

Analysis of Aluminum Alloy Surface Formed by Rust-preventive Additive Component of Coolant

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ABSTRACT

Coolant protects the engine water jacket against rusting, in other words, it acts as a rust preventive. The rust preventive performance depends upon the type and quantity of the additive.

Automotive coolants used in recent years can be broadly divided into three categories depending on the type of additive used: organic acid coolants, phosphate coolants, and silicate coolants.

In this research project, we studied coolant additives that provided aluminum with corrosion resistance, by combining organic acid coolant with organic additives that have a long heat-resistant life. The coolants were compared by analyzing the aluminum surface after the corrosion condition.

1. Introduction

In recent years, with the progress of rust prevention additive techniques, companies around the world have been applying coolants that have longer replacement intervals. In the 1990s, replacement was generally done every 2 to 3 years, but recently some coolants have recommended replacement periods of 5 years or even longer. This prolonging of coolant replacement life is the result of using an organic rust prevention additive with a long thermal life, a conventional inorganic rust prevention additive, and by optimizing the combination of additives.

As shown in Fig. 1, different regions have adopted different coolant formulations for quite some time^{(1), (2)}. Recently, Europe and North America have primarily used two types of coolants: an organic acid coolant that uses only organic additives or a silicate coolant that uses inorganic silicate.

Japan has used coolants that differ distinctly from those used in Europe and North America. Japan used an amine coolant through the 1980s and during the 1990s. Japan later adopted phosphate coolants that contain a combination of phosphates and organic acid salts.

	Year			
	1970	1980	1990	2000
Europe	Borate/Silicate/Nitrite → Organic acid			
U.S.A	Borate/Silicate/Phosphate → Organic acid			
Japan	Amine/Phosphate/Nitrite	Amine/Phosphate (Noen nitrite)	Phosphate/Organic acid (Non amine)	

Fig. 1 Coolant formation in each region

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There are some reports that state the use of organic acid coolant causes aluminum erosion-corrosion⁽¹⁾. In order to enhance the anti-erosion and corrosion performance of organic acid coolant, this study was designed to research the rust prevention additive component of coolants.

Furthermore, surface analysis was performed on the aluminum after the corrosion test condition to determine the difference in effects between the types of coolant additives.

2. Test Method

2.1. Investigation of Organic Acid Coolant

When investigating the rust prevention additive of a coolant, it is important to ensure that it can prevent aluminum rust under a lotic environment. In other words, that it has good anti-erosion and corrosion performance⁽¹⁾. Several types of organic acid coolants were created and their aluminum rust prevention performance was evaluated in flow of coolant.

The following items were considered for the selection of the combination of rust prevention additives.

- (1) Organic carboxylate, which has been used as a coolant rust prevention additive before, was selected as the base for the coolant.
- (2) Organic compounds that have chemical structures or functional groups with the potential to prevent rust in aluminum were used with the base coolant (1).

2.1.1. Sample preparation

Table 1 shows the evaluated coolant compositions. The base material for all of the compositions was ethylene glycol. Each formulation was diluted with water to a concentration of 30 volume % and adjusted to a pH of 7.5 - 8.0.

Phosphate coolant and silicate coolant were prepared for comparison.

2.1.2. Test method

A jet erosion-corrosion test apparatus (shown in Fig. 2) was used to evaluate the metal rust prevention performance of the coolants in flow of coolant⁽¹⁾. A metal test piece, regulated by JIS K2234⁽³⁾, was set in the test equipment. After circulating heated coolant for a determined amount of time, the aluminum test samples (AC2A) were checked for appearance and changes in weight.

2.2. Aluminum Surface Analysis after the Jet Erosion-Corrosion Test

A surface analysis was performed on each aluminum test piece after the jet erosion-corrosion test.

2.2.1. Sample and test piece

The aluminum test pieces used in the jet erosion-corrosion test with the three types of coolant below were selected for analysis.

- (1) Organic acid B coolant
- (2) Phosphate coolant
- (3) Silicate coolant

To observe changes in the surface of the test pieces before and after the test, the aluminum test pieces were polished to a mirror-surface finish prior to the test.

2.2.2. Analysis

Aluminum surface analysis methods are shown below.

