion rate at 1.00 mg/cm² /wk.

ASTM D1384: CORROSION TEST FOR ENGINE COOLANTS IN GLASSWARE

This test method covers a simple beaker-based procedure for evaluating the effects of engine coolants on metal specimens under controlled laboratory conditions [25]. In this test, specimens of metals typical of those present in engine cooling systems are totally immersed in aerated engine coolant solutions prepared with corrosive salts for 336 h at 88°C (190°F). The corrosion-inhibition properties of the test solution are evaluated on the basis of the weight changes experienced by the specimens. Each test is run in triplicate, and the average weight change is determined for each metal. This test method will generally distinguish between coolants that are definitely deleterious from a corrosion standpoint and those that are suitable for further evaluation. However, the results of this test method cannot stand alone as evidence of satisfactory corrosion inhibition. Only more comprehensive bench, dynamometer, and field tests can determine the actual service value of an engine coolant formulation.

Automobile manufacturers have accepted the specimens prescribed by this test method, but their compositions might not be the same as those of alloys currently used for engine cooling system components. Therefore, specimens other than those designated in this test method may be used with mutual agreement of the parties

involved. Test specimens of the following metals representative of cooling system metals, 1 in. by 2 in. in size, were used:

Steel, UNS G10200 (SAE 1020). The chemical composition of the carbon steel used was as follows: carbon, 0.17 % to 0.23 %; manganese, 0.30 % to 0.60 %; phosphorus, 0.040 % maximum; sulfur, 0.050 % maximum.

1. Copper, UNS C11000 (SAE CA110) or UNS C11300 (SAE CA113); cold-rolled.
2. Brass, UNS C26000 (SAE CA260).
3. Solder—a brass specimen coated with solder conforming to Alloy Grade 30 A (SAE 3 A).
4. Cast aluminum, conforming to alloy UNS A23190 (SAE 329).
5. Cast iron, conforming to alloy UNS F10007 (SAE G3500).

Tables 9 and 10 and Figs. 7 through 12 show the results of this test.

TABLE 9 ASTM D1384 [25] test results for specimen weight loss.

Specimen	Run 1	Run 2	Run 3	Average	Maximum
Copper (Cu), mg	0	0	1	0	10
Solder (70 % Pb), mg	1	2	2	2	30
Brass, mg	1	1	0	1	10
Steel, mg	0	0	0	0	10
Cast iron (Fe), mg	0	−1	0	0	10
Cast aluminum (Al), mg	5	10	0	1	30

TABLE 10 ASTM D1384 [25] test results for corrosion rates (calculated per JIS K2234 [26]).

Specimen	Run 1	Run 2	Run 3	Average
Copper (Cu), mg/cm ²	0.01	0.02	0.02	0.02
Solder (70 % Pb), mg/cm ²	0.05	0.07	0.06	0.06
Brass, mg/cm ²	0.02	0.03	0.02	0.02
Steel, mg/cm ²	0.00	0.01	0.00	0.00
Cast iron (Fe), mg/cm ²	−0.01	−0.02	−0.01	−0.01
Cast aluminum (Al), mg/cm ²	0.17	0.33	0.01	0.17

FIG. 7 ASTM D1384 metal specimens (copper).

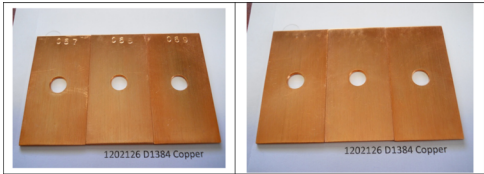


FIG. 8 ASTM D1384 metal specimens (solder).



FIG. 9 ASTM D1384 metal specimens (brass).

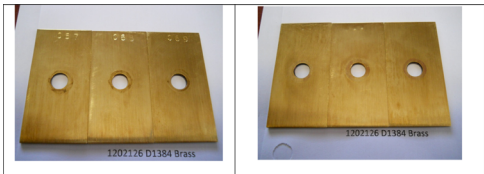


FIG. 10 ASTM D1384 metal specimens (steel).



FIG. 11 ASTM D1384 metal specimens (cast iron).



FIG. 12 ASTM D1384 metal specimens (aluminum).



ASTM D2570: SIMULATED SERVICE CORROSION TESTING OF ENGINE COOLANTS

This test method evaluates the effect of a circulating engine coolant on metal test specimens and automotive cooling system components under controlled, essentially isothermal laboratory conditions [27]. This test method specifies the test material, cooling system components, type of coolant, and coolant flow conditions that are considered typical in current automotive use. An engine coolant is circulated for 1064 h at 190°F (88°C) in a flow loop consisting of a metal reservoir, an automotive coolant pump, an automotive radiator, and connecting rubber hoses. Test specimens representative of engine cooling system metals are mounted inside the reservoir, which simulates an engine cylinder block. At the end of the test period, the corrosion-inhibiting properties of the coolant are determined by measuring the mass losses of the test specimens and through visual examination of the interior surfaces of the components. This test method, by virtue of its closer approach to engine cooling system conditions, provides better evaluation and selective screening of engine coolants than is possible from glassware testing (ASTM D1384 [25]). The improvement is achieved through controlled circulation of the coolant, the use of automotive cooling system components, and a greater ratio of metal surface area to coolant volume. Although this test method provides improved discrimination, it

cannot conclusively predict satisfactory corrosion inhibition and service life. If greater assurance of satisfactory performance is desired, it should be obtained from full-scale engine tests and from field testing in actual service. The same coupons used in ASTM D1384 are also used in this test.

Tables 11 through 13 and Figs. 13 through 22 show the results of this test, including the following:

- Metal corrosion coupons, front and reverse
- Water pump from test rig (post-test)
- Hose specimens
- Radiator sections

TABLE 11 ASTM D2570 [27] test results for specimen weight loss.

Specimen	Run 1	Run 2	Run 3	Average	Maximum
Copper (Cu), mg	2	2	2	2	20
Solder (70 % Pb), mg	9	8	8	9	60
Brass, mg	2	2	2	2	20
Steel, mg	1	1	1	1	20
Cast iron (Fe), mg	1	0	0	0	20
Cast aluminum (Al), mg	−2	−1	−2	−2	60

TABLE 12 ASTM D2570 [27] test results for corrosion rates (calculated per JIS K2234 [26]).

Specimen	Run 1	Run 2	Run 3	Average
Copper (Cu), mg/cm ²	0.08	0.08	0.07	0.07
Solder (70 % Pb), mg/cm ²	0.33	0.29	0.30	0.31
Brass, mg/cm ²	0.06	0.07	0.07	0.07
Steel, mg/cm ²	0.02	0.03	0.03	0.02
Cast iron (Fe), mg/cm ²	0.03	−0.01	0.01	0.01
Cast aluminum (Al), mg/cm ²	−0.06	−0.04	−0.05	−0.05

TABLE 13 pH and Reserve Alkalinity.

pH	Pre-test	7.62	Post-test	6.34
RA	Pre-test	1.9	Post-test	1.2

FIG. 13 ASTM D2570 metal specimens (copper).



FIG. 14 ASTM D2570 metal specimens (solder).



FIG. 15 ASTM D2570 metal specimens (brass).



FIG. 16 ASTM D2570 metal specimens (steel).

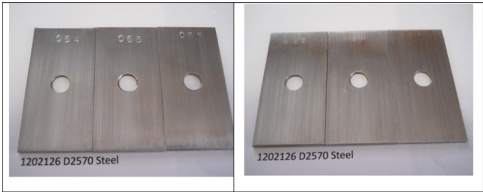


FIG. 17 ASTM D2570 metal specimens (cast iron).



FIG. 18 ASTM D2570 metal specimens (cast aluminum).

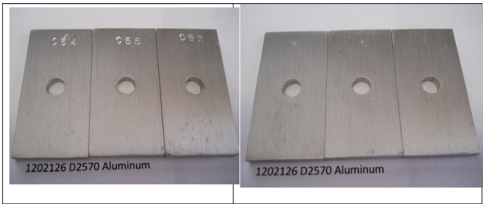


FIG. 19 Water pump (front).

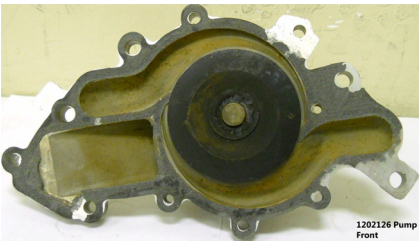


FIG. 20 Water pump
(cover).

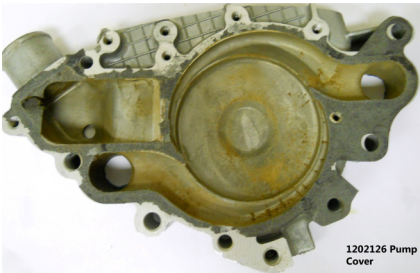


FIG. 21 Hose section
(post-test).

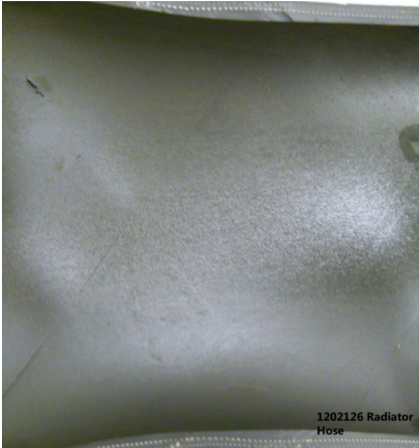
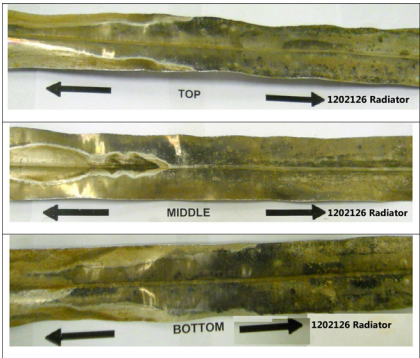


FIG. 22 Radiator tube
sections.



SCALING RESISTANCE OF ENGINE COOLANTS ON HOT STEEL SURFACES

This test method circulates coolant at 190°F past a stainless steel heater rod that is heated to 400°F for 96 h. The test fluid may be engineered to contain hard water minerals or other hot surface depositing species. At the conclusion of the 96-h exposure the heater rod is removed and dried. The weight of deposit is determined by comparing the weight of the prepared rod before exposure and after.

Development of this test method is published as “Scale and Deposits in High Heat Rejecting Engines” [28]. Table 14 shows the results of this test.

Performance in this test is rated based on agreements between supplier and customer. There is not, as yet, any industry standard for pass/fail in hot surface scale testing (Fig. 23).

TABLE 14 Scaling test results.

Weight before Exposure, g	Weight after Exposure, g	Net Weight Change, g
299.213	299.363	0.15

FIG. 23 Hot Surface Scale Rig (HSSR) rod.



Summary

Engine coolant using glycerin as the antifreeze molecule has been successfully formulated and tested to meet ASTM light- and heavy-duty engine coolant specifications. The coolant is formulated using slow-depleting corrosion inhibitors to offer users the benefits of extended service intervals. The experience in the test vehicles was very satisfactory, confirming the expectations predicted by standard ASTM engine coolant laboratory tests.

The glycerin engine coolant satisfied both ASTM D7714 and ASTM D7715 engine coolant specifications for light- and heavy-duty engines, respectively. We predict that the coolant will be used with satisfactory results in both light- and heavy-duty engine cooling systems.

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NEW ENGINE COOLANT TESTING

STP 1556, 2014 / available online at www.astm.org / doi: 10.1520/STP155620130111

Edward R. Eaton, Jr.¹ and Elvis Duvnjak²

Extending the Corrosion of Heat-Rejecting Aluminum Surfaces Test for Developing and Evaluating Extended Service Interval Engine Coolant Formulations

Reference

Eaton, Edward R., Jr. and Duvnjak, Elvis, "Extending the Corrosion of Heat-Rejecting Aluminum Surfaces Test for Developing and Evaluating Extended Service Interval Engine Coolant Formulations," *Global Testing of Extended Service Engine Coolants and Related Fluids*, STP 1556, Edward R. Eaton, Ed., pp. 121-130, doi:10.1520/STP155620130111, ASTM International, West Conshohocken, PA 2014.³

ABSTRACT

An independent testing laboratory has received numerous orders for modifications to the ASTM [D4340](#) test method. These changes alter the time, temperature, and coolant concentration of the coolant sample in an effort to better understand the behavior of the coolant on heat-rejecting aluminum surfaces over extended periods of time. It is also possible to modify the corrosive challenges to the coolant by modifying the coolant mixture from the published method. This paper explores the possible value of using variations of ASTM [D4340](#), including variations published in global original equipment manufactures (OEM) and industry specifications.

Keywords

antifreeze, engine coolant, water pump, extended service coolant, compatibility, cavitation, engine, long-life coolant, testing, hybrid, organic acid, carboxylate

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³ASTM Symposium on *Global Testing of Extended Service Engine Coolants and Related Fluids* on May 23, 2013 in Indianapolis, IN.

Introduction

Perhaps the most widely used coolant-performance screening test is the venerable ASTM D4340 [1]. The test method document describes the test as follows.

SCOPE

This test method covers a laboratory screening procedure for evaluating the effectiveness of engine coolants in combating the corrosion of aluminum casting alloys under heat-transfer conditions that may be present in aluminum cylinder head engines (Fig. 1).

Summary of Test Method

In this test method, a heat flux is established through a cast aluminum alloy typical of that used for engine cylinder heads while exposed to an engine coolant under a pressure of 193 kPa (28 psi). The temperature of the aluminum specimen is maintained at 135°C (275°F), and the test is continued for 1 week (168 h). The effectiveness of the coolant in preventing corrosion of the aluminum under heat-transfer conditions (hereinafter referred to as heat-transfer corrosion) is evaluated on the basis of the weight change of the test specimen [1] (Figs. 2 and 3).

The coolant to be evaluated sits on top of the aluminum puck and is heated through it. A satisfactory result (per ASTM D3306 [2]) is achieved when the coolant protects the aluminum so that a corrosion rate of less than 1.00 mg/cm²/week is

FIG. 1 ASTM D4340 hockey-puck-shaped specimen.



FIG. 2 Array of ASTM D4340 test stands.



measured. Unsatisfactory performance is defined as a corrosion rate in excess of $1.00 \text{ mg/cm}^2/\text{week}$ or visible pitting and erosion of the aluminum, or both (Fig. 4).

The following factors should be considered when determining whether results are satisfactory or unsatisfactory based on ASTM D3306 [2] specifications:

1. At the end of the test, there may be visible corrosion and precipitated material in the coolant.
2. The calculation of the R value determines whether a corrosion rate exceeds $1.00 \text{ mg/cm}^2/\text{week}$.
3. The coolant may have changed visibly. It may be cloudy or have other dramatic appearance changes that indicate possible reactions, instability, or corrosion.
4. The aluminum specimens often manifest visible surface changes due to corrosion (Fig. 5).

The desired outcome after an ASTM D4340 test is for nothing to have changed.

1. The coolant appears “as new” with no precipitation (Fig. 6).
2. The aluminum specimen appears “as new” and there is little weight loss.
3. The pH change is small.

Existing Modifications to ASTM D4340 Already Published in the Literature

FORD WSS M97B44D (OAT) SPECIFICATION

Coolant, Organic Additive Technology, Concentrate, for Passenger Car and Light Truck

- Adds a requirement that ASTM D4340 testing be performed on the fluid after ASTM D2570 [3] simulated service testing.

FIG. 3 Some specimens after exposure.



- ASTM [D2570](#) testing is run at 44 % antifreeze in ASTM standard corrosive water.
- This is a logical extension of testing for ESI coolant formulations, as they are expected to be capable of protecting for much longer periods than pre-1995 formulations.

General Motors Global Coolant GMW3420

- The new GMW3420 specification [4] includes a very comprehensive matrix of testing for the protection of aluminum heat-rejecting surfaces by ASTM [D4340](#) ([Table 1](#)).
- These tests are far more exhaustive than was previously required, a reflection of the extensive use of aluminum in modern powertrain components.
- Provides a definition for compatibility with ASTM [D4340](#) testing.
- “Raises the bar” by reducing the pass/fail limit substantially relative to ASTM [D4340](#).

FIG. 4 Unsatisfactory example.



FIG. 5 Corrosion of aluminum specimen.



FIG. 6 Satisfactory test result: clear fluid, no deposit, no weight loss.



- Introduces a second testing environment—50 % concentrate in de-ionized water. This test has proven counterintuitively difficult to pass for some formulations.

Hyundai/Kia MS 591-08

- The Hyundai specification [5] reduces the antifreeze concentration to 20 % from 25 % (Table 2).
- Hyundai accepts no weight change of more than 0.30 mg/cm²/week, a 70 % tighter requirement.

Mazda-MES MN 121

- Mazda changes the weight loss standard to a weight change standard (± 1.0) [6].
- Mazda extends the test period from 168 h to 1000 h (no pass/fail limit specified at 1000 h).

Two trends can be observed in the OEM specification (Table 3):

TABLE 1 GM Global ASTM D4340 testing matrix.

Coolant Mix	Reference Section	Test Conditions	Maximum Corrosion Rate, mg/cm ² /Week	
			Water-Cleaned	Acid-Cleaned
Candidate	3.4	25 % concentrate, 100 ppm chloride	0.3	1.0
Candidate	3.4	50 % concentrate, de-ionized water	1.0	2.0
Candidate and approved 1:3	3.4.1	25 % concentrate, 100 ppm chloride	0.5	1.0
Candidate and approved 1:1	3.4.1	25 % concentrate, 100 ppm chloride	0.5	1.0
Candidate and approved 3:1	3.4.1	25 % concentrate, 100 ppm chloride	0.5	1.0

TABLE 2 Hyundai ASTM D4340 coolant testing.

Corrosion of Heat-Rejecting Surfaces (Section 4.16)		
	ASTM Standard	Hyundai/Kia
Coolant mixture	25 % concentrate	20 % concentrate
Corrosive salts	100 ppm chloride	100 ppm chloride
Maximum corrosion rate, mg/cm ² /week	1.00 maximum	±0.30

- Longer exposure periods for extended life coolants (ELC) formulations
- Reduced tolerance for corrosion weight loss

Flux Compatibility Test Modification

In late February 2010, an ASTM D15 Work Group convened to address a situation reported to occur in both light- and heavy-duty vehicles equipped with aluminum heat exchangers. Some end users have reported unsatisfactory durability of heat exchangers. Symptoms associated with the reports include the following:

- Ammonia odor from open cooling systems
- Leaks from heat exchangers resulting from corrosion or erosion
- Precipitates, especially of silicate

Preliminary investigations into the situation resulted in a probable-cause hypothesis of a negative chemical interaction between some coolants and fused flux left in the heat exchangers from the aluminum brazing process.

To address the problem, members of ASTM D15.21 Subcommittee on Extended Life Coolants have been developing test methods to evaluate the interaction of coolants, aluminum, and radiator flux materials. One of the methods under development is a simple modification of ASTM D4340. Research at a major North American OEM and their radiator supplier discovered that flux, a material used in the brazing

TABLE 3 Observations on OEM modifications to ASTM D4340.

Corrosion and Long-Term Corrosion of Heat-Rejecting Surfaces (Section 15.2)			
	ASTM Standard	Standard 168 h	Extended 1000 h
Coolant mixture	25 % concentrate	25 % concentrate	
Corrosive salts	100 ppm chloride	100 ppm chloride	
Maximum corrosion rate, mg/cm ² /week	1.00 maximum	±1.0	Report
Other parameters to report	pH before and after appearance	pH before and after, ΔpH, ΔReserve alkalinity (RA), appearance, precipitation	

of aluminum heat exchangers, may be left behind in the internal passages. Negative interactions with some engine coolant formulations are suspected of contributing to unsatisfactory cooling system durability.

The ASTM D4340 test described here draws its concentration from an OEM-reported measurement of 10 g (average) of residual fused flux (post-production flux) in radiators installed in systems with a 12-gal coolant capacity. Using that concentration as a model, a typical “in service” solution of 50 % prediluted engine coolant and fused flux (no other corrosive salts) is introduced into the ASTM D4340 test rig, which is otherwise prepared per the standard method. The objectives of this test are as follows:

- The flux test should be able to mimic what happens in the field. Silicate instability might not be the only issue. When flux is dissolved or dispersed from the inside of the radiator, several things can happen, especially with traditional or hybrid-based chemistry containing silicate.
- The test should ideally generate the following:
 - Extremely fast silicate depletion
 - Depletion of nitrite and, to some degree, nitrate
 - Formation of NH₄ and an increase in pH
 - Glycol level appears to be inversely proportional to flux compatibility

Figure 7 shows the results of testing with a known problematic coolant. The photo in Fig. 8 shows that the reaction begins very quickly.

A presentation by Solvay to the ASTM D15 committee provided evidence that the test method is reasonably modeling other investigations (Fig. 9). (Solvay manufactures much of the flux in question.)

FIG. 7 Flux compatibility of prediluted OEM heavy-duty fully formulated conventional coolant.

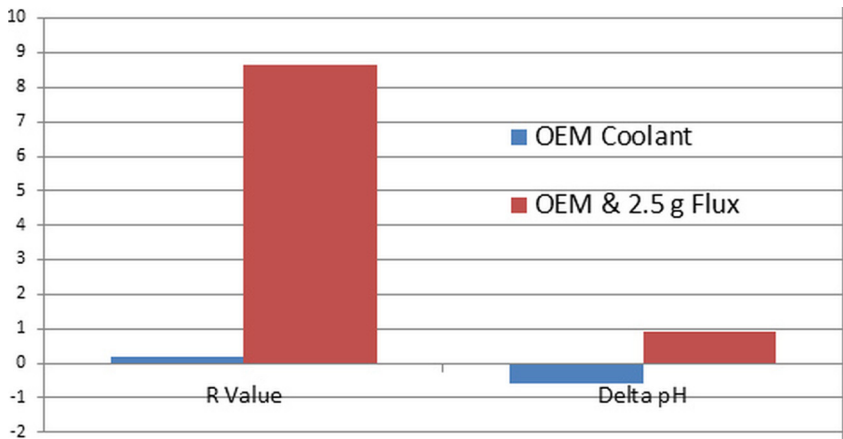
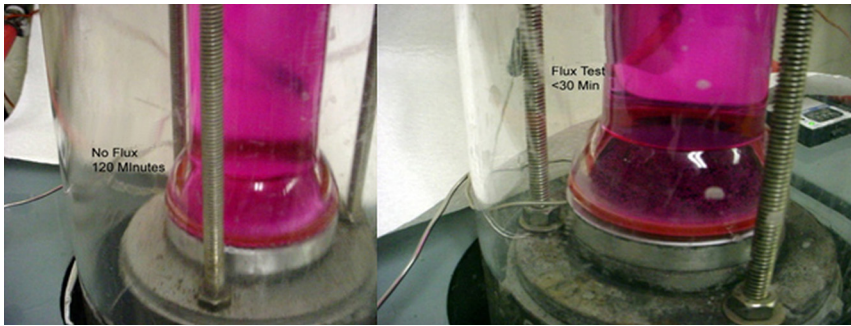


FIG. 8 Change in specimen appearance after 2 h.

STATUS OF THE ASTM D4340-STYLE FLUX INTERACTION MODIFICATION

A promising ASTM D4340-type flux-coolant interaction test method uses ASTM D4340 equipment to expose aluminum to prediluted (50 %) coolant with 10 g of fused flux per 12 gal of coolant (or another concentration specified by the requester) under standard ASTM 4340 test conditions. The usual observations of pH (in this case, before, after, and Δ pH), deposits, and R value are reported at the end of the test.

Amalgatech reported that the test was successful in differentiating between coolants that were observed to be compatible in the field and those that were not.

FIG. 9 Solvay test results reported to ASTM D15 committee.

Investigation of Interactions Between Silicate-Based Coolants and Brazing Fluxes



1. Interaction with flux powder – K-Al-F and K-Li-Al-F fluxes

Lab tests with powder (1g/l) in coolant/water (50/50 vol.)
Thermal cycling (one week) at 100°C / RT

Sample (1g/l)	pH	Si ppm	Al ppm	K ppm
Coolant (control sample)	7.9	116	0	172
NOCOLOK® post-braze Residue	7.7	12	20	453
NOCOLOK® Flux (as produced)	7.7	16	19	489
NOCOLOK® Li post-braze Residue	7.7	16	12	448
NOCOLOK® Li Flux (as produced)	7.7	12	18	468

↑
Silicon depletion

The use of ASTM [D4340](#) as a screening tool for the compatibility of coolants, aluminum, and fused aluminum potassium fluoride flux $[K_{(x)}AL_{(y)}F_{(z)}]$ has been demonstrated.

The test is in use for multiple vehicle and coolant manufacturers.

Consideration by the ASTM [D15](#) committee is in progress through efforts of an ASTM [D15.21](#) Work Group.

Summary

- ASTM [D4340](#) promises to be very useful for screening extended-life coolants.
- Modifications that include increases in the time of exposure are already specified by some vehicle OEMs.
- An effective adaptation to screen for coolant compatibility in the presence of fused potassium fluoride flux in aluminum heat exchangers has been developed and is in use.

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Extending the Corrosion in Glassware Test for Developing and Evaluating Extended Service Interval Engine Coolant Formulations

Reference

Eaton, Edward R. and Duvnjak, Elvis, "Extending the Corrosion in Glassware Test for Developing and Evaluating Extended Service Interval Engine Coolant Formulations," *Global Testing of Extended Service Engine Coolants and Related Fluids*, STP 1556, Edward R. Eaton, Ed., pp. 131–149, doi:10.1520/STP155620130075, ASTM International, West Conshohocken, PA 2014.²

ABSTRACT

An independent testing laboratory has received numerous orders for modifications to the ASTM D1384 "Corrosion in Glassware" standard test method. These requests alter the coupon metals, time, temperature, and coolant concentration of the coolant sample in an effort to better understand the behavior of the coolant on various metals employing glassware tests over extended periods of time. It is also possible to modify the corrosive challenges to the coolant by modifying the coolant mixture from the published ASTM method. This paper explores the possible value of using variations of ASTM D1384 including variations published in American and global OEM Standards and industry specifications such as Hyundai and JIS. It also explores the use of a coupon bundle that more closely approximates the metals in today's light-duty automotive systems. Some other changes include extended period and spaced interval options, different corrosive water formulas, and testing multiple antifreeze concentrations.

Keywords

antifreeze, engine coolant, corrosion, glassware testing, extended service, long life, flux, compatibility

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Introduction

The first corrosion in glassware test was developed in 1955 [1]. A typical cooling system in 1955 included a copper and brass radiator held together with lead tin solder. It contained cast iron blocks, cast aluminum water pump bodies, covers, and other steel components (Fig. 1). The test is run in triplicate with the test solution consisting of 33 % antifreeze and 67 % water; it is then finished with a corrosive water solution made up of a combination of 100 ppm each of chloride, sulfate, and bicarbonate. The test is run at 88°C (190 °F.) There are six metals in the current bundle: copper, solder, brass, steel, iron, and aluminum (Fig. 2).

