
REVIEWS

The Development of Corrosion Inhibitor Used in the Automotive Coolant

Vu Van Huy^{a,*}, Hoang Duc Quang^a, Adam Katolik^b,
Nguyen Trong Dan^a, and S. M. Gaidar^c

^a Vietnam-Russia Tropical Centre, Ho Chi Minh, 740300 Vietnam

^b McGill University, Montreal, Quebec, H3A0G4 Canada

^c Russian State Agrarian University, Moscow Timiryazev Agricultural Academy, Moscow, 127550 Russia

*e-mail: huy241989@gmail.com

Received August 4, 2021; revised December 16, 2021; accepted December 16, 2021

Abstract—This review features a brief history of coolant fluids, with a focus on changes to inhibitor and anti-freeze usage to enhance the corrosion protection of cooling system components. Additionally, forecasts are made concerning the development trends of coolant technologies, which are required to meet increasingly stringent environmental regulations.

Keywords: coolant, antifreeze, ethylene glycol, inhibitor, corrosion, organic acid

DOI: 10.1134/S1070427221120028

Automotive coolant, a mixture of antifreeze with water and inhibitor additives, is used to remove the heat, which is produced by the engine and transfer it into the cooling system. Besides its primary function to cool down the engine, the coolant also contains inhibitor additives that protect the metals and alloys of the engine and cooling system from corrosion, caused by a variety of factors (e.g. coolant flow, aeration, operating temperature, variable components of water used to dilute the antifreeze, corrosion product, antifreeze properties, galvanic corrosion of dissimilar metals, etc. [1, 2]).

Initially water was used as the cooling liquid considering its advantages (e.g. availability, low cost, good heat exchange). However, the use of water has some limitations including a great susceptibility of metals to corrosion in water, a high freezing point, and water expansion upon freezing. These can be overcome by the addition of antifreeze and corrosion inhibitors, but the low boiling point is still a difficult problem. There are a few ideas, which involve the use of a pressure cap to increase the boiling point of a coolant. However, the maximum pressure is limited by the materials of the radiator, and the solder used to seal joints in the radiator [3]. The use of glycol based fluid made primarily from ethylene glycol or propylene glycol greatly increases

the coolant boiling point. Over more than a century, the technology of manufacturing cooling liquids has made many advancements together with the development of test method and classification system.

There are many different ways to classify an automotive coolant, including: (i) national standards; (ii) international standards (ASTM, BS, GB, GOST); and (iii) specifications of motor vehicle manufacturers (GM, Mercedes, MAN, PSI, Renault, VW, Volvo). Nevertheless, in essence, these coolants only differ in the type of corrosion inhibitor. Antifreezes (ethylene glycol, propylene glycol, and glycerol) do not substantially affect the coolant quality. So to simplify the classification of coolants and patents, all engine coolants can be divided into three groups according to the type of corrosion inhibitor: (i) inorganic additive technology (IAT); (ii) organic acid technology (OAT); and (iii) hybrid organic acid technology (HOAT) [2, 3]. Changes in corrosion inhibitor usage during the development of coolants are a major emphasis of this article.

SHORT HISTORY OF COOLANT DEVELOPMENT

Arguably, engine coolant technology originated in 1885 when Karl Benz invented the first radiator to

circulate water for cooling the engine and limit coolant evaporation [2]. Ethylene glycol (EG) is the most widely used antifreeze due to its freezing point depression and boiling point elevation effects when combined with water. The first use of EG in the manufacture of coolant was in 1916 in the United Kingdom for cooling aircraft engines. In the United States, the application of EG based coolants took place in 1923. At that time EG was not as widely used as alcohol because many automobile manufacturers believed that EG based coolant leaked and was adverse to cylinder head gaskets and coolant pump seals. However, the fact is that the cylinder head bolts were not re-tightened after periods of operation. Moreover, alcohol (ethanol, methanol) would quickly evaporate at the point of leakage. Therefore, until the late 1940s, manufacturers continued using alcohol solutions because of their low cost, good freezing point and availability with corrosion inhibitors such as chromate, mercaptobenzothiazole (MBT), starch, sugar to cool car engines [1–3].

