Ethylene glycol-based coolant technologies for automotive applications: A critical review

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Abstract

Coolant fluids have been in use for almost a century. The use of cooling fluids is essential for heat transfer applications serving various purposes, such as protection against overheating or freezing. However, due to the heat stress conditions that occur inside such systems, these cooling fluids can also contribute to problematic issues, such as scaling/deposition of inorganic salts, and/or corrosion of critical equipment surfaces. The imperative to optimize the performance of coolant fluids has become increasingly pronounced. The dynamic changes in industry, technology, and environmental standards increased the demand for coolant formulations that not only deliver enhanced performance but also align with evolving global needs. This has led to an ongoing process of refining and optimizing the coolant technologies to meet the escalating requirements of a rapidly evolving world. In this review, our aim is to deliver a thorough and in-depth coverage of the ethylene glycol-based cooling fluids and the different coolant technologies used over the years. Through a meticulous examination of key concepts, recent advancements, and critical insights, this paper seeks to underscore the critical importance of coolant composition in determining the efficiency, material compatibility and sustainability of these products.

1. Introduction

Cooling fluids are widely used in several applications, such as power plants, radiators, automobile engines, heating ventilation and air conditioning (HVAC) systems and electronic devices [1]. The term "coolant" is mainly used in automotive and HVAC applications while the term "heat-transfer fluid" is commonly used in the industrial world, for high or low temperature manufacturing applications. The application of interest in this case is the car engine (see Figure 1). When a vehicle is in use, thermal energy (heat) is generated within the engine, which needs to be dissipated in order to avoid various catastrophic events. Therefore, it is essential to carefully address the heat dissipation mechanisms to obtain a balanced heat distribution inside the car engine. An efficient solution to handle the thermal challenges is circulation of a fluid with a high heat capacity that can facilitate heat transfer from the heat-generating components to the environment. Consequently, the fluid undergoes

convective cooling to dissipate the absorbed heat effectively [2]. Historically, water circulation was used in the first radiator for cooling the engine at the end of the 19th century and laid the foundation for the evolution of coolant technologies as we know them today [3].

Various coolant technologies have been developed over the years, containing a variety of chemical additives to provide solutions to diverse problematic issues. The main task of a coolant is to regulate the temperature of a system and achieve a critical temperature balance across various components. More specifically, its importance lies on its ability to draw heat away from the hot engine parts and transfer it to the environment. Concerning the automotive applications, only one third of the energy produced from the fuel combustion is actually utilized by the engine and converted to useful power. The remaining two thirds are converted into heat, half of which is removed through the exhaust. So, this leaves a significant car amount of heat in the engine block, which needs to be removed and diffused into the environment for efficient engine operation. If this excess heat is not immediately and properly removed from the engine, the consequences can be severe. Importantly, coolants play a significant dual role, *i.e.*, to prevent engine overheating during use, as well as freezing when the ambient temperature is too low. Protection against freezing is also an important requirement, especially in cold climates around the Planet.
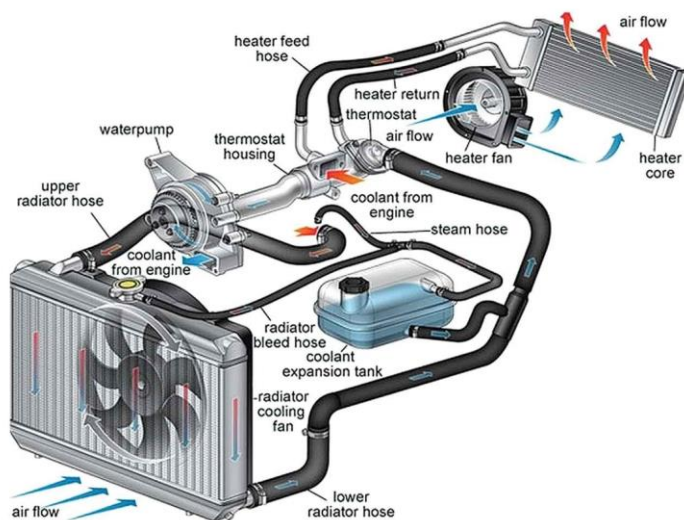

Figure 1. Schematic representation of an automobile engine. Adapted from https://www.powermag.gr

The key criteria for an ideal coolant are high heat capacity, thermal conductivity and efficient heat transfer, low viscosity, low-cost, non- or low-toxicity, chemical inertness, and environmental friendliness, as well as materials compatibility. Furthermore, a coolant should neither cause, nor promote corrosion of the metal-based components of the cooling system. However, the aggressive, heat-stress conditions occurring inside an operating car engine create a corrosive environment. Thus, the cooling fluid has a third function of vital importance, to protect the different metallic components of the cooling system against corrosion [4].

