

Technical Papers

Development of Non-Amine Type Engine Coolant

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In the recent years, environmental issues are drawing increasing attention on a worldwide basis. Engine cooling water (simply coolant) is by no means immune to this world trend and is required to be more and more environment-friendly. Against such backdrop, we have been intensively engaged in a development of coolant to respond to the requirement. This paper introduces the fruit of our development activities, i.e. an advanced non-amine and least polluting type coolant which has got rid of amine compounds, nitrite and borate that impose a burden on the global environment and which drastically reduced phosphate that could be a cause for enriching waste water. This innovative coolant is so designed that it is not only more friendly to the global environment, but also it improves heat resistant property of additives and deters scale in the engine cooling system that clogs the radiator fins. It is now widely in use, filling new machines in all the manufacturing plants of Komatsu in Japan, while on sale as Komatsu's genuine coolant under the brand name of AF-NAC.

Key Words: Engine Cooling Water, Coolant, Non-Amine Type, Low Pollution, Carcinogenic Substance

1. Introduction

In 1977, a danger was pointed out in Sweden that amine and nitrite contained in coolant as additives might produce a carcinogenic substance (nitrosamine) through their chemical reaction. It became such a controversial issue thereafter that as a solution, the use of amine for coolant was prohibited in the West, while the use of nitrite for the same purpose was made illegal in Japan. Then in 1987, the Norwegian government

imposed a total ban on the import of any coolant that contained amine¹⁾. Komatsu and the other manufacturers of construction equipment in Japan had to cope with the ban with dual measures that their export machines to Norway be filled with JIS Class 2 non-amine coolant and that anticorrosive be used at the same time. **Fig. 1** shows the world history of coolant issue since 1920²⁾.