Since 1950 the popularity of V8 engines with higher combustion pressures and numerous cylinder performance in cars forced manufacturers to use EG based coolants with higher boiling point and freeze-up protection to reduce engine sludge and wear. Coolants with higher boiling points are also required to ensure space heating in winter and improve fuel efficiency [3]. The market share of EG based coolants is steadily increasing and many studies on antifreeze using EG were carried out [4]. During this period, North American manufacturers used borates to buffer the pH and small quantities of corrosion inhibitors (e.g. MBT, arsenite, nitrite, molybdate and phosphate) to produce glycol based coolants [1]. In Europe and England, between 1950 and 1970, engine coolants were mainly produced according to the British Standards Institution, including BS 3150 (Ethanol amine + MBT) for engines of aluminum alloy construction, as well as BS 3151 (Nitrite + Benzoate) and BS 3152 (Borate) for engines of cast iron construction [5].

By the 1970s, three main approaches to corrosion inhibition development were established in the United States, Europe and Japan based on the actual conditions in those regions (e.g. water quality, cooling system, engine, and weather conditions). In other regions the market was composed of European, American and Japanese coolants because of technological assistance from cooperative companies [6]. Automakers from the United States

and Europe mainly used silicate technology coolants, which were classified as conventional coolants with a recommended change period from 48 000 to 64 000 km. By the early 1990s they began using hybrid low silicate-organic acid technology (OAT) and OAT coolants with recommended change periods of 160 000 to 168 000 km and 240 000 km respectively for protecting light metals from corrosion and increasing operating temperatures. Meanwhile, Japanese manufacturers used amine phosphate with a recommended change period of 29 000 to 58 000 km. They opted for this instead of silicates because of concerns of possible negative effects on water pump seal and limitations of the storage stability to protect the aluminum component of cooling system and the engine. They then switched to using phosphate OAT coolants in the 1990s, and low phosphate OAT coolants with recommended change periods of 160 000 to 200 000 km from the early 2000s [5, 6].

Moreover, nitrites were still used in combination with organic inhibitors to assist with cavitation corrosion in heavy-duty vehicles, which used diesel engines [7]. Glycerol and propylene glycol (PG) were also used as an alternative antifreeze due to its decreased toxicity and good freezing point depression. However, their use was not widespread because of limited supply and high cost [3, 7, 8]. Some coolant additives are presented in Table 1 based on previous research results. The corrosion protection ability of each additive is different for each metal, some additives can give good anticorrosive effect for these metals but show normal protective effects or even adverse effects for those metals. Good protective effect means that the presence of these additives ensures sufficient protection for those metals without the need for additional additives of the same type. Normal protective effect is understood that these additives have the ability to protect these metals to a certain extent, but still need to add additives of the same type.

ORGANIC ACID INHIBITORS

Since the 1990s, the use of organic acid inhibitors became widespread among corrosion inhibitors considering the key advantages of long life, high efficiency and environmental friendliness. American automakers, (General Motors, Ford and Chrysler), were the pioneers using OAT coolants as original factory fill coolants in their vehicles [3–5]. In Europe both OAT coolants and hybrid low silicate-OAT coolants that

Table 1. Engine coolant inhibitors: A list of the commonly used engine coolant inhibitors and their suitability to function with various engine construction materials