Water is an efficient (and cost-effective) heat-transfer liquid medium. For that reason, it still remains the main component of a coolant. Its high thermal capacity, low cost and wide availability make it suitable for use in heat-transfer applications. However, the use of water alone has certain limitations, including its high freezing point and its volume expansion upon freezing, as well as its relatively high corrosiveness towards metals that come in contact with it. Various ingredients (additives) are blended with it to optimize the performance and service life of the cooling medium, like glycols, scale and corrosion inhibitors, stabilizers, dispersants, sequestrants, pH buffering agents, antifoaming agents, dyes, *etc*. Alcohol solutions (ethanol and methanol) were used in the past because of their low cost, acceptable freezing point, and compatibility with corrosion inhibitors such as chromate, starch, sugar *etc*. to cool the car engines. However, the complexity of modern engines forced manufacturers to switch to ethylene glycol (EG)-based coolants with higher boiling point and freezing protection [5].

Glycol is added to increase the boiling point of the liquid in order to avoid undesirable consequences due to engine overheating, like accelerated distortion of the cooling fluid and the engine itself. At the same time the freezing point is decreased, thus protecting the engine and the cooling system from any damage due to freezing, when the ambient temperature is too low. Monoethylene glycol (MEG), which is the most common car antifreeze, was reported to be used for the first time in the coolant manufacture in the United Kingdom in the early 20th century, for cooling aircraft engines. Polyethylene glycol (PEG) or monopropylene glycol (MPG) are also used. A 1:1 MEG:water blend was adopted by the automakers as it showed high performance, maintaining a fine balance of the desirable features of the two components (water and antifreeze), as well as better compatibility with the other substances present in a cooling system [6]. Glycerol was also used as a base in an antifreeze at that time, but its use was rapidly decreased in the middle of the 20th century, mainly due to its high cost. Apart from cost considerations, there are several technical issues that need to be considered, including the higher viscosity of the aqueous glycerin coolants compared to the aqueous ethylene glycol coolants (especially at low temperature and higher antifreeze concentrations), and the lower freeze point depression for glycerin at an equivalent concentration. Douglas *et al*. have nicely summarized the technical differences between aqueous PG-based, EG-based and glycerin-based coolants [7].

Small amounts of other ingredients are also present in a cooling fluid, in addition to the main fluids, see Figure 2. While these components make up only a small fraction of the coolant, their role is crucial, as they are often used as a criterion for differentiating the various types of coolants present in the market [8]. Coolants with a wide variety of colours like blue, yellow, green, red, pink, orange, turquoise and purple can be found in the market. Dyes of different colours are added to a coolant to differentiate the type of the coolant. The Inorganic Additive Technology (IAT) coolants are mainly green-coloured. The common colours for Organic Additive Technology (OAT) coolants are pink, orange, blue, dark green and red. The typical colours for a hybrid coolant are yellow, turquoise, pink, blue, or purple. In recent days, however, coolant colour is no longer related to the additive technology, but determined

by the car manufacturer or end-user preference. Moreover, the presence of a pH-buffering agent is also beneficial, in order to avoid coolant "aging". Glycol-based cooling fluids were previously reported to be susceptible to thermo-oxidative degradation reactions. Organic acids like glycolic, oxalic, and formic were found to be the primary acidic degradation products formed in ethylene glycol solutions. Lactic and formic acids with minor amounts of acetic and oxalic acids were found to be the primary degradation products from the thermal oxidation of propylene glycol. These degradation products are responsible for pH decrease, and consequently, acceleration of metallic corrosion of the cooling system [9].
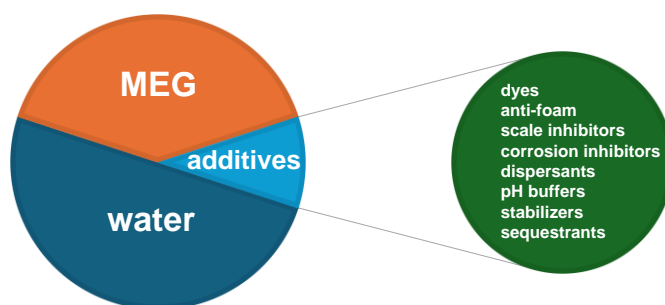

Figure 2. Basic composition of a MEG-based coolant.

The use of coolants, although necessary, may generate negative effects, such as corrosiveness of the fluid. Not unexpectedly, the formation of scale deposits commonly occurs in the cooling systems, mainly due to the presence of metal ions from the use of hard water used for dilution purposes. Furthermore, corrosion products can be formed in the cooling systems due to the presence of corrosive salts from various sources (the fabrication process itself, the use of corrosive water, and the driving environment) [10]. Adhesion of these deposits (scale and corrosion products) onto the critical equipment surfaces can lead to reduced heat-transfer efficiency and cause severe operational problems for the combustion engines. Partial blockage of the radiator could also occur due to excessive scaling, causing higher operating temperatures.