The modern vehicle cooling systems represented today have many different characteristics that may or may not be similar to one another. It is the purpose of this paper to compile what direction the industry is going to adapt the current method to their needs and to share the ideas that have been presented to modernize the method as it stands.

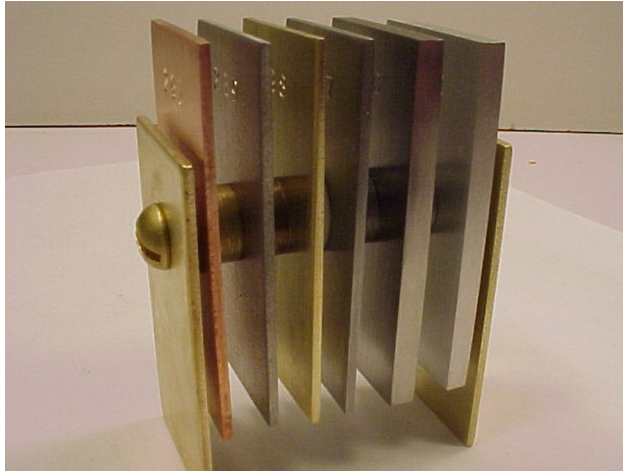
Alternatives

Some alternatives to the current ASTM D1384 [1] Corrosion Test for Engine Coolants in Glassware have shown interesting results. Some of the changes include tests run in duplicate [2], the test run in larger sets and harvested at different specified time periods (spaced interval testing), elevated temperature, different corrosive water formulations, extended exposure periods and different metals in the coupon bundles.

Cummins requires four variations of ASTM D1384 [3]:

FIG. 1 1955 DeSoto engine and cooling system.



FIG. 2 Typical corrosion coupon bundle.

- The Chrysler method [4] requires the addition of an isolated 3003 Al coupon added to the current coupon bundle, and in addition, the weight loss allowed on solder is tightened to 15 and 20 mg for aluminum.
- Next is a variation on the addition of 97 % lead solder in place of the standard solder the allowed weight loss for the 97 % solder is lowered to 20 mg.
- Each test is then also run under the same conditions with 70 % antifreeze

Electro-Motive Diesel (EMD) specification MI 1748 runs the standard ASTM D1384 with the addition of red brass to the coupon bundle (85 % Cu/15 % Zn). There is also an additional D1384 with red brass in hard water with total hardness 85–170 ppm, (standard ASTM D1384 corrosive salts are also present) (Table 1).

THE FORD MOTOR COMPANY METHODS WSS-M97B51-A1 (HYBRID) AND WSS-M97B44-D (OAT)

Compatibility with other coolants: the Ford methods contain a 50 % solution of the candidate coolant in ASTM Standard D1384 Corrosive Water (SCW) as well as a 50 % mixture of each current Ford approved coolant in SCW. They are covered and

TABLE 1 EMD requirements, corrosion in glassware.

Metal	D1384 Maximum Loss, mg / Specimen
Fe. Steel	5
Cu, Brass, Red Brass, Al, 70 % Solder	10

TABLE 2 GM requirements—corrosion in glassware.

Metal	D1384 Maximum Loss, mg / Specimen
Cu, Brass, Fe. Steel	10
Al, 70 % Solder	20
97 % Solder	Report

left alone to stand in room temperature and the absence of light for 48 h. The solutions that form any precipitate shall be tested according to the standard ASTM [D1384](#) procedure with the same weight loss limits imposed.

GENERAL MOTORS GMW3420 AND GM6277M METHODS

The method is run at the standard D1384 freeze point and at 50 %. High lead Solder (97 % Pb, 2.5 % Sn, and 0.5 % Ag) is also used in the coupon bundle ([Table 2](#)).

General corrosion compatibility with other coolants: the candidate engine coolant shall also meet the ASTM [D1384](#) requirements when tested with the following: 1:3, 1:1, and 3:1 volumetric mixtures with coolant approved to GM6277M/GMW3420 and any other coolant type as selected by the Coolant Committee.

HYUNDAI / KIA SPEC NO. MS 591-08; 4.14.1

Corrosion Method A shall conform to ASTM [D1384](#). The test is run at $98 \pm 2^{\circ}\text{C}$. Section 4.14.2 Corrosion Method B Shall conform to ASTM [D1384](#) except use the specified corrosive water in place of ASTM corrosive water.

Hyundai specified corrosive water can be prepared by dissolving the following amounts of reagents in 1 l of water ([Table 3](#)).

JIS K2234

The Japanese Industrial Standard follows ASTM [D1384](#) with the following exceptions: the antifreeze concentration will be 30, not 33 %. The laboratory reports change of mass as corrosion rate (mg/cm^2). The appearance of specimens and

TABLE 3 Hyundai corrosive water formulation.

Ion	Concentration, ppm	Salt Form	mg Per Liter
Cl^-	200	NaCl	318
SO_4^{2-}	200	Na_2SO_4	296
NO_3^-	45	NaNO_3	62
Fe^{3+}	0.3	$\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$	1.5
Cu^{2+}	1.0	$\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$	2.7
Zn^{2+}	5.0	ZnCl_2	10.4

TABLE 4 JIS K2234 requirements—corrosion in glassware.

Items				Class	
				Class 1	Class 2
Metal corrosion property 30 vol. % test solution 88 ± 2°C 336 ± 2 h	Metal test piece (specimen)	Change of mass mg/cm ²	Cast Aluminum	± 0.60	± 0.30
			Cast Iron	± 0.30	± 0.15
			Steel	± 0.30	± 0.15
			Brass	± 0.30	± 0.15
			Solder	± 0.60	± 0.30
			Copper	± 0.30	± 0.15
		Appearance	There shall be no visually noticeable corrosion on the test piece, excluding the part contacting with the spacer, but change in colour is permissible.		
	Properties of solution after test	Foaming property during test	No foam flooding out of the cooler.		
		pH value	6.5–11.0		
		Change in pH value	± 1.0		
		Liquid phase	No significant change of colour. No significant change liquid such as separation, or gel.		
			Amount of precipitation vol. %	0.5 % max.	

liquid phase (precipitation, color change, gel) should be reported after the test. The pH values should be reported before and after, and Δ pH. Report foaming of fluid, especially if the fluid over-foams (Table 4).

NAVISTAR BT-3 CORROSION TEST

This test should be tested in the same manner as ASTM D1384 with the following exceptions: run at 50 % antifreeze concentration (or as recommended by supplier for service concentration). Run the test for 2500 h exposure (104 days). Report the test data per ASTM D1384.

RENAULT 41-01-001

This test should be tested in the same manner as ASTM D1384 with the following exceptions: test at 20, 33, and 65 % antifreeze concentrations. Four aluminums will be tested: cast aluminum AC2B, Al 3003, Al 7072, and Al 4343. All results are reported in mg/cm².

VOLKSWAGEN

This test should be tested in the same manner as ASTM D1384 with the following exceptions: report Δ mass in g/m²; the loss must be < 3, except Al < 2, and with mass increase limited also < 1 except Al < 2.

A Major Effort by ASTM Committee D15 to Evolve the Glassware Test for Extended Service Coolants

ASTM subcommittee D15.06 on glassware tests conducted an interlaboratory study in June 2010. Six coolants were compared against the standard test method and a method resembling the Hyundai test method. Four of six volunteer laboratories were able to complete the project and submit data for review. The intent of this study was to learn if extending the D1384 from 14 to 30 days, increasing the test temperature 10°C, and using a more aggressive corrosive salt package would provide any data helpful to predicting the useful service life of a coolant candidate. In particular, it was hoped that the test would discriminate between coolants requiring replacement after one to two years and coolants capable of 5 or more years of service.

Experimental

In this test method, specimens of metals typical of those present in engine cooling systems were totally immersed in aerated engine coolant solutions for 336 h at 98°C (208°F). The corrosive salt package was changed to the more aggressive Korean formulation. Each test was run in triplicate, and the average weight change was determined for each metal. The capabilities of the coolant to protect metals tested were evaluated on the basis of the weight changes incurred by the specimens calculated and reported as mg/cm² (Fig. 3).

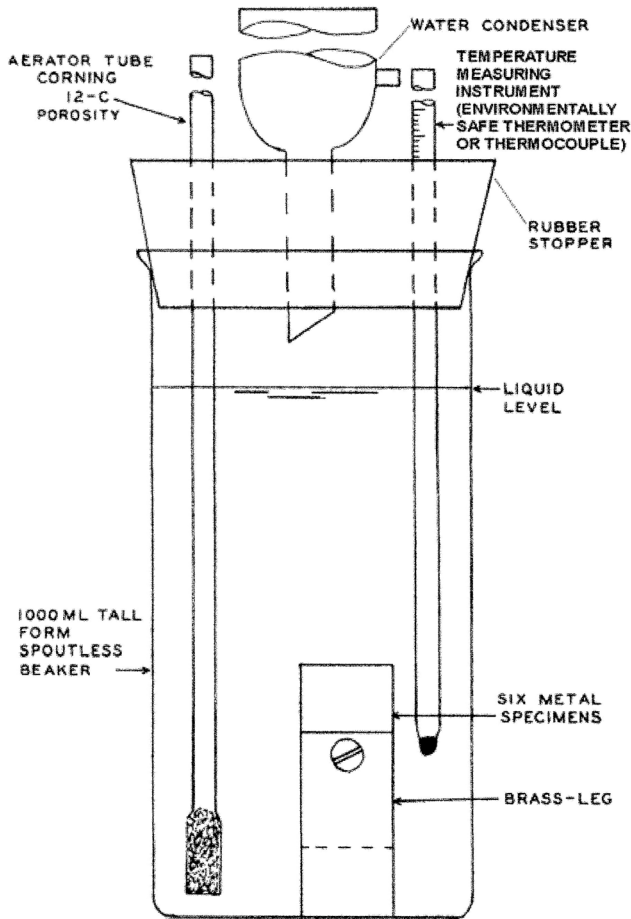
It was hypothesized that this test method would generally distinguish between coolants that were incapable of more than two years' service and those that are suitable for further evaluation as extended service intervals (5 or more years). This method is more severe than the current ASTM D1384. This method is similar to method defined in Hyundai MS 591-08. Even so, the results of this test method would not stand alone as evidence of satisfactory corrosion inhibition. As has always been the case, the actual service value of an engine coolant formulation can be determined only by continuing with more comprehensive simulated service, dynamometer, and field tests.

TEST METHOD

The D1384 "Corrosion in Glassware" apparatus, specifically:

Container—A 1 L, tall-form, spoutless beaker, made of heat-resistant glass, for containing the engine coolant solution and test specimens. The beaker shall be tightly closed with a No. 15 rubber stopper, having drill holes to accommodate a water condenser, an aerator tube, and a thermometer. Optionally, an all-glass apparatus may be used.

Condenser—A water condenser of the reflux, glass-tube type, having a 400-mm (16-in.) condenser jacket.

FIG. 3 Corrosion in glassware apparatus.

Aerator Tube—A gas-dispersion tube, porosity size 12-C, to ensure continuous aeration without plugging.

Temperature Measuring Instrument (Thermometer or Thermocouple)—An ASTM partial immersion temperature measuring instrument having a range from -20 to $+150^{\circ}\text{C}$ (0 to 302°F) and conforming to the requirements for thermometer 1C (1F), as prescribed in Specification E1 or thermocouple as summarized in ASTM Specification E230.

Heater—A constant-temperature bath containing a high-boiling liquid that is capable of giving continuous service with the specified temperature control. The size of the bath will be determined by the number of corrosion tests that are to be run concurrently.

METAL TEST SPECIMENS

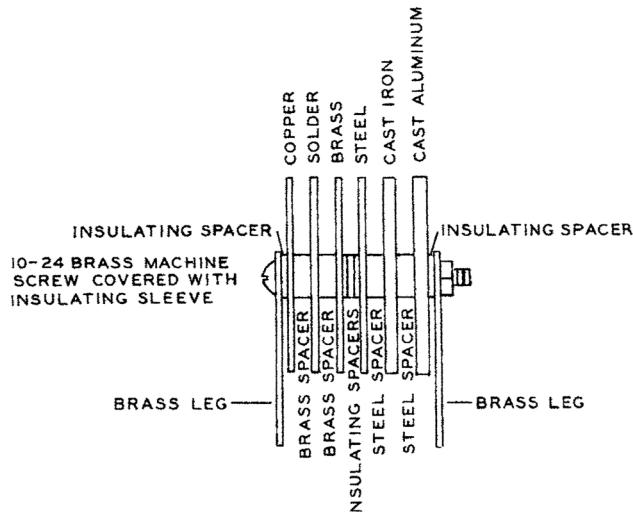
Note that the specimens prescribed in this test method have been accepted by automobile manufacturers; however, their composition may not be the same as that of alloys currently used for engine cooling system components. Therefore, specimens other than those designated in this test method may be used by mutual agreement of the parties involved.

Type—The following metal test specimens representative of cooling system metals shall be used:

1. *Steel*, UNS G10200 (SAE 1020),² or SPCC-B (JIS G3141) cut from 1.59-mm (1/16-in.) cold-rolled sheet stock to size 50.8 by 25.4 mm (2 by 1 in.). Chemical composition of the carbon steel is as follows: carbon, 0.17 to 0.23 %; manganese, 0.30 to 0.60 %; phosphorus, 0.040 % maximum; sulfur, 0.050 % maximum.
2. *Copper*, conforming to UNS C11000 (SAE CA110)⁸ or UNS C11300 (SAE CA113)⁸ or C1100P (JIS H 3100). Cold-rolled, cut from 1.59-mm (1/16-in.) sheet stock to size 50.8 by 25.4 mm (2 by 1 in.).
3. *Brass*, conforming to Alloy UNS C26000 (SAE CA 260). Half-hard, or C2680P (JIS H 3100) cut from 1.59-mm (1/16-in.) sheet stock to size 50.8 by 25.4 mm (2 by 1 in.).
4. *Solder* (two options)
 - a. A brass specimen as described in 6.1.3, coated with solder conforming to Alloy Grade 30 A (SAE 3 A) of Specification B 32 Solder-coated specimens may be prepared, or used specimens recoated for reuse, by the procedure given in ASTM D1384 Annex A1.
 - b. A solid solder specimen cut from 1.59-mm (1/16-in.) sheet stock of Alloy Grade 30 A (SAE 3 A) to size 50.8 by 25.4 mm (2 by 1 in.) or H30A (JIS Z 3282) may be used subject to mutual agreement of the parties involved. The use of a solid solder specimen must be reported along with the metal specimen weight loss results.
5. *Cast Aluminum*, conforming to Alloy UNS A23190 (SAE 329)⁸ or AC2A-F (JIS H5202). Specimen size, 50.8 by 25.4 by 3.18 mm (2 by 1 by 1/8 in.).
6. *Cast Iron*, conforming to Alloy UNS F10007 (SAE G3500)⁷ or FC200 (JIS G5501). Specimen size, 50.8 by 25.4 by 3.18 mm (2 by 1 by 1/8 in.).

Metal Specimen Arrangement—None of the hardware used in metal specimen arrangement (metal specimen, screws, washers, metal spacers, insulating sleeves, insulating spacers, and nuts) can be reused for a test. The metal test specimens shall be drilled through the center with a 6.75-mm (17/64-in.) drill to accommodate a 50.8-mm (2-in.) Between 10 and 24 brass machine screws covered with a thin-walled insulating sleeve. Tetrafluoroethylene tubing with a 6.35-mm (1/4-in.) o.d. 1.59-mm (1/16-in.) wide and a wall thickness of 0.4 mm (1/64-in.) is satisfactory. Two half-hard brass legs shall be cut from 1.59-mm (1/16-in.) sheet stock to size

² UNIFIED numbering system for metals and alloys, SAE-ASTM, July 1995.

FIG. 4 Metal specimen bundle arrangement.

50.8 by 25.4 mm (2 by 1 in.). A 6.35-mm (1/4-in.) diameter hole shall be drilled in each leg with the center 6.35 mm (1/4 in.) from the top and 12.7 mm (1/2 in.) from each side. The test “bundle” shall be made up on the insulated screw with the specimens in the following order: brass leg, copper, solder, brass, steel, cast iron, cast aluminum, and brass leg. The specimens shall be separated by 4.76-mm (3/16-in.) thick solid metal spacers having a 6.75-mm (17/64-in.) inside diameter and a 11.11-mm (7/16-in.) o.d. Insulating spacers made from tetrafluoroethylene shall be used between the brass legs and the specimen “bundle” and between the brass and steel specimens. Brass spacers shall be used between the brass, solder, and copper specimens, and steel spacers between the cast iron, steel, and cast aluminum specimens. The nut shall be tightened firmly to ensure good electrical contact between the test specimens in each section of the “bundle” (Fig. 4).

Alternate Metal Specimen Arrangements—When agreed upon between the supplier and the customer, alternate metal specimen arrangements may be used to evaluate multiple alloys.

Alternative 1: High lead Alloy Grade L50113⁹ consisting of 97 % lead, 2.5 % tin, 0.3 % silver, concurrently with Standard Alloy Grade 30 A or 30B (70 % Pb). It is recommended that the metal specimen arrangement be modified by replacing the copper specimen with the 97 % lead solder specimen and arranging specimens in the bundle as in Table 5:

Alternative 2: Additional aluminum alloy, such as Al 3003. It is recommended that the metal specimen arrangement be modified by adding the AL 3003 alloy

TABLE 5 Coupon bundle with 97 % Pb solder specimen.

97 % Pb	Brass	70 % Pb	Steel	Cast	Cast
Solder		Solder		Fe	Al

specimen electrically isolated from the rest of the coupons and arranging specimens in the bundle as in [Table 6](#):

Preparation of Test Specimens

Sand the cast iron and cast aluminum specimens on the 25.4 by 50.8-mm (1 by 2-in.) cut surfaces with “coarse” grade (No. 1) emery cloth. Remove any burrs from coupon edges and hole. Scrub all specimens vigorously, using a moistened bristle brush and ground pumice powder or fine silicon carbide grit until the entire metal area is bright, shiny, and free from any visible oxide film or tarnish. Rinse the specimens thoroughly with tap water; then rinse with acetone, dry, and weigh to the nearest 1 mg. Cast aluminum specimens should be dried in a 100°C oven for 1 h, to a constant weight, prior to recording the weight. If the test specimens are not to be used immediately, keep them in a desiccator until required.

Test Solutions

The concentration of the engine coolant to be tested shall be as follows:

1. *Engine Coolant*—The engine coolant shall be mixed with the proper quantity of corrosive water to give a 20 vol. % antifreeze concentrate coolant test solution.
2. *Corrosive Water*—The corrosive water shall contain 200 ppm each of SO_4^- , and Cl^- , 45 ppm NO_3^- , 0,3 ppm Fe^{3+} , 1.0 ppm Cu^{2+} , and Zn^{2+} .
3. *Preparation of Sample*—The preparation of the sample shall be done in accordance with the section on Preparation of Solutions Requiring Inclusion of Separated Solids and Liquids in Test Method D1176, except that the corrosive water shall be used for dilution instead of distilled water. Thus, any insoluble materials will be included in the representative sample.

Note that the specified corrosive water can be prepared by dissolving the anhydrous salts listed in [Table 5](#) in one liter of distilled or deionized water ([Table 7](#)).

TABLE 6 Coupon bundle with aluminum 3003 specimen.

97 % Pb	Brass	70 % Pb	Steel	Cast	Cast Al	3003
Solder		Solder		Fe		Al

TABLE 7 Corrosive water formulation for proposed ELC glassware test (1l @ 20°C).

Sodium Sulfate Na_2SO_4	296 mg
Sodium chloride NaCl	318 mg
Sodium Nitrate NaNO_3	62 mg
Ferric chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	1.5 mg
Cupric chloride $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	2.7 mg
Zinc Chloride ZnCl_2	10.4 mg

Test Conditions

1. *Beaker Assembly*—The arrangement of the assembled metal specimens with relation to the aerator tube and other components is shown in Fig. 3. Note that the tip of the condenser just emerges from the bottom of the rubber stopper.
2. *Test Temperature*—The test solution shall be maintained at a temperature of $98 \pm 2^\circ\text{C}$ ($208 \pm 5^\circ\text{F}$).
3. *Aeration Rate*—The aeration rate shall be $100 \pm 10\text{ mL/min}$. The aerator tube should be located at least 12.7 mm (1/2 in.) away from the test “bundle” to avoid direct contact with the metal specimens.
4. *Test Duration*—The test shall be run continuously for 2 weeks (336 h).

Procedure

1. Make triplicate tests concurrently on each engine coolant solution in accordance with the following procedure:
2. Carefully clean the test beaker, condenser, rubber stopper, and aerator tube, and thoroughly rinse with water.
3. Bolt the specimens together in the order given in step 2 and place the “bundle” in the test beaker as shown in Fig. 4.
4. Pour 750 ml of the prepared test solution into the 1000-ml beaker.
5. Fit the condenser and aeration tube to the beaker, and set the aeration rate at 100 mL/min, using a flow meter or other suitable device.
6. Raise the temperature of the test solution to 98°C (208°F). Pass water through the condenser at a rate sufficient to maintain adequate cooling.
7. Check the tests once each working day to ensure proper solution temperature, aeration rate, and solution level. The tests may operate unattended on weekends and holidays. Make up evaporation losses during the corrosion tests by addition of distilled or deionized water.
8. At the end of the test, *immediately disassemble* specimens and brush very lightly with a soft bristle brush and water to remove loosely held corrosion products. To remove the more tenacious corrosion products and films, the individual specimens shall then be subjected to additional cleaning treatments as follows:
9. *Iron and Steel*—Remove adherent deposits by means of a brass scraper or brass bristle brush, followed by scrubbing with a wet bristle brush and fine pumice to clean the specimen completely.

10. *Copper and Brass*—Dip in a 1 + 1 mixture of concentrated HCl (sp gr 1.19) and water for 15 s to remove tarnish films, rinse with tap water to remove acid, and scrub with a wet bristle brush and fine pumice powder (*Warning*: HCl is a strong acid. Avoid contact with skin and eyes. Handle in a fume hood).
11. *Aluminum*—In a fume hood, dip for 10 min in an aqueous solution containing 4 parts concentrated nitric acid (HNO₃, 70 mass %) plus one part distilled water at 25°C (76°F). Rinse thoroughly with water, and then brush very lightly with a soft bristle brush to remove any loose films, and again rinse with water³. Dry the specimen in a 100°C oven for 1 h, to a constant weight prior to recording the weight (warning: HNO₃ is a strong toxic oxidant and acid. Avoid contact with skin, eyes, and clothing. Do not breathe vapor. Handle in a fume hood).
12. *Solder*—Immerse for 5
13. in boiling 1 % glacial acetic acid. Rinse in water to remove the acid, and brush very gently with a soft bristle brush to remove any loosened material. (warning: avoid contact with skin and eyes with glacial acetic acid. Handle in a fume hood).
14. The acid dip times given in 10.1.7 for the cleaning of nonferrous specimens are average values found to be adequate in most cases. Other times, suggested by experience, may be used if necessary if gross weight losses are adjusted by the appropriate tare.
15. Follow each of the four operations noted above by thorough rinsing, first in tap water and then in acetone. Then dry and weigh the specimens to the nearest 1 mg. Store in desiccator specimens that cannot be weighed immediately.
16. Because cleaning methods and materials may vary among laboratories, occasionally determine cleaning losses obtained by a particular operator on an untested set of triplicate metal specimens. Deduct the average cleaning losses from gross weight differences to determine actual corrosion losses.

Report

1. Report corrosion rate (loss) as a positive value and rate of weight gain rate as a negative value. If no sign is given to the value it will be interpreted as a rate of loss.

EXAMPLE

Initial weight of a brass specimen after cleaning was 405 mg. At the end of the test after cleaning, it was 398 mg. The cleaning blank was determined by taking the weight of a brass specimen after the initial cleaning, 406 mg, and then cleaning it alongside of the brass specimen removed at the end of the test, 404 mg. Using the equation below, we calculated the corrosion rate of the specimen. The total surface area was $(5.0 \times 2.5) = 12.5 \text{ cm}^2$ per each of two sides plus 2.25 cm^2 along the edges for a total of 14.75 cm^2 total surface area.

³ A round-robin evaluation of nitric acid cleaning of aluminum specimens is available from ASTM Headquarters. Request RR: D15-1018.

$$(W_I - W_{EOT}) - W_{CB})/S_A = R_C$$

where:

W_I = the initial weight of the coupon,

W_{EOT} = the weight of the coupon after the test,

W_{CB} = the weight loss of the cleaning blank,

S_A = the total surface area of the coupon, and

R_C = the reportable rate of corrosion.

For example: (Brass) $R_C = [(405 \text{ mg} - 398 \text{ mg}) - (406 \text{ mg} - 404 \text{ mg})] / 14.75 \text{ cm}^2$
= 0.34 mg / cm² (Final Result to Report)

(positive value means that it is a weight loss)

2. Report the corrected corrosion rate weight changes of individual specimens to the nearest 0.01 mg for each test.

3. Report the average corrected metal corrosion rate for triplicate tests on each engine coolant solution. A single corrosion rate that appears completely out of line should be dealt with as described in ASTM [E178](#).

Results and Discussion

Six coolants were created for the analysis. The hope was that the coolants considered capable of only one or two years' service in cars would perform much poorer than the coolant chemistries that simulated commercial extended service products. As is the usual situation, no commercial coolant formulations were used and the coolants were subjected to all of the requirements for ASTM [D3306](#). These six profiles roughly represent basis inhibition conventions that exist today in the coolant industry. Some would be expected to require more maintenance than others. All six were tested by the standard ASTM [D1384](#) and then again by the proposed method.

The six coolants had inhibitor general profiles as follows in the "antifreeze concentrate" form ([Table 8](#)):

Six laboratories were recruited to participate in the interlaboratory study (ASTM Work Item WK25881). Four of the labs reported data for consideration. (Tables [9-14](#)).

TEST RESULTS

It would appear that the proposed modifications to ASTM [D1384](#) for testing extended service life coolants is more challenging to aluminum and possibly solder. The other four metals performed very close to their performance in the standard ASTM [D1384](#) test method. The method might be useful for evaluating the ability of a coolant to protect aluminum alloys for longer periods of time.

USCAR Magnesium Adaptation

Another modification to the ASTM [D1384](#) bundle that has been used to generate research data involves the addition of magnesium alloys. Magnesium alloys are of

TABLE 8 Experimental coolant chemical properties: units in ppm—formulations are approximate.

	pH	NO ₂	NO ₃	PO ₄	Mo	B	Si	BZT	MBT	TTZ	Benzoate	Sebacic
1	10.4	900	1200	1300		500	350			1000	1100	
2	8.0									2400	7600	9600
3	7.6		2600	2700				3600	6500			43 000
4	10.5	2800	1300			1000	350			1200		
5	8.1	1000			1200					2500	8300	10 000
6	8.1	800	3300			900				1000		

TABLE 9 Coolant #1: Phosphated Hybrid.