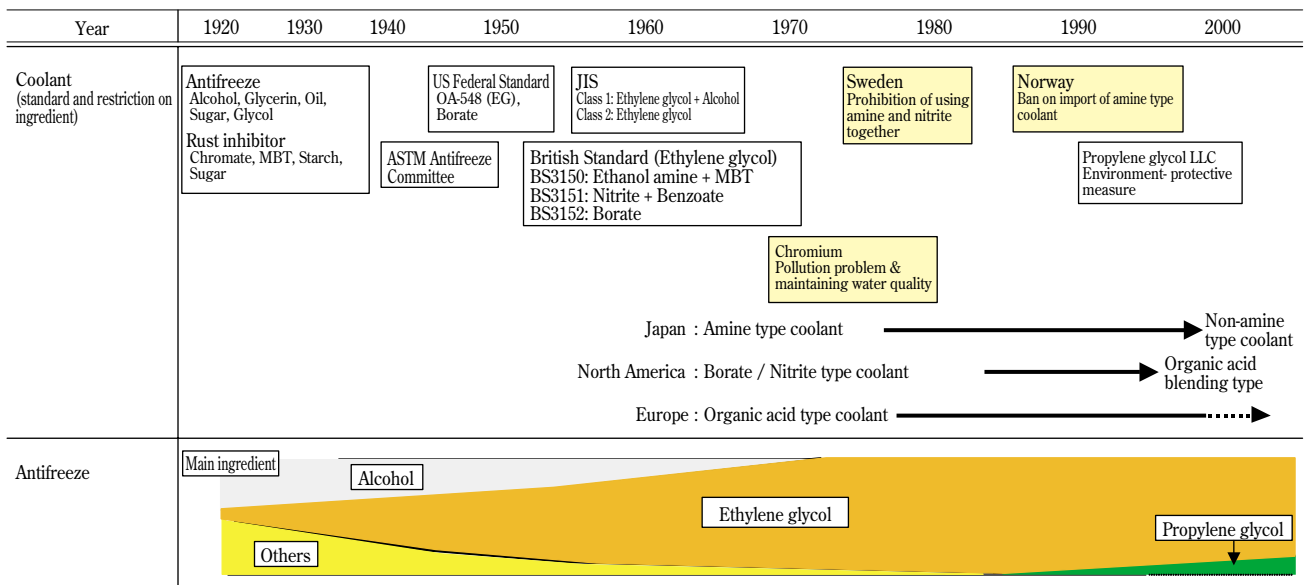


Fig. 1 History of worldwide coolant issue

In the meantime, Komatsu developed KES (Komatsu Engineering Standards) Class 3 amine coolant named AF-ACL³⁾ that far surpassed JIS Class 2 coolant in anticorrosive property and durability, and used for filling new machines in its domestic plants as well as introduced in the market as genuine Komatsu coolant, leaving a good track record. Even so, there was a strong desire for KES Class 3 non-amine type coolant, replacing the KES Class 2 coolant, to meet with heightening environmental expectations worldwide. Indeed amine is an excellent additive particularly for ferrous parts as far as anticorrosive property is concerned, and as such it was no easy job to find a substitute for amine. In an effort to find out a new additive for our next environmentally friendly coolant, we went back to the drawing board. And we finally came up with a least polluting type KES non-amine type coolant and which had a heightened heat resistant property at the same time.

2. Function of additive in coolant

As readily understood from Table 1, an engine cooling system uses a wide variety of materials²⁾. In selecting an additive, conformity with each of those ingredients must be carefully examined.

Table 1 Materials making up parts for engine cooling system

Part Name	Material Used
Water pump	Cast iron, Phenol resin, Nylon, Aluminum, Ultra-hard carbon
Oil cooler	Cast iron, Stainless steel, Aluminum
Cylinder block	Cast iron VMQ, NBR, EPDM, CR
Cylinder head	Cast iron, Brass
Thermostat	Brass, Aluminum, Cast iron
Radiator	Brass, Solder
Hose	SBR, NBR, EPDM, VMQ
Aftercooler	Copper, Copper-based cladding

Generally, a coolant is diluted by city water and well water. Since the quality of the waters is largely differ from place to place, a special care must be exercised when a corrosive water, which includes a lot of sulfate ion and chlorine ion, or a hard water, which includes a large of calcium and magnesium, is used. Fig. 2 shows general quality of water used for diluting coolant in the major areas of the world²⁾. It is understood from this graph that while the quality of water in Japan is regarded as generally good, water in Europe and Asia is hard and that in America the chance is high that water containing a high degree of sulfuric acid ion and chlorine ion is used for dilution. When selecting additives, we gave due consideration to the possibility of such coarse water being used.

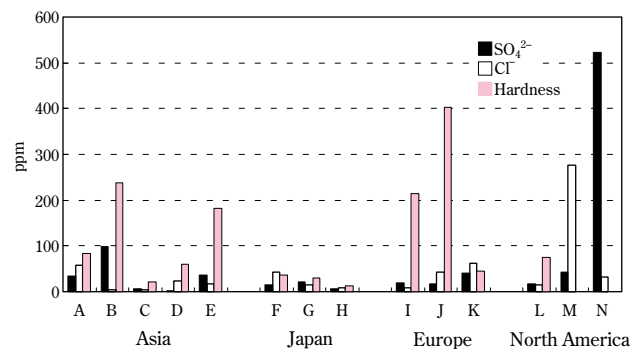


Fig. 2 World water used for coolant dilution

Generally, additives for coolant are classified into the following four types. The first is called an anode type that becomes immobilized after forming an oxidation film or adsorption film on a metal surface. The second is called a cathode type that covers the metal surface with hydroxide deposited due to a chemical reaction or electrochemical reaction and thereby inhibits rust. The third is called an adsorption type that forms an anticorrosive film of a single molecule through combining with metal. The last is a film-forming type that forms insoluble polymer after reacting to copper⁴⁾.