2. Corrosion

Corrosion of the metallic components of a cooling system is one of the most critical issues faced by the coolant manufacturing companies. Moreover, corrosion was reported to increase proportionally as the metal surface temperature is increased. Thus, as the engine combustion heat is transferred through the cylinder head to the coolant, it becomes imperative to ascertain its impact on the corrosion of the metallic surfaces, as well as to discern the role of coolant additives in modulating this corrosion process. Corrosion-related problems may result in disastrous operational and environmental issues. One of the main issues associated with heat-transfer corrosion of the aluminum castings is the deposition of corrosion products on the interior surfaces of the radiator tubes leading to the formation of an insulating film, which will substantially reduce the heat transfer efficiency of the cooling system. In certain cases, this process can occur rapidly, potentially leading to engine overheating within approximately

10,000 miles. Therefore, it is imperative to control and/or prevent corrosion of the critical interior surfaces using a properly balanced coolant formulation [11].

As documented in the literature, it was found that glycol, apart from the freezing point depression, is able to reduce, to some extent, the corrosion rate of metallic surfaces. Studies suggest that this effect can be attributed to the dilution of water, which is essential for metallic corrosion and/or passive film formation reactions. The addition of glycol diminishes the effective water concentration available for these reactions. Conversely, water, an inherent component of glycol-based cooling fluids, introduces several potential challenges. The quality of water can vary significantly, necessitating an understanding of how certain dissolved inorganic salts impact heat-transfer corrosion. Chlorides, in particular, emerge as some of the most corrosive ions encountered in water, capable of inflicting damage (commonly localised corrosion) on metals. In regions such as the Southwest US, it is not uncommon for water to contain chloride levels reaching up to 500 ppm [11].

Furthermore, in order to meet increasingly demanding fuel consumption specifications, automotive manufacturers have dramatically increased the use of aluminum alloys for the construction of heat exchanger systems, in order to reduce the weight of automobile parts [10, 12, 13]. A protective oxide layer is formed on ferrous metal surfaces (*e.g.*, certain aluminum-containing alloys) in the presence of neutral or slight alkaline solutions. Unfortunately, this protective layer can be degraded when aggressive anions (*e.g.*, chloride) are present, by mechanical impact (physical contact/friction) or by random film breaking down, leaving the metal surface exposed to the corrosive medium, therefore leading to corrosion. Several factors, such as aggressive anions or local pH, are likely to prevent repair of the oxide layer. Localised forms of corrosion of the critical surfaces, such as pitting and crevice corrosion, have been observed due to the extensive use of aluminum and other light metals for the components of the cooling system [14].

Different approaches for corrosion protection of metallic surfaces are available to shield the surface from the corrosive environment. Solution chemistry modifications are often implemented to slow down the corrosion process at the metal-solution interface with the use of corrosion inhibitors [15]. The corrosion inhibitor is a chemical substance that is purposely added to the cooling medium to reduce the corrosion rate of the metal surfaces in the operating cooling system. Sodium phosphate, sodium tetraborate, sodium silicate, and sodium nitrate are frequently encountered in coolants formulated to provide comprehensive cooling system protection and are key components of inhibitor packages found in numerous commercially available coolants.

The most common molecular mechanisms of corrosion protection induced by inhibitors are:

(a) passivation of the metal surface,
(b) formation of a thin barrier (film) of the inhibitor on parts or on all metal surfaces, or on the protective oxide layer, and
(c) formation of thick barriers (coatings) of the inhibitor on the metal surface.

Inorganic ions such as chromate, nitrite, molybdate *etc.* are categorized as passivators, and their corrosion inhibitory activity relies on their ability to cause a large anodic shift of the corrosion potential, to stabilize the protective oxide layer on the metal surface, to repair the damaged spots, to reinforce the passive oxide layer by incorporation, and to hinder adsorption of aggressive ions. Nonetheless, many of these additives show several unwanted features, like unacceptable toxicity and strong oxidizing action. One of the corrosion protection mechanisms is the formation of a thin barrier through physi- and/or chemi-sorption on the metal surface. Compounds like silicates can be homogenously adsorbed onto the metallic surface, thus isolating it from the corrosive medium and preventing leaching of metal ions from the surface to the liquid medium. Salts of organic acids, on the other hand, can be selectively adsorbed at the anodic spots, forming strong metal-carboxylate surface bonds. Shieling of the anodic spots also substantially decreases the release of metal ions. Additionally, thick insoluble protective layers can be formed on the metallic surfaces, blocking both anodic and cathodic spots, in the presence of carbonates or non-stabilized phosphate [16].

The efficiency of a corrosion inhibitor also depends on the extent of adsorption of the inhibitor on the metal surface through the mechanism of physisorption, chemisorption, or both (see Figure 3). In the case of physisorption (physical adsorption), weak polar interactions (van der Waals) occur between the inhibitor molecules and the charged metal surface. On the other hand, in the case of chemisorption, the inhibitor molecules are accumulated on the surface and this process is enhanced by formation of chemical bonds. In the latter type of adsorption, the forces that are responsible for the creation of chemical bonds are very strong and include ionic or covalent bonds and certain types of intermolecular forces (see Figure 3) [17, 18].
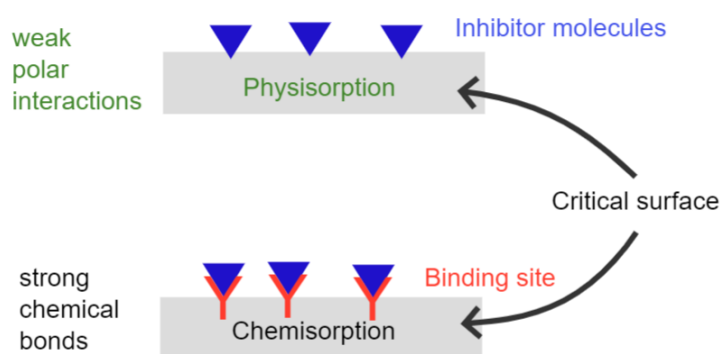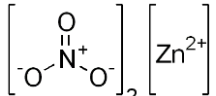