- Magnified appearance of surface:
Magnified appearance of surface using a microscope

Table 1 Test coolant composition

Test coolant Additive composition	Organic acid coolant						Comparative	
	A	B	C	D	E	F	Phosphate coolant	Silicate coolant
Carboxylate-a	●							
Carboxylate-b	●	●	●	●	●	●	●	●
Carboxylate-c		●	●	●	●	●	●	●
Amino acid			●					
Organic nitride				●				
Organic sulfide					●			
Saccharide						●		
Phosphate							●	
Silicate								●
Triltriazole, etc	●	●	●	●	●	●	●	●
Others		●	●	●	●	●	●	●

- Chemical composition analysis of surface:
Analysis of chemical composition in the direction of surface depth using glow discharge spectroscopy

2.3. Aluminum Surface Changes when Coolant was Replaced

Two types of coolant, with different compositions, were used to examine the affect on the aluminum surface when a coolant with a different additive is used during a jet erosion-corrosion test.

2.3.1. Sample

Phosphate coolant and organic acid B coolant were selected as the test coolants.

2.3.2. Test method

After coolant was circulated for a fixed time in the jet erosion-corrosion test apparatus of Fig. 2, in which a metal test piece has been placed. The coolant was replaced by one with a different composition and further circulated. The external appearance and change in mass of the aluminum after the test were checked.

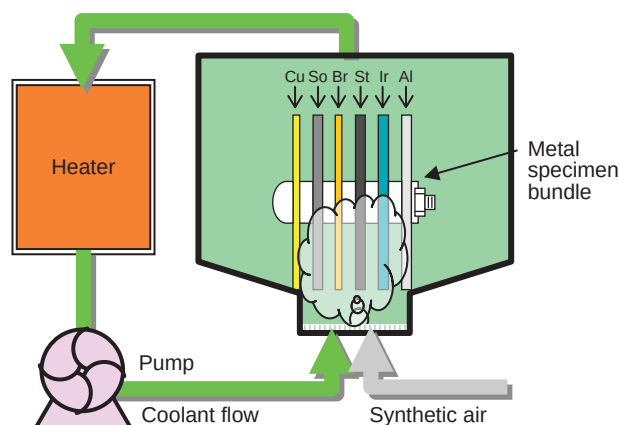


Fig. 2 Jet erosion-corrosion test apparatus

Test 1: Phosphate coolant

The coolant was replaced by organic acid B coolant in the middle of the test.

Test 2: Organic acid B coolant

The coolant was replaced by phosphate coolant in the middle of the test.

3. Results and Considerations

3.1. Investigation of Organic Acid Coolant

Table 2 shows the results of change in mass and external appearance of aluminum after the test. The reduction of mass of the metal test piece is considered to be caused by elution of the metal composition into the coolant. Therefore, coolants with lower amounts of mass reduction are judged to have better rust prevention performance.

Organic acid A coolant mainly uses organic carboxylate as rust prevention additives and its aluminum erosion-corrosion performance was found in previous evaluations^{(1), (4)}. From the test result, it was found that the mass of aluminum was greatly reduced by organic acid A coolant. In contrast, organic acid B coolant, which also includes organic carboxylate, was able to inhibit the mass reduction up to -0.02 mg/cm^2 .

The result of organic acid coolants C through F showed no enhancement of aluminum rust prevention performance, even though new organic materials were used.

On the other hand, the aluminum maintained a shiny silver external appearance similar to the initial appearance. In addition, the mass reduction of aluminum was low and results obtained were more favorable than organic acid formula coolants.

In this study, organic carboxylate and various organic compounds were combined to create organic acid coolants and the coolants were evaluated. Mass reduction was present in all organic acid coolants tested. This research did not lead to finding a coolant that has better aluminum rust prevention performance than phosphate or silicate coolants.

This investigation resulted in a reconfirmation that, although the organic acid coolant can inhibit the aluminum mass reduction, phosphate and silicate coolants are more effective at aluminum rust prevention than organic acid formula coolant.

Table 2 Results of coolant test

		Mass	Appearance
Organic acid coolant	A	-0.83 mg/cm^2	Black
	B	-0.02 mg/cm^2	Black
	C	-0.05 mg/cm^2	Black
	D	-0.08 mg/cm^2	Black
	E	-0.17 mg/cm^2	Black
	F	-0.05 mg/cm^2	Black
Comparative	Phosphate coolant	$+0.01 \text{ mg/cm}^2$	Silver
	Silicate coolant	$+0.01 \text{ mg/cm}^2$	Silver

3.2. Aluminum Surface After the Jet Erosion-Corrosion Test

3.2.1 Appearance of surface under magnification

Figure 3 shows magnified pictures and external appearances of the aluminum test pieces before and after the test. Electron Probe X-ray Micro Analyzer (EPMA) analysis confirmed that the areas on the test samples that look black and grey were precipitates of silicon and copper. These are components of the aluminum alloy.

For phosphate and silicate coolants, there were no significant changes in the external appearance or under magnification of the aluminum surface after testing.

