

## Comparative Analysis of Technical Standards Regulating the Requirements for Antifreeze Coolants Based on Monoethylene Glycol

*N.Y. Bashkirceva, O.Y. Sladovskya, Y.S. Ovchinnikova and R.R. Mingazov*

Kazan National Research Technological University, Kazan, Russia

**Abstract:** To assess the main deviations between Russian and Foreign Technical Standards regulating requirements and norms to physical-chemical and operating characteristics of coolants and their test methods, the comparative analysis has been performed. The study results have revealed the need to improve the Russian base of standardization, renewing the list of assessment criteria and unification of the methods and conditions for test conditions and their assessment. This has been caused by technical progress in machinery industry and fast development of assembling foreign automotive industry in Russia. Russian market of coolants is highly competitive. However, Russian market is characterizing by large number of fake and low quality products. To solve this problem there is a necessity to develop the joint national standard instead of existing GOST 28084-89. Moreover this problem can be enhanced by Russia joining the WTO that will results in appearance of variety of international brands of coolants on the Russian market which authentication can become another problem related with recognition of their product quality certificates and trial test results in Russia. This all can significantly affect the Russian market of coolants.

**Key words:** Ethylene glycol % Coolant concentrate % Coolant % Physical and chemical characteristics % operational properties % Test methods

### INTRODUCTION

In the past decade, development of the automotive industry in Russia has accelerated the modernization of related industries such as metallurgy, machine building, petrochemical, etc. Modern car manufacturers are the initiators of development to improve the requirements for the materials, component parts and technical liquids used for the production and maintenance of automotive vehicles. For example, environmental degradation related with increased emissions of the fuel combustion products into the atmosphere, have resulted in a tightening of the requirements for the quality of petrol and diesel fuels, which are reflected in the national standards of all major countries.

**The Main Part:** This article provides a comparative analysis of Russian and international normative documents regulating the requirements, standards, methods for testing of physical, chemical and operation characteristics of low-freezing fluids based on monoethylene glycol.

### Following Standards Have Been Analyzed National Standards:

- С GOST 28084-89 Low-freezing coolants. General technical requirements (Russian Federation),
- С ASTM D 3306-10 Standard Specification for Glycol Base Engine Coolant for Automobile and Light Duty Service (USA),
- С ASTM D 4985-10 Standard specification for low silicate ethylene glycol base engine coolant for heavy duty engines requiring a pre-charge of supplemental coolant additive (SCA) (USA),
- С ASTM D 6210-08 Standard specification for fully-formulated glycol Base engine coolant for heavy duty engines (USA).

### Industry Standards and Specifications:

- С TTM 1.97.1172-2004 Coolant concentrate. Technical requirements. (OAO "AVTOVAZ", Russian Federation),

- С TTM 327.2-2005 Antifreeze. Technical requirements. (OAO "IzhAvto", Russian Federation),
- С SPEC No 9.55523-04 Procurement specification. Antifreezes. (Fiat Auto, Italy),
- С MS 591-08 Material specification. Antifreeze-for factory fill. (HYUNDAI and KIA MOTOR, Korea),
- С WSS-M97B44-D Engineering material specification. Coolant, organic additive technology (OAT), concentrate for passenger car and light truck (Ford Motor Company, USA).

### Most Standards Classify the Coolants into Two Main Types:

- С Concentrate containing at least 85% vol. of glycol,
- С Ready to use coolant, concentrated and diluted with water.

A part of water dilution in different coolants depending on the country is normalized as follows:

	Russian standards [1]			International standards [2, 3]			
	coolant	coolant-40	coolant-65	type I	type II	type III	type IV
Concentrate (based on monoethylene glycol),% vol.	100	56	65	100	–	50	–
Concentrate (based on propylene glycol),% vol.	–	–	–	–	100	–	50
Water,% vol.	–	44	35	–	–	50	50

Apparently, the international standards [2, 3] cover a wide range of antifreezes and normalize the demands for liquids based on both monoethylene glycol (type I-concentrate and type III-diluted concentrate 50% vol.) and based on propylene glycol (respectively, type II and type IV). However, the Russian standards normalize the requirements only for ethylene glycol antifreezes.

The General Requirements for Operating Characteristics of Low-freezing Fluids Include

**High Cooling Capacity:** This feature characterizes the efficiency of involved "heat-transfer material" in the heat transfer processes and is ensured by the optimal values of heat-absorbing and heat-transfer parameters such as heat capacity, heat of vaporization, thermal conductivity, diffusivity and convective heat transfer [4], that directly depend on the choice of glycol in the antifreeze and its ratio with water in the final product.

