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Study of the anticorrosion properties of a carboxylate inhibitor in a coolant formulation

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Abstract. The operation of internal combustion engines (ICE) using water as a liquid heat carrier leads to intense corrosion and deposit formation. Therefore, it is advisable to incorporate a corrosion inhibitor with a high protective effect into the coolant composition. The study aimed to evaluate the efficiency of a coolant containing a carboxylate corrosion inhibitor and the corrosion resistance of metal elements in an ICE cooling system. The authors developed a prototype coolant, VN-RU-30, with the following composition: 48% water, 48% ethylene glycol, and 4% carboxylate corrosion inhibitor. The prototype was compared with commercially available coolants, OZh-40 LENA and CoolStream Standard 40. According to GOST 28084-89, the physicochemical parameters of VN-RU-30, OZh-40 LENA, and CoolStream Standard 40 were determined, and their corrosive effects on samples of M1 copper, POS-40-2 solder, L-63 brass, St3 steel, SCH-20 cast iron, and AK-7 aluminum alloy were compared under static conditions. The protective effect of the VN-RU-30 prototype was found to be comparable to the reference coolants. To evaluate the protective efficiency of the VN-RU-30 coolant, the authors conducted tests on a model simulating an engine cooling system subjected to corrosion for 336 hours. It was established that VN-RU-30 neutralizes corrosion products on metal surfaces and effectively inhibits further corrosion processes (protective effect exceeding 98%). Field corrosion tests lasting 46 months demonstrated the integrity of the metal components in the ICE cooling system when using VN-RU-30, compared to water, which intensified corrosion and deposit formation. The results confirm the high protective efficiency of the VN-RU-30 coolant for ICE cooling systems; it is advisable for use in engine operation, restoration, and long-term preservation.

Keywords: coolant; internal combustion engine (ICE); coolant efficiency; inhibitor; carboxylate corrosion inhibitor; corrosive effect

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Изучение антикоррозионных свойств карбоксилатного ингибитора в составе охлаждающей жидкости

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Аннотация. Эксплуатация двигателей внутреннего сгорания (ДВС) с использованием воды в качестве жидкого теплоносителя приводит к интенсивной коррозии и образованию отложений. Целесообразно в составе охлаждающей жидкости применять ингибитор коррозии с высоким защитным эффектом. Исследования проведены с целью оценки эффективности охлаждающей жидкости, содержащей карбоксилатный ингибитор коррозии, и коррозионной стойкости металлических элементов системы охлаждения ДВС. Разработанный опытный образец охлаждающей жидкости VN-RU-30 имеет следующий состав: вода – 48%; этиленгликоль – 48%; карбоксилатный ингибитор коррозии – 4%. Опытный образец сравнивали с предлагаемыми на рынке ОЖ-40 «ЛЕНА» и CoolStreamStandard 40. Согласно ГОСТ 28084-89 определили физико-химические показатели VN-RU-30, ОЖ-40 «ЛЕНА» и CoolStreamStandard 40 и сравнили их коррозионное воздействие на образцы меди М1, припоя ПОС-40-2, латуни Л-63, стали Ст3, чугуна СЧ-20 и алюминиевого сплава АК-7 в статических условиях. Защитный эффект опытного образца VN-RU-30 оказался на уровне исследуемых жидкостей. С целью оценки защитной эффективности охлаждающей жидкости VN-RU-30 проведены испытания на модели, имитирующей систему охлаждения двигателя, подвергнутой коррозионному разрушению, в течение 336 ч. Установлено, что VN-RU-30 нейтрализует продукты коррозии на металлических поверхностях и эффективно подавляет дальнейшее развитие коррозионных процессов (защитный эффект – более 98%). Натурные коррозионные испытания длительностью 46 месяцев показали сохранность металлических элементов системы охлаждения ДВС при использовании VN-RU-30 в сравнении с водой, способствующей интенсификации коррозии и образованию отложений. Полученные результаты подтверждают высокую защитную эффективность охлаждающей жидкостиVN-RU-30 системы охлаждения ДВС, и ее можно применять при эксплуатации, восстановлении и длительной консервации двигателя.