Figure 3. Schematic representation of physisorption and chemisorption.

Moreover, the ability of an additive (corrosion inhibitor) to achieve corrosion protection of a metallic surface is greatly dependent on the chemical composition of the surface (type of metal or alloy used). Inhibitors that offer excellent corrosion protection to one metallurgy, may show lower anti-corrosive or even enhanced corrosive effects to other metals. Commonly used coolant additives and their suitability for certain engine construction

materials are presented in Table 1 (for inorganic inhibitors) and Table 2 (for organic inhibitors) [5].
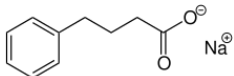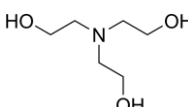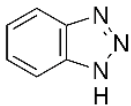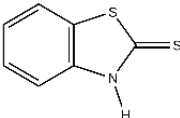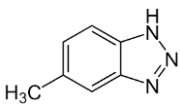
Table 1. Commonly used inorganic coolant additives and their suitability for certain engine construction materials. Adapted from Ref. 5.
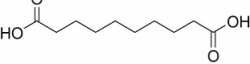
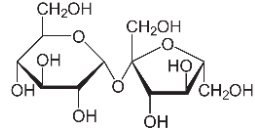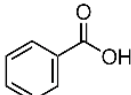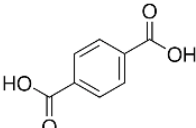| Inhibitor (chemical name)	Inhibitor (basic structure)	Anti-corrosion performance						Additional properties
		Steel	Cast iron	Aluminum	Copper	Brass	Solder	
Monosodium phosphate	(structure)	☑☑	☑☑			☒		pH buffer
Disodium phosphate	(structure)	☑☑	☑☑			☒		pH buffer
Sodium tetraborate	(structure)	☑☑				☑	☑	pH buffer
Sodium carbonate	(structure)							pH buffer
Sodium hydroxide	(structure)							pH buffer
Sodium nitrite	(structure)	☑☑	☑☑			☒		cavitation protection
Sodium molybdate	(structure)	☑☑	☑☑	☑	☑	☑	☑	
Sodium nitrate	(structure)			☑☑			☑	
Sodium silicate	(structure)	☑	☑	☑☑	☑	☑		
Sodium chromate	(structure)	☑☑	☑☑					

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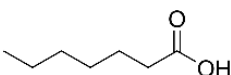| Inhibitor (chemical name)	Inhibitor (basic structure)	Anti-corrosion performance						Additional properties
		Steel	Cast iron	Aluminum	Copper	Brass	Solder	
Zinc nitrate		☑	☑					

☑ = level of protection, ☒ = corrosive.

Table 2. Commonly used organic coolant additives and their suitability for certain engine construction materials. Adapted from Ref. 5.

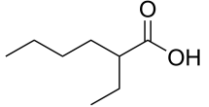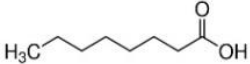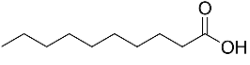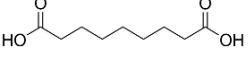| Inhibitor (chemical name)	Inhibitor (basic structure)	Anti-corrosion performance						Additional properties
		Steel	Cast iron	Aluminum	Copper	Brass	Solder	
Sodium phenylbutyrate		☑☑	☑☑					
Triethanolamine		☑☑	☑☑		☒			pH buffer
Benzotriazole				☑	☑☑	☑		
Mercapto Benzothiazole				☑	☑☑	☑		
Tolyltriazole				☑	☑☑	☑		
Sucrose				☑	☑	☑		
Benzoic acid		☑☑	☑	☑			☑	
Terephthalic acid		☑	☑	☑	☑	☑		
Heptanoic acid		☑	☑	☑	☑	☑		

Inhibitor (chemical name)	Inhibitor (basic structure)	Anti-corrosion performance						Additional properties
		Steel	Cast iron	Aluminum	Copper	Brass	Solder	
2-Ethylhexanoic acid		☑	☑	☑	☑	☑		
Octanoic acid		☑	☑	☑	☑	☑		
Decanoic acid		☑	☑	☑	☑	☑		
Nonanedioic acid (Azelaic)		☑	☑	☑	☑	☑		
Decanedioic acid (Sebasic)		☑	☑	☑	☑	☑		

☑ = level of protection, ☒ = corrosive.