On the other hand, there were significant changes in the external appearance and under magnification of the aluminum surface after testing using the organic acid coolant. The aluminum portion had all changed to black. The silicon that precipitated into rod shapes in the alloy appeared to be white and floating. This is believed to be because the aluminum surface was slightly corroded by flow of

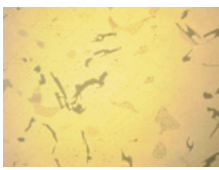
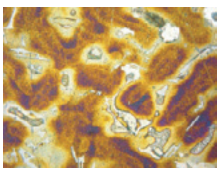
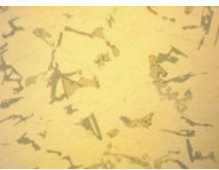
	Reference	After test		
		Organic acid coolant	Phosphate coolant	Silicate coolant
Appearance				
Magnification (x 1200)				
Mass	—	-0.02 mg/cm^2	$+0.01 \text{ mg/cm}^2$	$+0.01 \text{ mg/cm}^2$

Fig. 3 Appearance and mass of aluminum after coolant test

coolant. As for silicon, which is harder than aluminum, it was not corroded and therefore remained intact.

These results provide that the mass reduction of the aluminum test piece for organic acid coolant was caused by slight corrosion of the aluminum surface.

3.2.2 Chemical composition of the surface in the depth direction

Figure 4 shows chemical composition measurement results in the depth direction of the aluminum surface before testing. It is generally known that aluminum forms a very thin, passive, oxide layer on its surface that protects aluminum, in open air, from corrosion⁽⁵⁾. Therefore, the layer of aluminum and oxygen detected on the surface prior to testing is an aluminum oxide layer.

This aluminum oxide layer was maintained on the aluminum surface after testing with phosphate and silicate coolants (Figs. 5 and 6).

Aluminum and oxygen were detected on the surface using the organic acid coolant. However, a thick oxygen layer was also formed, which has different characteristics from that of phosphate or silicate coolants (Fig. 7). From Raman spectral analyses or X-

ray analyses, this thick oxygen layer is considered to be a layer formed primarily of aluminum hydroxide^{(1), (6)}.

The surface under magnification in Fig. 3 shows that the surface layer of aluminum formed by the organic acid coolant was slightly corroded by the flow of the coolant. Therefore, the thick aluminum hydroxide layer formed when using organic acid coolant could peel easily in flow of coolant, compared to the aluminum surface layer found with the phosphate coolant and silicate coolants (Fig. 8).

3.3. Aluminum Surface Changes when Coolant is Replaced

When coolant was replaced, the external appearance of the aluminum changed to brown-red in both tests 1 and 2, and there was also mass reduction seen in each test. In addition, a slight change in color and roughness of the aluminum surface was found when observed under magnification (Fig. 9).

As to the chemical composition in the direction of surface depth, a surface layer with a thick oxygen layer was confirmed. This layer is similar to the one found after testing with only organic acid coolant (Figs. 10 and 11).

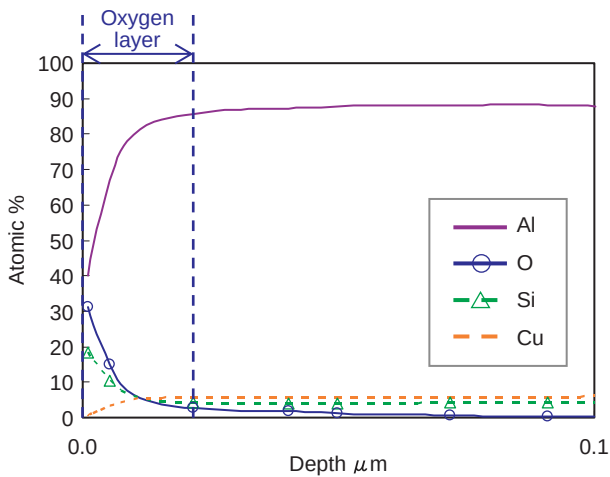


Fig. 4 Depth profile of each component of aluminum surface before coolant test

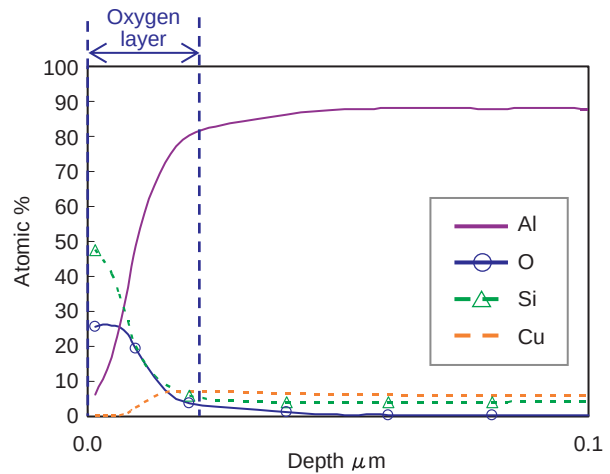


Fig. 6 Depth profile of each component of aluminum surface after silicate coolant test