Table 2 Main coolant additive and function

Additive	Chemical formula	Main Function					Remarks	
		Anticorrosive property						Other
		Fe	Al	Cu	Brass	Solder		
Inorganic inhibitor	Phosphoric acid	H ₃ PO ₄				×	pH buffer	
	Sodium monohydrogen phosphate	Na ₂ HPO ₄	◎			×	pH buffer	Anode type
	Sodium polyphosphate	NaH ₂ PO ₄	◎			×	pH buffer	Anode type
	Sodium borate	Na _{n-2} P _n O _{3n-1}	◎				Scale inhibitor	Cathode type
	Boric acid sodium	Na ₂ B ₄ O ₇	◎	×			pH buffer	
	Sodium carbonate	NaCO ₃					pH buffer	
	Sodium hydroxide	NaOH					pH buffer	
	Sodium nitrite	NaNO ₂	◎			×		Anode type
	Sodium molybdate	Na ₂ MoO ₄	◎	○	○	○	○	Anode type
	Sodium nitrate	NaNO ₃		◎			○	
	Sodium silicate	Na ₂ SiO ₃	○	◎	○	○		Anode type
	Zinc nitrate	ZnNO ₃	○	○				Anode type
	Sodium chromate	Na ₂ CrO ₄	◎					Anode type (now out of use)
Organic inhibitor	Sodium benzoate	NaC ₇ H ₅ O ₂	◎	○			○	Anode type
	p-tert-Butyl sodium	C ₁₀ H ₁₁ NaO ₂	◎					Anode type
	Triethanolamine	N(CH ₂ CH ₂ OH) ₃	◎		×			pH buffer Adsorption type
	Benzotriazole (BT)	C ₆ H ₅ N ₃		○	◎	○		Film-forming type
	Mercapto benzothiazole (MBT)	C ₇ H ₅ NS		○	◎	○		Film-forming type
	Tolytriazole (TT)	C ₇ H ₇ N ₃		○	◎	○		Film-forming type
	Organic acid (Sebacic acid, Terephtharic acid)	HOOC(CH ₂) ₈ COOH		○	○	○		
	Polymethacrylate	(C ₂ H ₃ COOCH ₃) _n						Dispersal of scale
	Polyalcohol							Antifoaming agent
Silicate stabilizer							Silicate precipitate inhibitor	

◎: Very effective ○: Effective ×: Adversely effective

For readers' reference, **Table 2** lists representative additives. Some additives demonstrates an anticorrosive effect with plural metals, while others are effective only with a specific single metal but gives a negative impact on the other metals as the case with hydrogen phosphate sodium. A good balance must be established in blending additives.

Meanwhile, **Table 3** shows toxicity of each of the major additives. As a precondition for our development efforts this time, we denied ourselves the use of borate that is suspected of biological toxicity, not to mention amine compounds that may produce carcinogenic substances and nitrite. In addition, we limited the volume of phosphate used that is presumably responsible for enriching wastewater and for depositing scale in the engine cooling system.

Table 3 Toxicity of main additives

Additive	Toxicity against Environment
Inorganic inhibitor	
Phosphoric acid, Phosphate	Enriching wastewater
Borate	Biological toxicity, Environmental toxicity
Nitrite	Generating carcinogenic substance (nitrosoamine), Environmental toxicity
Chromate	Heavy metal toxicity (prohibited by law)
Organic inhibitor	
Amine	Generating carcinogenic substance (nitroso amine)

3. Market proven track record

The ban on the use of amine for coolant in Norway prompted coolant manufacturers in Japan to develop non-amine type coolant thereafter, but they were mostly for automobiles and not intended for construction equipment that constantly encounter rigorous working conditions. **Photo 1** testifies the condition of a cylinder liner of an engine which used a commercially available coolant⁵⁾. A large number of cavitation pitching has occurred across all the surface of the cylinder liner, which evidences that the used coolant was impotent against cavitation pitching.

This fact taught us that an anti-cavitation pitching property was as important as an anticorrosive property for coolant for engines of construction equipment. Meanwhile, clogging of the radiator due to scale was noticed here and there across the section of the radiator top tank. **Photo 2** shows this clogging status. An analysis using fluorescent X-rays revealed that the ingredient of this scale was a substance composed mainly of phosphate iron⁶⁾. (See **Fig. 3**)

Phosphorus is presumed to originate in the coolant. It follows, therefore, that in order to deter scale from accumulating, it is essential to limit the use of phosphorus which in turn deters phosphate iron from being produced.