Diverse coolant technologies have been developed over the years using inorganic or organic-based inhibitors to protect engine components from excessive scaling and corrosion, depending on the requirements of each geographical area. By the end of the 20th century, three main approaches to corrosion inhibition were established in the United States, Europe and Japan based on water quality, cooling system type, engine type, and weather conditions in those regions. In Europe, for example, the water used for dilution of the coolant concentrate was found to be rich in metal cations such as Ca^{2+} and Mg^{2+}. These metal cations are known to interact with phosphate anions (used as inorganic corrosion inhibitors in coolants) forming metal phosphate scales and deposits. Excessive deposit formation onto critical surfaces forced certain coolant technologies to go "phosphate-free" [8].

Silicate-based coolants, which were classified as "conventional coolants", were used in United States and Europe. Later on, organic acid or hybrid low silicate/organic acid-based coolants were preferred by the automakers for enhanced corrosion protection at higher operating temperatures. Meanwhile, Japanese automakers preferred amine/phosphate-based coolants instead of silicates. The reason for this was the concerns for potential operation-compromising effects, such as amorphous silica precipitation on various components of the cooling system and inefficient corrosion protection due to decreased storage stability. Later on, phosphate/organic acid or low phosphate/organic acid-based coolants were selected [5]. In Asia, scaling problems causing decreased heat transfer led to the prohibition of coolants containing silicate (also used as inorganic corrosion inhibitor in coolants).

There are many different ways to classify an automotive antifreeze coolant, including national or international standards, specifications of automotive manufacturers *etc*. However, the coolants mainly differ in the type of scale and corrosion inhibitors added. The type of antifreeze used does not substantially affect the quality of the coolant. Therefore, the

engine coolants can be classified into three main categories according to the type of corrosion inhibitor [5]:

(i)   Inorganic Additive Technology (IAT) coolants,
(ii) Organic Additive Technology (OAT) coolants, and
(iii) Hybrid Organic Acid Technology (HOAT) coolants.

These will be presented in detail below.

2.1. Inorganic additive technology coolants (IAT)

For several years different combinations of inorganic inhibitors, including phosphates, silicates, molybdates, borates, nitrites and nitrates were used for reducing corrosion effects in the cooling systems. The desired multi-metal corrosion protection of these inhibitors is achieved through effective adsorption of these compounds on the metal surfaces. Thus, a protective layer is formed onto the critical surfaces of the cooling systems acting as a physical barrier insulating the metal surfaces from the cooling fluid and preventing any further corrosion effects. IAT coolants, also called "traditional" or "conventional" coolants, even though they are considered outdated for the demands of modern engines, are still used in older cars [10].

2.1.1. Borate, nitrate and molybdate

Borate (in the form of tetraborate) is considered as one of the best buffers for pH control and is one of the most common ingredients included in coolants. According to Wiggle *et al.* tetraborate showed no corrosion protection activity against general corrosion [19]. Nitrate is considered as a very effective inhibitor against pitting and crevice corrosion of aluminum surfaces and is usually an important additive (mainly in combination with silicate) in engine coolants used for aluminum-built equipment [20, 21]. Molybdate was found to be amongst the most broadly applicable corrosion inhibitors, mainly due to its efficacy to protect both ferrous and non-ferrous metals and its relatively low toxicity [22]. It was proposed that molybdate is adsorbed on the native oxide layer on the metal surface, producing a layer impermeable to other aggressive anions (*e.g.*, Cl^- and SO_4^{2-}). More often, molybdate is added in combination with synergistic compounds, like film-forming agents. These agents provide a primary passivating film more readily than does molybdate alone. The addition of molybdate promotes primary film formation, resulting in better quality barrier films [19].

2.1.2. Silicate

Silicate was reported to exert outstanding corrosion protection for several metallurgies, forming a stable protective film on the metal surface, when present in the solution at sufficiently high concentrations. According to a published study, silicate at a dosage >0.2 g/L (as $Na_2SiO_3 \cdot 9H_2O$, 42 ppm expressed as SiO_2), and in the presence of other inorganic inhibitors such as tetraborate and phosphate, achieved efficient corrosion

protection [11]. Later on, Van de Ven *et al.* [23] established that for conventional coolants 0.04% w/w (as $Na_2SiO_3 \cdot 9H_2O$, 115 ppm expressed as SiO_2) was the minimum concentration of silicate required in the coolant solution for efficient corrosion protection of aluminum heat-transfer surfaces, according to well-known protocols (ASTM D). The corrosion products formed on aluminum-containing metal surfaces presumably interact with the silicates to form thin, stable aluminum-rich silicate surface films. These films were reported to successfully impede the corrosive attack. Additionally, it was suggested that silicate-based coolant technology was superior in performance and a well-stabilized silicate-containing coolant passivates an aluminum surface more rapidly than other coolant technologies. Nevertheless, a poorly stabilized silicate-containing coolant, with lower active silicate levels, showed decreased corrosion protection efficiency. At lower silicate concentrations, the abovementioned protective film is no longer effective, and corrosion is more likely to occur, together with the formation of corrosion debris [24]. Furthermore, heat-transfer corrosion tests showed that as soon as the soluble silicate levels drop below 115 ppm, the corrosion protection is compromised. Pre-treatment of the aluminum surfaces with mixtures containing higher silicate levels was found to be ineffective. It is, therefore, important to have sufficient amount of active (soluble) silicates in the cooling system so that they can continuously repair the protective film and maintain its integrity in an otherwise aggressive alkaline environment [23].