Coolant #1 Phosphated Hybrid							
		Lab 1	Lab 2	Lab 3	Lab 4	Average	SD
Cu	D1384	−1	1	1	1	1	1
	Proposed	0	2	1	1	1	1
Solder	D1384	10	5	2	2	5	4
	Proposed	0	5	4	3	3	2
Brass	D1384	2	1	3	1	2	1
	Proposed	0	2	1	1	1	1
Steel	D1384	−1	0	1	0	0	1
	Proposed	0	0	15	2	4	7
Fe	D1384	0	−1	1	−1	0	1
	Proposed	0	−1	25	6	8	12
Al 319	D1384	−3	0	1	−1	−1	2
	Proposed	0	8	21	13	6	13

interest to the automotive industry because they offer weight savings potential when compared to aluminum. Of course, experienced engineers are well aware of the corrosion potential for magnesium alloys, so evaluating alloys for interaction with engine coolants is necessary when using the alloys to replace aluminum components in automobiles is contemplated. To that end, the United States Council on Automotive Research has been working with ASTM test methods that might be adapted as useful tools to predict the behavior of magnesium alloys and engine coolants. The specimen arrangement developed for USCAR is illustrated in [Fig. 5](#).

TABLE 10 Coolant #2: Sebacic Acid OAT.

Coolant #2 Sebacic Acid OAT							
		Lab 1	Lab 2	Lab 3	Lab 4	Average	SD
Cu	D1384	0	1	1	1	1	1
	Proposed	0	2	1	0	1	1
Solder	D1384	−1	0	2	0	0	1
	Proposed	30	0	9	8	12	13
Brass	D1384	0	1	1	1	1	0
	Proposed	1	2	1	1	1	1
Steel	D1384	−1	0	1	0	0	1
	Proposed	−1	1	1	−1	0	1
Fe	D1384	0	−2	0	0	−1	1
	Proposed	−2	0	1	2	0	2
Al 319	D1384	3	0	9	2	3	4
	Proposed	7	38	201	92	85	85

TABLE 11 Coolant #3: Sebacic Acid Hybrid.

Coolant #3 Sebacic Acid Hybrid							
		Lab 1	Lab 2	Lab 3	Lab 4	Average	SD
Cu	D1384	1	1	2	1	1	1
	Proposed	0	2	4	2	2	2
Solder	D1384	0	0	1	−1	0	1
	Proposed	−1	0	1	−1	0	1
Brass	D1384	1	1	1	0	1	0
	Proposed	1	1	2	1	1	1
Steel	D1384	0	0	1	1	0	1
	Proposed	0	0	1	−1	0	1
Fe	D1384	−1	−2	−1	1	−1	1
	Proposed	−2	−2	0	−1	−1	1
Al 319	D1384	−2	−1	−1	−2	−1	0
	Proposed	−2	15	16	8	9	8

Testing of magnesium alloys in coolants by D1384 using the USCAR configuration provided evidence that the method is capable of sorting the most corrosive combinations from those that were much less corrosive. Weight losses of 0 to almost 500 mg were recorded during the extensive research [5].

Spaced Interval Modification to D1384

This method is currently a pure research method, it has insufficient experience and no ILS data to correlate its results to “real world” experience. It is derived from the

TABLE 12 Coolant #4: Fully Formulated Conventional.

Coolant #4 Fully Formulated Conventional							
		Lab 1	Lab 2	Lab 3	Lab 4	Average	SD
Cu	D1384	1	2	2	1	2	1
	Proposed	0	6	2	0	2	3
Solder	D1384	11	11	5	6	8	3
	Proposed	15	14	4	4	9	6
Brass	D1384	2	2	2	1	2	0
	Proposed	2	3	1	2	2	1
Steel	D1384	0	0	1	1	1	0
	Proposed	1	1	10	0	3	5
Fe	D1384	0	−2	0	1	0	1
	Proposed	−2	−3	24	3	5	13
Al 319	D1384	−2	0	−1	−1	−1	1
	Proposed	11	4	20	17	5	15

TABLE 13 Coolant #5: Nitrite, Molybdate OAT (Heavy Duty).

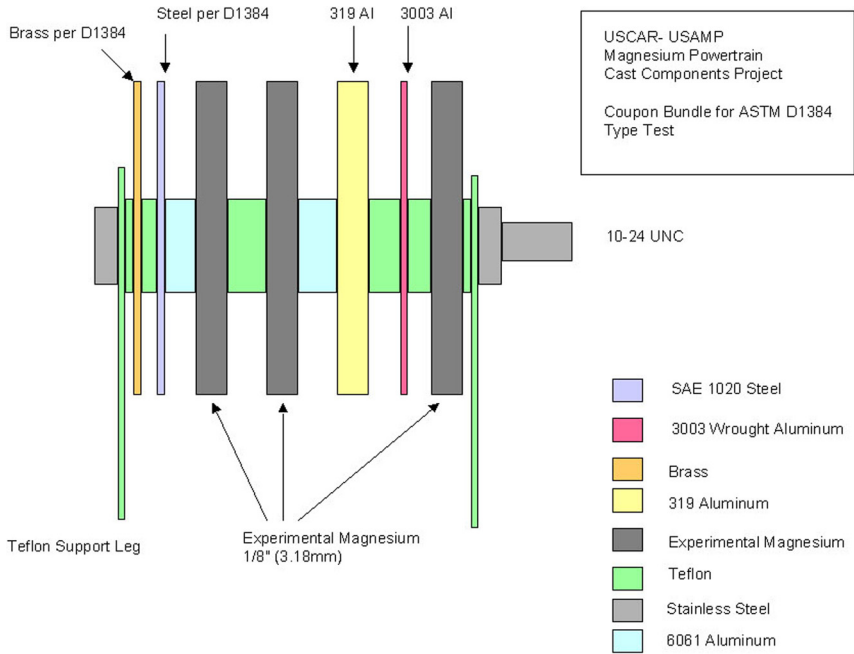
Coolant #5 Nitrite, Molybdate OAT (Heavy Duty)							
		Lab 1	Lab 2	Lab 3	Lab 4	Average	SD
Cu	D1384	1	3	2	1	2	1
	Proposed	−1	3	2	1	1	1
Solder	D1384	9	1	1	3	3	4
	Proposed	25	1	153	15	40	77
Brass	D1384	1	1	0	1	1	1
	Proposed	0	2	2	0	1	1
Steel	D1384	1	0	0	0	0	1
	Proposed	−1	1	1	−3	0	2
Fe	D1384	2	−1	−1	0	0	1
	Proposed	−2	−2	−2	−1	−2	1
Al 319	D1384	5	1	6	2	3	2
	Proposed	15	4	82	23	21	43

discussion of spaced interval test in ASTM G31-72 (1999), Standard Practice for Laboratory Immersion Corrosion Testing of Metals, an ancestor of ASTM D1384. This test method evaluates the effect of engine coolant on metal test specimens under controlled, essentially isothermal laboratory conditions. This test method modifies classical ASTM D1384 beaker-type procedure for evaluating the effects of engine coolants on metal specimens under controlled laboratory conditions. In this test method, specimens of metals typical of those present in engine cooling systems are totally immersed in aerated engine coolant solutions prepared with corrosive

TABLE 14 Inorganic Phosphate Free.

Inorganic Phosphate Free							
		Lab 1	Lab 2	Lab 3	Lab 4	Average	SD
Cu	D1384	1	1	0	1	1	1
	Proposed	0	3	1	0	1	1
Solder	D1384	0	18	9	7	9	7
	Proposed	1	20	4	11	9	9
Brass	D1384	2	2	1	1	1	1
	Proposed	0	2	1	1	1	1
Steel	D1384	0	1	1	1	1	1
	Proposed	3	1	48	4	14	23
Fe	D1384	−1	1	5	1	2	3
	Proposed	6	−2	9	11	3	8
Al 319	D1384	3	3	8	9	6	3
	Proposed	3	10	20	15	12	7

FIG. 5 USCAR magnesium testing corrosion bundle.



salts at 88°C (190°F). The corrosion inhibition properties of the test solution are evaluated on the basis of the weight changes incurred by the specimens versus time. Twelve coupon bundles are prepared and immersed in the candidate coolant prepared per the standard ASTM D1384 test method. Each test is run in duplicate, and the average weight change is determined for each pair of metal specimens as they complete their term of exposure at 2-week intervals (total test time is 12 weeks). This test method will produce a record of the corrosion mass loss plotted against time and shall also be reported as a corrosion rate (mg/cm²/week). At the end of each two-week interval, the corrosion-inhibiting properties of the coolant are determined by measuring the mass losses and rate of corrosion of one pair of test specimens and by visual examination and photography of the surfaces of the removed specimens. The mass losses and rates of corrosion are tabulated and graphed to aid in observing how the corrosion behavior is changing, or not, with time. This information may be useful in predicting the long-term (extended service) capabilities of a coolant. Much more cooperative research would be necessary to evolve this method for general use.

Summary and Conclusions

There are many ASTM D1384 modifications to be considered:

- The inclusion of an alternate specification for a modern, aluminum-and-magnesium focused bundle.
- Testing to include options for extended and spaced interval options.
- The possibility of different corrosive water formulas.
- Adding allowances for different antifreeze concentrations.

Where can we move with a research discussion? Ideas to make the tests more severe, thereby better simulating longer service periods, need to be addressed (corrosive water formulation, lower weight loss limits, reporting results in mg/cm^2). Many OAT test results show the mass increase on some metals. Weight additions need to be limited and meaningful limits to the gains should be determined. As the consumer market uses more and more coolants in their vehicles and the OEM's introduce multiple acceptable coolants, there is a need for compatibility variations and standards to address these issues.

ASTM [D1384](#) is used globally. As ASTM becomes a more global organization it is our responsibility to adapt to the global demands and requests that the industry requires. Many OEM'S already have variations of ASTM [D1384](#) in their testing requirements. ASTM [D15](#) can learn and adapt the OEM test speciation's to begin developing useful test methods for evaluating coolant compatibility.

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Elmo Trevino Jr.¹ and Edward R. Eaton V¹

Extending the Simulated Service Test for Developing and Evaluating Extended Service Interval Engine Coolants

Reference

Trevino, Elmo Jr. and Eaton V, Edward R., "Extending the Simulated Service Test for Developing and Evaluating Extended Service Interval Engine Coolants," *Global Testing of Extended Service Engine Coolants and Related Fluids*, STP 1556, Edward R. Eaton, Ed., pp. 150–160, doi:10.1520/STP155620130100, ASTM International, West Conshohocken, PA 2014²

ABSTRACT

ASTM Committee D15 on Engine Coolants and Related Fluids has discussed numerous possible updates or modifications to the ASTM [D2570](#) test method. Many of these modifications are suggested by published Japanese and Korean methods that use similar test rigs. These requests alter the coupon metals, time, temperature, and coolant concentration of the coolant sample in an effort to better represent the behavior of the coolant on various metals in glassware tests over extended periods of time. The test is already performed with modifications required by JIS K2234 coolant specifications and Hyundai coolant specifications. It is possible to modify the corrosive challenges to the coolant by modifying the coolant mixture from that in the published method, as has been proposed by engineers at Korean Testing & Certification. This paper explores the possible value of using modifications to ASTM [D2570](#), including variations published in global original equipment manufacturer and industry specifications such as JIS K2234 and Hyundai specifications. It also explores the use of a coupon bundle that more closely approximates the metals in today's light-duty automotive systems. Finally, it invites the global automotive community to focus a coordinated effort on updating this test method, even if that results in multiple

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²ASTM Symposium on *Global Testing of Extended Service Engine Coolants and Related Fluids* on May 23, 2013 in Indianapolis, IN.

embodiments for different types of coolant service (i.e., light duty versus heavy duty).

Keywords

glycerin, glycerol, engine coolant, antifreeze, extended service, heavy duty, organic acid technology, OAT, carboxylate

Introduction

This paper describes several possible approaches that could be used to address the challenge of improving the existing ASTM [D2570](#) Simulated Service Test to better model modern cooling systems and to better predict which coolant formulations may remain in service for the “new norm” of at least 5 years before being replaced. Careful review of historical work has been completed, and the documented historical discoveries of industry experts have been considered. Result harvesting including both traditional “snapshot” and trend-analysis types of evaluations is debated. Regardless of the direction(s) explored, substantial work to refine the test methods and develop repeatability, reproducibility, precision, and bias will be needed before a final method can be adopted. This paper is a continuing step along the journey.

Background

ASTM Committee D15 published the first version of ASTM [D2570](#) in 1966 [1]. The method creates a model of an engine cooling system. Between 1966 and 1977, the method was updated and improved [2]. The first attempts to develop repeatability, reproducibility, precision, and bias statements proved challenging. Three inter-laboratory studies before 1977, including one conducted using a “marginally acceptable coolant,” documented acceptable repeatability within individual laboratories but disappointing reproducibility between laboratories [3]. It is somewhat awkward to confess that ASTM [D2570](#) offers poor reproducibility because it is required by most major ASTM and North American manufacturers’ coolant specifications [4]. Nevertheless, the industry in 1979 felt strongly that the method was valuable, and ASTM Committee D15 has made no attempt to purge or significantly revise it since [3].

Several issues identified by Choinski and Maxwell at the ASTM [D15](#) symposium in 1979 potentially still challenge the ASTM [D2570](#) method today. They are the following:

1. Lack of uniformity between the test stands from lab to lab.
2. Possible variations in the metal specimens.
3. Too much flexibility in the choice of automotive components.
4. Variations in cleaning procedures from lab to lab.
5. Preconditioning of the test rig with the test coolant for a day or two before the beginning of testing (no longer included in the instructions).

- 6. Rowe commented in a discussion of the presentation by Choinski and Mazwell that increasing the concentration to 44 % antifreeze from 33 % antifreeze was helpful but still did not yield the desired reproducibility, although the reproducibility was probably similar to that achieved by other corrosion tests [3].

The biggest issues in reproducibility experienced in Choinski and Mazwell’s research were related to aluminum and solder corrosion results. In 1986 Hudgens and Hercamp published their discovery that these softer metals are sensitive to the effects of high flow rates, and that their discovery in ASTM D2570 testing correlated with field failures in aluminum elbows in which turbulence and high flow rates resulted in rapid failure [5]. They observed that ASTM D2570 did not reproduce the high flow rates experienced in heavy-duty engines and argued for a new ASTM D3306 type of document for heavy-duty applications that would better model the heavy-duty diesel engine cooling system.

The debate on the merits of ASTM D2570 subsided for a while after 1986, except for discussions by Bradley regarding recycling technologies in 1993 [6] and 1999 [7]. In 2002 ASTM Committee D15 again conducted an interlaboratory study, but this time a well-proven conventionally inhibited coolant formulation was prepared from the GM 6038 formula. One batch was prepared and shared with six labs, five of which returned ASTM D2570 data (Table 1) [8].

Confirming earlier Achilles’ heel issues, this interlaboratory study also reported disappointing reproducibility for aluminum and solder. It was encouraging that all of the labs passed the GM formula, based on both ASTM D3306 and GM 1825M [9] requirements. Nevertheless, this was a coolant known to perform very well in the field, and corrosion losses on aluminum were inconsistent with field experience. Especially puzzling is that the laboratory repeatability was good for corrosion testing, in spite of surprisingly high aluminum weight loss (Table 2).

TABLE 1 Data from the 2002 interlaboratory study of ASTM D2570.

ASTM D15.09 Simulated Service Subcommittee							
ASTM D2570 Simulated Service Interlaboratory Study							
	A	B	C	D	E	Average	S.D.
Aluminum	5	−9	45	45	6	18	25.0
Iron	3	1	−3	6	−3	1	3.9
Steel	3	2	2	8	−1	3	3.3
Brass	4	1	4	7	−1	3	3.1
Solder	11	31	1	10	1	11	12.3
Copper	3	0	0	5	−1	1	2.5
pH before		8.0	7.7	7.8	7.8	7.8	0.1
pH after		7.8	8.8	8.8	8.0	8.4	0.5
Reserve Alkalinity before		9.4	10.5	10.2	10.8	10.2	0.6
Reserve Alkalinity after		9.8	4.7	5.6	8.9	7.2	2.5

TABLE 2 2002 data from one lab reporting high aluminum mass loss, but reflecting satisfactory laboratory repeatability.

ASTM D2570 Simulated Service Round-Robin Repeatability				
Aluminum	39.2	46.9	47.7	45
Cast iron	−0.6	−5.5	−2.1	−3
Steel	1.6	3.5	1.6	2
Brass	3.4	4.9	3.7	4
Solder	0.9	0.9	0.6	1
Copper	0.1	−0.1	0	0

Note: negative numbers indicate a weight gain.

Establishing Objectives for ASTM D2570 Updates

What does the industry need from a circulating simulated service test? Considering the history of the existing version of ASTM D2570, what are the points that we need to focus on?

1. Improve reproducibility from lab to lab and continent to continent.
2. The current design reflects North American 20th century practices; the update needs to reflect 21st century global technologies.
3. It is desirable not only to standardize test stands but also to facilitate the procurement of parts anywhere on the planet.
4. Address the problem of specific parts becoming obsolete.

What have other testing organizations offered as possible improvements?

There are at least two Asian circulating simulated service test methods to consider. They are the variation to ASTM D2570 as published in JIS K2234 and the circulating simulated service test method required by Hyundai. Section 8.7 of JIS K2234 [10] states that the parts for building the test stand are to be sourced from a 1.61 ± 0.21 vehicle's cooling system, in contrast to ASTM D2570, which allows a "1.6 to 5.0 liter range." The actual parts specified in ASTM D2570-10 fit a GM 2.8-l V-6 engine. The JIS test rig setup is similar to that described in ASTM D2570-10, but there are some notable exceptions. The main heated reservoir, referred to in JIS K2234 as the "heating bath," is stainless steel, whereas in ASTM D2570 the reservoir is to be made of SAE G3500 Gray Iron for Automotive Castings. The antifreeze concentration is 30 %, as opposed to 44 % in ASTM D2570. There is a note included in ASTM D2570-10 that comments on the 44 % concentration:

"NOTE 4—The test solution concentration of 44 % by volume was selected to improve the precision of the test method. Previously, the concentration had been 33 % by volume. The precision of the test, both intra-laboratory and inter-laboratory, improved at the higher concentration. Using this test at concentrations lower than the 44 % will result in a decrease in precision, with a corresponding need to evaluate any test limits selected for use in a specification" [2].

TABLE 3 Summary of some existing simulated service test requirements.

	ASTM D2570	JIS K2234 Class 1	JIS K2234 Class 2	Hyundai MS 591-08 LLC-2/LLC-5	Hyundai MS 591-08 LLC-5																				
Test solution	44 % concentrate in corrosive water	30 % concentrate in corrosive water	30 % concentrate in corrosive water	20 % concentrate in corrosive water	50 % concentrate in corrosive water																				
Time and temperature	1176 h total, 1064 88°C; two 8-h stoppages per week	336 h, 88°C	1000 h, 88°C	LLC-2, 1000 h, 88°C; LLC-5, 1000 h, 98°C	2000 h, 98°C																				
Cu	≤20 mg	±0.3 mg/cm ²		0.15 mg/cm ²																					
Mass lost	(0.72 mg/cm ²)																								
Solder	≤60 mg					±0.6 mg/cm ²		0.30 mg/cm ²																	
Mass lost	(2.15 mg/cm ²)																								
Brass	≤20 mg									±0.3 mg/cm ²		0.15 mg/cm ²													
Mass lost	(0.72 mg/cm ²)																								
Steel	≤20 mg													±0.3 mg/cm ²		0.15 mg/cm ²									
Mass lost	(0.72 mg/cm ²)																								
Fe	≤20 mg																	±0.3 mg/cm ²		0.15 mg/cm ²					
Mass lost	(0.66 mg/cm ²)																								
Al	≤60 mg																					±0.6 mg/cm ²		0.30 mg/cm ²	
Mass lost	(1.89 mg/cm ²)																								
Appearance of metal specimens	Report	There shall be no visually noticeable corrosion on the test piece, excluding the part contacting with spacer, but		There shall be no noticeable appearance change on the metal pieces.																					

TABLE 3. Continued

	ASTM D2570	JIS K2234 Class 1	JIS K2234 Class 2	Hyundai MS 591-08 LLC-2/LLC-5	Hyundai MS 591-08 LLC-5
		change in color is permissible.			
Reserve alkalinity value		Report before and after			
Δ Reserve Alkalinity				$\leq 30\%$	
pH value	Report Before and after	6.5–11.0		7.0–9.0	
Δ pH		± 1.0		± 1.0	
Coolant appearance: liquid phase	Report Before and after	No significant change		No noticeable change	
Water pump	Report	No seal failure; no corrosion		No seal abrasion or noise; no corrosion	
Condition of hoses	Report				
Condition of radiator	Report				No noticeable corrosion on the tube
Copper anticorrosion additive remaining					60 % minimum 4000 ppm minimum
Precipitate	Report	Report		1.0 vol. % maximum	

JIS K2234 specifies two durations: 336 h for winter coolants, and 1000 h for extended life technologies. (Realistically, today's technologies would all fall into the 1000-h category.) JIS K2234 also directs that the test run continuously for 1000 h, and ASTM D2570 specifies one 8-h "cooldown" per week to provide thermal stress to the system. ASTM D2570 calls for a 24-h presoak before the start of the test, whereas JIS K2234 does not. Finally, the results are reported a little differently. ASTM D2570 reports mass lost in milligrams per coupon (average of three), and JIS K2234 reports mass lost as milligrams per square centimeter (average of three).

The Korean (Hyundai) method (MS 591-08) [11] is interesting in that it changes several parameters relative to both ASTM and JIS methods. MS 591-08 defines two service interval categories, LLC-2 and LLC-5. These represent the requirements for two-year and five-year service interval coolants, respectively. The simulated service test requirement is defined in Section 4.17.1 of the standard. The first requirement is that there "[s]hall be no noticeable appearance change on the metal pieces." Analytical testing before and after is required because copper protection must remain at 60 % of the initial concentration. The simulated service exposure must be performed on two different solutions. The first solution is 20 % antifreeze exposed continuously for 1000 h. This is required for both LLC-2 and LLC-5 coolant categories, but the test temperature is 88°C for LLC-2 and 98°C for LLC-5. The LLC-5 candidates must also endure and pass a second trial with 50 % antifreeze for 2000 h at 98°C.

The ASTM G1 Committee on Corrosion employs a concept referred to as "spaced interval corrosion" in ASTM B117 [12] and perhaps some other standards. The concept is simple; it involves exposing numerous corrosion test specimens over time, harvesting one or more of the specimens at designated intervals, and recording the mass lost due to corrosion as a function of time. This is intriguing because many corrosion tests provide essentially a "snapshot" of the corrosion behavior at the end of a standard test period. Conversely, the concept of spaced interval testing offers information at multiple points in time, perhaps leading to a better understanding of the corrosion (or corrosion protection) behavior. Questions such as "How quickly does corrosion progress?" or "How quickly is passivation realized?" may be answered. Further, if the test period is sufficiently long, the effective period of corrosion protection may be observed or estimated. The concept of spaced interval testing in ASTM D2570 was introduced into actual research practice by Beal [13]. In Beal's embodiment, the number of coupon bundles in the test rig is increased from three to six. The standard exposure is 7 weeks, so one bundle is removed at the end of every week except week 6. The final bundle is removed at week 7. This approach sacrifices the repetition of results at any one given time (such as the end of the test) but offers twice the number of data points and further provides corrosion behavior information as a function of time.

Another variation of the test involves using four bundles. Three bundles are exposed per the standard method. The fourth bundle is harvested and replaced at specified intervals. Again, the intent is to understand the corrosion behavior of the

specimen in the fluid over time. As the coolant ages, the rate of corrosion increases as the capability of the coolant to protect metals wears out. At the end of the test the traditional three bundles are reported per the method.

The time intervals and total time of exposure may be extended by agreement between customer and supplier so as to provide the most useful set of information.

Study Using Spaced Interval Corrosion Testing

The following data were generated by observing the corrosion behavior versus time of a new extended life coolant technology using spaced interval simulated service testing. The evaluation was used in addition to a standard ASTM [D3306/D6210](#) testing protocol [4,14]. In this test, five bundles of corrosion coupons were used and a bundle was harvested and processed every two weeks. The data were tabulated (Table 4) and graphed (Fig. 1).

How do other coolants compare?

A coolant used as a negative control is the “synthetic used coolant” described by Bradley. When subjected to the spaced interval test, this coolant behaves much as expected.

It is the authors’ opinion that the practice of spaced interval testing holds promise. They further believe that changes to the alloys, in particular aluminum alloys, included in the coupon bundle should be considered. The authors have no data for additional aluminum coupons to report at this time, but it is noted that research and some original equipment manufacturer specifications have involved multiple solder and aluminum coupons.

Summary

The industry has recognized shortcomings in the current version of ASTM [D2570](#). Several potential improvements have been identified and offered for development. These include updates to the metal coupons in the corrosion test bundle and investigating the harvesting of dynamic corrosion behavior data by using spaced interval test methods.

TABLE 4 Data from spaced interval simulated service test.

Specimen Corrosion Weight Loss versus Time					
Specimen	2 weeks	4 weeks	6 weeks	8 weeks	10 weeks
Copper, mg	1	1	1	1	2
30a solder, mg	1	1	1	1	−1
Brass, mg	1	1	1	2	2
Steel, mg	0	1	1	1	1
Cast iron, mg	0	0	0	0	−1
Cast aluminum, mg	2	2	3	3	4

TABLE 5 Spaced interval data for negative control coolant.

Specimen Corrosion Weight Loss versus Time						
Specimen	0 weeks	2 weeks	4 weeks	6 weeks	8 weeks	10 weeks
Copper, mg	0	10	12	20	28	42
30a solder, mg	0	48	78	88	92	93
Brass, mg	0	2	5	10	12	14
Steel, mg	0	12	30	35	37	39
Cast iron, mg	0	25	54	75	86	92
Cast aluminum, mg	0	27	39	49	67	87

TABLE 6 Proposed alternative corrosion coupons.

97 % Pb solder	Brass	70 % Pb solder	Steel	Cast Fe	Cast Al	3003 Al
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FIG. 1 Graph of spaced interval data.