Ключевые слова: охлаждающая жидкость; ДВС; эффективность охлаждающей жидкости; ингибитор; карбоксилатный ингибитор коррозии; коррозионное воздействие

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Introduction

The issue of corrosion resistance in internal combustion engine (ICE) cooling systems remains a critical challenge. The use of dissimilar metals and alloys, including aluminum alloys, cast iron, steel, copper, brass, and solder – within cooling systems provides conditions conducive to galvanic and localized corrosion when exposed to electrolytes and dissolved salts [1]. Furthermore, employing hard water as a coolant in ICE systems without highly effective corrosion inhibitors leads to accelerated electrochemical corrosion, deposit formation, and reduced heat exchange efficiency [2, 3, 4].

A comprehensive analysis of coolants and corrosion inhibitors [1] reveals that the type and combination of inhibitors are paramount in determining the protective anticorrosive properties of coolants. Inhibitors can be broadly categorized into three types: inorganic, organic, and mixed. Each category possesses distinct advantages and limitations, particularly concerning the protection of aluminum alloys and solder [5, 6, 7].

Conventional silicate and phosphate inhibitors effectively protect cast iron and steel. However, they may form problematic gel-like deposits on hot aluminum surfaces, thereby impairing heat transfer [8, 9]. In contrast, organic carboxylate inhibitors are widely adopted due to their high efficiency in heat exchange systems [10]. Their protective mechanism relies on the selective adsorption of carboxylate ions at areas with a damaged protective oxide film. This process safeguards the metal without forming a continuous insulating layer, thus preventing heat transfer degradation. This mechanism is particularly crucial for aluminum alloys commonly employed in the cylinder heads of modern engines [11].

However, most published works present results from laboratory tests of coolants in new or idealized cooling systems [12]. There is a notable lack of data regarding the coolant's influence on cooling systems that have already undergone corrosive damage or have been subjected to prolonged storage – conditions highly relevant to real-world operation and seasonal equipment use.

Therefore, field tests on the corrosion resistance of metals and alloys used in cooling systems, utilizing a carboxylate corrosion inhibitor-containing coolant, are essential to validate the hypothesis of its protective and stabilizing effect on metal surfaces within the cooling system [13, 14].

The research objective is to evaluate the efficacy of a coolant, enhanced with an organic carboxylate inhibitor for superior anticorrosion protection, within ICE cooling systems, employing both GOST methodologies and field trials.

Materials and methods

The coolants investigated included VN-RU-30 (a prototype formulated with a carboxylate corrosion inhibitor) and two commercially available products: OZh-40 LENA and CoolStream Standard 40. The optimal composition of VN-RU-30 was determined following GOST 28084-89 guidelines.

Physicochemical properties of all coolants were assessed using standard methods recommended by GOST 28084-89. These included generally accepted measurement techniques for density, freezing point, boiling point, pH, foaming characteristics, and alkalinity. The coolants' performance indicators were evaluated through comprehensive testing, encompassing both laboratory analyses and field studies to determine their operational properties.

Corrosion effects were studied in accordance with GOST 28084-89. The study examined six types of metal specimens: M1 copper (GOST 859-2014), POS-40-2 solder (GOST 21931-1976), L-63 brass (GOST 931-90), St3 steel (GOST 380-2005), SCH-20 cast iron (GOST 1412-85), and AK-7 aluminum alloy (GOST 1583-93), with three specimens of each metal used. Corrosion losses were determined by measuring the mass of the samples before and after the tests.

To evaluate the protective efficiency of the coolant, tests were conducted on a model simulating cooling system conditions that had undergone corrosive degradation due to the use of hard water. The tests were performed in the laboratory of the Joint Vietnam-Russia Tropical Science and Technology Research Center. The water used as a heat transfer fluid exhibited the following parameters: pH – 7.2; total hardness (as $CaCO_3$) – 33.8 mg/L; chloride ion (Cl-) content – 8.8 mg/L; total iron content – less than 0.02 mg/L.

Results and Discussion

The first phase of the investigation focused on determining the optimal composition of the VN-RU-30 coolant. The ideal ratio of water, ethylene glycol, and inhibitor should balance heat capacity, low-temperature performance, and anticorrosive properties, while adhering to the primary requirements of GOST 28084-89.

Initially, a coolant concentrate was prepared, consisting of a solution of the carboxylate corrosion inhibitor in ethylene glycol. Distilled water was then added in various proportions. The characteristics of the prepared coolant solutions and their corrosive effect on the specimens (determined by mass loss in g/m² · day) are presented in Table 1.