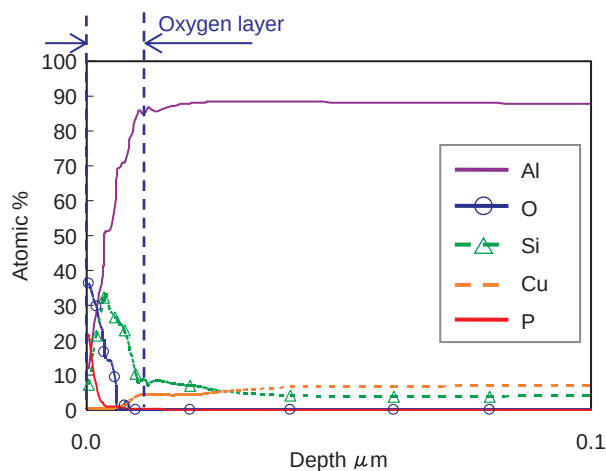


Fig. 5 Depth profile of each component of aluminum surface after phosphate coolant test

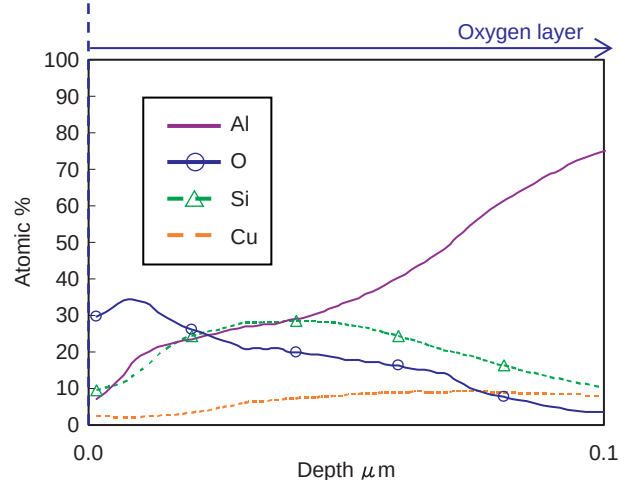


Fig. 7 Depth profile of each component of aluminum surface after organic acid coolant test

From these results, it was found that when phosphate coolant was used and then replaced by the organic acid coolant, the thin aluminum oxide layer on the surface was not maintained and the surface changed to the thick layer similar to that formed by the organic acid coolant.

It was found that when the organic acid coolant was used and then replaced by the phosphate coolant, the surface layer maintained the characteristics formed by the organic acid coolant and was not significantly changed by the phosphate coolant.

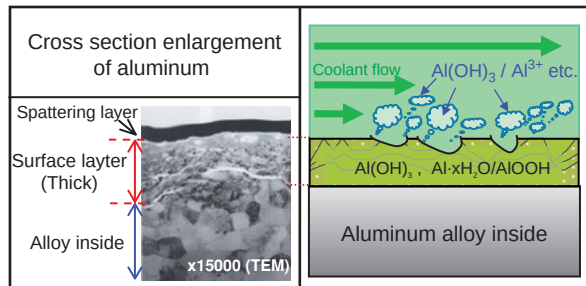


Fig. 8 Aluminum exfoliation mechanism in organic acid coolant flow

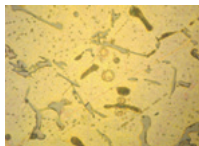
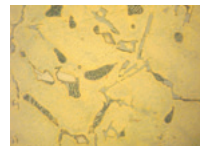
Beginning	Organic acid coolant	Phosphate coolant
Replacement	Phosphate coolant	Organic acid coolant
Appearance		
Magnification (x 1200)		
Mass	-0.06 mg/cm ²	-0.03 mg/cm ²