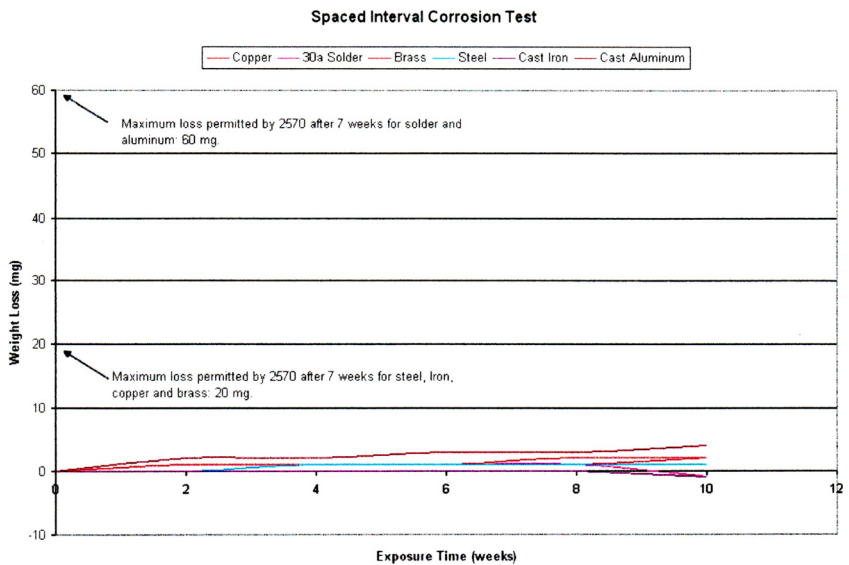
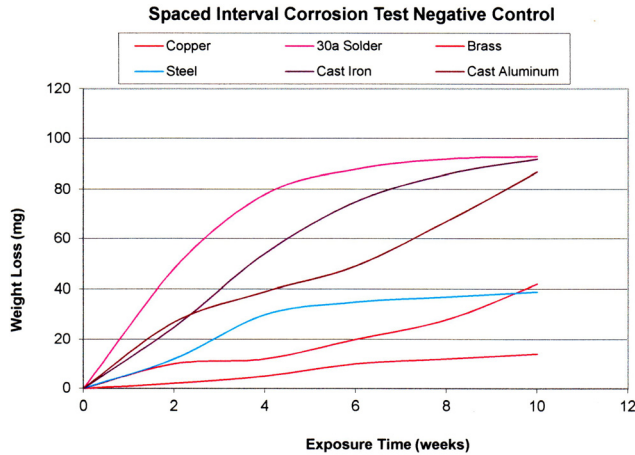


FIG. 2 Graph of data for negative control coolant.

Global vehicle manufacturer specifications also offer food for thought. Various specifications require testing of different antifreeze concentrations. Some dispense with the cooldown periods, and others extend the exposure time. These practices are good directions for ASTM Committee D15 to explore as the need to update ASTM [D2570](#) intensifies.

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Edward R. Eaton, Sr.¹

Protocol for Evaluating the Compatibility of Engine Coolants

Reference

Eaton, Edward R., Sr., "Protocol for Evaluating the Compatibility of Engine Coolants," *Global Testing of Extended Service Engine Coolants and Related Fluids*, STP 1556, Edward R. Eaton, Ed., pp. 161-172, doi:10.1520/STP155620130064, ASTM International, West Conshohocken, PA 2014.²

ABSTRACT

In the mid-1990s, the first North American specification for carboxylate-inhibited engine coolant that was accompanied by a recommended change interval of 5 years/ 100 000 miles was published. Others followed. Part of the testing protocol in these specifications require prospective suppliers to evaluate and report the compatibility of proposed formulations with previous, conventionally inhibited engine coolants, in particular widely referenced and manufactured formulations. Industry experience with the test methods required by these original equipment manufacturers (OEMs) has been the root cause of heated debate in the industry as to the definition of "compatibility" in light of the tremendous push of "all Makes All models" coolants. This paper compiles the compatibility tests that are, or have been, specified by OEM specifications and also reports research work performed by other companies in an attempt to identify possible problematic behaviors. Tests of intentionally mixed coolants are modified from standard OEM, ASTM, and JIS methods. Some test methods evaluate the effect of mixed coolants on unpassivated metal surfaces while others seek to assist in understanding of the effect of mixed coolants in systems that have been operated for some time on a single coolant technology (the "top up" environment).

Keywords

compatibility, engine coolant, antifreeze, extended service, heavy duty, organic acid technology, OAT, carboxylate

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²ASTM Symposium on *Global Testing of Extended Service Engine Coolants and Related Fluids* on May 23, 2013 in Indianapolis, IN.

Introduction

This paper considers development of an extended life coolant compatibility testing protocol. Since the introduction of carboxylate-inhibited coolants, often referred to as “long life,” “extended service interval,” or “extended life” formulations, some manufacturers have included new compatibility tests in their engine coolant specifications. This paper will review many of the OEM compatibility testing requirements in an effort to discover what behaviors are of interest to the manufacturers, supposing that they have cause to be interested. In general, tests that have been discussed and conducted include:

1. Tests that evaluate the corrosion protection behavior of coolant mixtures on new, unpassivated metals.
2. Tests that evaluate the corrosion protection behavior of coolant mixtures on passivated metals. This might be considered the applicability of the formulation in “top-up” situations such as “quick lube” facilities where small amounts of coolant are added to multiple makes and models of cars and light trucks.
3. Tests that evaluate the behavior of coolants and/or coolant mixtures on non-metallic materials such as elastomeric materials.

At the end of the paper, the author will summarize the existing compatibility test requirements and propose a possible protocol for general coolant qualification, perhaps as an addition to Coolant Specifications including ASTM [D3306](#) [1] and ASTM [D6210](#) [2].

Background

In the author’s area there is a well-respected, locally owned independent auto repair chain that operates five or six locations. Recently, a family member had an opportunity to present an American-made vehicle filled with a European-style hybrid coolant for routine service. Although requested to “leave the cooling system alone,” the well-meaning service technician “topped up” the coolant reservoir with coolant taken from the service facility’s inventory. Intent on preventing compatibility issues in the prized, out-of-warranty and paid-off vehicle, the owner mercilessly interrogated the innocent Service Writer regarding the specifics of the coolant used for “top-up.” The Service Writer surrendered the remainder of the gallon used in hopes of appeasing the owner. Little did he know.

To make a long story short, the coolant was not a “major brand” coolant. It advertised compliance on the label with a very long list of OEM specifications, including GM 6043, GMW3420 [3] and GM 6277M [4]; Ford WSS-M97B51 A1 and FordWSS-M97D44-D; Chrysler MS-7170 and MS-9769. By all label appearances, it was not recycled. Now, as many of the readers of this paper are familiar with these specifications, one will perhaps recognize that some are for conventionally inhibited, some are for hybrid formulation, and others are specifically for carboxylate inhibited engine coolant formulations. In reading the specifications, an observant person will quickly discover that full compliance with all of the requirements of

these specifications using one formula is not possible. Furthermore, analysis of the coolant discovered chloride, sulfate, metals, formate, and glycolate concentrations that confessed that the base glycol was certainly not compliant with ASTM E1177 [5], and contaminants disqualified the blended formulation from compliance with ASTM D3306 [1] even without any performance testing. Again, this experience was in a very well-respected shop that believed the claims of the product's label and salesperson. Most consumers trust their vehicles to professional service facilities, and few are aware of the pitfalls that are possible if poor quality or poorly selected formulations are used.

Since the close of the last century, vehicle and engine manufacturers have been recommending and using new coolant formulations. These formulations may offer good solutions for global manufacturers who want to implement global fluids programs throughout their product line. It is easy to understand how a single fluid, capable of providing satisfactory service in any given system in any part of the world, would be convenient both for the manufacturer and the vehicle operators. The author has personally witnessed consumers confused as to the use of engine coolant concentrates, which are intended to be used in conjunction with water, typically blended at 50 % each. Many consumers add concentrate products to cooling systems undiluted. Some people believe that “more is better,” or at least that adding straight antifreeze is acceptable, but that is an incorrect concept when applied to engine coolant concentrates. Therefore, we learn that simplicity in the marketplace is desirable to facilitate owner-operator vehicle maintenance.

The author encourages ASTM Committee D15 on Engine Coolants and Related Fluids to debate possibly expanding ASTM D3306 [1], ASTM D6210 [2], and similar specifications to include compatibility testing. Of course, Committee D15 would have to define “compatibility,” develop a testing protocol, and guide the industry in making appropriate disclosures to the motoring public.

Discussion

It would appear that most manufacturers advise against mixing different types of coolants. Of course, aftermarket applications will involve performance of mixtures on “seasoned” or “passivated” metal surfaces. The OEM research is likely conducted on new metal surfaces with unused coolants. Predictably, each OEM has a strong preference for the coolant formulations that they have meticulously qualified and selected for factory-fill. Here are six examples of published advice to car buyers from major manufacturers:

SIX OEM POSITIONS ON MAINTAINING AND MIXING ENGINE COOLANTS

General Motors

“When adding coolant, it is important that you use only DEX-COOL (silicate-free) coolant. If coolant other than DEX-COOL is added to the system, premature

engine, heater core, or radiator corrosion may result. In addition, the engine coolant will require change sooner at 30 000 miles (50 000 km) or 24 months, whichever occurs first. Damage caused by the use of coolant other than DEX-COOL is not covered by your new vehicle warranty”[6].

Ford Motor Corporation

“Adding engine coolant—when adding coolant, make sure it is a 50/50 mixture of engine coolant and distilled water. Add the mixture to the coolant reservoir, when the engine is cool, until the appropriate fill level is obtained. If coolant is filled to the COLD FILL RANGE or FULL COLD level when the engine is not cool, the system will remain underfilled.

DO NOT MIX different colors or types of coolant in your vehicle. Make sure the correct coolant is used.

DO NOT MIX recycled coolant and new (unused) coolant together in the vehicle. Mixing of engine coolants may harm your engine’s cooling system. The use of an improper coolant may harm engine and cooling system components and may void the warranty. Refer to Maintenance product specifications and capacities in this chapter” [7].

Also, Ford’s position is made clear in the following advice to owners:

“Due to the complexity of cooling systems, no coolant has been approved to work in all vehicles. ‘Universal’ coolants generally do not contain silicates and nitrites, both of which are required for Ford vehicles equipped with Motorcraft Premium Gold Engine Coolant. Thus, these ‘universal’ coolants may not be suitable for use in vehicles originally equipped with Motorcraft Premium Engine Coolant.... Use of non-approved ‘universal’ coolants may lead to eventual engine damage or failure” [8].

Ford publishes a quick reference “Service Coolant Usage Chart” to assist owners available online.³ The guide helps Ford owners choose the correct Ford formulation from the five different coolants that Ford has used since 1998.

Chrysler

“Adding Coolant—When adding coolant, or refilling the system, a minimum solution of 50 % recommended HOAT (author’s note: Hybrid Organic Acid Technology) ethylene glycol engine coolant (antifreeze) (MS-9769) and distilled water should be used. Use higher concentrations (not to exceed 70 %) if temperatures below -34°F (-37°C) are anticipated” [9]. Change in 2013 model year: “We recommend you use MOPAR Antifreeze/Coolant 10 Year/150 000 Mile Formula OAT (Organic Additive Technology). (MS 12 106)” [10]. The new Chrysler OAT coolant has some very clear language included:

³Available at <https://www.fcsdchemicalsandlubricants.com/main/quickref/scucEN.pdf>.

Limitations on Usage—This coolant is to be used in vehicles equipped designed to use OAT coolant. It must not be used in any other Chrysler Group engine or cooling system. This coolant is an OAT coolant and is not compatible with HOAT coolants like MS-9769. This coolant will not contain 2-EH [11].

Toyota

“Your Toyota is equipped with Genuine Toyota Super Long-Life Coolant. The replacement intervals for engine coolant recommended in this booklet are based on replacement with Genuine Toyota Super Long-Life Coolant or similar high-quality non-silicate, non-amine, non-borate ethylene-glycol coolant with long-life hybrid organic acid technology (i.e., a combination of low phosphates and organic acids). If another type of ethylene-glycol coolant is used, replacement intervals may be different” [12].

Nissan USA

“When adding or replacing coolant, be sure to use only Genuine NISSAN Long Life Antifreeze/Coolant (blue) or equivalent. Genuine NISSAN Long Life Antifreeze/Coolant (blue) is pre-diluted to provide antifreeze protection to -34°F (-37°C).... The use of other types of coolant solutions other than Genuine NISSAN Long Life Antifreeze/Coolant (blue) or equivalent may damage the engine cooling system.

The life expectancy of the factory-fill coolant is 105 000 miles (168 000 km) or 7 years. Mixing any other type of coolant other than Genuine NISSAN Long Life Antifreeze/Coolant (blue), including Genuine NISSAN Long Life Antifreeze/Coolant (green), or the use of non-distilled water will reduce the life expectancy of the factory-fill coolant. Refer to the Nissan Service and Maintenance Guide for more details” [13].

Volkswagen

“The right coolant will help prolong the service life of the engine. The coolant required for your Volkswagen is only available at your Volkswagen dealer. Coolant additive is the special fluid for the cooling system of a liquid-cooled engine. It protects the engine and cooling system. The vast range of modern materials and high engine performance demand a special coolant additive. G12+ remains thermally stable to a temperature of $+135^{\circ}\text{C}$ and its anti-corrosion composition provides for better heat dissipation to alloy components such as an aluminum cylinder head. A cylinder head that cools as designed will help to prolong the engine’s service life” [14].

SIMPLE PRECIPITATION TESTING IN GLASSWARE MODIFIED FOR COOLANT COMPATIBILITY RESEARCH

Hyundai/Kia offer the following [15] screening test entitled “*Compatibility with Mixing*”:

Dilute samples of the candidate coolant and the approved coolant with equal parts of corrosive water (as described in ASTM D1384 [16]). Mix 100 ml of the candidate antifreeze solution with 100 ml of the approved coolant solution in a 250 ml beaker. Heat the mixture to 90 ~ 95°C. Cover, remove from the heat and let stand 16 ~ 24 h at room temperature in the absence of light. There shall be no precipitation or separation.

Why do the manufacturers feel so strongly about engine coolants? What can happen if you mix dissimilar coolants? The author is not aware of any published information from vehicle manufacturers that reports cooling system failures attributed to mixing dissimilar coolants. However, a clue is provided in that several of the manufacturers' specifications require corrosion testing of coolants in ASTM standard tests. In particular, test methods ASTM D4340 [17] and ASTM D1384 [16] are modified to check compatibility (see Table 1).

REVIEW OF THE TESTING PROTOCOLS

ASTM D4340 [17] Standard Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions Modified for Coolant Compatibility Research.

This test method covers a laboratory screening procedure for evaluating the effectiveness of engine coolants in combating corrosion of aluminum casting alloys under heat-transfer conditions that may be present in aluminum cylinder head engines.

In this test method, a heat flux is established through a cast aluminum alloy typical of that used for engine cylinder heads while exposed to an engine coolant under a pressure of 193 kPa (28 psi). The temperature of the aluminum specimen is maintained at 135°C (275°F) and the test is continued for 1 week (168 h). The effectiveness of the coolant for preventing corrosion of the aluminum under heat-transfer conditions (hereafter referred to as heat-transfer corrosion) is evaluated on the basis of the weight change of the test specimen.

To evaluate compatibility, three to five runs are conducted. The coolants are mixed either per three mixtures or five mixtures preferences and a total of 25 % total antifreeze concentrate is mixed with ASTM Standard Corrosive Water per the method. The antifreeze component is prepared before mixing for compatibility testing as in Table 2.

It is supposed, of course, that satisfactory Standard ASTM D4340 [17] data exist for both coolants. Nevertheless, some researchers will perform standard control runs on the candidate and approved coolants to establish baseline data.

An example of using this method for research is presented by Weisenberger and Hadjat [18].

ALTERNATE D4340 METHOD MODIFICATION

Preconditioning and/or Use of Higher Antifreeze Concentrations

It is generally known in the coolant industry that testing certain mixtures of OEM-approved engine coolants per the ASTM D4340 [17] method described above does

TABLE 1 Examples of OEM Compatibility Requirements.

Manufacturer	ASTM D4340 [17]	ASTM D1384 [16]	Other Compatibility Test
GM 6277M [4]	(25 % total coolant concentrate, 100 ppm chloride) in 1:3, 1:1 and 3:1 volumetric mixtures with a GM 6277M/GMW 3420 approved coolant and any other coolant selected by the GM Coolant Committee.	1:3, 1:1 and 3:1 volumetric mixtures with the following: Coolant approved to GM6277M/ GMW3420 and any other coolant type as selected by the Coolant Committee.	Non Metallic Testing. Candidate engine coolant (alone, not mixed) as normally used in cooling systems shall have no deleterious effects on hoses, gaskets, seals, O-rings, and coatings and other cooling system components and materials.
GMW3420 [3]			
Ford Motor Company	WSS-M97B51-A1 hybrid 10 %/90 %, 30 %/70 %, 50 %/50 %, 70 %/30 % and 90 %/10 % of test coolant and each coolant currently supplied to the market in which the coolant is to be used for both initial fill and after market applications.	WSS-M97B51-A1 hybrid 10 %/90 %, 30 %/70 %, 50 %/50 %, 70 %/30 % and 90 %/10 % of test coolant and each coolant currently supplied to the market in which the coolant is to be used for both initial fill and after market applications.	WSS-M97B44-D (OAT) Precipitation test with 50 % Ford approved coolant. If precipitation observed then D1384 % 50-50. Compatibility with radiator flux.
Chrysler	1.3 Limitations on Usage - This coolant is to be used in vehicles equipped designed to use OAT coolant.		
MS12106	It must not be used in any other Chrysler Group engine or cooling system. This coolant is an OAT coolant and is not compatible with HOAT coolants like MS-9769.		
(Sebacic Acid as Primary Inhibitor)	This coolant will not contain 2-EH.		
VW TL 774	"Miscibility: The different types of coolant additives must be miscible with each other in any ratio with all coolants of the same type without any degradation of the functional characteristics."		

produce results that exceed the corrosion rate maximums established by ASTM D3306 [1]. One such report is included by Weisenberger and Hadjat [18]. Some industry researchers argue that the use of the standard ASTM D4340 [17] is a poor model of the aftermarket environment because we are really trying to understand what happens if you "top up" a system that has been in service for some time with a candidate coolant formulation. A modification has been researched and experiments performed.

TABLE 2 Two commonly requested compatibility testing protocols.

Antifreeze Concentrate Mixtures for Compatibility Testing	
Three Sample Method	Five Sample Method
1. 25 % Candidate/75 % Approved	1. 10 % Candidate/90 % Approved
2. 50 % Candidate/50 % Approved	2. 33 % Candidate/67 % Approved
3. 75 % Candidate/25 % Approved	3. 50 % Candidate/50 % Approved
	4. 67 % Candidate/33 % Approved
	5. 90 % Candidate/10 % Approved

The modification is performed by exposing the aluminum specimen under standard ASTM D4340 [17] conditions for 48 h. The test is then stopped and the coolant is modified so as to represent a mixture as described in Table 2. The test is then resumed and run to completion. The author has observed that this modification results in calculated corrosion rates that are less severe than tests performed per the standard method. Some researchers also feel that the total antifreeze concentration in a compatibility test should be 50 %, not 25 %, to aggravate any potential instability or incompatibility problems. The author has not compared the 25 % antifreeze–preconditioning data to the 50 % antifreeze preconditioning data, but can report that if the specimen is preconditioned for 48 h with any OEM approved coolant, no unsatisfactory result has yet been observed in any test. This may be interpreted as demonstration of acceptable corrosion protection performance on passivated metal surfaces when coolants are mixed, or it may be interpreted that this test variation is too forgiving. This is a matter for the D15 Committee and subcommittees to debate, but Weisenberger and Hodjat [18] remind us that when new cooling system components are installed, there are unpassivated metals in the system and such metals are vulnerable to attack if the coolant chemistry is incapable of quickly passivating new parts [18].

ASTM D1384 CORROSION TEST FOR ENGINE COOLANTS IN GLASSWARE MODIFIED FOR COOLANT COMPATIBILITY RESEARCH [16]

This test method covers a simple beaker-type procedure for evaluating the effects of engine coolants on metal specimens under controlled laboratory conditions. In this test method, specimens of metals typical of those present in engine cooling systems are totally immersed in aerated engine coolant solutions prepared with corrosive salts for 336 h at 88°C (190°F). The corrosion inhibition properties of the test solution are evaluated on the basis of the weight changes incurred by the specimens. Each test is run in triplicate, and the average weight change is determined for each metal. This test method will generally distinguish between coolants that are definitely deleterious from the corrosion standpoint and those that are suitable for further evaluation. However, the results of this test method cannot stand alone as evidence of satisfactory corrosion inhibition. Only more comprehensive bench,

dynamometer, and field tests can determine the actual service value of an engine coolant formulation.

Automobile manufacturers have accepted the specimens prescribed in this test method, but their composition may not be the same as that of alloys currently used for engine cooling system components. Therefore, specimens other than those designated in this test method may be used by mutual agreement of the parties involved. The following metal test specimens, 1 by 2 in. in size, representative of cooling system metals, were used:

- 1. Steel, UNS G10200 (SAE 1020): Chemical composition of the carbon steel is as follows: carbon, 0.17 to 0.23 %; manganese, 0.30 to 0.60 %; phosphorus, 0.040 % maximum; sulfur, 0.050 % maximum.
- 2. Copper, conforming to UNS C11000 (SAE CA110) or UNS C11300 (SAE CA113). Cold-rolled
- 3. Brass, conforming to alloy UNS C26000 (SAE CA 260).
- 4. Solder—A brass specimen as described in 6.1.3, coated with solder conforming to Alloy Grade 30 A (SAE 3 A).
- 5. Cast Aluminum, conforming to alloy UNS A23190 (SAE 329).
- 6. Cast Iron, conforming to alloy UNS F10007 (SAE G3500).

To evaluate compatibility of one coolant with another, as with the modified D4340, three to five runs are conducted. The coolants are mixed either per GM (three mixtures) or Ford (five mixtures) preferences. It is supposed, of course, that satisfactory Standard ASTM D1384 [16] data exist for both coolants. Nevertheless, some customers will choose to perform control runs.

At the conclusion of the tests, results are generated as prescribed in the method. These methods can be compared to the performance of the coolants being tested when they are tested alone per ASTM D1384 [16] and also evaluated against the maximum weight losses published in ASTM D3306 [1] and various OEM specifications.

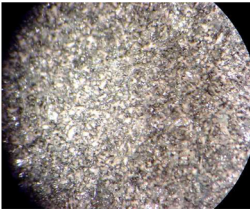
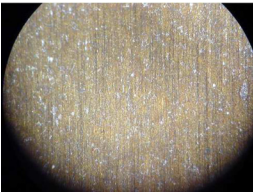
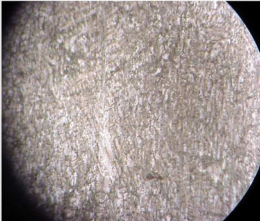
Satisfactory results must be agreed to between the customer and supplier. At a minimum, it seems logical and consistent to adopt the ASTM D1384 [16] weight loss maximums published in ASTM D3306 [1](Table 1). Examples of actual D1384 experimental results for aluminum coupons are shown in Table 3. These photos of aluminum specimens in Table 4 illustrate the variance that is possible in ASTM D1384 [16] testing.

TABLE 3 Mass loss maximums published in ASTM D3306 for D1384 testing.

	Copper (Cu)	Brass	Iron (Fe)	Steel	Aluminum (Al)	Solder
mg loss	10	10	10	10	30	30
Conversion to (mg/cm ²) ^a	0.36	1.08	0.36	1.08	0.36	1.08

^aClose approximation based on standard specimens used at Amalgatech; these numbers are provided for the convenience of readers more accustomed to these units. Note: these are NOT the JIS limits, these are the ASTM limits converted to mg/cm².

TABLE 4 Some examples of ASTM D1384 aluminum results.

	Photo	Micrograph 30X	mg Loss	mg/cm ²
Number 1			617	22.26
Number 2			167	6.02
Number 3			0	0.00
Number 4			18	0.65

These tests are formulations that contain silicate when mixed with lower pH carboxylate-inhibited formulations

Summary

Engine Coolant compatibility is being evaluated by and/or for engine manufacturers using stability and corrosion methods. The most commonly specified

methods include physical stability, modified ASTM D4340 [17] and modified D1384 [16] standard tests. Many manufacturers now include compatibility testing in their coolant specifications. Satisfactory performance in these tests is intended to provide evidence that two coolants, if mixed, will not cause problems such as precipitation of materials that could block cooling system passages and also that the mixture of two coolants does not result in an unacceptable loss of corrosion protection for the metals in the system. ASTM Committee D15 could debate the definition of compatibility as might be reasonably predicted by the tests discussed. Data could be required by, and included in, ASTM D3306 [1] and D6210 [2] testing protocols as “Report Only” because even though it is possible that a formulation that is highly desirable for one application might perform poorly in compatibility, it may nevertheless offer desirable properties as factory-fill. Therefore a coolant should not be disqualified from ASTM D3306 [1] based on its compatibility performance with other coolants. In the best case scenario, satisfactory performance of a candidate formulation mixed with an intelligently selected representative range of dissimilar formulations could support claims that the candidate may be satisfactorily used as a top-up in a variety of vehicles.

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INTERACTIONS IN ENGINE COOLING SYSTEMS

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The Effects of Residual Controlled Atmospheric Brazing Flux on Engine Coolants

Reference

Alverson, Fred C., Ranger, Mary, and DeBaun, Heather J., "The Effects of Residual Controlled Atmospheric Brazing Flux on Engine Coolants," *Global Testing of Extended Service Engine Coolants and Related Fluids*, STP 1556, Edward R. Eaton, Ed., pp. 175–194, doi:10.1520/STP155620130067, ASTM International, West Conshohocken, PA 2014⁴

ABSTRACT

Automobile and truck heat exchangers, including radiators, heater cores, oil coolers, charge air coolers, etc., are predominantly manufactured with aluminum alloys using a process known as controlled atmosphere brazing (CAB). In the CAB process, a fluxing agent (such as potassium fluoroaluminate), is applied to the surfaces to be joined. The fluxing agent melts, dissolves, and displaces the aluminum oxide layer that naturally formed on the aluminum surfaces and frees up and allows the metal filler to flow and form brazed joints. The presence of residual brazing flux in the heat exchangers, along with the high ratio of aluminum surface area to coolant volume within the internal tube surfaces, may affect the physical and chemical properties and corrosion protection of certain engine coolant formulations. The effects may include color fading, ammonia formation/odor, pH increase, rapid depletion of inorganic corrosion inhibitors (particularly nitrite, nitrate, molybdate, and silicate), formation of deposits, coolant passage blockage, and ultimately heat exchanger failure. Some of these effects have been exacerbated by newer, more efficient heat exchangers with smaller internal passages, heat exchangers with internal braze joints along the length of the tubes, and shipment of vehicles worldwide under stagnant coolant conditions. This paper summarizes some of these failure modes in aluminum

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CAB heat exchangers. It also covers the development of an aluminum heat exchanger screening test to assess the effects of residual brazing flux on engine coolant physical and chemical properties and corrosion protection after aging the engine coolant in a CAB heat exchanger at elevated temperature under stagnant conditions. Test results are provided on conventional, hybrid organic additive technology (HOAT), and extended life coolants (ELC) along with correlations to field performance of coolants. In addition, this paper introduces a test to assess the amount of residual brazing flux in heat exchangers.