Results obtained from exposing the test specimens to coolant solutions with varying carboxylate corrosion inhibitor concentrations are as follows (Table 1):

– The alkalinity of the coolant solution containing 30% distilled water was 9.0 mL (standard: 10 mL), and the foam volume was 32.5 mL (standard: 30 mL). The corrosive effect did not exceed the standard allowable value

– In a highly diluted solution (70% distilled water), alkalinity reached 20.0 mL, and foam stability exceeded the standard value (3 s) at 4.81 s. The corrosive effect remained within the specified limits.

– For solutions containing 40-60% distilled water, the parameters for foaming, pH, alkalinity, and corrosive effect met the requirements of GOST 28084-89.

Table 1

Coolant VN-RU-30 characteristics with varying water content

Indicator	Standard according to GOST 28084-89	Amount of distilled water in the coolant composition, % by volume				
		30	40	50	60	70
Density at 20°C, g/cm³	–	1.030	1.052	1.069	1.078	1.094
Freezing point, °C	–	–60	–50	–35	–25	–15
Boiling point, °C	–	105	106	108	112	118
Corrosive effect on metal, g/m²·day in the sample: Copper	≤ 0.1	0.010	0.014	0.016	0.011	0.022
Solder	≤ 0.2	0.000	0.000	0.000	0.000	0.000
Brass	≤ 0.1	0.015	0.015	0.014	0.012	0.014
Steel	≤ 0.1	0.000	0.000	0.000	0.000	0.000
Cast iron	≤ 0.1	–0.049	–0.049	–0.048	–0.045	–0.047
Aluminum	≤ 0.1	0.002	0.002	0.000	0.000	0.000
Foaming tendency: foam volume, cm³	≤ 30	32.5	28.0	25.0	27.5	30.0
foam stability, s	≤ 3	2.13	2.06	2.10	2.80	4.81
pH value	7.5 to11.0	8.5	8.4	8.4	8.3	8.0
Alkalinity, cm³, not less than	≥ 10	9.0	11.8	15.2	16.4	20.0

It should be noted that a reduction in distilled water content in the coolant solution leads to a lower boiling point and a higher crystallization temperature.

Diluting ethylene glycol with water improves the mixture's heat transfer due to water's higher specific heat capacity (4200 J/kg·K) compared to ethylene glycol (2433 J/kg·K), but this comes at the cost of reduced anticorrosive properties.

Based on the comprehensive set of performance indicators for the VN-RU-30 coolant (foaming, freezing and boiling points, heat transfer, and anticorrosive properties), the following composition recommended for practical application is as follows: water – 48%; ethylene glycol – 48%; carboxylate corrosion inhibitor – 4%.

The second phase of testing involved determining the physicochemical parameters of the three coolants according to GOST 28084-89. The results are presented in Table 2 and Figure 1.

Visual inspection of the samples tested for 14 days revealed a high protective effect from the coolants under study. Intense formation of corrosion products, localized damage, and surface degradation were not observed. It should be noted that negative values for the change in mass are due to the specifics of the post-testing cleaning of samples; they do not indicate the absence of corrosion processes. The consistency between visual and gravimetric data confirms the reliability of the assessment methods employed and the stable protective action of the coolants within the multi-element metallic system.

Corrosion test results for VN-RU-30 over 14 days at 88°C, as well as additional tests lasting 84 hours at 92°C, showed that the coolant maintained its transparency and stability. The corrosion rates for all investigated samples were significantly below the maximum allowable values specified by the standard. Based on the totality of physicochemical parameters, VN-RU-30 is comparable to OZh-40 LENA and CoolStream Standard 40 coolants.

The third stage of the research verified the hypothesis regarding the protective and stabilizing action of the VN-RU-30 coolant, containing a carboxylate corrosion inhibitor, on an in-use cooling system exhibiting signs of corrosion.

To assess the protective efficiency of VN-RU-30, the authors modeled conditions simulating the operation of an engine cooling system degraded by the use of hard water. This approach allowed for the simulation of realistic operating conditions where corrosion products are already present on metal surfaces.

Initially, corrosion tests were conducted on metal samples in water, adhering to GOST 28084-89 requirements. This simulated the operation of a cooling system using water as a heat transfer fluid and formed a corrosion-active surface on the metals.

Subsequently, the samples, pre-corroded in water, were immersed in VN-RU-30 coolant to investigate its ability to suppress further corrosion development.