The cooling capacity is a complex operating characteristic and there is no complex parameter to evaluate it. Therefore this feature is characterized by a relatively simple parameters such as initial boiling point, initial solid phase formation temperature and resistance to hard water.

**Continuous Circulation During Operation Process:** Describes the fluidity of liquid, its ability to provide the necessary circulation rate in the cooling system and ensured by optimal values of the viscosity-temperature, low and high temperature parameters [4].

The characteristic can be indirectly standardized by such indicators as density, crystallization temperature, pour point, boiling point and the purity.

**Compatibility with Structural Materials:** This characteristic describes the ability of the coolant to interact with structural and operational materials of engine cooling system, storage, transportation and refueling facilities [4].

It is standardized by corrosion aggressiveness, compatibility with polymer and finishing materials, pH and alkalinity.

**Resistance to Vapor Locks, High Temperature Foam Sedimentation:** This can be achieved by evaluation of probability of vapor locking and cavitation regime of fluid flow in the cooling system that characterizes the possible violation of the continuous flow of "heat-transfer material", accompanied by the breakdowns during the pumping and significant deterioration of heat removal from the walls of the engine to the coolant [4].

The characteristic is standardized by the volume and foam stability.

**Stability of Physical and Chemical Properties and Maintenance of Quality During Storage, Transportation and Operation:** Characterizes the ability of a liquid to keep the quality and operational characteristics affected by operating and storage conditions such as temperature, pressure, humidity, dusted atmosphere, structure and materials of storage, transportation and refueling equipment [4].

Can be evaluated by testing of the statistical parameters of quality change during experimental storage in various conditions and after tests in a real engine and non-engine experimental equipment. The results allow the determination of quality parameters

which are the most changeable and determine the complex parameter indicating the continuous quality- guarantee working life.

Thus, the following list of physical and chemical characteristics is a standard set for evaluation of the operational parameters of coolants: boiling point or fractional data; the temperature of initial crystallization; density; hydrogen ion concentration-pH; alkalinity; compatibility with structural materials of the cooling system; foaming; resistance to hard water; appearance; period of storage; installation tests in a real engine and non-engine experimental equipment.

Parameter "Boiling point" is normalized above 150-165°C for concentrates and above 108-110°C for coolants depending on the degree of water dilution. Quantitative characteristic of this parameter shows the ratio between glycol and water in the coolant which characterizes the cooling capacity of antifreeze ensuring the normal operation of the engine in the summer (heat capacity, heat of vaporization and thermal conductivity coefficient of water-sglycol mixture) including its "volatility" [4].

The method consists in determination of the equilibrium boiling point of coolants. The equilibrium boiling point indicates the boiling point of cooling system at equilibrium and atmospheric pressure [6-8].

The index "Fractional data" describes the composition of the coolant and is more informative in terms of ratio of water and other glycols in the finished coolants when the mass ratio of liquid distilled up to 150°C [1] or 190°C [9] is measured.

The index "Crystallization temperature" indicates the possibility of liquid implementation in the cooling system of an internal combustion engine during cold seasons. A ratio of water and glycol in the coolant indicates the quantitative characteristic of this index.

The index "Temperature of initial crystallization" i.e. the maximum temperature which appears as a visible initial crystallization [1] of coolant at standard conditions is normalized in the Russian regulatory documents. In international standards, the index of "Freezing-point" is normalized and indicates the temperature of initial crystallization in the absence of hypothermia, or the maximum temperature achieved immediately after the formation of crystal in the case of hypothermia, or the temperature at which solid crystals formed during cooling disappear and the temperature of the sample increases.

Despite of some distinctions in the determination methods, this index is determined as the temperature of initial crystallization determined only by visual [1] or graphical [10] methods.

Dilution in a ratio 1:1 and quantitative norm is a standard dilution for determination of crystallization temperature and in different standards varies from-34 to-36,4°C. In addition, the standards TTM 327.2 and MS 591 prescribe the tests of solution with 30% concentration (volumetric) with quantitative standard-above-14,5°C [7, 9] for countries with a temperate climate.

The most common brands in Russia are the coolant-40 and coolant-65 with appropriate temperatures of initial crystallization [1]. The temperature of initial crystallization [2, 3] is not considered in international regulations for classification of coolants. The solution of coolant concentrate and water prepared in a ratio 1:1 that ensures the temperature of initial crystallization-36-37°C is standard for implementation.