2.1.3. Phosphate

The use of phosphates (plural is used because various types of phosphates, *e.g*., ortho-, pyro-, and hexametaphosphate have been used) for corrosion control in boiler systems dates back to 1930 [25]. Phosphate is also well known for its ability to form protective layers on critical surfaces, protecting the various components of the cooling systems against corrosion. More specifically, phosphate has proven to be a good inhibitor against cavitation and erosion/corrosion for aluminum-based metallurgies, as well as for general corrosion protection for most metals in a cooling system [20]. Thermodynamic studies indicated that the adsorption of phosphate onto a metallic surface is a spontaneous process occurring through physisorption. As it was demonstrated by surface analysis methods, the inhibition mechanism of phosphate ions for steel surfaces was attributed to the formation of a passive film with a "double" layer on the surface. The inner layer was formed by iron oxyhydroxides, while the outer layer consisted of iron phosphate salts, like $FeHPO_4$, $Fe_3(PO_4)_2$ and $FePO_4$ formed via a dissolution-precipitation mechanism. Similarly, a highly adherent Al_3O_3 barrier is known to be formed on the surface of aluminum alloys [26]. In general, it is believed that phosphate-based inhibitors react with metal cations present, such as Ca^{2+}, forming metal phosphate precipitates. These precipitates are subsequently deposited onto the critical surfaces or adsorbed at the pit locations on the metal surface where corrosion has already been initiated, acting as a physical barrier, and impending the diffusion of aggressive ions [27]. However, if the process is not carefully controlled, thick metal phosphate layers may

be deposited on the critical equipment, inducing unwanted phenomena, such as inefficient heat transfer.

A significant disadvantage of this type of inhibitor system is its relatively short service life. Due to the formation of the protective layer and/or uncontrol scaling, these inhibitors are rapidly depleted from the cooling system [28]. Other disadvantages of inorganic inhibitors, including toxicity (chromate), low stability (silicates, phosphates) and selective protective action (nitrites), have led the research efforts towards the application of organic compounds as possible inhibitors [29].

2.2. Organic additive technology (OAT)

Organic-based corrosion inhibitors have been used as alternatives to "conventional" (inorganic) inhibitors due to several attractive features, such as their non-toxicity and low environmental impact, biodegradability, long service life, acceptable corrosion inhibition efficiency *etc.* [27] OAT was introduced in the late 80s and was based on the use of organic acid inhibitors, specifically neutralized carboxylic acids, commonly referred to as carboxylates. US manufacturers were the first ones to use organic acid inhibitors, followed by European automakers. Since the 90s the use of OAT-based coolants became widespread worldwide.

Corrosion protection in this case is achieved by chemical interactions of carboxylates with the metallic corrosion sites, rather than the formation of a protective layer covering the entire metallic surface (the latter being the case for inorganic inhibitors). Studies have shown that under the heat-transfer conditions occurring in an engine cooling system, carboxylates are chemically bonded to the metal surface forming a molecular film only at the anodic sites, where a high potential of corrosion exists. More specifically, adsorption of the carboxylate inhibitors at the spots where the oxide layer is destroyed leads to the formation of a temporary "patch" (<0.1 μm thickness), thus preventing further adsorption of aggressive ions and therefore inhibiting corrosion of the metal surface. It was reported that the inhibitor can either adsorb from the solution directly onto the anodic sites, or diffuse laterally to the anodic site, having already been adsorbed onto the metal surface. Importantly, this does not affect the heat transfer at the metal surface-cooling medium interface. As soon as the oxide layer is re-formed, the inhibitor is released back to the solution or moves to another nearby anodic spot [14]. Nevertheless, carboxylates were also reported to have a threshold value. Below this value, no net effect of aliphatic acids on the corrosion of the metal can be observed. Notably, the decreased corrosion protection observed for lower levels of inhibitors is much less intense for the carboxylates compared to the silicates [14].

Thus, carboxylates provide higher levels of stability and robustness, as well as better heat-transfer characteristics compared to the IAT coolants. These attractive features, along with the very low depletion rates of the carboxylate-based inhibitors, have led to the global use of the OAT coolant technologies. Furthermore, these organic acid inhibitors, also called "universal" inhibitors, are more environmentally friendly. They can be blended with other coolants of the same technology without any compromise in their performance. The OAT

coolants meet the Asian and European antifreeze requirements as they do not contain silicates or phosphates [10, 12].