The test results demonstrate a clear difference in the nature of the corrosion processes when using water (Fig. 2a) versus the coolant (Fig. 2b). After 336 hours of testing in a glass vessel with water, a significant amount of corrosion products (deposits) was observed,

Table 2

Coolant testing according to GOST 28084-89

Indicator	Standard according to GOST 28084-89	Coolant		
		OZh-40 LENA	**CoolStreamStandard40**	**VN-RU-30**
Appearance	–	Clear homogeneous green liquid		
Freezing point, °C	–	<–40	<–40	<–40
Boiling point, °C	–	108	108	108
Corrosive effect over 336 h at 88°C on the sample, g/(m² · day):				
Copper	≤ 0.1	0.790	0.005	0.005
Solder	≤ 0.2	0.053	0.007	0.009
Brass	≤ 0.1	0.026	0.005	–0.007
Steel	≤ 0.1	0.000	0.013	0.000
Cast iron	≤ 0.1	–0.163	–0.295	–0.059
Aluminum	≤ 0.1	0.050	0.006	0.000
Corrosive effect over 84 h at 92°C on the sample, g/(m² · day):				
Copper	–	0.252	0.000	0.032
Solder	–	0.019	0.000	0.038
Brass	–	0.000	0.000	0.065
Steel	–	0.000	–0.077	–0.065
Cast iron	–	– 0.280	–0.183	–0.140
Aluminum	–	0.071	–0.044	0.056
Foaming tendency:				
foam volume, cm³	≤ 30	20	25	25
foam stability, s	≤ 3	1.9	2.3	1.8
pH value	7.5 to 11	9.5	8.0	8.4
Alkalinity, cm³, not less than	≥ 10	13.7	2.3	14.6

precipitated on the sample surfaces and at the bottom of the vessel.

The sample surfaces underwent intense degradation (Fig. 2a). The highest corrosion rate, 8.84 g/(m² · day), was recorded for the steel sample. Compared to the requirements of GOST 28084-89, the corrosion rate for steel exceeded the standard value by a factor of 88.4, for cast iron by a factor of 53.2, for solder by a factor of 28.7, and for aluminum by a factor of 23.6.

When using VN-RU-30 coolant, the sample surfaces remained practically unchanged after 336 hours of testing, and the corrosion zones did not expand (Fig. 2b). The solution remained transparent, with no formation of sediment or corrosion products. Quantitative corrosion impact data are presented in Table 3.

Visual analysis and the results of quantitative measurements (Table 3) indicate a stabilization of the metallic surfaces, with no propagation of corrosion foci or secondary deposit formation. This suggests that VN-RU-30 exhibits not only a preventive but also a stabilizing effect in previously used cooling systems. The protective effect of VN-RU-30 against ferrous and non-ferrous metals exceeded 98%.

The fourth stage of the research involved field tests simulating the long-term storage of an engine cooling system.

The objective of these field tests was to comprehensively assess the corrosive behavior of a multi-element engine cooling system during prolonged storage when using water and VN-RU-30, and to determine the protective efficiency of the VN-RU-30 coolant.

Sets of samples for long-term corrosion tests were prepared in accordance with GOST 28084-89 requirements. Each set of samples was placed in a separate 1-liter glass vessel filled with the respective fluid. Tests were conducted in two media: water and VN-RU-30 coolant.

The glass vessels were hermetically sealed and stored for 46 months in a covered warehouse, simulating the conditions of long-term engine cooling system storage. Upon completion of the tests, the samples were extracted and cleaned according to GOST 28084-89 requirements. Corrosion was assessed based on visual analysis of the sample surface condition and determination of mass loss. The test results are presented in Figure 3 and Table 4.