Keywords

antifreeze/coolant, brazing flux, controlled atmospheric brazing, potassium fluoroaluminate flux, heat exchangers

Introduction

Automobile and truck radiators, heater cores, charge air coolers, oil coolers, and other heat exchangers are now widely made with aluminum alloys which provide excellent cooling performance at reduced weight [1]. These heat exchangers consist of alternating layers of tubes and corrugated fins in a frame with end tanks and are commonly manufactured using a process known as controlled atmosphere brazing (CAB) [2].

The CAB process involves assembly of the heat exchanger (tubes, fins, side supports, and header plates) in a fixture that is carried along a conveyor belt through degreasing/cleaning, flux application, and blow-off stations and brazing oven. A fluxing agent (such as potassium fluoroaluminate) is applied to the heat exchanger to facilitate the formation of joints. The function of the fluxing agent is to displace the oxide film naturally present on aluminum surfaces, allow the filler metal to flow, and protect the surfaces from re-oxidizing during the brazing operation [3].

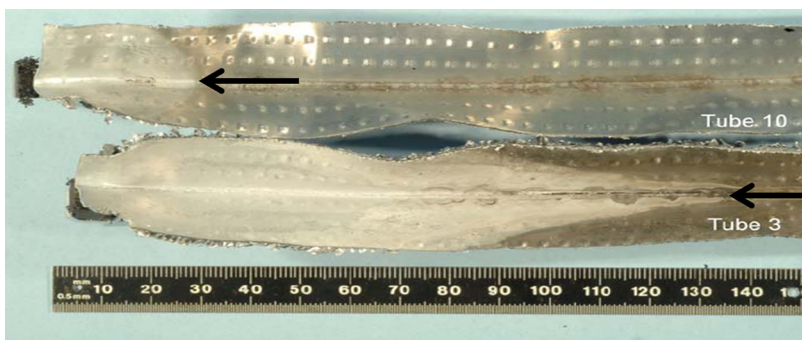
The CAB process requires the use of aluminum brazing alloys/brazing sheets for aluminum components to be brazed in the heat exchanger. Aluminum AA 3003 alloy or modified AA 3003 alloys containing minor amounts of other elements (i.e., copper, manganese, zinc, chromium, etc.) are commonly used for the base or core alloy for tubes and fins. The core alloy is clad on one or both sides with an aluminum brazing filler metal (i.e., aluminum alloys with silicon in the AA 4000 series such as AA 4343 or AA 4045). This material is used to make seam welded tubes or brazed tubes. The water side of the tube material may also be clad with AA 7072 (aluminum alloyed with zinc) or AA 1050 (aluminum 99.5 %) for improved corrosion resistance performance [3]. The fins are made from unclad stock.

During the CAB process, brazing flux is applied to the heat exchanger by a variety of methods including low pressure spray, flooding, dipping, roll coating, brushing, and electrostatic (dry fluxing). The application method depends on several factors: heat exchanger design and aluminum alloys, surface wettability, lubricants / degreasing, floor space, and personal choice. For flat radiator and heater core tubes, low pressure spray application is the most common means in which multiple

nozzles direct the spray on to the tubes and fins. Separate nozzles and brazing flux concentrations are sometimes used for the headers. With spray application, precautions should be taken to prevent nozzles from spraying brazing flux into the inlets/outlets of the tubes. For radiator, heater core, and other heat exchangers using folded B tubes, which have an internal middle wall, the application method may involve dipping, roll coating, and/or electrostatic application to coat the internal wall in the tubes for brazing. From an engine coolant perspective, engine coolants may be exposed to a greater amount of brazed aluminum surface area and/or post brazing flux in internally brazed tubes [3].

The most common brazing flux agent is a mixture of potassium aluminum fluorides which has a general formula of $K_{1-3}AlF_{4-6}[(H_2O)_n]$. As sold, it typically consists of a mixture of $KAlF_4$ (70–80 %) and $K_2AlF_5 \cdot H_2O$ (20–30 %). The brazing flux is a white powder substance that is mixed with water at a concentration of 5 %–25 % to form a slurry. The brazing flux slurry is then applied to the metal surface to be bonded at a coating (flux loading) of approximately $3\text{--}5\text{ g/m}^2$, which reportedly provides $1\text{--}2\text{ }\mu\text{m}$ tightly adherent non-corrosive residue. Due to very low solubility in water, the brazing flux slurry requires constant agitation to prevent the flux from settling. After flux application, the heat exchanger sometimes goes through an air blow-off step which pushes the flux into the center core to provide a uniform coating. The blow-off step should also remove excess flux and prevent pooling/puddling of flux. The brazing flux application method and amount are critical since too little brazing flux may result in poor metal filler flow and poor/weak joint formation; too much flux may result in pooling of flux, grey substance formation, and visible flux on surfaces [3]. Figure 1 shows the internal surfaces of two tubes from the same radiator after spray flux and blow off of the welded tubes (in the post-braze condition). The arrows indicate the unintentional flux intrusion into the tubes—intrusion in the top tube (tube 10) is $\sim 1\text{ in.}$ while intrusion in the bottom tube is $\sim 5.5\text{ in.}$ (tube 3). This shows the variability in the amount of

FIG. 1 Unintended flux intrusion in radiator tubes.



unintended internal flux based on possible process variability (air knives for tube 3 were configured such that air was blowing the flux into the tube).

After fluxing, blow-off, and subsequent drying for complete removal of slurry water, the heat exchanger passes through a brazing oven generally consisting of three zones: pre-heat, brazing, and cooling. In the pre-heat zone, the heat exchanger is heated to approximately 200°C to remove all water and moisture. During the brazing zone, from approximately 564°C–572°C, the brazing flux melts and reacts, dissolves, and displaces the aluminum oxide layer that naturally formed on the aluminum alloy surface. As the temperature reaches approximately 577°C (depending on the choice of filler metal alloy), the filler metal (clad) melts, flows, and forms the brazed joints. During cool down, the brazed joints solidify and any excess brazing flux left on the surface also solidifies and remains on the surface as a residue. CAB brazing is conducted in a controlled atmosphere (dew point < –40°C and oxygen concentration < 100 ppm) using an inert gas such as nitrogen. The controlled atmosphere conditions minimize oxygen and moisture to prevent re-oxidation of aluminum surface and formation of corrosive HF gas and the high temperature results in sublimation of KAlF_4 although some KAlF_4 will remain on the surface [3].

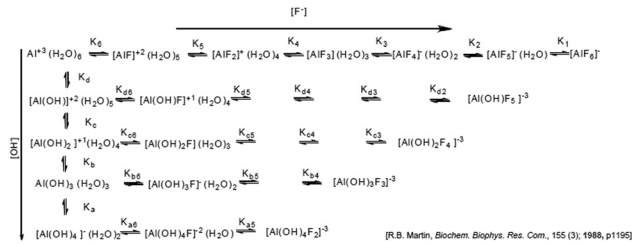
The majority of automotive and truck radiator tubes, heater core tubes, and charge air cooler tubes are made using welded flat tubes or folded and brazed B tubes. The folded B type tube with the internal wall braze joint offers benefits in providing greater structural integrity and durability, which allows the use of smaller coolant passage width and wall thickness, greater amount of turbulators (dimples) to promote turbulence and heat transfer, and greater aluminum surface area for increased heat transfer. Trends in tubes with smaller coolant passages and wall thicknesses (regardless if flat tubes or folded B tubes) tend to increase the potential for plugging from any debris or deposits in the cooling system, and accelerate pitting corrosion through the metal. The newer brazing alloys/cladding along with increased severity of operating conditions (high coolant flow rates/surface velocities and higher temperatures) increase the potential for erosion–corrosion and removal of sacrificial linings.

HYDROLYSIS OF POST BRAZING FLUX RESIDUES

Recent industry studies have shown that brazing flux residues are slightly soluble in water and may leach out potassium, fluoride, and aluminum fluoride ions. Figure 2 shows that $\text{K}_x\text{Al}_y\text{F}_z$ flux residue may undergo dissolution and hydrolysis. Aluminum and fluoride can form six compounds in aqueous solutions, and aluminum can form four compounds with hydroxyl groups. This results in a total of 24 compounds which have limited solubility in water, lower solubility in engine coolant solutions, and may form aluminum precipitates that can plug narrow coolant passages in heat exchangers [4].

Studies at Ford Motor Company have also shown that post brazing flux is partially soluble in commercial engine coolants and will leach out fluoride, potassium, and aluminum ions. Figure 3 shows flux solubility observed in four vehicles at 500

FIG. 2 Dissolution of $K_xAl_yF_z$ fluxes.



and 14 000-mile intervals for fluoride and potassium (the coolant formulation did not contain potassium). The concentration of potassium in solution continued over time, as shown. Determining the actual amount of dissolution in engine coolant can be problematic. Some coolant formulations contain potassium that can compound the amount, aluminum can form hydroxides and come out of solution as precipitates, and fluoride is very reactive and can interact with aluminum oxides and free aluminum.

ENGINE COOLANT INTERACTION WITH CAB HEAT EXCHANGERS AND POST BRAZING FLUX

Post-braze flux solubility and interactions with engine coolant can enhance the corrosion of metals in electrochemical and ASTM D1384-12 [5] Standard Test Method for Corrosion Test for Engine Coolants in Glassware tests [6–9]. In a Ford engine test stand study, three operating condition variables (flux concentration, temperature, and aeration) were evaluated to determine the effects on corrosion pitting of aluminum heater core and radiator tubes. Test results (Table 1) showed that the

FIG. 3 Dissolution of $K_xAl_yF_z$ fluxes in four vehicles.

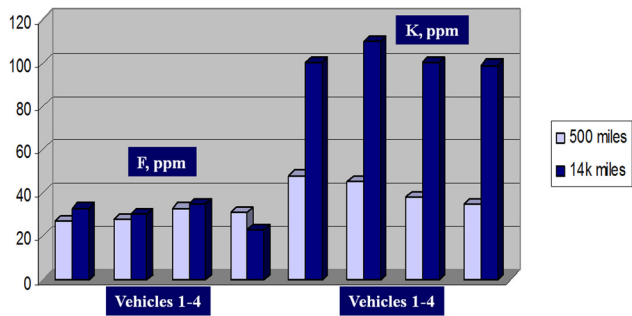


TABLE 1 Engine test stand study: effects of flux, temperature, and aeration on corrosion.

Operating Condition	Base	Test 1	Test 2	Test 3	Test 4
Flux	Design	+50 g	Design	Design	+50 g
Temperature	Design	Design	+8° C	Design	+8° C
Air	Design	Design	Design	+1.5 psi	+1.5 psi
Pit Depth, %					
Heater Core	1.6	3.3	6.1	9.1	12.0
Radiator	2.1	3.8	4.3	5.3	6.4

combination of increased brazing flux, elevated temperature, and increased aeration resulted in the greatest pitting depths of heater core and radiator tubes [10].

In actual vehicle service, flux-coolant interaction has been documented showing that brazing flux is soluble in engine coolants and can cause corrosion at fluxed surfaces, increased general corrosion, and crevice corrosion under flux [11]. Figures 4 and 5 show an example of crevice corrosion that was observed in the channel of a radiator header underneath a build-up of post-braze residual flux. The radiator was exposed to a HOAT engine coolant.

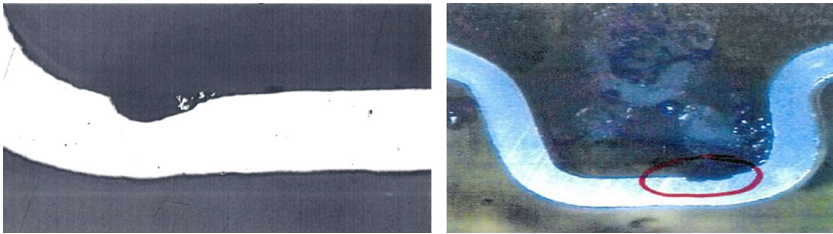
Figure 6 shows radiator tubes following Ford-modified ASTM Standard Test Method for D2570 [12] Simulated Service Corrosion Testing of Engine Coolants testing with an organic additive technology (OAT) engine coolant. Following testing, orange deposits were observed at ends of the tubes where flux ingress had occurred. Interestingly, the deposits were only located at the interface of fluxed and non-fluxed surfaces (flux resulted from unintended intrusion during spray and blow off). The darkened center portion is where the flux was present in the tubes. Metallurgical analysis of the tubes revealed extensive corrosion attack—via intergranular corrosion with pitting—associated with areas underneath the deposits, as shown in Fig. 7.

Under dynamic conditions, ASTM D2809-09 [13] Standard Test Method for Cavitation Corrosion and Erosion-Corrosion Characteristics of Aluminum Pumps With Engine Coolants testing was conducted on two extended life coolants (OAT)

FIG. 4 Post-braze flux residue in radiator header channel.



FIG. 5 Cross-sectional views of crevice corrosion in radiator channel underneath deposits.



with nitrite and without nitrite with the addition of 100 ppm NaF and 100 ppm fused brazing flux. Test results (Table 2) indicate that the presence of fluoride ions may degrade ASTM D2809 cavitation erosion–corrosion protection by 1–2 values with the OAT nitrated coolant.

FIG. 6 Deposits observed in tubes post-internal corrosion testing.

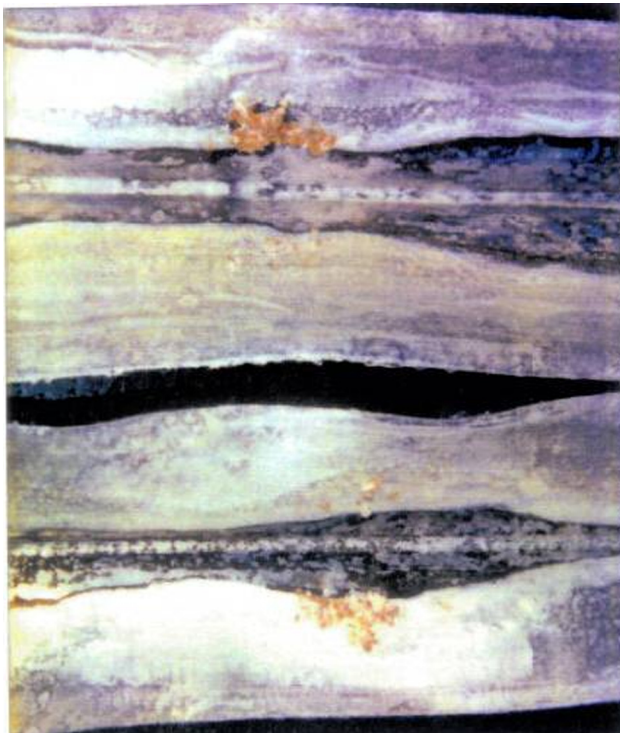
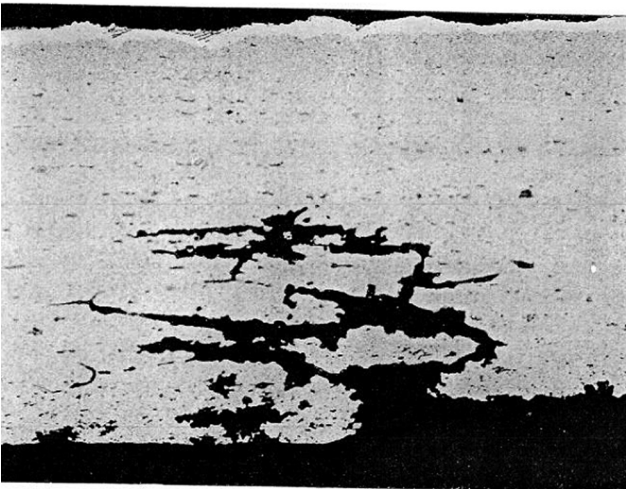


FIG. 7 Cross-sectional view of corrosion observed underneath deposits.



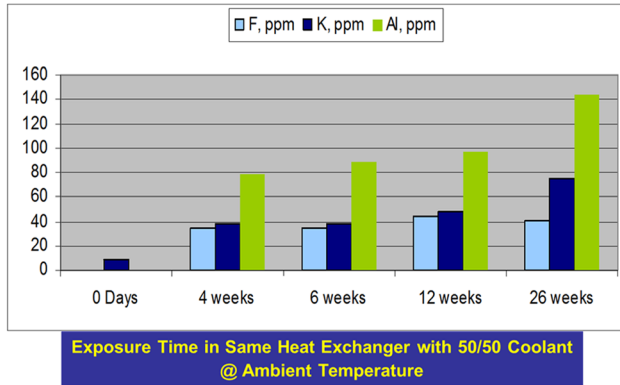
ENGINE COOLANT INTERACTION WITH CAB HEAT EXCHANGERS AND POST BRAZING FLUX

The industry as a whole has been observing greater engine coolant interaction with CAB brazed aluminum heat exchangers and post brazing flux. Figure 8 shows the flux solubility over time. The testing involved exposing engine coolant to post-braze flux in radiators at ambient temperature. Samples were collected over time and analyzed for potassium, fluoride, and aluminum. The radiators involved were manufactured by spraying flux and blowing off the excess.

The flux solubility and flux-coolant interaction along with high aluminum surface area may adversely affect physical and chemical properties and corrosion protection of certain types of engine coolants. The effects may include color fading, ammonia odor, pH increase, rapid depletion of corrosion inhibitors (particularly

TABLE 2 ASTM standard test method D2809 [13] test results for OAT coolants with fluoride.

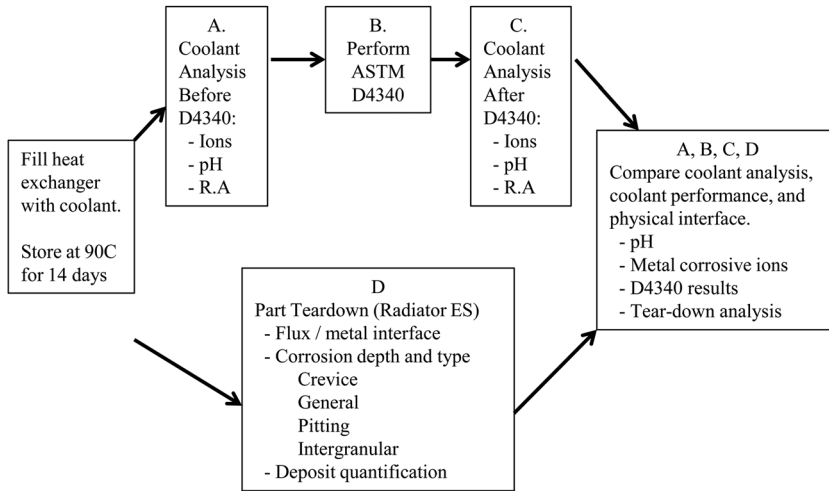
Coolant	ASTM D2809 Test Result
OAT Nitrite Reference Coolant	8
OAT Nitrite with 100 ppm NaF	7
OAT Nitrite with 100 ppm fused flux	6
OAT Nitrite Free Reference Coolant	8
OAT Nitrite Free with 100 ppm NaF	7
OAT Nitrite Free with 100 ppm fused flux	8
ASTM D 3306 Requirement Note: 1= High Corrosion / 10 = Low Corrosion	8 Minimum

FIG. 8 Flux solubility in engine coolant.

nitrite, nitrate, molybdate, and silicate), formation of deposits, coolant passage blockage, and ultimately heat exchanger failures. Figure 9 shows examples color fading of an OAT only coolant, a heavy duty OAT coolant with nitrite and molybdate, and a heavy duty fully formulated coolant following 2 week exposure to post-braze residual flux in a heat exchanger at $90 \pm 2^\circ\text{C}$.

As of this time, there are no standard industry tests to assess coolant interactions between CAB heat exchangers and post brazing flux. This paper covers development of an aluminum heat exchanger screening test to assess effects of residual brazing flux on engine coolant physical and chemical properties and corrosion protection after aging the engine coolant in a CAB brazed heat exchanger at elevated temperature under stagnant conditions. The test is based on Ford Laboratory Test Method BL-106-01 [14] “Stagnant Coolant Test For Aluminum and Fluorine and Its Effect on Aluminum Corrosion Under Heat Rejecting Conditions.” Figure 10 shows a flow chart of the test method. A modification of this test may also be used to provide a determination on the amount of post brazing flux that may be leached

FIG. 9 Coolant color change after exposure to post-brazed aluminum heat exchanger tubes.

FIG. 10 Flow chart of the Ford coolant flux stagnation exposure test.

into water solution. The modified test is run by filling the CAB brazed heat exchanger with deionized water, storing for 24 h at room temperature, and measuring the amount of potassium, fluoride, and aluminum in the post-test aqueous solution. This test method is described later in this paper.

Experimental

The test method involves filling a CAB brazed heat exchanger with 50/50 engine coolant prepared with deionized water and aging the heat exchanger in an oven for 2 weeks at $90 \pm 2^\circ\text{C}$. Engine coolant stability is assessed based on changes in coolant physical and compositional properties, and engine coolant corrosion is based on performance in the ASTM D4340-10 [15] Standard Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions.

If changes are noted in the coolant or the coolant post-stagnation fails ASTM D4340 [15] testing, the heat exchanger is torn down to look for deposits and analyzed metallurgically for evidence of corrosion attack. In addition, the stagnation portion can be run at ambient temperature for 2 or more months, if desired, to allow for the corrosion to progress.

The aluminum CAB brazed heat exchanger used in the test may be commercially produced or experimentally prepared by the heat exchanger supplier. With commercially produced heat exchangers, it is recognized that the aluminum alloying, flux loading during brazing, and particularly the amount of residual flux remaining in the part after CAB brazing may vary from part to part. Therefore, the

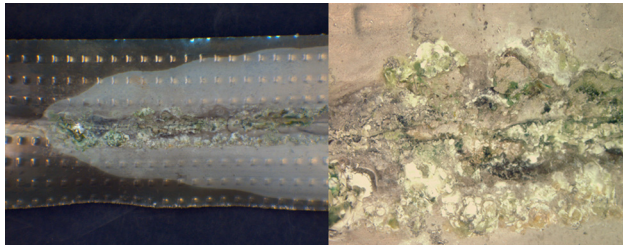
heat exchanger type, manufacturer, size, and other design parameters should be decided by mutual agreement of the parties using the test.

HEAT EXCHANGER STAGNATION TESTING WITH ENGINE COOLANTS— ACTUAL RESULTS

The sensitivity of the engine coolant and flux interaction was observed during a series of Ford coolant-flux stagnation tests of three HOAT formulations using radiators from two different manufacturers. One of the formulations—HOAT #1—exhibited compositional changes following stagnation testing and it failed the ASTM D4340 test [15]. The radiator was torn down to assess flux ingress and look for deposits. Heavy deposits were observed in ends of several of the tubes where flux intrusion had occurred, as shown in Fig. 11. Evidence of flux intrusion was observed up to 10–13 in. in length, total of both tube ends. The manufacturing process included spray fluxing followed by blow off and the tubes were welded. Tubes were cross-sectioned at the precipitates and metallurgically evaluated. There was no evidence of corrosion underneath the precipitates, following the 14-day exposure at $90 \pm 2^\circ\text{C}$.

The manufacturer made two iterations of changes to the fluxing process to improve the flux application. Coolant-flux stagnation testing was repeated with HOAT #1 formulation that initially failed, following both iterations of manufacturing changes. In addition, a known, less sensitive HOAT formulation—HOAT #2—was coolant-flux stagnation tested when the flux intrusion had been reduced as much as possible. In a second study, HOAT #3 and OAT #1 were tested in a radiator from a second manufacturer that also used spray flux and blow off of welded tubes. The tubes exhibited around 10 in. of flux ingress, average of both sides. At first, HOAT #3 failed and OAT #1 passed ASTM D4340 [15] post-stagnation testing. The manufacturer altered the process to obtain less than $\frac{1}{2}$ " of flux ingress, average of both sides, in the tubes. Retesting was performed. The HOAT #3 then passed ASTM D4340 testing post-stagnation.

FIG. 11 Precipitates observed in tubes following coolant-flux stagnation testing in the flux ingress zone of the tube.



All results are shown in Table 3. As shown, a reduction in internal flux residue can accomplish a significant reduction in weight loss during ASTM D4340 [15] testing for the HOAT formulations that exhibit sensitivity to flux loading. On the other hand, engine coolants that are robust to flux loading in ASTM D4340 are unaffected by reductions in residual internal flux.

Aluminum heat exchanger stagnation testing was conducted on two light duty OAT (LD OAT) and five light duty HOAT (LD HOAT) engine coolants with another heavily fluxed automotive radiator. The post-test coolants after radiator stagnation were analyzed and subjected to the ASTM D4340 test [15]. Test results presented in Table 4 show the two LD OAT coolants exhibited color changes from orange to pink, no change in OAT corrosion inhibitor levels, and passing ASTM D4340 results. LD HOAT coolants 1 through 4 contained moderate to significant amounts of precipitate after the test and significant reduction in silicate content. LD HOAT 1 coolant exhibited a pH increase whereas all of the other coolants exhibited pH decreases (some significant, some not significant). LD HOAT coolants 1 and 2 containing borate exhibited high levels of aluminum and fluoride, and failed the ASTM D4340 test requirement.

Aluminum heat exchanger testing was also conducted on heavy duty extended life (HD OAT) and traditional fully formulated (HD TFF) engine coolants with a truck radiator containing tubes with b-joints that had been dip fluxed. Test results in Table 5 show HD OAT 1 and HD TFF 1 exhibited color changes from red to pink and purple to pink, respectively. HD OAT coolants 1 and 2 exhibited significant pH increases and depletion of nitrite and nitrate, respectively, along with molybdenum, yet both coolants provided excellent corrosion protection in the ASTM D4340 test [15]. HD TFF 1 also exhibited a significant amount of precipitate after the stagnation test, and significant depletion of nitrite and silicate.

TABLE 3 Radiator stagnation test results with HOAT and OAT engine coolants.

Heat Exchanger Supplier	Round	Formulation	Flux Ingression Average Total Inches	Deposits	ASTM D4340 Post-Stagnation gm/cm2/wk
1	1	HOAT #1	12	Y	> 3
			13	-	> 3
	2	HOAT #1	8	N	> 2
	3		4	N	~ 1
	3	HOAT #2	4	N	-0.05
2	1	HOAT #3	10	N	> 2
			10	N	> 4
	2		0.5	N	0.76
2	1	OAT #1	10	N	-0.1
	2		0.5	N	0.05

TABLE 4 Radiator stagnation test results with light duty engine coolants.