Inhibitor	Formula	Protection level						Other
		steel	cast ion	Al	Cu	brass	solder	
Inorganic								
Disodium phosphate	Na ₂ HPO ₄	xx	xx			o		pH buffer
Monosodium phosphate	NaH ₂ PO ₄	xx	xx			o		pH buffer
Sodium borate	Na ₂ B ₄ O ₇	xx				x	x	pH buffer
Sodium carbonate	Na ₂ CO ₃							pH buffer
Sodium hydroxide	NaOH							pH buffer
Sodium nitrite	NaNO ₂	xx	xx			o		Cavitation protection
Sodium molybdate	Na ₂ MoO ₄	xx	xx	x	x	x	x	
Sodium nitrate	NaNO ₃			xx			x	
Sodium silicate	Na ₂ SiO ₃	x	x	xx	x	x		
Zinc nitrate	ZnNO ₃	x	x	x				
Sodium chromate	Na ₂ CrO ₄	xx	xx					
Organic								
<i>p</i> -tert-Butyl sodium	C ₁₀ H ₁₁ NaO ₂	xx	xx					
Triethanolamine	N(CH ₂ CH ₂ OH) ₃	xx	xx			o		pH buffer
Benzotriazole	C ₆ H ₅ N ₃			x	xx	x		
Mercapto benzothiazole	C ₇ H ₅ NS			x	xx	x		
Tolyltriazole	C ₇ H ₇ N ₃			x	xx	x		
Saccharose	C ₁₂ H ₂₂ O ₁₁			x	x	x	x	
Aromatic acid								
Benzoic acid	C ₆ H ₅ COOH	xx	x	x			x	
Terephthalic acid (1,4-dihydroxybenzoic)	C ₆ H ₄ (COOH) ₂	x	x	x	x	x		
Monocarboxylic acid (> C ₄)								
Axit heptanoic	CH ₃ (CH ₂) ₅ COOH	x	x	x	x	x		
2-Ethylhexanoic acid	CH ₃ (CH ₂) ₃ CH(C ₂ H ₅)COOH	x	x	x	x	x		
Octanoic acid	CH ₃ (CH ₂) ₆ COOH	x	x	x	x	x		
Decanoic acid	CH ₃ (CH ₂) ₈ COOH	x	x	x	x	x		
Dicarboxylic acid (> C ₅)								
Azelaic acid	(CH ₂) ₇ (COOH) ₂	x	x	x	x	x		
Sebacic acid	(CH ₂) ₈ (COOH) ₂	x	x	x	x	x		
Mono- + di-carboxylic acid + aromatic acid		xx	xx	xx	x	x	x	
Polyalcohol								AntiFoam
Organosiloxane	R ₂ SiO							Silicate stabilizer

R: Organic group, xx: Good, x: Normal, o: adverse

do not contain other inorganic inhibitors were used in place of conventional coolants. Conversely, in Japan, there was concern that OAT coolants offered insufficient protection against aluminum corrosion. Therefore the combination of organic acid inhibitors and phosphates was applied. This avoided aluminum surface blackening effects, which were caused by formation of an aluminum oxide layer, which featured an amorphous and porous structure [9].

Hersch, et al. [10] describe the mechanism by which carboxylate ions (organic acid inhibitors) protect ferrous metals. The presence of neutral and alkaline solutions forms an oxide film on the surfaces of steel and cast iron, which can be destroyed by various means (e.g., aggressive anion, mechanical impact) leading to corrosion. The introduction of carboxylate ions prevents the adsorption of these aggressive ions to the spot where the oxide layer was destroyed by forming a temporary patch (protective layer). This releases from the surface after a new oxide film is formed [10, 11]. This mechanism can also explain the aluminum corrosion protection. Specifically, carboxylate inhibitors do not form a protective layer (gel) over the entire surface of a metal component, they are only adsorbed in spots where corrosion occurs, and form protective layers ($< 0.1 \mu\text{m}$). Therefore, this does not affect the heat transfer process.

The first studies on the corrosion resistance of carboxylates for ferrous metals were carried out in a 1955 patent (US 2726215). This presented the use of up to 3 wt % dicarboxylic acid salts (sebacic or azelaic) to protect ferrous metals in aqueous solution [12]. In a follow up 1961 study, Hersch, P. et al. [10] reported the use of salts of mono and di-carboxylic acids as corrosion inhibitors for steel in aqueous solutions. Results showed that the best protective effects were obtained with carboxylic acids containing 8–10 carbon atoms.