Photo 1 Example of using commercially available coolant (at 500 h in engine bench test)



Photo 2 Radiator clogged with scale (section of radiator top tank side)

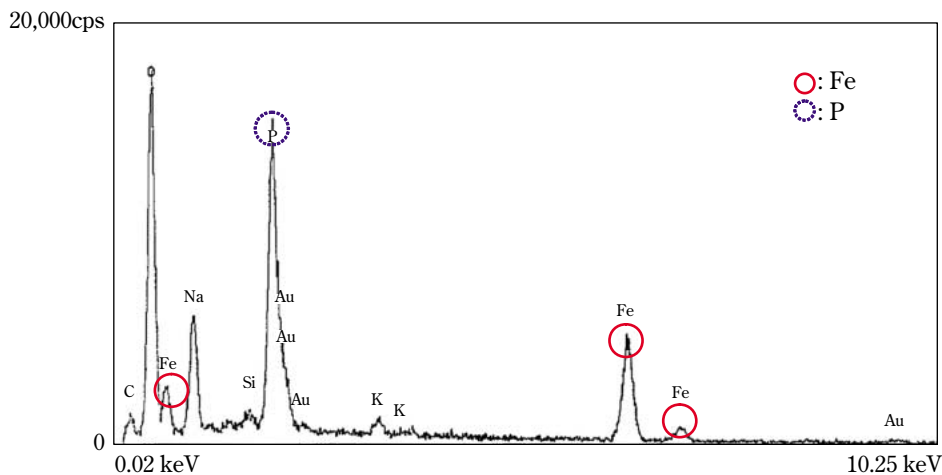


Fig. 3 Result of analyzing scale with fluorescent X-rays (qualitative)

4. Preliminary test

Prior to writing out a prescription for coolant additives, we carried out a series of common preliminary tests that were composed of tests for general properties like specific gravity, acidity (pH), etc. and the JIS water pump cycling corrosion test. In addition to them, we also carried out a metal corrosion test of our own. At that time, it was ensured that a boiling point and vapor pressure be higher than those in the KES Class 3 amine type coolant, since they could give an impact on the occurrence of cavitation pitching on a cylinder liner.

This cylinder liner cavitation pitching means a phenomenon that air bubbles are generated in the coolant and are disrupted due to vibrations of the cylinder liner, whereby a jet water current is created and runs against the surface of the cylinder liner, causing mechanical damage on the surface locally. To prevent cavitation pitching on a cylinder liner surface, we contrived a solution as outlined in the Fig. 4. It consists of the following steps.

- ① To use thickener to increase coolant viscosity, thereby lowering the destructive force of air bubbles
- ② To use surface-active agent to reduce coolant surface tension, thereby lowering the destructive force of air bubbles

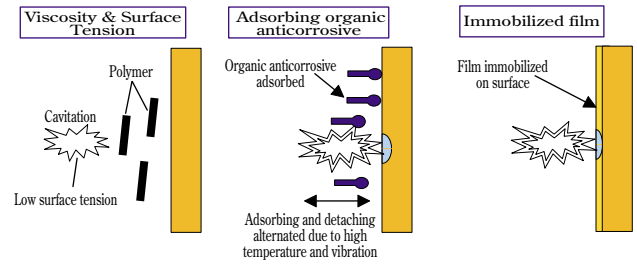


Fig. 4 Conceptual drawing on cavitation preventive mechanism

- ③ To protect metal surfaces by adsorbing organic anticorrosive
- ④ To protect metal surfaces by forming an immobilized film

Table 4 shows rate items and the meaning of each item. Except for an engine test, each of them was given a full review in the preliminary test. Furthermore, each elastomers was also subjected to a dipping test to check their compatibility with the additive. As a result, a satisfactory result was obtained in comparison with an amine type coolant and no problem was identified, as shown in Fig. 5.

Table 4 Main test item and effect

Main Test Item ☆: Specific Item	Check Point	Comparison with common JIS coolant (○: Equivalent ◎: Better)
Freezing temperature	Prevention of freezing	○
Boiling point	Prevention of cavitation	○
Extent of foaming	Prevention of cavitation	○
Pre-alkalinity	Prevention of corrosion	○
Metal corrosion test	Prevention of corrosion	○
Water pump circulation test	Prevention of corrosion on water pump	○
☆Boiling corrosion test	Prevention of corrosion	◎
☆Cavitation test	Prevention of cavitation	◎
☆Crevice corrosion test	Prevention of corrosion	◎
☆Long time corrosion test	Prevention of corrosion and extension of life	◎
☆Blending stability test	Providing corrosion resister and blending other coolant	◎
☆Rust preventing test	Rust inhibitive property	◎
☆Engine test	Checking by installing on actual engine	◎
☆Additive concentration	Low polluting and conformity with environment	◎