It should be noted that water-ethylene glycol solution unlike water freezes by several steps. The crystals are forming in a liquid during cooling at relatively negative temperature. Then, the further cooling gradually increases the crystallization, appeared as so-called "slush ice," and finally becomes solid at the minimal final temperature. The initial temperature of the first crystal formation is the temperature of initial crystallization (freezing-point). The final temperature of the transition from the liquid to the solid phase is the temperature of fluidity loss or congelation point (pour point). For antifreezes coolant-40 used in Russian automobiles, the difference between the freezing point and pour point is about 10°C. Thus, antifreeze, which crystallizes at-40°C hardens only at-50°C.

Unwanted consequences such as sedimentation or gelation forming as a result of the interaction of the coolant components and hard water salts are important characteristic for coolants. This can result in a blockage of system channels and further, to significant reduce the circulation velocity of coolant, the coolant heat transfer efficiency and engine overheating in the cooling system of engine.

Therefore, the index "Resistance to hard water" is obligatory parameter in the Russian standards [1, 6, 7]. The method includes the observation of a phase of the coolant solution concentrate in hard water and visual determination of the possible separation or sedimentation in this solution during certain time at a certain temperature [1, 11].

Quantitative index “density” characterizes the ratio of glycol and water in coolants and used at shipment, acceptance and registration of coolants in mass units.

There are following standards of coolant’s density depending on water dilution rate and country of production:

Russian Standards [1, 6, 7] g/cm <sup>3</sup> , at 20 °C [13]			International standards [2–3, 9, 11–12] g/cm <sup>3</sup> , at 15,5 °C [14]	
concentrate	coolant-40 (56:44)	coolant-65 (65:35)	concentrate	coolant (50:50)
1,110–1,145	1,065–1,085	1,085–1,110	1,110–1,145	higher 1,065
1,110–1,150	1,075–1,085	1,075–1,110	1,130–1,150	

Effective anticorrosion protection of various structural materials of the cooling system is achieved by selection of corrosion inhibitors, which can be represented by a wide range of chemical compounds. However, industrial standards significantly restrict or prohibit the use of inorganic inhibitors such as amines, silicates, borates, nitrates and phosphates [7, 9, 12]. This is a result of higher loads in the engines of the latest generation and their capacity is exhausted at the run of 30.000 km and thus, further exploitation of engine becomes harmful for both the engine and environment.

Therefore, the majority of motor-car manufacturers use at the stage of the input control only modern antifreezes produced by organic additive technology (OAT).

The presence of anticorrosion additives causes the protective properties of the coolants which are assessed by the index “Corrosion degree of the metals.” The method consists of the bearing of metal samples represented in the cooling systems of the engine, in the aerated solution of the test coolant during certain time at certain temperature [1, 15].

The steel, iron, aluminum, copper, brass and solder samples are usually included to the standard test set. However, the brand range of these samples in different standards is different and depending on the type of vehicles or on national standard requirements where the most used samples are recommended.

In addition, the test conditions are different: the dilution rate of the test fluid with hard water, the composition of synthetic hard water and application of additional characteristics in some of the standards such as an appearance of the plates after tests and the final properties of coolant solution after the test [7, 9].

Different size units are used depending on the method of assessment:

- С g/m<sup>2</sup>\*day-characterizes the velocity of corrosion, i.e. the loss of mass per square unit per day [1];
- С mg-characterizes the change in mass of the metal sample for the entire duration of the test [2, 3, 5, 6];
- С mg/cm<sup>2</sup>-characterizes the change in mass of the metal sample per square unit for the duration of the test [7, 11, 12].

Conversion of measurement units of corrosion is shown below:

1	Velocity of corrosion, Y g/m <sup>2</sup> *day 2	Mass loss (m1–m2) mg 3	Mass loss per square unit mg/cm <sup>2</sup> 4
GOST 28084			
cooper	0,100	3,815	0,140
brass	0,100	3,815	0,140
steel	0,100	3,815	0,140
cast iron	0,100	4,130	0,140
aluminium	0,100	4,130	0,140
solder	0,200	7,630	0,280
ASTM			
cooper	0,253	10,000	0,354
brass	0,253	10,000	0,354
steel	0,253	10,000	0,354
cast iron	0,233	10,000	0,326
aluminium	0,699	30,000	0,979
solder	0,759	30,000	1,063

The concentration of alkali functional (anticorrosion) additives in the coolant is indirectly characterized by "pH value" because water-glycol solution possesses a high pH and is chemically aggressive media causing the corrosion of cooling system elements. The presence of anticorrosion additives changes pH value, which should vary within an interval 7,5-11,0.