Fig. 9 Appearance and mass of aluminum after coolant change test

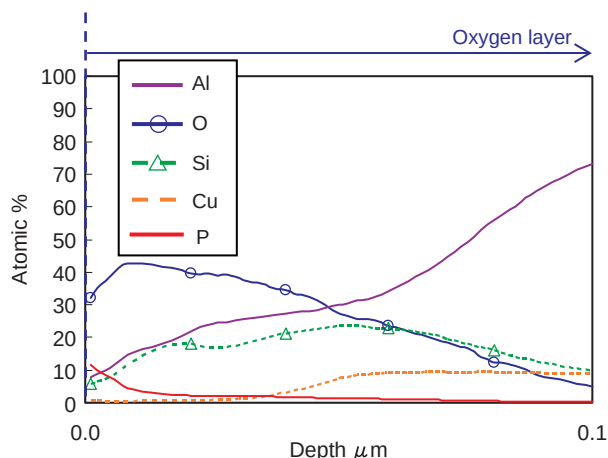


Fig. 10 Depth profile of each component of aluminum surface after coolant change test (phosphate → organic acid)

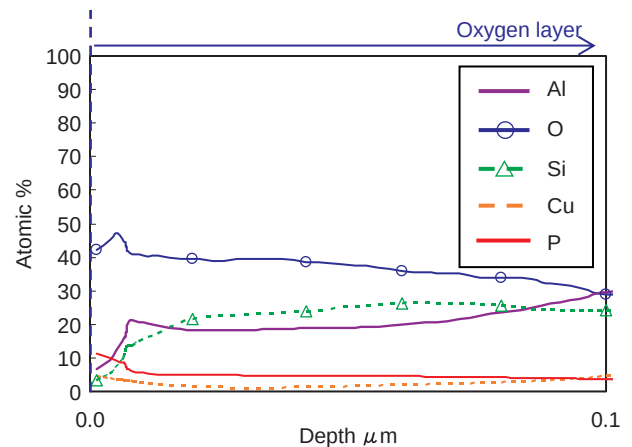


Fig. 11 Depth profile of each component of aluminum surface after coolant change test (organic acid → phosphate)

4. Conclusion

Through investigation of organic acid coolant and aluminum surface analysis, the following results were obtained.

- (1) Organic acid coolant was evaluated for rust prevention performance under a lotic environment, and it was able to inhibit the aluminum mass reduction. However, organic acid coolant could not achieve better results than phosphate or silicate coolants.
- (2) Organic formula coolant forms a thick layer on the surface of the aluminum. However, this layer peels easily in flow of coolant when compared to the aluminum surface layer found after testing with phosphate and silicate coolants.
- (3) When replacing phosphate coolant with organic acid coolant, the surface layer changed to a thick layer similar to that formed by organic acid coolant.
- (4) When replacing organic acid coolant with phosphate coolant, the surface layer maintained the thick layer formed by the organic acid coolant and was not significantly changed by the phosphate coolant.

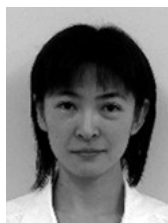
From these results, it can be stated that further research is needed to enhance aluminum anti-erosion and corrosion performance of organic acid coolants.

Lastly, it has been stated that silicate formula coolant has the effect of preventing aluminum from rusting. However, it has been reported that silicate affects the water pump seal⁽¹⁾ and that there are cases where it gels in solution⁽⁷⁾. Furthermore, since the silicate is consumed quickly⁽⁸⁾, it is necessary to consider its life of rust prevention performance.

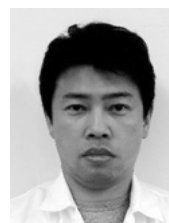
References

- (1) Osawa, M., Morita, Y., Nagashima, T.: A Study of Extension of Engine Coolant Life Using Low Phosphate Organic Acid Inhibitors, SAE 2003-01-2023 (2003)
- (2) Arguing over a few percentage points: The inhibitors Automotive cooling journal, May 1999, p. 22 (1999)
- (3) JIS K2234, Engine antifreeze coolant
- (4) Osawa, M., Fukuda, K., Ijima, T., Nagashima, T.: Development of Long Life Engine Coolant, HONDA R&D Technical Review, Vol. 12, No. 2, p. 159-164
- (5) Masuko, N.: A theory of Rust, Japanese Standards Association, p. 27-30 (1997)
- (6) Wagner, F. T., Moylan, T. E., Simko, S. J., Militello, M. C.: The Composition of Incipient Passivating Layers on Heat-Rejecting Aluminum in Carboxylate and Silicate Inhibited Coolants—Correlation with American Society for Testing and Materials D4340 Weight Losses, American Society for Testing and Materials D-15 Engine Coolant Committee Fourth Symposium on Engine Coolants, p. 11-12 (1997)
- (7) Hercamp, R. D., Hudgens, R. D.: Silicate Gelation in Heavy-Duty Diesel Engine Cooling Systems, SAE 852327 (1985)
- (8) Washington, D. A., McMullen, A. F., et al.: Performance of Organic Acid Based Coolants in Heavy Duty Applications, SAE 960644 (1996)

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