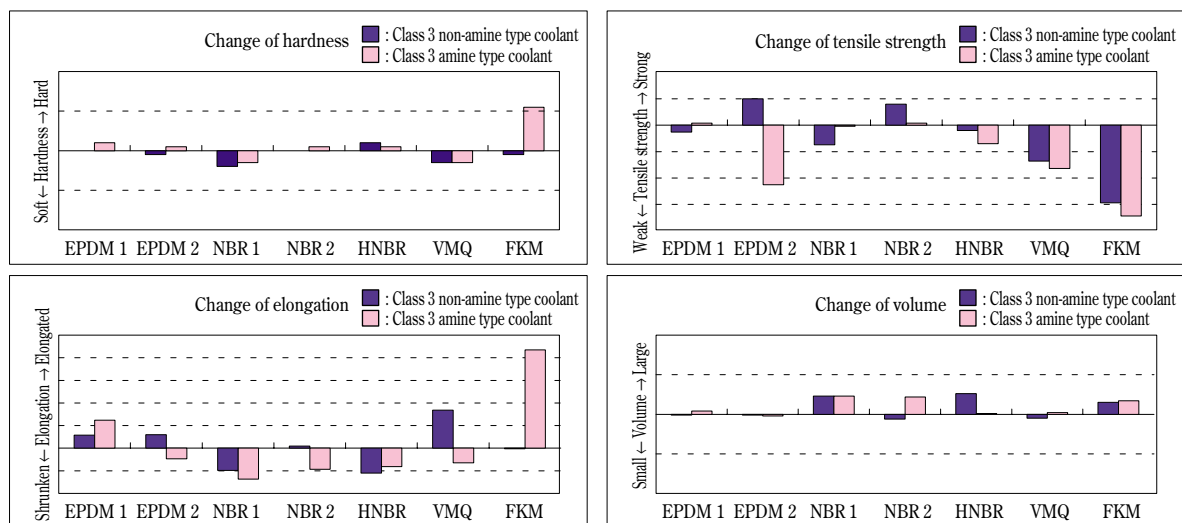


Fig. 5 Result of dipping test for elastomer

5. Engine test

Then we went ahead with a quality check of those candidate coolants through a bench test, after confirming their basic performance through a preliminary test. Items of the quality check are liner cavitation-induced pitching resistant property, anticorrosive property, compatibility with seals, antirust property, etc., apart from the extent of deterioration and decrease of coolant additives.

5-1 Engine test for evaluating cavitation pitching resistant property

An evaluation of cavitation pitching resistant property should be based on a cavitation pitching laboratory test. However, a mechanism of cavitation occurrence and prevention is not necessarily the same as that to be obtained through a preliminary test. Thus at the initial stage of our development activities, we could not simulate cavitation pitching on an actual machine in a cavitation pitching laboratory test.

Photo 3 shows the result of a prototype non-amine coolant in an engine test, after confirming the performance through a cavitation pitching laboratory test.

As understood from **Fig. 6**, this prototype non-amine coolant has demonstrated as good cavitation pitching resistant property as the KES Class 3 amine coolant in the cavitation pitching laboratory test. But in an engine test, cavitation pitching developed on a cylinder liner surface, which prompted us to again review the conditions of a preliminary test as well as working conditions of the additives. Consequently it became known that dissolved oxygen in the coolant gives a great impact. That is, it was discovered that indeed some of the additives used in the prototype non-amine type coolant work properly if there is dissolved oxygen, but they do not sometimes work well under the condition of no dissolved oxygen.