Currently, the index "Alkalinity" is the most controversial among the all existing characteristics of antifreezes. The method for the determination of the index mainly describes the content of alkaline inhibitors (alkaline buffers) such as phosphates and borates. Modern coolants developed according to the technology of organic additives without buffer agents characterize with low "Alkalinity" varying from 3 to 8 cm<sup>3</sup>, but providing perfect anticorrosion protection of the metals. Therefore, the value "alkalinity reserve" in the coolant is hardly a criterion for determining its protective properties and identification the lifetime of the coolant.

In the Russian standards, "Alkalinity" (or alkalinity reserve) is normalized to a minimum of 10 cm<sup>3</sup> [1, 6, 7] and this parameter is not standardized in ASTM standards and substituted by actually received value [2, 3, 5] in the tables of coolant test results. Thus, the parameter "Alkalinity" is used as formal parameter for identification of the coolant, because it easily and quickly measured [1, 16].

The parameter of "Foaming" which is estimated by volume of foam formed after blowing air through the coolant [1, 17], presents in all considered standards.

Foreign concentrates and ready-to-use coolants are usually diluted by synthetic water before the tests [2, 3, 5]; Russian coolant-40 and coolant-65 are tested without dilution. The dilution degree of concentrate for testing and the quantitative limits of parameter are normalized in each individual standard. Test conditions were similar for the temperature, air flow rate and blow time for all regulations and the greater differences were observed in the composition of synthetic water used for dilution.

Several parameters characterizing the compatibility of coolants with elements of the cooling system, parts of the vehicle or other technical fluids can be normalized in some standards and completely absent in others.

For example, the parameter "Compatibility with polymeric materials" which evaluates the properties of the rubber samples after exposure to the test solution of coolant [8, 18] is mandatory for Russian and industry standards [1, 6, 7, 9, 11, 12] and shows the possibility of adverse effects such as the rupture of rubber sealants or hoses with subsequent depressurization of the system, or

crumbling, leading to contamination of the coolant and the blockages that limit the normal pumping of fluid and heat transfer in the system.

The parameter "Ash" or "Ash content", which is the ratio of the mass of ash obtained after evaporation and burning of coolant to the mass of tested coolant sample, expressed as a percentage, is normalized only by the ASTM standards [2, 3] and the technical requirements of "AvtoVAZ".

Stability of antifreezes and coolants during storage at higher temperature, expressed by absence of separation, sludge and gelation are standardized by industry standards TTM 1.97.1172, TTM 327.2, MS 591 and WSS M97B44-D.

The interaction of coolants at accidental mixing of fluids of different manufacturers during exploitation is important for automobile manufacturers. Therefore, the majority of industry standards express the conditions for the tests in such the parameters as "Compatibility with mixtures" or "Compatibility with previously approved coolants" [6, 7, 9, 12].

Some standards, besides the physical, chemical and operational characteristics describe the tests of coolant in conditions simulating the actual operation of the engine and cooling system, so-called bench and road tests.

Thus, there is a method prescribed by ASTM D 2570 to assess the corrosion-erosion impact of coolant on structural materials of the cooling system, which assesses the weight loss of metal and changes of fluid quality during circulation in non-motorized stand simulating a car engine. This is a subject of TM 1.97.1172, MS 591, WSS-M97B44-D, ASTM D 3306, ASTM D 6210 and ASTM D 4985 standards.

Program of road tests of coolants is embedded in TTM 1.97.1172, MS 591 and WSS-M97B44-D standards.

These tests are designed to assess the state of the coolant after prolonged use and the condition of the cooling system of the engine such as cavitation on an aluminum water pump, change the surface of aluminum cylinder heads, radiator and heater.

## CONCLUSION

Thus, the comparative analysis of national, industrial Russian and international standards and technical documents allowed the following conclusions:

- C Russian national and international standards [1-3, 5] are uniform regulations for all types of coolants, showing a general list of requirements for quality without dividing of coolants to the types according to chemical composition of additives.