2.3. Hybrid organic acid technology (HOAT)

Recently, the need was apparent to overcome the negative effects of inhibitor depletion occurring in IAT coolants, to ensure extended life performance, and to manage/control multi-metal systems. Hence, the synergetic effect of the above mentioned organic and inorganic inhibitors was exploited, introducing the so called "hybrid" coolants [23]. These include either a traditional coolant (containing inorganic inhibitors) that includes a minimum amount of organic inhibitors, or an OAT coolant with the addition of synergistic inorganic inhibitors. The latter type includes coolants with inorganic co-inhibitors such as silicate or phosphate, in addition to the organic acid inhibitors, in order to optimize performance.

The protective film formed in the presence of carboxylates (OAT-based coolants), provides good protection against corrosion of the aluminum heat-rejecting surface. At high silicate levels, the silicate film showed the same corrosion protection efficiency. For intermediate silicate levels though, this film is no longer effective in preventing corrosion of the aluminum surface. Nevertheless, it was reported that the formation of the silicate layer precedes the formation of the organic acid adsorption layer. At low silicate levels, the protective silicate layer initially formed, is gradually replaced by a layer of corrosion products. If no alternative aluminum corrosion inhibitor is present, the surface will readily corrode. However, in the presence of carboxylates, the silicate layer when broken down is replaced by a carboxylate protective layer [14].

Therefore, more efficient corrosion inhibition was reported for hybrid coolant technologies compared to OAT or IAT coolants, as both anodic and cathodic inhibition was achieved. The high stability and non-consuming behavior provided by organic inhibitors was reinforced by the efficient, inexpensive multi-metal protection provided by silicate or phosphates [10].

3. Scale Formation and Deposition

Cooling systems often suffer from inorganic scale formation and deposition [7]. Under high-stress conditions thick layers of scale can be deposited onto critical heat-transfer surfaces, causing several catastrophic impacts, such as decreased thermal efficiency of heat exchangers, flow oscillations or flow blockage, cavitation and underdeposit corrosion of the metal components. Additionally, cracked heads, warped engine blocks and cooling system fans' malfunction can occur resulting to overheating due to inefficient operation of the cooling system. Thus, it is apparent that scale deposition impairs the operation of the cooling equipment leading to challenging operation problems such as frequent and difficult repairs, costly overhauls, and related system outages [30].

The formation of these deposits in a cooling system is strongly influenced by various parameters such as water hardness or system metallurgy. The presence of metal ions in a cooling system, due to the water used for dilution of the coolant concentrate or due to

leaching of metal ions from the metallic surfaces, can cause excessive precipitation. For example, calcium and magnesium, as well as aluminum, iron and copper ions can form insoluble salts or gels in the presence of carbonates, phosphates, and silicates. The water used for coolant dilution purposes can vary considerably in composition, depending on the geographical location around the globe. Another factor that affects scale formation is the system operational temperature [31]. Most common scales that deposit onto heat-transfer surfaces, are those that exhibit inverse solubility with temperature (*i.e.*, their propensity to form increases with increasing temperature), like calcium carbonate, calcium phosphate and various metal silicates. More specifically, these types of scale-forming salts can be completely soluble at lower temperatures. But, as the temperature of the system is increased the solubility of those scales is drastically decreased leading to supersaturation, especially in the higher-temperature areas of the cooling fluid, near the heat transfer surfaces. Thus, their propensity to drop out from the working fluid increases and precipitation on the hot surfaces occurs [3]. Additionally, normal solubility salts (whose solubility increases with increasing temperature), such as colloidal/amorphous silica may form and deposit during cooling processes. Moreover, deposit formation can also be influenced by fluid velocity and residence time, concentration of oxygen, pH, and the presence of corroded surfaces. Scale generally tends to form in areas with low flow and high dissolved oxygen levels. Common scales encountered in cooling systems include calcium carbonate, calcium sulphate, calcium phosphate, silica, and metal silicates. Scales and deposits that are of particular interest for the engine coolant applications include amorphous silica, metal silicate and metal phosphate scales.

Silica is the most infamous example of amorphous scale precipitation. Silicates are added in the coolant concentrate as chemical additives, due to their ability to provide efficient corrosion protection for various metal surfaces. Unfortunately, long term stability of the soluble silicate species in coolants is difficult, leading to excessive precipitation in the cooling systems, as well as depletion of the corrosion inhibitor (active silicate). Removal or dissolution of such precipitates is particularly difficult, time consuming and expensive. Currently, limited information is available about the polycondensation process of silicic acid taking place in a coolant environment. According to a recent publication, however, it was established that silicate is rapidly polymerized in a coolant environment, and that its condensation is faster and more efficient than that in pure water systems [30]. When implementing approaches for the mitigation of silica scaling, the presence of certain ions, such as Mg^{2+}, Fe^{3+} or Al^{3+} should be carefully considered as well [32, 33]. When pH levels exceed neutral, silica is present in the form of silicate anions (*e.g.*, $(HO)_3SiO^-$, which is the mono-deprotonated form of silicic acid) that readily react with metal ions, such as Mg^{2+}, Fe^{3+} or Al^{3+}, to form insoluble metal silicates. In fact, it has been shown that silica can precipitate at concentrations below its saturation limit when such metal cations are present [34, 35]. Thus, the presence of these metal cations and their hydroxides have been reported to aggravate silicate fouling, especially at high pH regions, leading to massive precipitation [31, 35]. In some cases, aluminum-containing siliceous precipitates have been observed to

adhere to industrial critical equipment [35]. Furthermore, corroded steel surfaces (*e.g.*, corroded pipes or heat exchanger tubes) are prone to silicate fouling. Corrosion products such as iron oxides/hydroxides present on metallic surfaces may act as a deposition matrix for siliceous deposits. Again, to the best of our knowledge, limited research has been conducted on metal-silicate scale formation and stabilization in coolant or MEG environment.