Nitrite and amine compounds used in the conventional coolant can demonstrate a high anticorrosive property even when there is no dissolved oxygen. Engine cooling water in an actual engine contains little dissolved oxygen because the high water temperature deaerates it. On the other hand, a preliminary test is based an open system, which allows sufficient dissolved oxygen to still exist. Guided by this observation result, we proceeded with improving the preliminary test method like removing dissolved oxygen beforehand and continued with the test. After confirming the basic performance through an improved cavitation pitching laboratory test, we again conducted a test for the improved prototype coolant in a 200 hour cyclic mode using an engine of 220 kW output. The test conditions are shown in **Table 5** and the way the test was conducted is shown in **Photo 4**.

Table 5 Condition for coolant bench test Using engine

Item	Condition
Engine output (kW)	220
Test mode	Cyclic mode
Test time (hr)	200
Kind of coolant	Class 3 non-amine type coolant
Coolant concentration	1/2 of standard concentration
Quality of diluting water	Coarse water



Photo 3 Result of engine bench test for non-amine type coolant (cylinder liner cavitation pitching at initial stage of development)

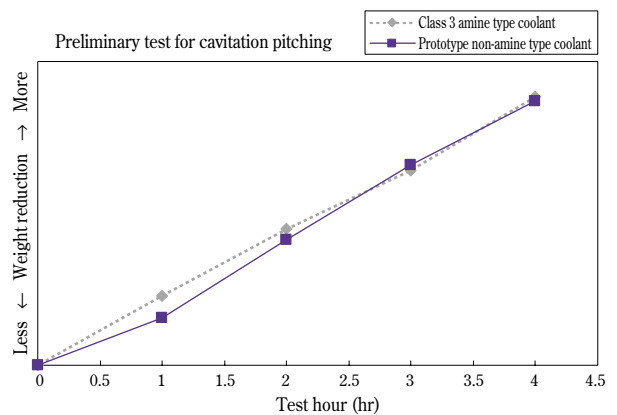


Fig. 6 Result of laboratory test for cavitation pitching

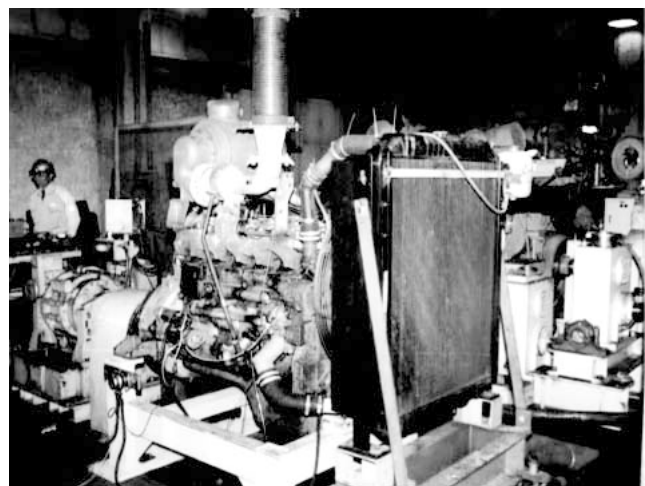


Photo 4 Engine bench test

The test result was that cavitation pitching on the cylinder liner surface was successfully prevented, but cavitation was noticed on a seal at the lower part of the cylinder liner. (See **Photo 5**) This is presumably because we have made a slight change in the composition of the additives to solve cylinder liner cavitation pitching.

Once again we started with a dipping test of various elastomers with a main focus on the seals on which cavitation occurred. A series of the tests have proved that there is no such problem any more. Encouraged by the fact, we again tried a test using an actual engine with the final results that cavitation pitching occurs on none of the cylinder liners, water pump and seals any more. Thus the new coolant was judged a success. (See **Photo 6**)

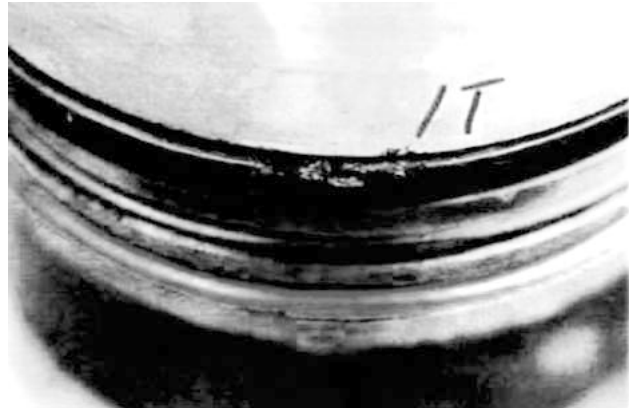


Photo 5 Result of on-engine test for prototype non-amine type coolant (cavitation on seal at initial stage of development)



a) Acceptable as no cavitation pitching, rust, etc. are noticed on cylinder liner surface.