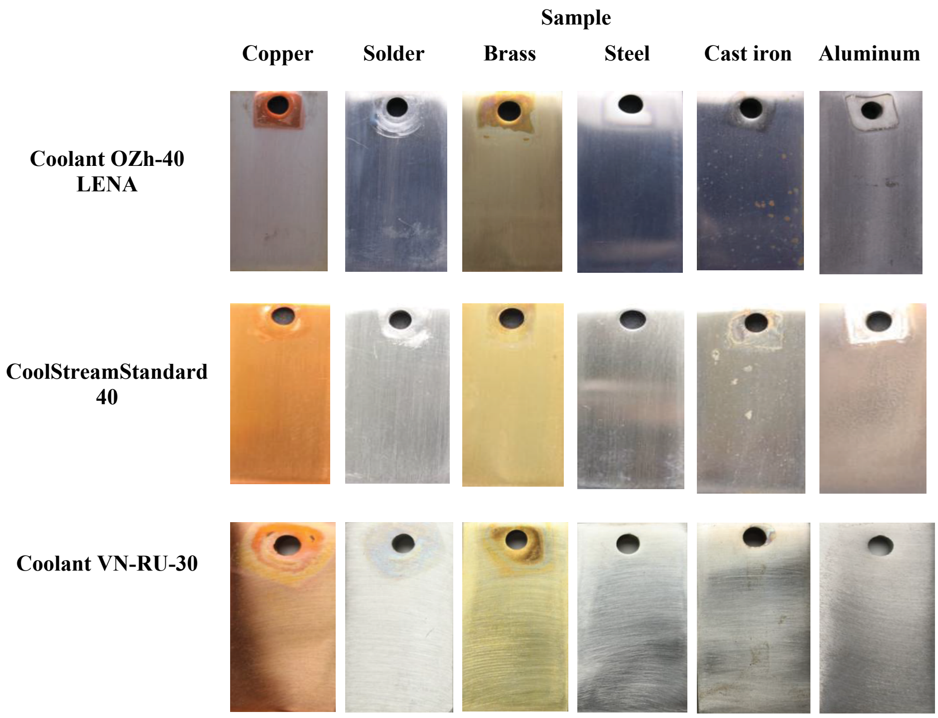

Fig. 1. Appearance of samples after 336 h (14 days) of testing according to GOST 28084-89

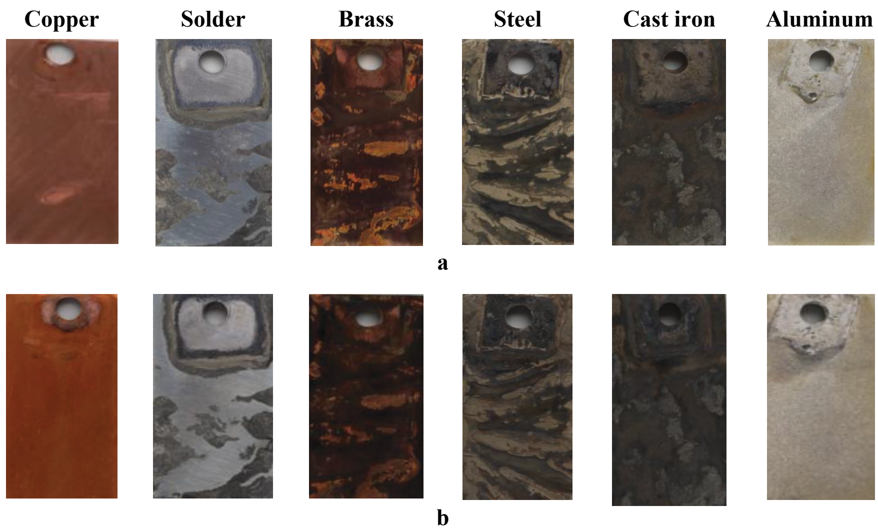

Fig. 2. Appearance of samples after 336 h of corrosive exposure:
a – in water (Stage 1); b – in VN-RU-30 coolant (Stage 2)

Table 3

Corrosive effects of water and VN-RU-30 on samples over 336 h

Medium	Corrosive Effect on Samples g/(m²·day)					
	Copper	Solder	Brass	Steel	Cast iron	Aluminum
Water	0.18	2.87	0.15	8.84	5.32	2.36
VN-RU-30	0.08	0.04	0.12	0.05	0.30	0.16

Analysis of Figure 3 and the data in Table 4 leads to the following conclusions. In water, signs of active corrosion processes were observed early in the tests. After one week, the solution turned yellow, and after one month, a significant amount of corrosion products was detected at the bottom of the vessels and on the sample surfaces. Throughout the entire test period, corrosion processes were intense and accompanied by deposit formation. Upon completion of the 46-month tests, the sample surfaces exhibited pronounced corrosive degradation, particularly for solder, steel, cast iron, and aluminum. The most intensive corrosion was observed for cast iron