Phosphate is another well-known additive used in certain coolant formulations as an effective corrosion inhibitor. As discussed in detail above, efficient corrosion protection of the metallic surfaces is achieved through the formation of a protective phosphate-containing layer. Furthermore, in the presence of metal ions, especially Ca^{2+}, a thin film of metal phosphate scale deposit has been observed to form on critical surfaces, in the cooling systems [37]. If the process is not carefully controlled, thick metal phosphate layers may be deposited on critical equipment, causing catastrophic events such as reduction of the heat-transfer capacity or flow blockage. Moreover, metal phosphate precipitates are typically less soluble in neutral or alkaline conditions [36, 38] while the pH of a coolant is typically ~8–9, which is the edge of calcium phosphate scale solubility in aqueous systems. Apart from pH, temperature is another factor that may influence the precipitation of metal phosphate scales. Calcium phosphates (both crystalline and amorphous) exhibit inverse solubility characteristics with increased precipitation observed at higher temperatures [39]. The presence of organic solvent was also found to enhance calcium phosphate formation. The solubility of two crystalline forms of calcium phosphate precipitates was reported to decrease in mixed ethanol/water solutions (higher pK_{sp} values) [40]. Interestingly, the presence of polyethylene glycol (PEG) [41] and glycerol [39] during calcium phosphate precipitation was reported to favour amorphization.

The use of phosphates, albeit necessary, usually leads to the formation of highly insoluble calcium phosphate deposits which harm the critical equipment of industrial systems, like heat exchangers. These precipitates are frequently attributed to hydroxyapatite [$Ca_5(PO_4)_3(OH)$, HAP]. Among the various calcium phosphates, tricalcium phosphate and hydroxyapatite are the most commonly observed scales in cooling systems [42]. It was reported that, if sufficiently high alkalinity is achieved (above 200 ppm, in the form of the hydroxide ion, OH^-), phosphate will combine with the available Ca^{2+} to form HAP, which appears in the form of soft voluminous particles and can be easily removed. If, however, there is insufficient hydroxide ion present, the Ca^{2+} ions react with the phosphate to form tricalcium phosphate [$Ca_3(PO_4)_2$]. The latter is a very dense, hard, grey deposit that forms a tenacious scale on critical metal surfaces. In cases of water softener failure, metal ions such as Ca^{2+} and Mg^{2+} (from the use of hard water) will combine with hydroxide ions forming metal hydroxides. Thus, the hydroxide ions will no longer be available for the formation of hydroxyapatite and the calcium ions will combine with the available phosphate, forming the undesirable tricalcium phosphate [43]. Apart from Ca^{2+}, the presence of other metal ions, including Mg^{2+} (from hard water), $Fe^{3+/2+}$ or Al^{3+} (leaching form metallic surfaces due to uncontrolled corrosion), is responsible for the formation of tenaciously adhering metal

phosphate scale forming on various equipment parts (piping, pumps, heat exchanger, aerators, *etc.*) [44, 45].

Deposition of calcium phosphate on heat exchangers, as well as iron phosphate on radiators has been reported as a problem that must be combated when phosphate is present in a coolant, although limited knowledge is available in the literature [31]. Thus, the use of scale inhibitors is necessary to reduce the potential deposition and control the scale layer thickness [46]. However, there are no available research studies focused on scale inhibitors used in the cooling fluids.

4. Conclusions

For a cooling system to be able to operate properly, the following actions need to be implemented: (a) control of problems related to corrosion, scaling, fouling and biological growth, (b) maintenance of balanced chemical composition and operation parameters in the recommended range, (c) cost-effectiveness, (d) safeguarding of human health, as well as (e) adherence to environmental requirements and restrictions. Various factors that need to be considered for the selection of chemical additives as scale or corrosion inhibitors and/or dispersants include compatibility with formulation ingredients, water composition (*i.e.* hardness), additive stability and performance under heat-stressed conditions, and environmental acceptability. The need for both efficient and environmentally friendly inhibitors has led to continuous research to achieve improved performance [47]. In order to apply the most suitable scale and corrosion inhibitor(s) in a cooling system several factors must be taken into account: the system operating conditions, the type of metallurgy and other surfaces that come in contact with the cooling medium, the water quality being used, as well as the potential problems/contaminations that may occur under normal operation conditions [48].

Conflicts of interest

The authors declare no conflict of interest.

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