	Appearance		pH		Flux		% Inhibitor Remaining After Test								D4340 mg/cm2/week (1.0 Maximum)
Coolant	Pre Test	Post Test	Pre Test	Post Test	Δ Al ppm	Δ F ppm	B	NO ₂	NO ₃	Si	P	Mo	OAT		
LD OAT 1	Orange	Pink	8.6	7.7	18	47	—	—	—	—	—	—	100	0.1	
LD OAT 2	Orange	Pink	8.0	7.0	< 1	12	—	—	—	—	—	—	100	0.0	
LD HOAT 1	Yellow	Yellow ^a	8.3	9.8	18	87	100	8	4	2	—	—	99	6.8	
LD HOAT 2	Yellow	Yellow ^a	8.3	8.2	44	82	100	—	—	58	—	—	100	2.1	
LD HOAT 3	Yellow	Yellow ^a	8.7	7.8	14	26	—	—	100	39	—	—	100	0.0	
LD HOAT 4	Pink	Pink ^a	8.9	7.5	1	< 5	—	—	—	12	—	—	94	0.5	
LD HOAT 5	Red	Red	7.6	7.5	2	98	—	—	98	—	88	100	100	0.1	

^aPost test coolant samples exhibited precipitate.

TABLE 5 Radiator stagnation test results with heavy duty engine coolants.

Coolant	Appearance		pH		Flux		% Inhibitor Remaining After Test						D4340 mg/cm2/week (1.0 Maximum)
	Pre Test	Post Test	Pre Test	Post Test	Δ Al ppm	Δ F ppm	B	NO ₂	NO ₃	Si	Mo	OAT	
HD OAT 1	Red	Pink	8.3	9.5	9	91	—	0	—	—	8	100	0.06
HD OAT 2	Yellow	Yellow	8.6	9.2	4	38	—	—	57	—	10	100	0.07
HD OAT 1+AF	Red	Red	8.3	8.0	< 1	40	—	98	100	—	100	100	Not Run
HD OAT 2+AF	Yellow	Yellow	8.6	8.3	< 1	65	—	—	100	—	100	100	Not Run
HD TFF 1	Purple	Pink ^a	10.3	10.6	128	328	100	24	100	17	—	—	Not Run

^aPost test coolant samples exhibited precipitate.

In view of potential coolant inhibitor interaction and reduction in CAB heat exchangers containing significant amounts of post brazing flux, certain coolant suppliers have developed anti-flux additives to minimize brazing flux–coolant inhibitor interaction. Addition of a proprietary organic/inorganic anti-flux additive (AF) to HD OAT 1 and HD OAT 2 showed good retention of coolant corrosion inhibitor levels after the radiator stagnation test. Based on the resulting no effect to the corrosion inhibitor package upon exposure to post-braze flux, it was decided it was not necessary to run the ASTM D4340 test [15] on these coolants.

With today's high aluminum content in engines and cooling systems, the engine coolant pH and the aluminum corrosion protection package are extremely important. The Pourbaix diagram for aluminum, shown in Fig. 12, indicates that a protective aluminum oxide film may be maintained between pH 4 and 9. Aluminum decomposes water to form hydrogen in acid solutions and aluminates plus hydrogen in alkaline solutions. The radiator stagnation test results indicate the high aluminum surface area and/or presence of brazing flux may impact the pH and overwhelm the corrosion protection package of an engine coolant (see Fig. 13). In the radiator stagnation tests where pH increases occurred, the pH increases may reflect several possible reactions: conversion of nitrite and/or nitrate to ammonia with nitrated/nitrated coolants, partial hydrolysis of dissolved flux to $[K]^+$ and $[F]^-$ ions and subsequent ion exchange between $[F]^-$ and $[OH]^-$ from $Al(OH)_3$ or other metal hydroxides like shown in Fig. 2. The radiator stagnation test results, however, also showed that some formulations can overcome a pH reaction. For example, the corrosion inhibitor packages in HD OAT coolant 1 and 2 were robust enough to provide satisfactory corrosion protection in the ASTM D4340 [15] at elevated pH.

Since aluminum automotive and truck heater cores are also often manufactured using the CAB process and are generally less expensive than respective radiators,

FIG. 12 Pourbaix diagram for aluminum.

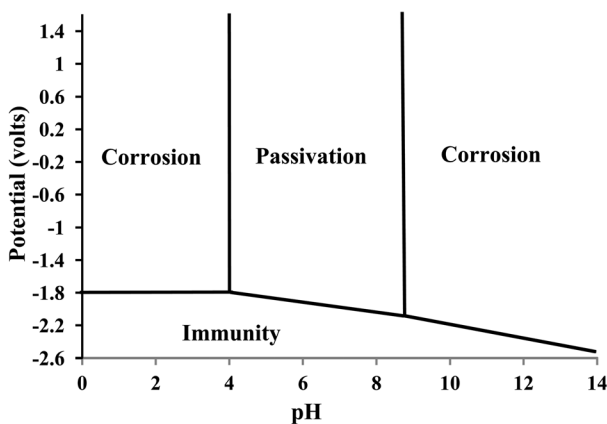
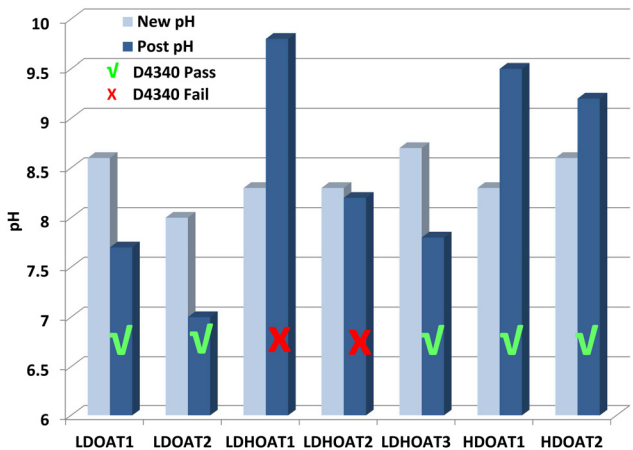


FIG. 13 Effect of coolant type on pH and corrosion protection after stagnation testing.



heater cores were used in a round of coolant stagnation testing (sometimes this requires the use of more than one heater core to obtain the required amount of post-stagnation coolant for ASTM D4340 [15] testing.) In a specific study, the coolant-flux stagnation test was performed without ASTM D4340 because it was already known that there was no impact to this test, although the coolant additive package and other attributes were affected. A study in heater cores with two HD OAT and two HD TFF coolants are shown in Table 6. Testing produced similar effects on certain coolant properties including precipitate formation, pH elevation, fluoride and aluminum leaching, and depletion of certain inhibitors. The two HD TFF coolants contained significant amounts of precipitate after the test and exhibited total silicate depletion. It is also noted that engine coolants containing borate in the three heat exchanger tests (automotive radiator, truck radiator, and truck heater core) showed the highest amounts of fluoride leaching into the coolant, which appears to support work done by Solvay Fluor that the use of coolants containing borate increases flux solubility [16].

ALUMINUM HEAT EXCHANGER STAGNATION TESTING WITH DEIONIZED WATER

In order to assess the sensitivity of engine coolant to post-braze flux in the coolant-flux stagnation test, it is important to use heat exchangers that contain a typical level of post-braze residual flux. Several studies of water solubility testing were used to determine if there is a typical or at least a minimum value for post-braze flux.

Aluminum heat exchanger flux solubility testing was conducted on different type of CAB heat exchangers: radiators (high and low temperature), heater cores, and oil and charge air coolers. The heat exchangers were filled with deionized water,

TABLE 6 Heat exchanger stagnation test results with heater cores.

Coolant	Appearance		pH		Flux		% Inhibitor Remaining After Test					
	Pre Test	Post Test	Pre Test	Post Test	Δ Al ppm	Δ F ppm	B	NO ₂	NO ₃	Si	Mo	OAT
HD OAT 1	Red	Pink	8.6	9.7	5	57	—	45	—	—	96	100
HD OAT 2	Red	Red	8.7	8.5	1	19	—	—	100	—	75	100
HD TFF 1	Purple	Pink ^a	10.9	11.3	14	201	98	63	96	2	—	—
HD TFF 2	Purple	Pink ^a	11.0	11.8	33	265	100	30	65	2	—	—

^aPost test coolant samples exhibited precipitate.

TABLE 7 Heat exchanger flux solubility in water test results.

Heat Exchanger	Post Test	Post Test Flux Components Solubility		
	pH	F, ppm	Al, ppm	K, ppm
Radiator B - Tube	7.0	119	34	122
Radiator B - Tube	7.2	69	22	84
Radiator B - Tube	7.0	152	34	124
Radiator B - Tube	6.6	147	41	147
Low Temperature Radiator B - Tube	—	136	36	140
Heater Core B - Tube, Dip Flux	7.0	466	95	387
Heater Core B - Tube, Electrostatic Flux	6.4	113	47	186
Heater Core - Welded Tube, Spray Flux	7.2	176	65	189
Charge Air Cooler - Many Internal Joints	7.2	144	43	147
Engine Oil Cooler - Many Internal Joints	—	91	43	74

slightly tipped back and forth a few times and then stored for 24 h at room temperature. After the 24-h period, the water was removed and analyzed. Table 7 provides information on the heat exchangers and the amount of potassium, fluoride, and aluminum leached from post brazing flux residues in the post-test water solutions.

The test results show substantial amounts of fluoride, aluminum, and potassium were leached from all five categories of CAB heat exchangers tested (high temperature radiators, low temperature radiator, heater cores, charge air cooler, and engine oil cooler). As reported in Solvay Fluor’s Technical Bulletin, the most reliable ion for measuring flux solubility appears to be potassium since fluoride is extremely reactive with aluminum and aluminum ions may form aluminum hydroxide, which has limited solubility in water. At this time, studies are in progress to establish a recommended minimum level of leached potassium to conduct compatibility of candidate engine coolants with the candidate CAB heat exchangers. The overall data herein suggest a potassium level of 125 ppm minimum may be a good starting point.

The heat exchanger flux solubility test with water may also be used by heat exchanger manufacturers or OEMs as a manufacturing quality control test to determine and control the amount of residual post brazing flux in heat exchangers. For

TABLE 8 Navistar heat exchanger internal cleanliness test results.

Heat Exchanger	Post-Cleanliness Test in Water		
	F, ppm	K, ppm	Al, ppm
Heavy Duty Radiator A	40	50	7
Heavy Duty Radiator B	300	280	60
Heavy Duty Radiator B, after additional processing	21	35	4

instance, Navistar utilizes an internal cleanliness specification TMS-9502 to control the amount of internal residual flux in CAB heat exchangers. Heat exchangers with results in excess of the TMS-9502 limits may require processing to meet the specification. Table 8 shows results of heavy duty heat exchangers after Navistar internal cleanliness testing.

Conclusions

- During the course of normal vehicle operation, engine coolants are exposed to dynamic and stagnation conditions in CAB brazed aluminum heat exchangers, which may result in leaching of potassium, fluoride, and aluminum ions from residual internal flux into the engine coolant. This leaching of ions from the post-braze flux can affect color stability, pH, corrosion inhibitor levels, corrosion protection performance, and precipitate formation.
- A heat exchanger stagnation test has been developed as a screening test to assess the effects of post brazing flux and high aluminum surface area on engine coolant physical, chemical, and performance properties. This test can also be used to assess effects on the heat exchanger from the flux-coolant interaction.
- Heat exchanger stagnation test results obtained on OAT coolants showed excellent corrosion inhibitor stability and corrosion protection after coolant-flux stagnation testing in both CAB radiators and heater cores.
- Certain HOAT and traditional fully formulated coolants showed effects that could include significant precipitate formation, pH changes, reduced corrosion inhibitor levels, and reduced hot surface aluminum corrosion protection.
- The heat exchanger coolant-flux stagnation test may be a beneficial screening test for both OEMs and coolant suppliers to assess coolant compatibility with CAB heat exchangers during vehicle design.
- The heat exchanger flux-water solubility test may also be used as a quality control test to assess the amount of residual post brazing flux in CAB brazed heat exchangers after manufacture.

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The Effect of Long-Term Intermittent Service on Elastomers in Aqueous Engine Coolants

Reference

Hertz, Daniel L., Jr., Hertz, Daniel L. III, and Cook, Harold, "The Effect of Long-Term Intermittent Service on Elastomers in Aqueous Engine Coolants," *Global Testing of Extended Service Engine Coolants and Related Fluids*, STP 1556, Edward R. Eaton, Ed., pp. 195–216, doi:10.1520/STP155620130070, ASTM International, West Conshohocken, PA 2014.²

ABSTRACT

Synthetic rubber (elastomeric) o-ring seals are widely used in modern CI and SI power systems. They are increasingly challenged by higher thermal inputs, design considerations, and long-term warranty issues. This paper presents comprehensive, quantitative aging data for evaluating popular elastomers used for sealing coolants. Three categories of commercial heavy-duty (HD) engine coolants were used as test media. The commercially available elastomers tested in this study were: fluoroelastomers (FKM-type 2), tetrafluoroethylene-propylene rubber (FEPM), and hydrogenated nitrile rubber (HNBR). The study sought to duplicate the effects of multiple engine startups and shutdowns. The test protocol involved 100 twenty-four hour cycles consisting of 16 h operation at 150°C and an 8-h cool down. The test fixtures, run in triplicate, provide O-rings sealing axially (flange seal design), radially (piston seal design), and a straight thread port seal. The test fixtures subjected seals to saturated vapor on one side and liquid on the other. Data was developed and reported in accordance with ASTM D1414-94 and ASTM D412-06a. Compressive stress relaxation is reported in accordance with ASTM D6147. To monitor degradation of the fluoroelastomers, coolant was monitored for fluoride ion activity. A brief

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discussion on polymer stability in high pH aqueous and nonaqueous fluids is included.

Keywords

coolant, high temperature, elastomers

History

During the past 10 years, diesel engine performance has significantly increased in terms of kW/l. Power and heat are interrelated so engine coolants might be subjected to 25 % higher heat rejecting surfaces, often complicated by nucleate boiling. EPA Tier requirements, in some instances, have necessitated the use exhaust gas recycling (EGR). The gas temperature of 700°C is reduced to 160°C, resulting in an additional thermal load to the engine coolant system. The result is a possible 25 %–35 % increase in thermal load to be dissipated by the cooling system [1].

Basic chemistry posits that heat accelerates reactions. Thus, the increased thermal load on coolants and the associated seals in conjunction with longer engine warranties is a precursor for warranty issues associated with marginal sealing materials. Warranty periods of 1.0 Mkm (mid-size engines), 1.6 Mkm (large-bore engines), 20 000 h (stationary engines), and 9 year service requirement (locomotives) are not uncommon. Warranty problems associated with coolant seals are not uncommon either.

Coolants Studied

Three general categories of commercial heavy-duty (HD) engine coolants were used as test media:

1. Organic Acid Technology Coolant (OAT)
2. Propylene glycol 50/50 premix (PG)
3. Deionized Water with Corrosion Inhibitors (W/CI)

OAT and PG coolants are commonly used for on and off-road service. W/CI coolant is often found in HD diesels for locomotive service.

The coolants used are all alkaline. The OAT coolant is an ethylene-glycol based coolant stabilized with carboxylic acid complexes for long-life service with a pH of 8 or more. The PG coolant is a propylene-glycol based coolant with pH of 9 or more and is considered more environmentally acceptable. Finally, the W/CI coolant is stabilized with inorganic complexes to suppress corrosion, with a typical pH of 10 or more.

A 1,2-glycol can be easily cleaved under mild conditions. One mechanism is oxidative cleavage, catalyzed by a metal, into an aldehyde, ketone, or both [2]. In the actual glycol-based coolants, oxidation of the glycol forms glycol degradation organic acids such as glycolic, formic, oxalic, etc. [3].

These coolants act as either aqueous and or non-aqueous electrolytes working in a system of various metals and insulators and as such can be modeled as a nucleophile or electron-pair donors (i.e., Lewis base).

Elastomers Studied

A number of elastomers have been successfully used in the past at lower operating temperatures. Those materials and their ASTM D1418 [4] designations are nitrile (NBR), silicone (VMQ), ethylene-propylene (EPDM), and fluoroelastomers (FKM-type 1). However, at elevated temperatures and high pH, these materials degrade quickly. The more severe operating environment and longer warranty requirements have warranted consideration and use of

1. Hydrogenated nitrile rubber (HNBR)
2. Vinylidene fluoride-tetrafluoroethylene-hexafluoropropylene rubber (FKM-type 2)
3. Tetrafluoroethylene-propylene rubber (FEP)

Elastomers are long-chain molecules polymerized from combinations of C₂ (ethylene), C₃ (methylene), and C₄ (butadiene) gases, with or without substitutions upon the carbon chain. This basic monomer structure is a good indicator of both thermal and chemical reactivity with adequate descriptions of possible chemical reactions to be found in an introductory Organic Chemistry textbook.

Proprietary compounds of comparable modulus were examined. Relative changes in properties are reported to otherwise normalize inherent differences in the viscoelastic response of the base polymers.

HNBR

Hydrogenated NBR is a copolymer of butadiene (which has been hydrogenated to a level ranging from 80 %–99 %) and acrylonitrile. This process enhances heat stability of the butadiene component by saturating double-bond carbons. The acrylonitrile component (a substituted ethylene with a cyano group-CN) is a critical organic component imparting material properties such as oil resistance and strength. However, a fundamental reaction of nitrile is hydrolysis to a carboxylate in the presence of a base (supplied by the coolant) and heat (supplied by the engine). The end result is high swelling of the elastomer due to the water soluble characteristic of a carboxylate and loss in shear modulus [5]. The reaction typically becomes apparent after 1200 h at lower temperatures (125°C) and can be duplicated in a lab after 1000 h @ 135°C.

FKM TYPE 2

The FKM type 2 fluoroelastomer is a terpolymer of vinylidene fluoride-tetrafluoroethylene-hexafluoropropylene. The elastomer is primarily vinylidene fluoride, technically a 1,1-disubstituted ethylene (i.e., there are two fluorine atoms substituted on the first carbon). The hydrogen atoms adjacent to the fluorine atoms on this vinyl are very acidic and a strong base under mild conditions can readily abstract them leaving a carbon-carbon double bond and a hydrogen fluoride byproduct. The presence of tetrafluoroethylene greatly minimizes this tendency but does not eliminate it. Thus, measurements of fluoride ion released into the coolant are included in this study.

FEPM

The most popular FEPM class elastomer is a copolymer of tetrafluoroethylene (a fully substituted monomer) and propylene (a non-substituted monomer). This elastomer exhibits remarkable stability in a high pH environment. The material is sometimes faulted for a relatively high temperature stiffening value (T_g , 0°C), but possesses a remarkably low brittle temperature (−58°C) [6]. The high T_g can be a limitation if a truly rubbery characteristic is required at below freezing temperatures. Notwithstanding, the FEPM elastomer has been widely used in HD diesel engine service, including power cylinder seals, for over 10 years.

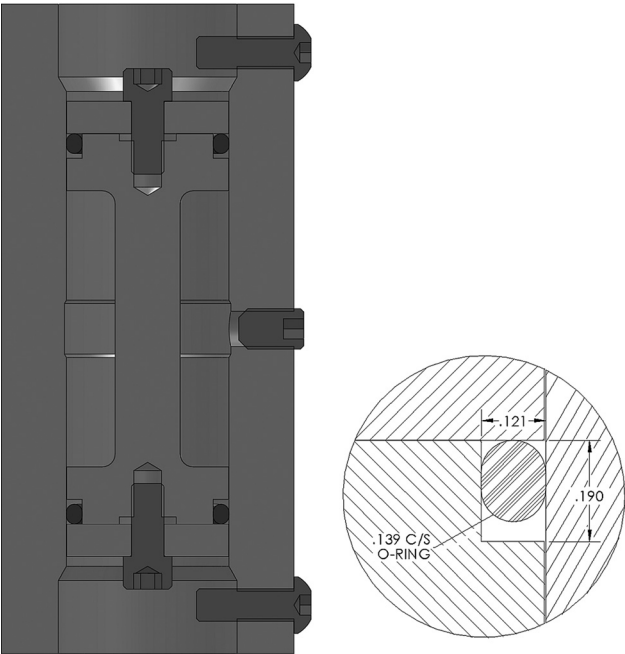
Test Protocol

SPECIMENS

O-rings are commonly used for sealing, and as such test fixtures were designed to simulate conventional seal applications which include both radial and axial deformations. The O-ring aging fixtures were designed for AS568-214 standard dimension O-rings and deform the O-rings in either the radial or axial direction. Fixture SK2264, in Fig. 1, is used for radial deformation.

Fixture SK2451, in Fig. 2, applies axial deformation to three separate specimens.

FIG. 1 SK2264, radial deflection of O-rings.



AS568-225 O-rings are subject to axial deflection serving as cap seals in the aging vessel (see Fig. 3).

TEST METHODS

ASTM D1414 [7] ("Standard Test Methods for Rubber O-rings") procedure was used to determine tensile strength and elongation of AS568-214 O-rings before and after aging.

ASTM D412-06 [8] ("Vulcanized Rubber... - Tension") procedure was used to determine tensile strength, M25, and elongation of standard dumbbells before and after aging.

ASTM D2240-05 [9], Type M indenter was used to measure hardness.

Compressive stress relaxation (CSR) data, comporting to ASTM D6147-94 [10], was determined at 25 % deformation using an in-house procedure. Fixture SK1303 (see Fig. 4) contains a 250 in. deflected sphere of the subject elastomer and can be mounted on a pressurized manifold with pressure gage. The fixture fits inside test vessel SK2451-V for aging in coolant.

The pH values and fluoride ion were measured using a Hanna Instruments (HI-3222) pH bench meter and an HI-4110 fluoride ion half-cell electrode according to established procedures.

AGING CYCLES

To more closely simulate engine service the test chamber is programmed to run a 24 h cycle, ramping from room temperature (RT) to 150°C. After 16 h elapsed time,

FIG. 2 SK2451, axial deflection of O-rings.

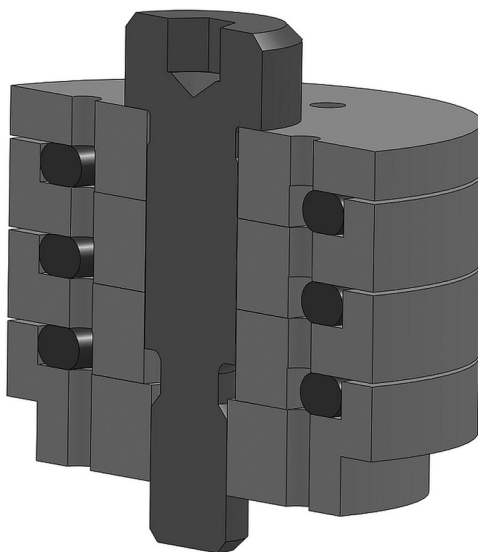
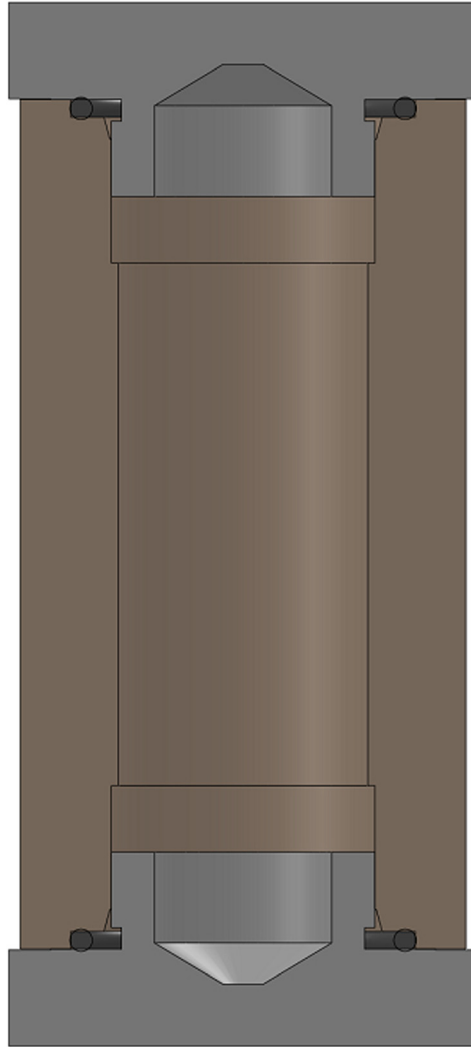


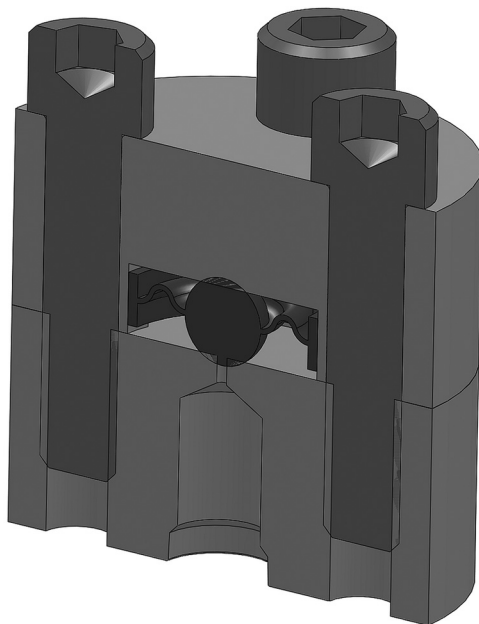
FIG. 3 SK2451-V gray iron aging vessel.



power is shut off and the oven chamber is allowed to cool to ambient over the next 8 h. This is considered 1 cycle. Test data results are summarized for periods of 4, 10, 20, 40, and 100 cycles.

TEST VESSELS

The gray iron test vessels (SK2451-V), in Fig. 3, are designed to develop specific sets of information. Test O-rings are either deformed 13 % in the radial direction (see

FIG. 4 SK1303 CSR fixture.

fixture SK2264) or 22 % in the axial direction (see SK2451). Heat rejecting surfaces commonly create nucleate boiling, so test fixtures were designed to isolate and age O-rings in either the saturated vapor (the top o-ring) and saturated liquid phase (the bottom o-ring) of the coolant.

The test vessels, SK2451-V and SK2264, are placed perpendicular in the chamber after being charged with 50 and 30 ml of coolant, respectively, and identified “top” and “bottom.” The top seal is subject to a saturated vapor from within the vessel and dry-heat oxidative exposure from outside. The bottom seal is subjected to liquid coolant internally and oxidative exposure externally. Any unusual appearance of the o-ring, such as groove pitting, corrosion, staining, or leakage, is reported. D412 dumbbells were fully immersed in fluid during the aging process.

BASELINE DATA

Data are noted in the Tables 1 and 2.

Results

Reported values are the calculated mean value unless indicated otherwise.