From 1961, multiple patents and studies disclosed the use of different carboxylic acids in manufacturing engine coolants. Patents [13–22] reported the use of metal salts of dicarboxylic acids ($\text{C}_3\text{--C}_6$ aliphatic: adipic, glutaric, succinic, malonic; $\text{C}_8\text{--C}_{12}$ aliphatic: suberic, azelaic, sebacic, undecanedioic, dodecanedioic, methylene azelaic, 1,2-naphthalenedicarboxylic, dicyclopentadiene; $\text{C}_7\text{--C}_{12}$ aromatic) or their mixtures in presence of benzoic acid with triazoles, and silicate, phosphate (FR 2489355B3 [13], US 4578205A [16]), amin (EP 0077767B2 [19], US 4584119A [17]), molybdate (US 4561990A [15], JP 4980534B2 [22]) as

corrosion inhibitors for engine coolants. Some patents used combinations of diazole (imidazole, benzimidazole, imidazoline) and triazole (tolyltriazole or benzotriazole) for protecting copper. The patent US 4561990A [15] disclosed that inhibitors, which comprised dicarboxylic acids and inorganic inhibitors provided good corrosion protection for high lead solders and ferrous metals in aqueous systems. Unlike monocarboxylic acids, they did not increase brass corrosion in the absence of triazoles. A similar result was also obtained by mixing the OA coolant with a silicate conventional coolant in a 3 : 1 ratio [8]. The result of the D1384 test [23] showed that increasing the amount of organic acid coolant mixed with corrosive water containing Cl^- , $(\text{SO}_4)^{2-}$ and $(\text{HCO}_3)^{-}$ led to an increase in the amount of corroded solder [8, 24]. Moreover, US 4578205 [16] discovered that the salt of methylene azelaic acid did not precipitate and fell out of the coolant using hard water, unlike other salts of dicarboxylic acids (e.g., $\text{C}_{10}\text{--C}_{12}$ aliphatic dicarboxylic acids).

Patents [25–35] disclosed the use of metal salts of monocarboxylic acids containing 8–20 carbon atoms (heptanoic, octanoic, nonanoic, decanoic, undecanoic, dodecanoic, oleic, palmitic, stearic, myristic, linoleic, 2-ethylhexanoic, 3,5,5-trimethylhexanoic, *p-tert*-Butylbenzoic), aromatic mono- or polycarboxylic acid (benzoic, alkylbenzoic, alkylbenzoic, phthalic, trimellitic) or their mixtures with triazoles (tolyltriazole or benzotriazole) and other compositions such as inorganic inhibitors (US 4759864: borate) and amines (US 4342596A [25]: alkanolamine, cyclohexylamine; diisopropylamine; morpholine) for producing engine coolant. Octanoic, 2-ethyl hexanoic and benzoic acids were widely used together and most of the above patents described the possibility of using $\text{C}_8\text{--C}_{12}$ aliphatic dibasic acids with or in place of mono acids as metal corrosion inhibitors. However, some automakers avoid using 2-ethyl hexanoic acid, which is prone to damage the plastics (e.g., nylon 6.6), which are employed to make inlet manifolds, gaskets and radiators [1]. EP1747254A1 [32] proposed the use of salt of 3-hydroxypropionic acid and $\text{C}_1\text{--C}_4$ alkyl ester to producing an engine coolant, but the results of corrosion tests were not presented. EP1087004A1 [30] found that a mixture of lower carbon carboxylates (e.g., $\text{C}_1\text{--C}_2$ and $\text{C}_3\text{--C}_5$) with good solubility in salt solutions provided a synergistic frost protection.