b) Acceptable as no cavitation is noticed on seal

Photo 6 Result of coolant bench test

5-2 Durability test on engine and field test

After finishing the quality confirmation process through a preliminary test and engine bench test, the next stage of development was to carry out a bench test for confirming durability and a field test. When these tests were finished, all of the engines used for bench test were overhauled for checking, while in the case of field test, two engines of the test machines were dismantled and overhauled. In the course of the check, we implemented an analysis of how much the additives had reduced, not to mention an analysis of the coolant conditions.

These analyses revealed that the life of cylinders in terms of pitching far exceeded the specified overhaul time as shown in **Photo 7** meaning the new coolant was a success as a product. There was no problem of water leak with the water pump and the seals, either. Meanwhile, additives for the new coolant showed a smaller rate of reduction while in use, better heat resistant property and longer durability as compared with those in the conventional amine type coolant. **Fig. 7** shows additive reduction curves of both types of coolant. Indeed slight differences are noticed in the case of non-amine type depending on an additive, but it is understood from them that the non-amine type coolant shows superiority, showing longer durability.



Photo 7 Result of field test of non-amine type coolant

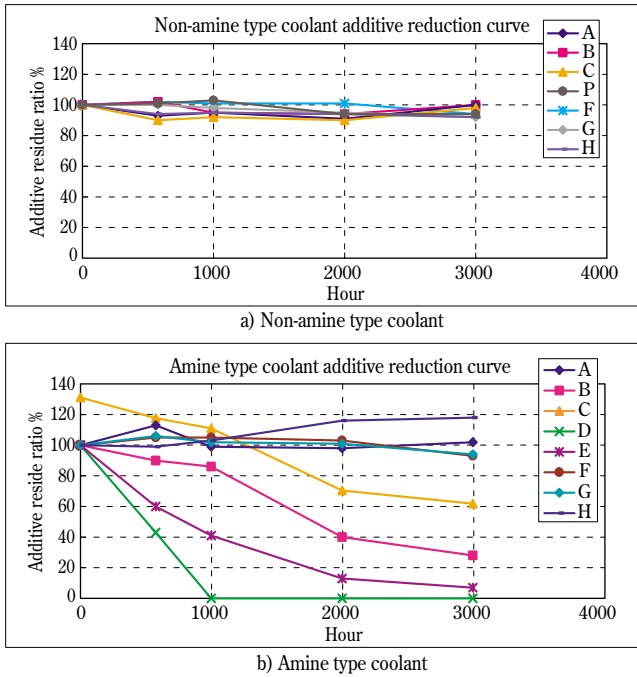


Fig. 7 Coolant additive reduction curve

6. Conclusion

Development of new coolant at Komatsu was remotely triggered by an incident of carcinogenic substance contained in coolant in Sweden and directly initiated by the total ban on the use in coolant by the Norwegian government, and arrived at the new KES Class 3 non-amine type. As a matter of course, it does not contain amine compounds the use of which is prohibited. For that matter, it does not contain nitrite and borate, either, that are feared of their toxicity while lowering the level of use of phosphate that threatens to enrich wastewater. It may well be rated as an innovative coolant a step ahead of the time. It was introduced as genuine Komatsu coolant under the brand name of AF-NAC (Photo 8) in the markets world over in August 2001, while in use for filling new machines across all the domestic plants.



Photo 8 Komatsu genuine non-amine type coolant

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[A few words from the writers]

Frankly speaking, the new non-amine type coolant was a result of anything but a proactive development activity in a sense that it was initiated to cope with a ban on the use of amine in Europe. Such being the case, the final product is a product of low pollution in that it not only has got rid of banned substances, but also either removed or restricted others that impose a burden on the global environment. The next target is a still less polluting coolant of far longer life. We will sustain an aggressive approach toward this goal.