The reported % change calculation is set forth in Eq 1

$$(1) \quad \% \text{ Change} = \frac{\text{Property Value}_{\text{aged}} - \text{Property Value}_{\text{original}}}{\text{Property Value}_{\text{original}}}$$

TABLE 1 D1414 baseline values (AS568-214 O-rings).

Baseline Data			
	FEPM	FKM	HNBR
Tensile Strength (MPa)	17.1	8.4	18.7
Elongation (%)	133	173	155
Durometer (points)	77	72	67

The reported % retained calculation is set forth in Eq 2

(2)
$$\% \text{ Retained} = \text{Property Value}_{\text{aged}} / \text{Property Value}_{\text{original}}$$

When a material became incapable of evaluation due to degradation, the data series was terminated at that point.

TENSILE STRENGTH

The % retained values in tensile strength (at break), per ASTM D1414 [7], after aging in OAT, PG, and W/CI coolants are plotted for the AS568-214 O-rings in Figs. 5–7, respectively.

FEPM exhibits the greatest stability in both the liquid and vapor phase of all three coolants as observed in Figs. 5–7.

The % retained values in tensile strength (at break) after aging in OAT, PG, and W/CI coolants are plotted for the D412 dumbbells in Figs. 8–10, respectively.

The retention of tensile strength in the FEPM D412 dumbbells after aging in all three coolants exhibits greater stability than either FKM or HNBR. This observation coincides with the same observation made using the D1414 O-rings.

ELONGATION

The % retained values in elongation (at break) after aging in OAT, PG, and W/CI coolants are plotted for the AS568-214 O-rings in Figs. 11–13, respectively.

TABLE 2 D412 baseline values (D412 Dumbbells).

Baseline Data			
	FEPM	FKM	HNBR
Tensile Strength (MPa)	21.7	17.2	23.8
Elongation (%)	139	252	270
Durometer (points)	82	75	73
M-25	3.23	1.69	1.48

FIG. 5 D1414 retained tensile after aging in OAT.

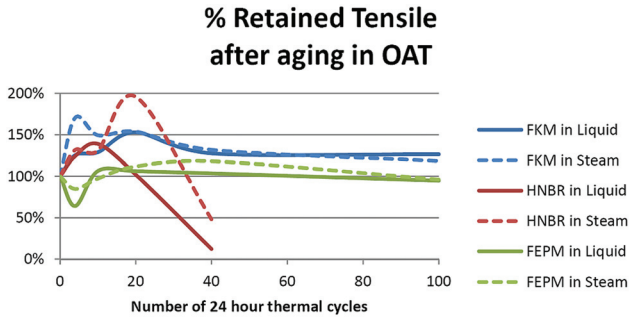


FIG. 6 D1414 retained tensile after aging in PG.

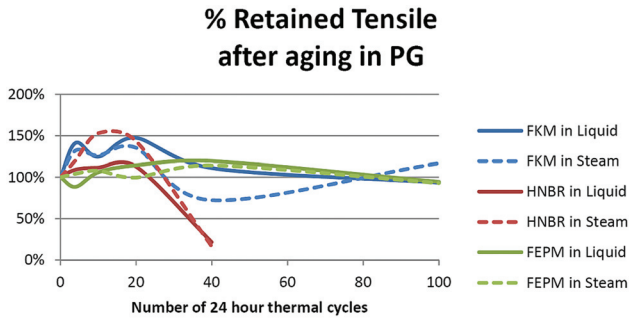


FIG. 7 D1414 retained tensile after aging in W/Cl.

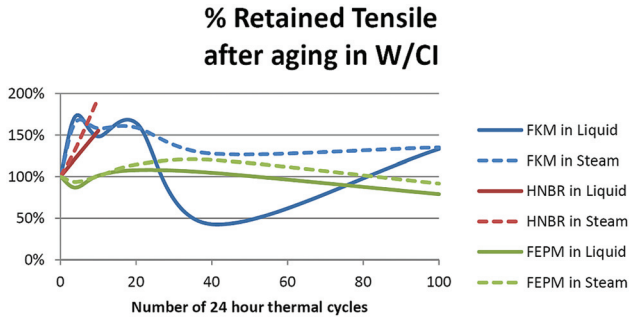


FIG. 8 D412 retained tensile in OAT.

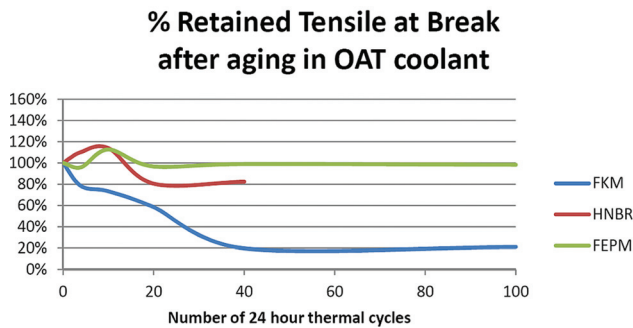


FIG. 9 D412 retained tensile in PG.

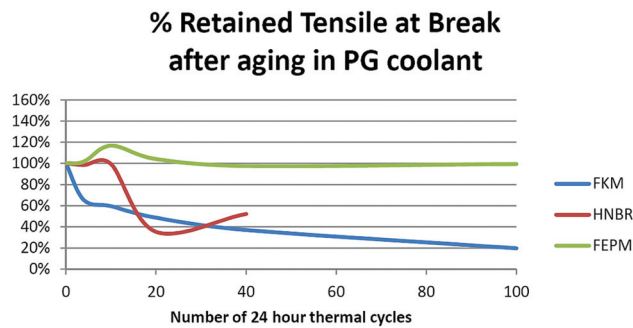


FIG. 10 D412 retained tensile in W/CI.

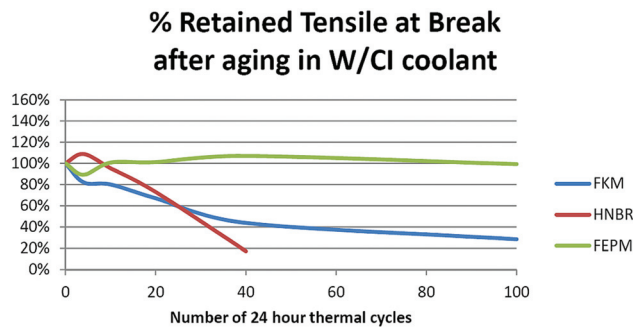
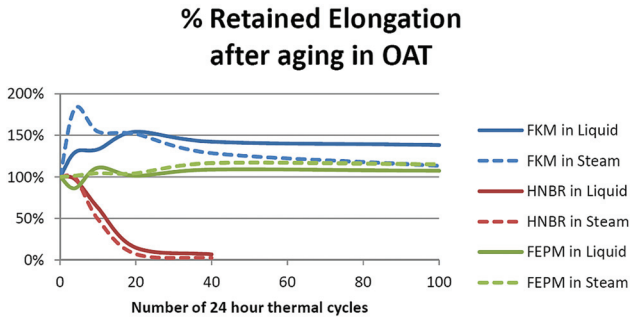


FIG. 11 D1414 retained elongation in OAT.



The retention of elongation in the FEPM D1414 O-rings, after aging in all three coolants, exhibits greater stability than either FKM or HNBR.

The % retained values in elongation (at break) after aging in OAT, PG, and W/CI coolants are plotted for the D412 dumbbells in Figs. 14–16, respectively.

The retention of elongation in the FEPM D412 dumbbells after aging in all three coolants exhibits greater stability than either FKM or HNBR. This observation coincides with the same observation made using the D1414 O-rings.

M25-STRESS AT 25 % ELONGATION

The % retention of stress at 25 % strain (M25) after aging in OAT, PG, and W/CI coolants are plotted for the D412 dumbbells in Figs. 17–19, respectively.

The FKM D412 dumbbells exhibit the greatest stability while the HNBR appears remarkably unstable.

FIG. 12 D1414 retained elongation in PG.

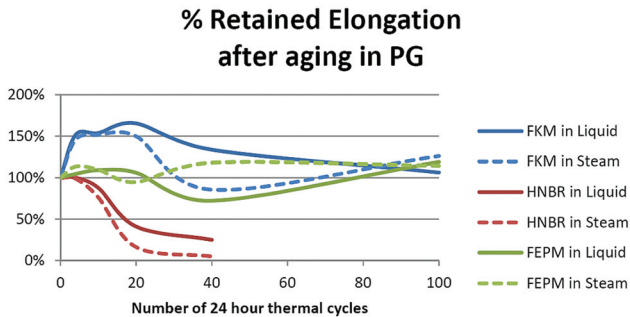


FIG. 13 D1414 retained elongation in W/Cl.

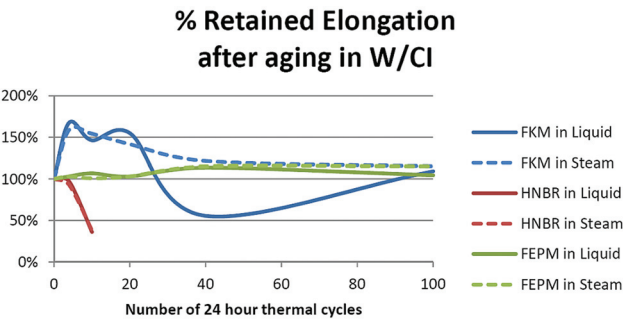


FIG. 14 D412 retained elongation in OAT.

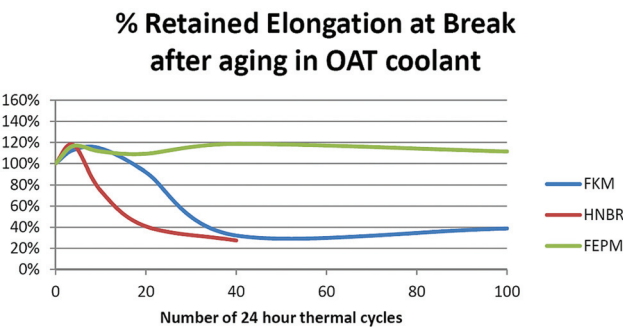


FIG. 15 D412 retained elongation in PG.

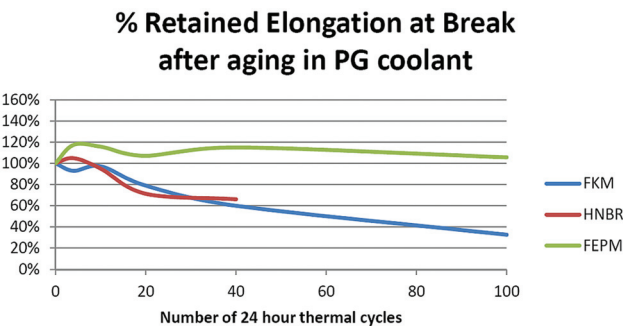
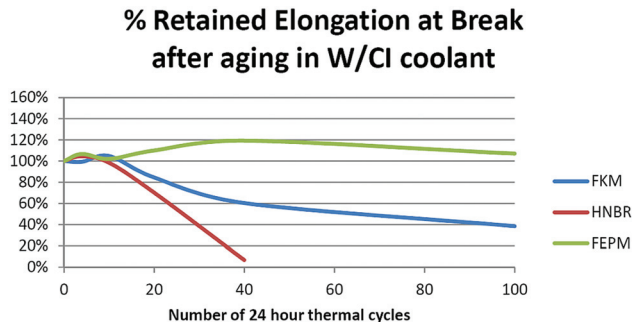


FIG. 16 D412 retained elongation in W/CI.



COMPRESSION SET

Radial compression set of the AS568-214 O-rings from fixture SK2264 is plotted for both steam phase and liquid phase exposure in Figs. 20–22.

Axial compression set of the AS568-214 O-rings from fixture SK2451 in the liquid phase is plotted in Figs. 23–25.

Axial compression set of the AS568-225 cap O-rings from the vessel SK2451-V is reported for both dry/steam phase and dry/liquid phase exposure: HNBR exhibited excessive compression set characteristics relative to FKM and FEPM (26–28).

HARDNESS (TYPE M)

The change in hardness relative to baseline after aging in OAT, PG, and W/CI coolants are measured from D412 dumbbells and plotted in Figs. 29–31, respectively.

FIG. 17 D412 retained M25 in OAT.

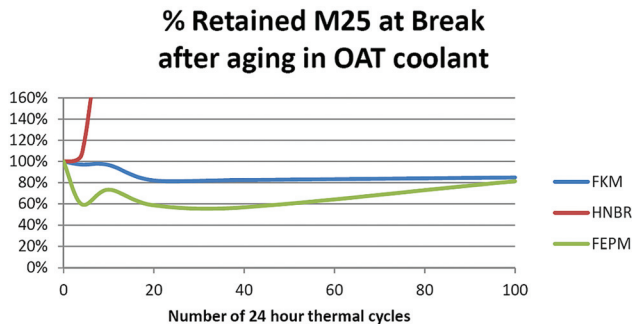


FIG. 18 D412 retained M25 in PG.

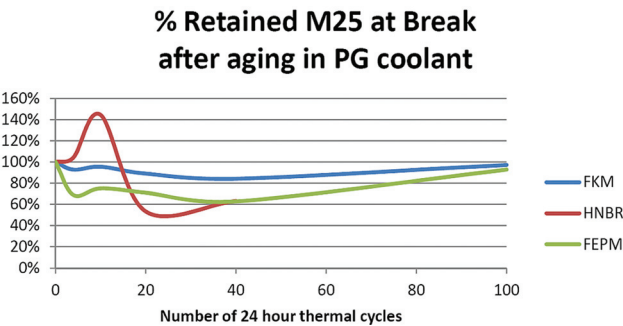


FIG. 19 D412 retained M25 in W/Cl.

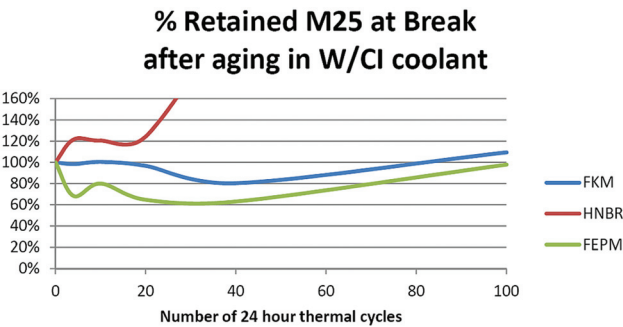


FIG. 20 Radial compression set in OAT.

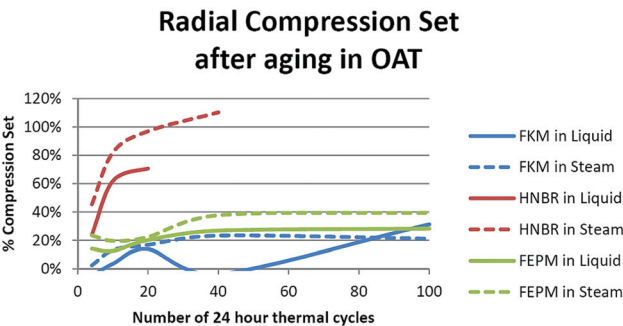


FIG. 21 Radial compression set in PG.

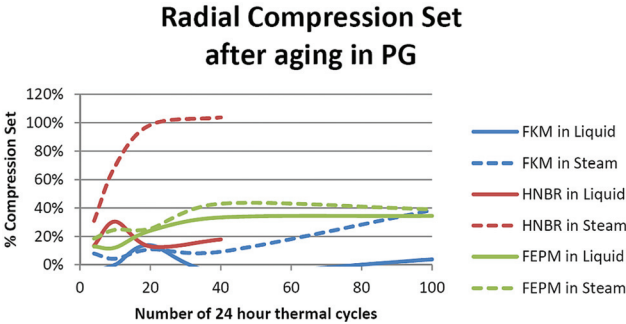


FIG. 22 Radial compression set in W/CI.

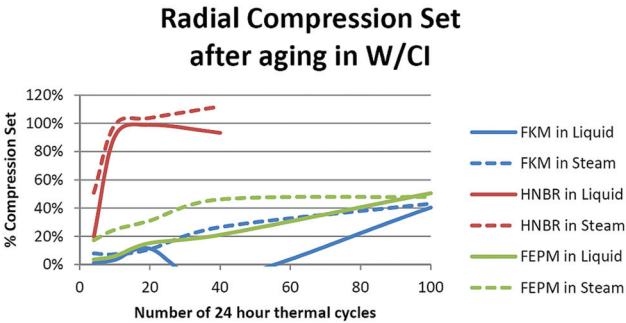


FIG. 23 Axial compression set in OAT.

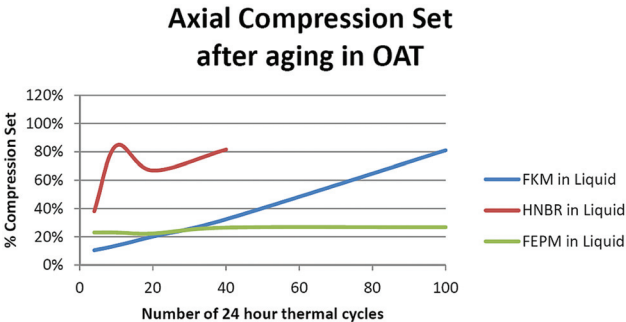


FIG. 24 Axial compression set in PG.

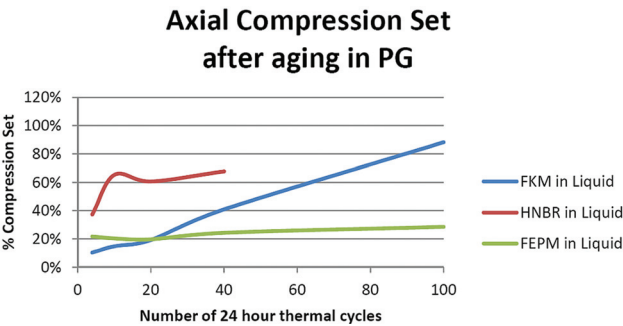


FIG. 25 Axial compression set in W/Cl.

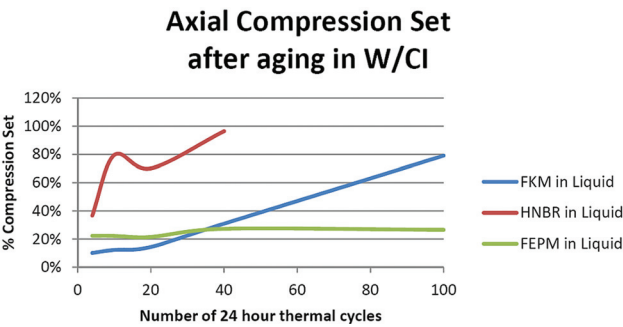


FIG. 26 Axial compression set in OAT.

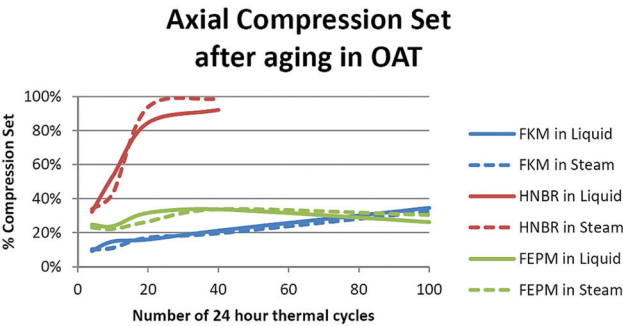
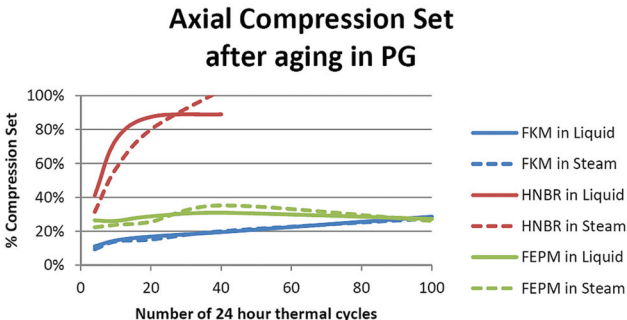


FIG. 27 Axial compression set in PG.



Remarkable changes in the durometer of HNBR were noted after aging in OAT and PG.

COMPRESSIVE STRESS RELAXATION

The median value of % retained contact stress (as tested in SK1303) is reported. See Figs. 32–34.

Remarkable increases in retained contact stress of HNBR are observed indicative of a material instability.

Remarkable drops in pH of the coolants in contact with FKM (see Figs. 35–37) indicate chemical interaction between the polymer and coolant (See Figs. 38–40).

The increase in measured fluoride ion associated with FKM in each coolant coincides with the measured reduction in pH . This observation corroborates the premise of chemical interaction between FKM and hot alkaline coolants.

FIG. 28 Axial compression set in W/Cl.

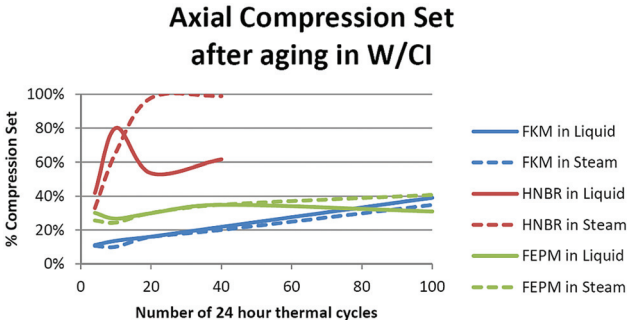


FIG. 29 Change in hardness after aging in OAT.

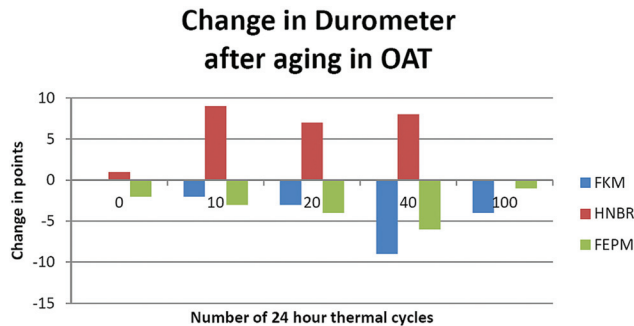


FIG. 30 Change in hardness after aging in PG.

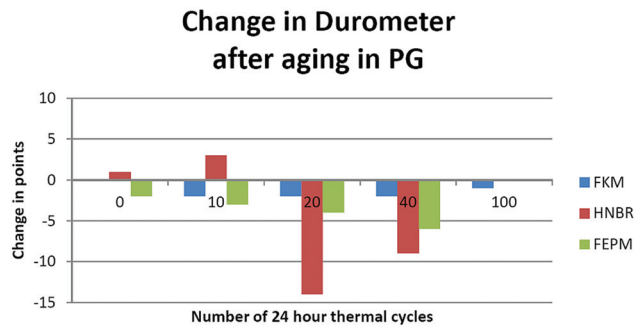


FIG. 31 Change in hardness after aging in W/CI.

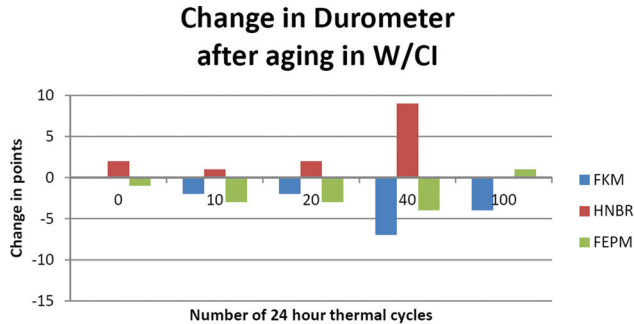


FIG. 32 Retained contact stress in OAT.

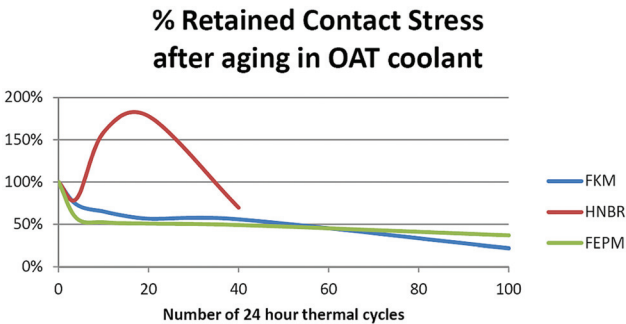


FIG. 33 Retained contact stress in PG.

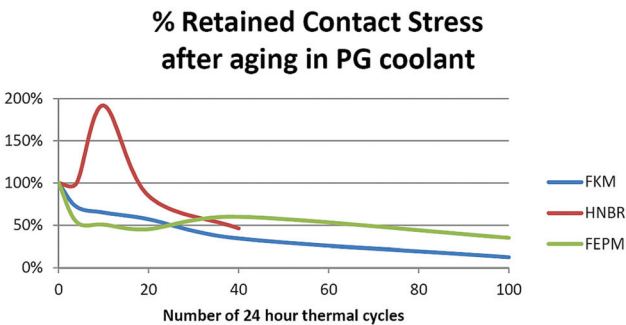


FIG. 34 Retained contact stress in W/Cl.

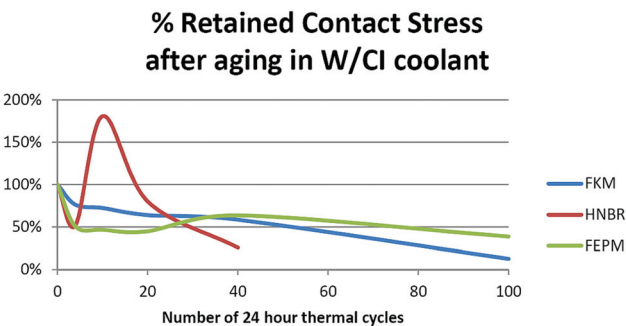


FIG. 35 pH of aged OAT coolant.

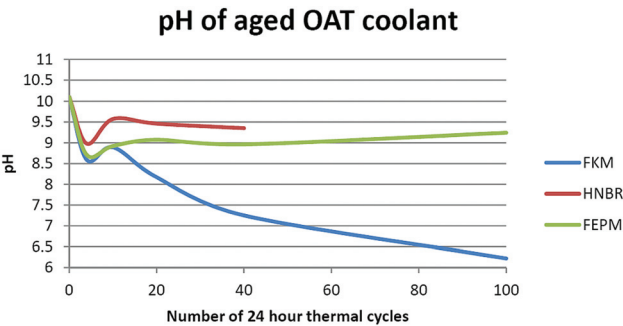


FIG. 36 pH of aged PG coolant.