Other patents [34–45] dealt with combining the metal salts of C_5 – C_{16} (preferably C_8 – C_{12}) monocarboxylic acids (aliphatic: octanoic, nonanoic, decanoic, undecanoic, dodecanoic, 2-ethylhexanoic, neodecanoic; cyclohexanecarboxylic, isononanoic; aromatic: benzoic) and C_4 – C_{16} (preferably C_7 – C_{12}) dicarboxylic acids (aliphatic: suberic, azelaic, sebacic, undecanedioic, dodecanedioic; aromatic: 1,4-dihydroxybenzoic, 2,4-dihydroxybenzoic, 2,6-dihydroxybenzoic) in the presence of triazoles (tolyltriazole, benzotriazole) and typical inorganic inhibitors (e.g. borate, silicate, molybdate) as inhibitors for engine coolant. US 9328278B2 [45] disclosed the use of isononanoic acid as an inhibitor provided good protection of ferrous metals from pitting corrosion. Furthermore, the use of isononanoic acid in place of sodium nitrite also improved the corrosion resistance of aluminum, brass, and solder. WO 2014180886A1 [44] presented good synergistic effects from isononanoic and sebacic acid in 1,3-propanediol based coolants which are non-toxic and meet environmental requirements. US 6846431B1 [43] also introduced biodegradable engine coolants comprising of succinic acid, acetic acid and ethanol ensured a freezing point of -30°C after mixing with water. All major components of this type of coolant can be obtained by fermenting renewable resources and are degraded by microorganisms in the natural environment.

The synergistic effects of monoacid/diacid combinations were initially reported in US 4647392 [36] and studied in detail by J.W. Darden et al. [48]. Reportedly, monoacid/diacid combinations (e.g., octanoic acid/sebacic acid) with an optimal molar ratio ($[\text{octanoic acid}]/[\text{sebacic acid}] = 0.57x_a$, a : positive integers) afforded good protection of aluminum from pitting and crevice corrosion. One explanation is that complex formation improved due to hydrogen bridging. Alternatively, the electrodensity characteristics changed at some mole ratios. These ratios are different for other acid pairs and specific to the chain length, which is the most important parameter in determining the ability to prevent corrosion. The inhibitor effectiveness of mono carboxylate salts improved when increasing the carbon number in the backbone. Thus, 2-ethylhexanoic acid, a C_8 acid, has a lower protective effect than C_8 octanoic acid and similar effectiveness as C_6 hexanoic acid. The use of acids with high carbon numbers is limited by their solubility in water, while lower carboxylic acids are readily soluble in water due to hydrogen bonding

and can be used with increased concentrations. This explains why octanoic acid (C_8 acid) is more commonly used than C_9 – C_{12} acids in producing engine coolant.

FUTURE TRENDS

Automobile manufacturers are aiming to maximize fuel economy, resulting in the use of light alloys (e.g. aluminum and magnesium) for cooling system components. However, aluminum is more active than other metals and susceptible to several types of corrosion. These include pitting corrosion in the thin sheet of radiator and heater cores as well as crevice corrosion at cylinder head. For a long time, silicate was known to be a good inhibitor for aluminum, but the use of silicate is limited by the reduction of heat transfer efficiency, which happens even for hybrid low silicate-OAT coolants. This is due to the formation of a gel layer on the aluminum surface and depletion thereof over time [5, 49]. Therefore, the discovery of synergism of combinations of mono and diacids is an important step forward in making long life coolant for new generation cars using light alloys in cooling systems. Moreover, Regis J. Pellet et al. [50] reported that carboxylate can also be used to replace nitrite in heavy-duty coolants to protect the iron cylinder liner from cavitation. Unlike nitrites, carboxylate salt depletion is slower so there is no need to periodically use supplemental coolant additives (SCA's) [51, 52].

Another way to decrease fuel consumption is to reduce the radiator size by using a more efficient engine coolant called nanofluid. It is obtained by dispersing nanoparticles in usual coolants, resulting in increasing thermal conductivity and heat transfer performance [53–57]. Enhancing the thermal conductivity of base fluids with nanoparticles due to a large surface to volume ratio and Brownian motion effect was discovered by Choi in 1995 [53]. Since then, there have been many studies on the application of nanoparticles (e.g. Al_2O_3 , Fe, Fe_2O_3 , Cu, CuO, SiC, TiC, ZnO, C etc.) in the engine production [58–60].