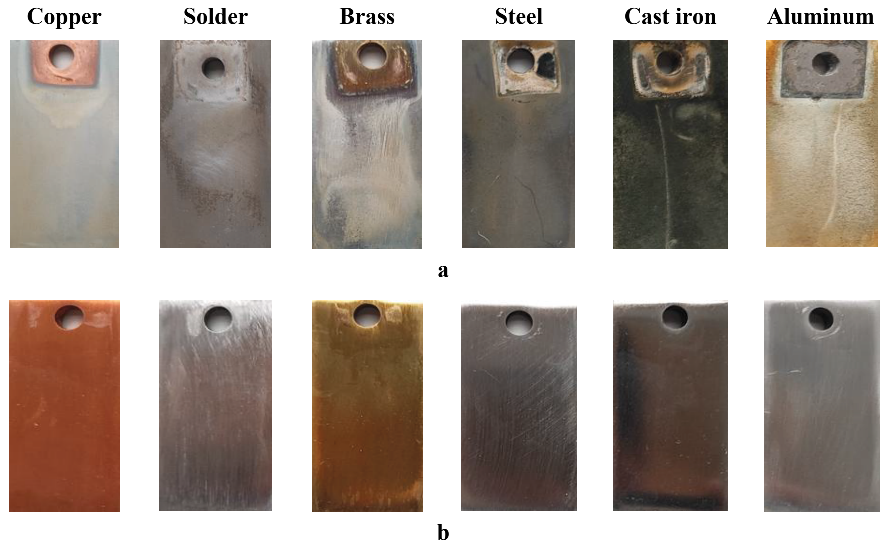

Fig. 3. Sample surfaces after 46 months of field testing in water (a) and VN-RU-30 coolant (b)

Table 4

Corrosive effects of two media on the cooling system over 46 months

Medium	Corrosive effect on samples g/(m²•day)	Samples					
		Copper	Solder	Brass	Steel	Cast iron	Aluminum
Water	Mass loss, mg	–4.0	66.7	–1.1	129.0	273.6	47.7
	Corrosion rate over the storage period, g/m²	1.42	21.53	0.41	48.69	85.61	13.33
VN-RU-30	Mass loss, mg	–1.0	–1.6	–0.7	–1.3	–6.2	–0.7
	Corrosion rate over the storage period, g/m²	0.34	0.52	0.26	0.49	1.94	0.20

and steel, with mass losses of 273.6 and 129.0 mg, respectively, and corrosion rates of 85.61 and 48.69 g/m².

In the VN-RU-30 coolant, a pronounced protective effect was observed. The solution remained transparent and chemically stable throughout the 46-month test period. The samples showed no signs of uniform or localized corrosion, and no deposits formed. For all investigated samples, mass loss and corrosion rates were minimal. This effect can be attributed to the formation of stable protective films and the stabilization of electrochemical processes on the surfaces of metals and alloys.

The results of the 46-month field tests confirm the highly effective anticorrosion properties of the VN-RU series coolants. In contrast, the use of water leads to intense corrosion and the accumulation of deposits.

The totality of results from both comprehensive laboratory and field tests allows VN-RU-30 coolant to be considered an effective agent for use in ICE cooling systems. The application of a theoretically grounded methodology for comprehensive validation, oriented towards real operating conditions, enabled a reliable assessment of ICE coolant effectiveness.

Conclusions

The organic carboxylate corrosion inhibitor incorporated into the coolant formulation maintains its anticorrosive properties. The recommended coolant composition (48% water, 48% ethylene glycol, 4% corrosion inhibitor) ensures a balance between corrosion protection and thermophysical properties.

The corrosion rates of copper, brass, solder, steel, cast iron, and aluminum alloys in the VN-RU-30 coolant medium are significantly lower than the maximum allowable values stipulated by regulatory documents, which attests to the high effectiveness of the employed corrosion inhibitor.

Model tests of a cooling system previously subjected to corrosive degradation demonstrated that VN-RU-30 coolant not only prevents the development of new corrosion effects but also stabilizes the condition of already damaged metallic surfaces, effectively suppressing the further propagation of corrosion foci.

46-month field tests, simulating the storage process of an engine cooling system, showed intense corrosion and deposit formation when water was used. In contrast, VN-RU-30 ensured a stable condition of metal elements and alloys without corrosive damage.

The comprehensive set of obtained results provides grounds to recommend VN-RU-30 coolants for use in both new and previously operated engine cooling systems, including modes of operation, restoration, and long-term preservation.

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