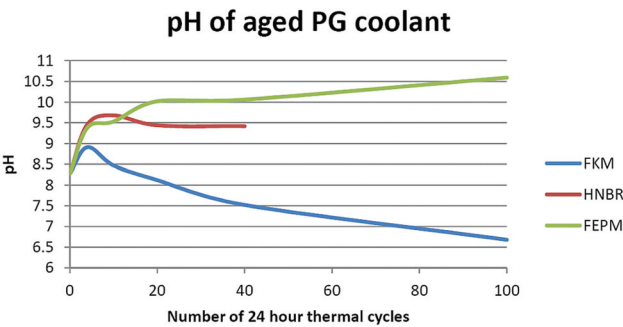


FIG. 37 pH of aged W/Ci coolant.

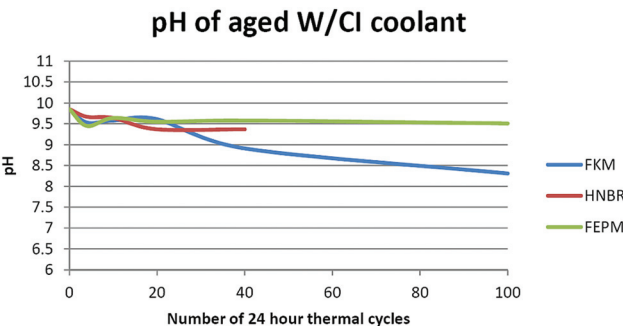


FIG. 38 Fluoride ion of OAT coolant.

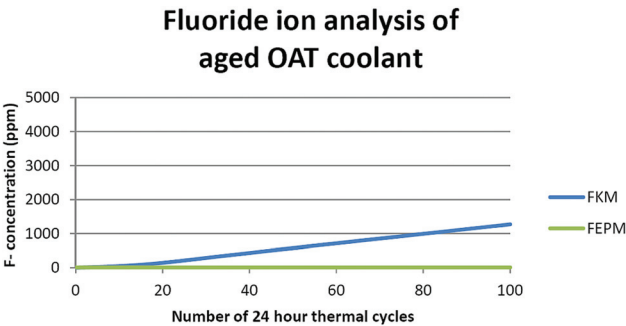


FIG. 39 Fluoride ion of PG coolant.

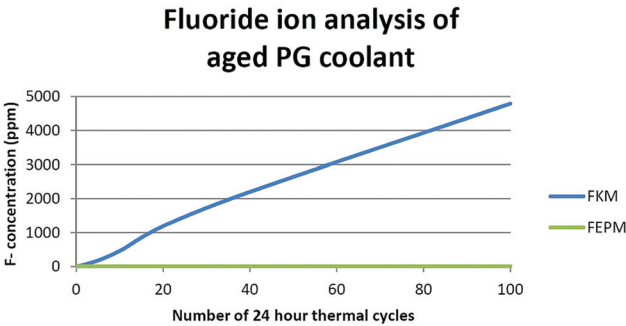
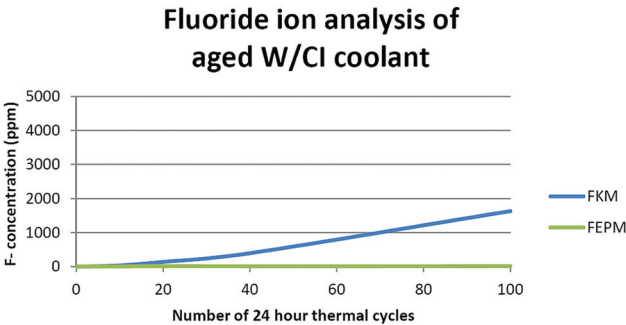


FIG. 40 Fluoride ion of W/CI coolant.



Conclusions

The test results indicate that HNBR is not a suitable elastomer for high temperature service ($\sim 150^{\circ}\text{C}$) in the three coolants examined.

Absent data to the contrary, data based on 40 cycles (1000 h) of testing indicates FEPM and FKM are suitable materials in the coolants studied. However, the increasing trend in fluoride ion, and associated reduction in $p\text{H}$, indicates longer term testing and validation of FKM in hot coolant is warranted.

ACKNOWLEDGMENTS

The writer expresses his gratitude and acknowledgment for the substantial effort and contribution of Samuel Iskander, Harold Cook, and Daniel Hertz III in the compilation of this study and paper.

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STP 1556, 2014 / available online at www.astm.org / doi: 10.1520/STP155620130071

Loring A. Weisenberger¹ and Yahya Hodjat²

Investigation of the Effects of Mixtures of Dissimilar Engine Coolant Inhibitor Chemistries on Automotive Water Pump Durability

Reference

Weisenberger, Loring A. and Hodjat, Yahya, "Investigation of the Effects of Mixtures of Dissimilar Engine Coolant Inhibitor Chemistries on Automotive Water Pump Durability," *Global Testing of Extended Service Engine Coolants and Related Fluids*, STP 1556, Edward R. Eaton, Ed., pp. 217–228, doi:10.1520/STP155620130071, ASTM International, West Conshohocken, PA 2014.³

ABSTRACT

Modern aftermarket water pumps are engineered to provide at least 100 000 miles of service. Most of these pumps are manufactured with aluminum alloys with cast aluminum cases being particularly common. Other pump components may contain cast or extruded aluminum, cast iron, stamped steel, or plastic. Failures of aftermarket water pumps are typically indicated by excessive coolant loss through the weep hole. An investigation into the root cause of the failures was conducted. Areas of focus for determining the root cause of premature failures included investigations of various destructive mechanisms including physical erosion and evaluations of the corrosion behavior of new, unconditioned metals in the water pumps. Of particular interest was the possibility of corrosion when parts are exposed to engine coolant solutions that contain mixtures of North American factory-fill coolants. All of the North American original equipment manufacturers (OEMs) recommend against mixing coolants, but no

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³ASTM Symposium on *Global Testing of Extended Service Engine Coolants and Related Fluids* on May 23, 2013 in Indianapolis, IN.

data concerning the effects of mixing could be found. Nevertheless, consumer or installer mixing of dissimilar coolant formulations is common, because many coolant formulations are marketed for use in “All Makes, All Models” of vehicles and/or are labeled “Mixes with Any Color Antifreeze.” It is assumed that these claims are well researched and are for top-off applications. However, the target of this investigation is the capability of coolant mixtures to protect previously unpassivated metals, especially those in aftermarket water pumps. For this research, four common but dissimilar OEM factory-fill coolant formulations were obtained. Coolants were mixed with each other and the ASTM “Water Pump, Corrosion in Glassware,” and “Corrosion of Heat Rejecting Aluminum Surfaces” test methods were used to learn what the effects of the coolant mixtures are. This paper reports the results of those tests and provides support for a position by the water pump supplier that dissimilar coolant formulations should not be mixed when new cooling system components are installed. It also provides data for ASTM Committee D15 on Engine Coolants and Related Fluids to consider in possibly drafting a coolant compatibility standard.

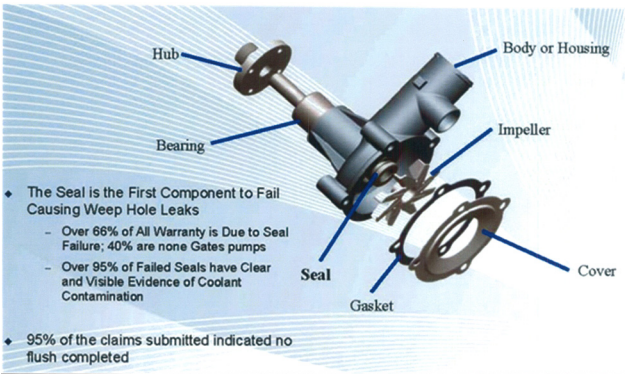
Keywords

antifreeze, engine coolant, water pump, extended service coolant, compatibility, cavitation, engine, long life coolant, testing, hybrid, organic acid, carboxylate

Introduction

Modern water pumps include a combination of cast aluminum, ferrous metal, ceramic, rubber, and plastic parts. **Figure 1** is an exploded view of a typical water pump. Data accumulated from customer returns over recent years reflects a failure rate that warrants investigation, especially for pumps with mileages well below the engineered life of the pumps. These aftermarket water pumps are engineered to

FIG. 1 Exploded view of a typical water pump.

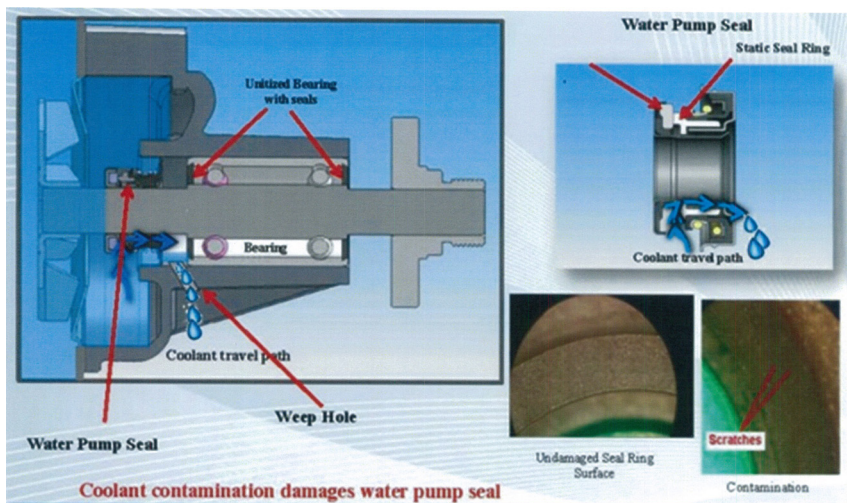


provide at least 100 000 miles of service. Most pump bodies are manufactured with common cast aluminum alloys. Other pump components may contain cast or extruded aluminum, cast iron, stamped steel, or plastic. Water pump warranty returns are typically complaints of excessive coolant flow through the weep hole. Whereas some coolant flow through the weep hole is normal and expected, excessive coolant flow is typically because of damage to the ceramic seal. The potential root causes of the damaged seal and contributions from coolant system corrosion are investigated in this work. **Figure 2** is a cross section of a typical water pump assembly showing the path of the coolant as it cools the assembly.

The authors and team members discovered that the failures are manifested as mechanical failures, typically scoring or other physical damage to the ceramic seal. Physical examinations of the parts indicate that the damage to the seals is caused by debris from the cooling system. The source of the debris could be the result of physical wear (erosion), chemical attack (corrosion), or a combination of both.

One area of focus in determining the root cause of premature failures was the evaluation of the behavior of the new, unconditioned metals in the water pumps when exposed to engine coolant solutions that contained mixtures of different types of North American factory-fill coolants. North American OEMs recommend against mixing coolant types but no data as to the effects of mixing could be found. Nevertheless, consumer and installer mixing of dissimilar coolant formulations are common in the market because many coolant formulations are marketed for use in “All makes, All Models” and/or are labeled “Mixes with Any Color Antifreeze.” It is

FIG. 2 Cross section of water pump showing path of coolant through seals as well as damaged of ceramic seal.



assumed that these claims are well researched for top-off applications, but this investigation seeks to understand the capability of coolant mixtures to protect previously unpassivated metals, especially those in aftermarket water pumps.

Experimental

PHYSICAL WEAR, EROSION, ABRASION

The failures of newer water pumps caused the technical group to investigate the procedures commonly employed in removing and replacing failed water pumps in modern vehicles. In general, the first step in the repair process is the removal of the old coolant from the system. Investigators learned that coolant removal procedures can be grouped into three stages with many service outlets only completing stage 1 or 2:

- (1) gravity drain,
- (2) water flush at city water pressure, and
- (3) power flush or pulse power flush with water applied at significant pressure.

To better understand the efficiency of each approach, a 2003 Mercury Sable was serviced by gravity drain, flushing at city water pressures, and then power flushing. The coolant was filtered at the engine exit, radiator exit, and heater core exit for each method. Note that this vehicle was not experiencing any cooling system malfunction. It is probably a good representation of a well-used family vehicle in typical family service. This cooling system had never been serviced or repaired. The car had accumulated 61 000 miles (97 600 km). The photos in [Fig. 3](#) document what was collected at each stage of flushing. The data in [Table 1](#) reflect that the particles in the filters are of varied sizes, but about half are large enough to be retained by the first screen and would probably act as abrasives if caught in the moving parts

FIG. 3 Photographs of debris collected after simple flushing (top) and power flushing (bottom) for the three different collection points.

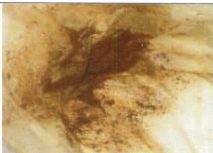
Engine	Radiator	Heater Core
Hose Flush Alone	Hose Flush Alone	Hose Flush Alone
		
Pulse - Power Flushing	Pulse - Power Flushing	Pulse - Power Flushing
		

TABLE 1 Summary of particle sizes accumulated from flushing coolant system.

Mesh	Size (μm)	Wt. %	Weight (g)
40	420	55.98	2.48
60	250	18.96	0.84
80	177	8.13	0.36
100	149	5.87	0.26
200	74	7.45	0.33
400	37	2.71	0.12
500	26	0.68	0.03
Pan		0.22	0.01

or seal areas of a water pump. Obviously, it is not desirable to leave abrasive materials in the system when a new water pump is installed. The presence of these particles would likely shorten the service life of the new pump. Researchers observed that the pulsating power flush method would remove the most debris and also insure the most complete coolant exchange possible when preparing a cooling system for a new pump and coolant.

The material from the Sable was collected and classified. It was dried, weighed, and then sifted using standard laboratory screens to classify the particle sizes in the flushed material. [Table 1](#) is a summary of these results.

Some of the filtered material was dissolved in acid and then analyzed consistent with ASTM [D6130](#) [1] "Standard Test Method for Determination of Silicon and Other Elements in Engine Coolant by Inductively Coupled Plasma-Atomic Emission Spectroscopy." This method is capable of determining most of the elemental content of the material. The [D6130](#) [1] method is for metallic elements. The analysis actually provides content for both corrosion metals and some additives. The results are reported in [Table 2](#).

The results are not surprising. The aluminum is from erosion or corrosion of any number of cooling system components. The iron is from rust in the engine block and other ferrous parts. The silicon is consistent with the factory-fill coolant, which for the Sable was European style hybrid technology coolant. The cooling system has little or no copper or brass. Clearly, there is potential for the debris in the system to negatively impact the durability of the water pumps. The debris is a result of corrosion and other coolant-related deficiencies. The benefits of the pulsating flush procedure during water pump and other cooling system service are obvious.

EFFECTS OF ENGINE COOLANT ON WATER PUMP DURABILITY

This research also included experiments relating to corrosion protection of coolant mixtures on unpassivated (new, unused) metal surfaces. ASTM International offers several test methods that expose new, unused metals to engine coolant under

TABLE 2 Summary of ICP-AES determination of elements in flushed material.

Test Performed	This Sample
Boron (mass % B)	<0.1
Molybdenum (mass % Mo)	<0.1
Silicon (mass % Si) by	0.82
Aluminum (mass % Al)	3.30
Calcium (mass % Ca)	0.15
Copper (mass % Cu)	<0.1
Iron (mass % Fe)	35.50
Magnesium (mass % Mg)	<0.1
Lead (mass % Pb)	<0.1
Zinc (mass % Zn)	<0.1

controlled and accepted test conditions. Two relatively easy and short methods were selected to aid in this investigation that specifically evaluates aluminum behavior. These were of interest because the water pumps involved in the failures contain cast aluminum as a primary material. The methods chosen were:

- ASTM [D4340](#) [2] “Standard Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions” (modified for coolant compatibility research).
- ASTM [D2809](#) [3] “Standard Test Method for Cavitation Corrosion and Erosion-Corrosion Characteristics of Aluminum Pumps with Engine Coolants.”

Results and Discussion

ASTM [D4340](#)

ASTM [D4340](#) [2] is a laboratory screening procedure for evaluating the effectiveness of engine coolants in combating corrosion of aluminum casting alloys under heat-transfer conditions that may be present in aluminum cylinder head engines.

In this test method, a heat flux is established through a cast aluminum alloy typical of that used for engine cylinder heads while exposed to an engine coolant under a pressure of 193 kPa (28 psi). The temperature of the aluminum specimen is maintained at 135°C (275°F) and the test is continued for 1 week (168 h). The effectiveness of the coolant for preventing corrosion of the aluminum under heat-transfer conditions (hereafter referred to as heat-transfer corrosion) is evaluated on the basis of the weight change of the test specimen.

The standard test evaluates 25 % engine coolant in water for 100 h. To evaluate the effects of mixed coolants on aluminum, different coolant types were mixed at 1:1 ratio and then diluted the mixture to 25 % with water. Fresh aluminum samples

were exposed to each of the different combinations of coolant types. All of the coolants used were advertised as compliant with ASTM D3306 [8], so it was assumed that they pass the test and were not tested individually in this study. Compliance with ASTM D3306 [8] indicates that the calculated “R” value, a rate of corrosion, is less than 1.0 mg/cm²/week, when tested alone.

Four coolants were selected to represent general formulation “families.” Three are used by various automobile manufacturers as factory fill at the time of the research. They are likely to be exposed to aftermarket service and possible mixing with other coolants. The fourth is widely available in the aftermarket and was used as factory fill by North American car manufacturers until as recently as 2001. The four families represented are:

1. Conventional Technology

This technology has a well-documented history and was used by Adamowicz and Falla in the comparison evaluation of conventional and carboxylate coolant technologies as reported in STP 1192 [4].

2. A European-Style Hybrid Formulation

This formulation has been well documented and is used by many European manufacturers as well as two major North American manufacturers. Inclusion of this formulation is especially important because it is at least part of the justification for a challenge to advertising claims regarding broad compatibility between coolants. In 2005, the Better Business Bureau’s National Advertising Board (NAB) published this decision in the matter:

“The NAB also concluded that the advertiser’s Ford 300 h ASTM D2809-based test results provided a reasonable basis for its intended claim [3], e.g., that in laboratory testing, the use of organic acid technology (OAT) chemistry in an application that is designed to accommodate (or has approved of the use of only) HOAT chemistry, can be potentially damaging to the water pump” [5].

3. Carboxylate Inhibited “Oat” Technology

There are several manufacturers who fill new vehicles with formulations colloquially referred to as organic acid technology (OAT) coolants. This technology is also well documented with numerous references possible, but one good overview is offered by Mercer in STP 1192 [6]. A frequently observed approach is to use 2-ethylhexanoic acid, sebacic acid, tolyltriazole, and primary inhibitor ingredients.

4. Asian Hybrid Technology

The European hybrid employs silicate and avoids phosphate. The Asian hybrid is often the reverse; it chooses phosphate as an inorganic component and prohibits silicate [7]. Like the European formulation, the carboxylate of choice is benzoate. Because the number of Asian-nameplate vehicles in North America as well as

TABLE 3 Summary of the results of the D4340 testing.

ASTM D4340 [2] Coolant Test Results		
Coolant Mixture	R value (mg/cm ² /week)	Appearance
Standard conditions: 25 % antifreeze in ASTM SCW		
OAT and Euro hybrid—50/50 mix	6.05	Black aluminum surface with deposits
OAT and conventional—50/50 mix	9.12	Black aluminum surface with moderate deposit
Asian and conventional—50/50 mix	10.56	Black pitted surface with moderate deposit; dense population of suspended precipitates

Note: ASTM R value limit = 1.0 mg/cm²/week (rate of corrosion).

globally is significant, the risk for mixing coolant types with the Asian hybrid technology is high and therefore this family is included in this study.

The results of ASTM D4340 [2] tests are reported in Table 3. The corrosion rate is identified in the test as the “R value,” which is expressed in mg/cm²/week [8]. In ASTM coolant specifications, the limit for the R value is set at 1.0 mg/cm²/week [8]. Visual observations are also reported because precipitation of additive components is significant in understanding compatibility of dissimilar formulations. The aluminum specimens in ASTM D4340 [2] are discs of cast alloy cut from a rod. Corrosion damage in testing can often be observed with the naked eye. Figure 4 are photographs of specimens representing light and heavy corrosion. Results in Table 3

FIG. 4 Examples of aluminum test disks used in D4340 [2]. Acceptable result (top), heavy corrosion (bottom).

Good Results – $R \leq 1.0 \text{ mg/cm}^2/\text{week}$ compatible?	
Bad results – $R > 1.0 \text{ mg/cm}^2/\text{week}$ not compatible?	

and Fig. 4 clearly demonstrate that mixtures of dissimilar coolants may result in insufficient corrosion protection.

ASTM D2809

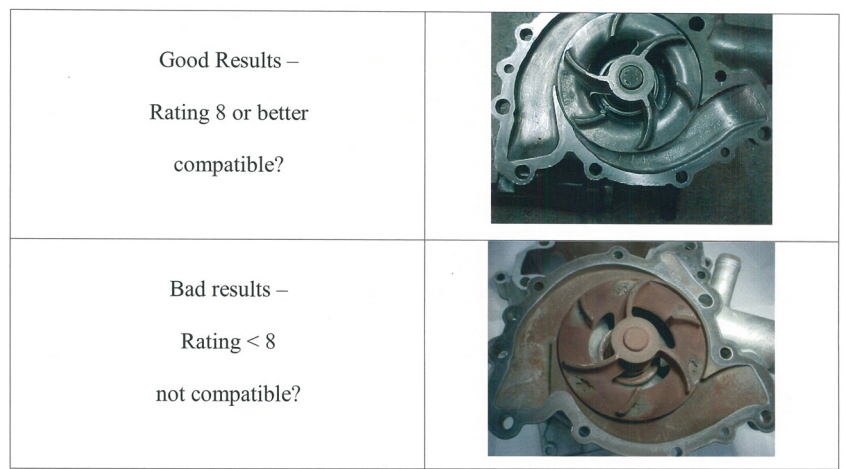
This test method [2] consists of pumping a dilute coolant in water solution at 113°C (235°F) through a pressurized 103-kPa (15-psig) simulated automotive coolant system. The specimen is an aluminum automotive water pump driven at 4600 r/min by an electric motor. The pump circulates the coolant solution to evaluate the cavitation erosion–corrosion effect of the coolant mixture under test. The pump is examined to determine the extent of cavitation erosion–corrosion damage and is rated according to the system given in Table 4.

This test method is used in this case to distinguish between coolant mixtures that contribute to cavitation corrosion and erosion–corrosion of aluminum automotive water pumps. A particular rating number, as determined from this test, is not meant to be equivalent to a certain number of miles in a vehicle test. However, limited correlation between bench and field service tests has been observed with single-phase coolants. Field tests under severe operating conditions should be conducted as the final test to determine the actual effects of a coolant on cavitation corrosion and erosion–corrosion. It is also possible, with proper control of the test

TABLE 4 ASTM D2809 [3] rating system.

10	No corrosion or erosion present; no metal loss. No change from original casting configuration. Staining permitted.
9	Minimal corrosion or erosion. Some rounding of sharp corners or light smoothing or both, or polishing of working surfaces.
8	Light corrosion or erosion may be generalized on working surfaces. Dimensional change not to exceed 0.4 mm (164 in.).
7	Corrosion or erosion with dimensional change not to exceed 0.8 mm (132 in.). Random pitting to 0.8 mm permitted.
6	Corrosion or erosion with dimensional change not to exceed 0.8 mm. Depressions, grooves, clusters of pits, or scalloping, or both, within 0.8 mm dimensional change limit permitted.
5	Corrosion or erosion with dimensional change not to exceed 1.6 mm (116 in.). Small localized areas of metal removal in high-impingement regions or random pits to 1.6 mm permitted.
4	Corrosion or erosion with dimensional change not to exceed 1.6 mm. Small localized areas of metal removal in high-impingement regions, clusters of pits within 1.6 mm dimensional change. Random pits to 2.4 mm (332 in.) permitted.
3	Corrosion or erosion with dimensional change not to exceed 2.4 mm. Depressions, grooves, clusters of pits or scalloping, or both, permitted.
2	Corrosion or erosion with any dimensional change over 2.4 mm, and short of pump case failure.
1	Pump case leaking caused by corrosion or erosion.

FIG. 5 Examples of water pumps tested according to D2809 [3]. Acceptable result (top), heavily corroded and eroded (bottom).



variables, to determine the effect of pump design, materials of construction, and pump operating conditions on cavitation.

The results of the D2809 [3] tests are reported as semi-subjective rating. A rating is from “1” to “10” and is determined by examining and measuring the damage to the internal aluminum surfaces of the water pump. In ASTM coolant specifications, an “8” or higher is required from this test. Example results are illustrated in Fig. 5. Results in Table 5 and Fig. 5 clearly indicate that dissimilar coolants may result in insufficient corrosion protection.

TABLE 5 Summary of results from D2809 testing.

ASTM D2809 [3] Coolant Test Results		
Coolant Mixture (50 % “A” and 50 % “B” Mixes)	Rating ^a	Appearance
Standard conditions: 17 % total antifreeze in ASTM SCW (8.5 % “A” and 8.5 % “B” in this set of experiments)		
OAT and Euro hybrid	2	Pump impeller perforated
OAT and conventional	8	Cavitation less than 0.4 mm
Asian and conventional	9	Minor wear on impeller surfaces
Euro hybrid and conventional	9	Minor wear on impeller surfaces
OAT and Asian	10	Like new

^aASTM D3306 [8] rating limit = 8, minimum.

Conclusions

Researchers have examined the literature published by various technical organizations, as well as the opinions and specifications of engine and vehicle manufacturers and regulatory bodies. Experiments have been conducted to better understand the root causes of premature water pump failure, especially in aftermarket replacement situations. The conclusions of the research are as follows:

1. Water pump failure is generally indicated by excessive coolant from the weep hole. The excessive fluid is the result of scoring of the ceramic seal by particulates in the coolant. Particulates are typically corrosion products from various metal parts. Metal parts corrode because of insufficient corrosion protection from the additives in the coolant. Coolant corrosion protection is apparently compromised by mixing different types of coolants.
2. When replacing a water pump, it is best to thoroughly flush the cooling system of old coolant and then use fresh coolant after installing the new water pump. Removing as many particles from the system before installing the new water pump is essential to the longevity of the pump. The pulsating pressure flushing tool provides superior results in removing harmful particles from the cooling system.
3. Selection of the coolant is important. OEM coolant is formulated differently. It is not possible to formulate a coolant that “meets all OEM requirements.” Not only would it be difficult to justify the cost to test a coolant to meet all OEM requirements for all models in every model year, some specifications are mutually exclusive. At least one manufacturer states this clearly in their new coolant specification [9].
4. Mixing dissimilar coolants may result in premature failure caused by corrosion or cavitation on unpassivated aluminum surfaces. The best practice when replacing a water pump is to fill the repaired system only with the coolant recommended for the vehicle by the original manufacturer after thoroughly flushing the system.

Although issues apparently do exist when mixing certain OEM factory-fill coolants, it might be possible to formulate a coolant capable of satisfactory performance across a range of vehicles. One such effort is presented for consideration by Skrobul et al. in ASTM STP 1491 [10]. Such a coolant would still not “meet all manufacturers’ specifications” in the literal sense, but may accommodate the variations from one manufacturer to another adequately to provide protection.

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