Lee et al. [58] investigated the effect of CuO on thermal conductivity of EG. Their results suggested that a 23% thermal conductivity enhancement was obtained in EG in the presence of CuO. Eastman et al. [63] reported that about 40% of thermal conductivity enhancement could be obtained by using a nanofluid, which consists of EG and 0.3 vol % Cu nanoparticles, with sizes less than 10 nm. Hussein et al. [59] studied

the thermal conductivity TiO₂-Water and SiO₂-Water nanofluids as coolants in automotive radiators. They reported about 11 and 22.5% enhancement in the thermal conductivity respectively. Meanwhile, Jinmao Chen et al. [61] investigated the application of TiO₂ in commercial coolants and found only a 3% thermal conductivity enhancement and above 10% convective heat transfer enhancement could be gained at 1 wt % TiO₂. Gefei Wu et al. [62] investigated the use of graphite particles to increase the thermal conductivity of commercial antifreezes produced by OAT, phosphate free long-life hybrid technology and phosphate-silicate free organic acid technology. It was found that a nanofluid obtained by dispersing graphite particle in OAT coolant using proper dispersant levels could pass the compatibility and storage stability tests (CID AA-52624 A) plus corrosion tests (ASTM D1384 and ASTM D4340) and achieved a 25% enhancement in the thermal conductivity at 2 vol % particle loading.

Thus, nanofluids can be considered as a promising applicant to produce engine coolants in the future due to good thermal characteristics, which allow automobile manufactures to use smaller radiators and decrease the weight and fuel consumption. However, in practice, there are still many issues that need to be considered carefully before using nanoparticles. For instance, nanofluids with higher density and viscosity cause a pressure drop, which leads raises the pumping power. This together with the presence of nanoparticles can accelerate cavitation corrosion of the water pump [61]. High density particles increase the heat-transfer coefficient of the nanofluid, but they can settle down and clog radiator channels in stagnant state of engine [62, 63]. Besides, corrosion can also occur on the submerged components. This is because of the flow and impact of nanoparticles with cooling system parts in the active state of an engine and the influence of nanoparticles on the effectiveness of corrosion inhibitors. Moreover, production costs constitute one of the main reasons preventing the application of nanofluids. They are produced by one or two steps methods, and require modern and sophisticated equipment.

Environmental protection regulations are becoming more stringent and that forces manufacturers to eliminate or limit harmful substances in their engine coolants. In addition to replacing inorganic inhibitors with organic acid inhibitors considering their shortcomings (e.g. biological toxicity of chromate and borate, conversion to carcinogenic substances including

nitrites and amines, phosphate enriching wastewater) automobile manufacturers are also concerned about the health effects and environmental issues associated with antifreeze substances [61, 63]. EG, a good freezing point depressant with a sweetish taste and attractive smell to children and pets, is most commonly used by automobile manufacturers. However, the U.S. Department of Health and Human Services (HHC) and the U.S. Environmental Protection Agency (EPA) have established that EG is toxic to humans and animals. The toxicity is caused by the conversion of EG to glycoaldehyde and subsequently to glycolic acid, which leads to metabolic acidosis in the presence of alcohol dehydrogenase (ADH), when ingested. A portion of the glycolic acid further metabolizes to glyoxylic acid (glyoxylate), and then to oxalic acid (oxylate), which precipitates as crystals of calcium oxalate when combined with serum calcium in the bloodstream. This can cause a range of symptoms, including hypocalcemia, cardiac failure, and acute oliguric renal failure. To solve this problem, some automakers have released embittered coolant, which contains a small amount of bittering agents, which make it taste bitter and therefore not attractive to children and animals [1]. For example, denatonium benzoate can be added at 30 ppm to create his bittering effect. WO 2002072728A1 [66] also disclosed that the toxicity of the EG based coolant can be reduced by adding polyhydric alcohol (e.g., glycerol or PG), which acts as an alcohol dehydrogenase enzyme inhibitor that prevents the conversion of EG into glycoaldehyde when ingested. So propylene glycol can be used to replace EG as a freezing point or in combination with it to decrease toxicity of engine coolants.

CONCLUSIONS

Over more than a century, the coolant industry has made great strides in research and manufacturing different types of engine coolant. The period 1885–1990 marked a strong development of conventional coolants manufactured using inorganic acid inhibitors having short service intervals and high toxicity to humans and the environment. Since 1990, automobile manufacturers began to use organic acid inhibitors to produce coolants with long life service and less environmental pollution. Some commonly used coolants are OAT coolants, hybrid low silicate-OAT and low phosphate OAT coolants.