The implementation of inorganic inhibitors such as amines, silicates, borates, nitrates, phosphates is significantly restrict or prohibit only by the industry standards [7, 9, 12]. These normalize the requirements for “carboxylate” (technology of organic additives-OAT) or “hybrid” (the technology of organic additives with permissible content of some inorganic additives) types of antifreezes.

- C The total list of physicochemical and operational requirements for coolants in Russian and international standards are identical. Quantitative standards for these requirements are also a comparable with insignificant differences in dimensions and test conditions.
- C Foreign national standards cover a broader assortment row, where both well-known monoethylene glycol and propylene glycol which is more promising in terms of environmental safety are considered as the basis of antifreeze.
- C Foreign national standards represent a broader range of required operational characteristics, in particular for tests with simulation conditions [19] and evaluation of the cavitation corrosion [20], while in Russia it is described in industry standards (specifications for automobile manufacturers).

According to the analysis it can be noted that the Russian base of standards needs to be improved dictated by the progress of the automobile industry and in particular, the modernization of design of highly accelerated engines. In addition, the methods and test conditions require the unification what is caused by the mass development of foreign car assembly plants in Russia.

The Russian market of coolants is highly competitive and represented by more than 200 brands. However, the Russian market characterizes by great number of fake and low-quality products. This problem indirectly confirms the need for a single national standard in stead of existing GOST 28084-89 which was approved in Soviet Union.

This problem can also be exacerbated by the recent entry of Russia into the WTO, which will result in the appearance of a huge number of foreign production coolants on the market, which authenticity will be a difficult problem related with the recognition of the product test results after production and Russia's recognition of foreign certificates issued to the manufacturer without proper quality assurance for supply to Russia.

## ACKNOWLEDGEMENT

The study was performed within the integrated project on high-technological industry development (resolution no. 218) and financially supported by the Ministry of Education and Science of Russian Federation.

## REFERENCES

1. GOST 28084-89 Low Freezing Coolants. General Technical Requirements.
2. ASTM D 3306-10 Standard Specification for Glycol Base Engine Coolant for Automobile and Light Duty Service
3. ASTM D., 6210-08 Standard Specification for Fully-Formulated Glycol Base Engine Coolant for Heavy Duty Engines.
4. Safonov, A.S., A.I. Ushakov and V.V. Grishin, 2007. Chemmotology of Combustion-Lubricating Materials, NPIKTs, pp: 415-428.
5. ASTM D., 4985-10 Standard Specification for Low Silicate Ethylene Glycol Base Engine Coolant for Heavy Duty Engines Requiring a Pre-Charge of Supplemental Coolant Additive (SCA)
6. TTM 1.97.1172-2004 Coolant Concentrate. Technical Requirements. (OAO “AVTOVAZ”, Russian Federation).
7. TTM 327.2-2005 Antifreeze. Technical Requirements (OAO “IzhAvto”, Russian Federation).
8. ASTM D 1120-08 Standard Test Method for Boiling Point of Engine Coolants
9. MS 591-08 Material Specification. Antifreeze-for Factory Fill. (HYUNDAI è KIA MOTOR, Korea).
10. ASTM D 1177-07 Standard Test Method for Freezing Point of Aqueous Engine Coolants.
11. SPEC No 9.55523-04 Procurement Specification. Antifreezes. (Fiat Auto, Italy).
12. WSS-M97B44-D Engineering Material Specification. Coolant, Organic Additive Technology (OAT), Concentrate, for Passenger Car and Light Truck (Ford Motor Company, USA)
13. GOST 18995. 1-73 Chemical Liquids. Methods for Determination of Density.
14. ASTM D 1122-97. Standard Test Method for Density or Relative Density of Engine Coolant Concentrates and Engine Coolants By The Hydrometer.
15. ASTM D 1384-01 Standard Test Method for Corrosion Test for Engine Coolants in Glassware.
16. ASTM D 1121-07 Standard Test Method for Reserve Alkalinity of Engine Coolants and Antirust.

17. ASTM D 1881-97 Standard Test Method for Foaming Tendencies of Engine Coolants in Glassware
18. GOST 9.030-74 Unified System of Anticorrosion and Anti-Aging. Rubbers. Test Method for Resistance in a Relaxed State to the Liquid Aggressive Media.
19. ASTM D 2570-96 Standard Test Method for Simulated Service Corrosion Testing of Engine Coolants.
20. ASTM D 2809-94 Standard Test Method for Cavitation Corrosion and Erosion-Corrosion Characteristics of Aluminum Pumps with Engine Coolants.