Currently, the second wave of electric cars is strongly taking place. The largest car companies in the world have

greatly invested in electric cars research considering their many benefits, including zero environmental pollution, and a great fuel economy. Therefore, manufacturers are focused on finding solutions to limit the environmental pollution caused by coolants and increasing heat transfer properties to decrease the weight of cooling systems and fuel consumption, where nanofluids can be considered as a potential choice.

FUNDING

This article was supported by Vietnam-Russia Tropical Centre. We thank our colleagues who provided insight and expertise that highly assisted the research.

CONFLICT OF INTEREST

The authors have no conflict of interest.

REFERENCES

- Halderman, J.D., *Automotive Technology: Principles, Diagnosis, and Service*, US: Pearson, 2011.
- Hannigan, H.J., *Engine Coolant Testing*, 1993, vol. 3, pp. 6–10.
<https://doi.org/10.1520/STP25153S>
- Bosen, S.F.; Bowles, W.A.; Ford, E.A.; Perlson, B.D., *Antifreezes. Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim: Wiley-VCH, 2000.
- Hercamp, R., *SAE Technical Paper*, 1999, ID 01-2824.
<https://doi.org/10.4271/1999-01-2824>
- Yang, B., Gershun, A., and Woyciesjes, P., *Global Testing of Extended Service Engine Coolants and Related Fluids ASTM STP 1556*, 2014, pp. 3–38.
<https://doi.org/10.1520/STP155620130109>
- Egawa, H., Mori, Y., and Abel, M.L., *Engine Coolant Technologies*, 2008, vol.5, pp. 1–7.
<https://doi.org/10.1520/STP45560S>
- DeBaun, H.J. and Alverson, F.C., *Engine Coolant Technologies*, 2008, vol.5, pp. 8–16.
<https://doi.org/10.1520/STP45561S>
- Weir, T., Greaney, J., and Backenstrass, F., *SAE Technical Paper*, 1997, ID 971803.
<https://doi.org/10.4271/971803>
- Osawa, M., Morita, Y., and Nagashima, T., *SAE Technical Paper*, 2003, ID 01-2023.
<https://doi.org/10.4271/2003-01-2023>
- Hersch, P., Hare, J.B., and Robertson, A., *Journal of Applied Chemistry*, 1961, vol.11, no. 7, pp 251–265.
<https://doi.org/10.1002/jctb.5010110705>
- Weir, T. and de Ven, P., *SAE Technical Paper*, 1996, ID 960641.
<https://doi.org/10.4271/960641>
- US Patent 2726215A, 1955.
- France Patent 2489355B3, 1983.
- US Patent 4382008A, 1983.
- US Patent 4561990A, 1985.
- US Patent 4578205A, 1986.
- US Patent 4584119A, 1986.
- US Patent 4592853A, 1986.
- European Patent 0077767B2, 1988.
- European Patent 0739965B1, 2002.
- Japan Patent 4737585B2, 2011.
- Japan Patent 4980534B2, 2012.
- ASTM D1384-05(2019), Standard Test Method for Corrosion Test for Engine Coolants in Glassware, ASTM International*, West Conshohocken, PA, 2019.
- Van de Ven, P. and Maes, J., *SAE Technical Paper*, 1994, ID 940769.
- US Patent 4342596A, 1982.
- Patent 4759864A, 1988.
- European Patent 0251480B1, 1992.
- US Patent 5997763A, 1999.
- WIPO (PCT) 2000050532A1, 2000.
- European Patent 1087004A1, 2001.
- Germany Patent 10163337A1, 2003.
- European Patent 1747254A1, 2007.
- WIPO (PCT) 2012021204A2, 2012.
- US Patent 9051515B2, 2015.
- European Patent 2171014B1, 2015.
- US Patent 4647392A, 1987.
- US Patent 4657689A, 1987.
- US Patent 4851145A, 1989.
- US Patent 5085791A, 1992.
- US Patent 5085793A, 1992.
- European Patent 0564721A1, 1993.
- European Patent 0479470B1, 1995.
- US Patent 6846431B1, 2005.
- WIPO (PCT) 2014180886A1, 2014.
- US Patent 9328278B2, 2016.
- US Patent 9540558B2, 2017.
- Japan Patent 6537847B2, 2019.

48. Darden, J., Triebel, C., Maes, J., and VanNeste, W., *SAE Technical Paper*, 1990, ID 900804.
<https://doi.org/10.4271/900804>
49. Van de Ven, P. and Maes, J., *SAE Technical Paper*, 1994, ID 940498.
<https://doi.org/10.4271/940498>
50. Pellet, R., Bartley, L., and Hunsicker, D., *SAE Technical Paper*, 2001, ID 01-1184.
<https://doi.org/10.4271/2001-01-1184>
51. Hudgens, R., *SAE Technical Paper*, 1999, ID 01-0130.
<https://doi.org/10.4271/1999-01-0130>
52. Mercer, W.C., *Engine Coolant Testing*, 1993, vol. 3, pp. 44–62.
<https://doi.org/10.1520/STP25156S>
53. Choi SUS. *Enhancing Thermal Conductivity of Fluids with Nanoparticles*, American Society of Mechanical Engineers (ASME), Fluids Engineering Division (FED): San Francisco, CA; 1995. p. 99–105.
54. Choi, S., Zhang, Z.G., Yu, W., and et al., *Appl. Phys. Lett.*, 2001, vol. 79, pp. 2252–2254.
<https://doi.org/10.1063/1.1408272>
55. Erkan, A., Tüccar, G., Tosun, E., et al., *SN Appl. Sci.*, 2021, vol. 3, no. 365.
<https://doi.org/10.1007/s42452-021-04368-z>
56. Ahmad, A., Rad, S., Mehdi, S., Goodarz, A., et al., *Energy Conversion and Management*, 2015, vol. 101, pp. 767–777.
57. Li, X., Changjun, Z., and Aihua, Q., *International Communications in Heat and Mass Transfer*, 2016, vol. 77, pp. 159–164.
58. Lee, S., Choi, S., Li, S., and Eastman, J.A., *J. Heat Transfer*, 1999, vol. 121, pp. 280–289.
<https://doi.org/10.1115/1.2825978>
59. Hussein, M.A., Bakar, R.A., Kadrigama, K., and Sharma, K.V., *Int. Commun in Heat and Mass Transf.*, 2014, vol. 53, pp. 195–202.
<https://doi.org/10.1016/j.icheatmasstransfer.2014.01.003>
60. Vajjha, R.S., Das, D.K., and Namburu, P.K., *Int. J. Heat and Fluid Flow*, 2010, vol. 31, pp. 613–621.
<https://doi.org/10.1016/j.ijheatfluidflow.2010.02.016>
61. Jinmao, C. and Jianguang, J., *Materials Research Innovations*, 2017, vol. 21, no. 3, pp. 177–181.
<https://doi.org/10.1080/14328917.2016.1198549>
62. Wu, G., Turcotte, D.E., Dwornick, B.L., et al., *Global Testing of Extended Service Engine Coolants and Related Fluids*, *STP 1556*, 2014, pp. 57–70.
<https://doi.org/10.1520/STP155620130073>
63. Eastman, J.A., Choi, S., Li, S., and et al., *Applied Physics Letters*, 2001, vol. 78, no. 6, pp. 718–720.
<https://doi.org/10.1063/1.1341218>
64. Kouji, I., Satoshi, O. and Keisaku, I., *Komat's Technical Report*, 2002, vol. 48, no 149, p. 3.
65. Chen, J.M., Guan, J.L., Ru, J. Y., and Bo, G., *Applied Mechanics and Materials*, 2014, vol. 716–717, pp. 130–132.
<https://doi:10.4028/www.scientific.net/AMM.716-717.130>
66. WIPO (PCT) 2002072728A1, 2002.