World Applied Sciences Journal 20 (9): 1317-1321, 2012
ISSN 1818-4952
© IDOSI Publications, 2012
DOI: 10.5829/idosi.wasj.2012.20.09.2888

Anticorrosion Properties of Carboxylic Acids in Aqueous-Glycolic Solutions

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

Kazan National Research Technological University, Kazan,
Russia 420015 Russia, Tatarstan, Kazan, ul. Karla Marksa 68

Abstract: The sodium salts of carboxylic acids were investigated in order to evaluate their anticorrosion properties in aqueous-glycolic solutions by gravimetry and galvanostatic dilution methods using the metals applied in cooling systems. The composition of anticorrosion complexes and effective concentrations for inhibition of metals, have been determined. It has been revealed that anticorrosion aqueous glycolic complexes containing the sodium succinate and sodium sebacinate reveal the maximal anticorrosion effect. The study results on protection properties of considered anticorrosion inhibitor complexes in aqueous-glycolic solutions were compared and showed the high anticorrosion properties of carboxylic and dicarboxylic acids as regards to all studied metals and can be applied for composition of liquid coolants.

Key words: Aqueous-glycolic solution Corrosion inhibitors Carboxylic acids % Study % Properties

INTRODUCTION

The wide range of liquid coolants and working substances revealing the specific complexes of rheological, thermophysical, anticorrosion and other properties is applied in the modern machinery. However, the choice of basis liquid for these fluids among the chemical and petroleum products is limited due to various mutually exclusive requirements.

The water is most cheap coolant with variety of thermophysical properties and used in cooling equipment, heat supply systems and as the cooling agents in combustion engines. Significant application shortage of water is relatively low freezing point. The freezing point can be decreased by addition of nonorganic salts, glycerol and monoatomic alcohols (methanol, ethanol and isopropanol).

Table 1 demonstrates the high values of specific heat and thermal conductivity of salt-containing solutions ensuring the low freezing points of the fluids. However, the high corrosion activity enhancing by high salt concentrations is significant shortage [1]. Maximal corrosion activity can be observed in the contact places between the surface and leaches after permeation through the compressor junctions.

The coolants produced with the aqueous solutions of mono-, di-and triatomic alcohols and their derivatives are most applied. There are antifreezes with the main components as methanol, ethanol, n-propanol and isopropanol, furfural or its mixtures with these alcohols, mono-, di-and triethylene glycols and their mixtures, monoalkyl ethers of ethylene glycols, 1,2-propylene glycol and its monomethyl ethers and glycerol including its mixtures with glycols.

Besides the high thermophysical properties ensuring efficient machine cooling and low freezing points allowing the safety use the motor vehicles around a year, the coolants must possess the several physical and chemical properties and correspond to the following requirements [2, 3]:

C High boiling-point, ensuring the normal vehicle machine functionality during summer period and diminishing occurrence of vapor stoppers in cooling system;

Corresponding Author: Y.S. Ovchinnikova, Kazan National Research Technological University, ul. Karla Marksa 68, 420015 Kazan, Russia.

Table 1: Thermophysical properties of some coolants.

Properties	Water	23,1 % NaCl aqueous solution	20,6 % $MgCl_2$ aqueous solution	29,9 % $CaCl_2$ aqueous solution	60 % MEG aqueous solution	60 % DEG aqueous solution	60 % TEG aqueous solution
Freezing point, °C	0	-21,2	-33,6	-55,0	-49	-41,5	-40,0
Specific heat C at 0°C, cal/g•°C	1,0 at 20°C	0,79	0,72	0,65	0,71	0,72	0,74
Thermal conductivity $8 \cdot 10^3$ at 0°C, cal/cm•s•°C	1,43 at 15°C	1,28	1,21	1,25	0,94	0,89	0,87

- Minimal viscosity at low temperatures ensuring the regular machine start-up during cold seasons;
- Low corrosion activity to the all metal construction materials in engine cooling system preventing destruction of single elements and release of corrosion products, affecting the fluid circulation; index of corrosion effect of fluid on metals is significant for assessment of coolants quality;
- Low foaming ability because foaming of coolant results in drastic decrease of heat-transfer coefficient and as the result, to overheating of engine and release of coolant from cooling system and cavitation, destroying the water pump impeller;
- Inactivity to rubber and plastic products applied in engine cooling systems and to varnish of motor vehicles;
- Availability of alkaline reserve (buffer capacity) maintaining pH value within the interval 7,5-9,5 which effective for corrosion inhibition of some metals;
- Stability to hard water i.e. prevention of sedimentation of heavy salts and formation of scale in cooling system resulting in less efficient heat transfer from engine block to the coolant;
- No specific smell and low toxicity.

According to these requirements to the coolants, propose and application field of any alcohol as the basis for coolant, can be concluded. The fluids based on aliphatic monoatomic alcohols, in spite of several advantages (insufficient viscosity at low temperatures, inactivity to varnished surfaces, rubber and polymeric materials, low toxicity, oxidative resistance and etc.) have limited application as the coolants in motor engines due to low boiling-point. Similarly, the coolants based on 1,2-propylene glycol and glycerol satisfied to the most of requirements, are hardly widespread in the motor vehicle industry due to deficiency of raw materials and high viscosity at low temperatures. These fluids due to low toxicity are actively applied as the heat-transfer agents in food refrigerators and alcohols are widely used for production of synthetic uninflammable hydraulic fluids. In present, the world motor vehicle market implements the cooling fluids based on ethylene glycols which satisfy the necessary requirements such as low freezing-point, high heat capacity and boiling-point, relatively low viscosity and price.

However, the leaches and aqueous alcohol mixtures in continuous contact with the metal elements of heat-transfer systems cause their corrosion. Corrosion processes are repeatedly accelerating by the high temperatures and the constant circulation of the coolant. As the result, any coolant must contain anticorrosion complexes.

Some corrosion inhibitors have been applied to diminish corrosion influence of the coolants on construction materials. 2-mercaptobenzothiazole as the alkali element salts, benzotriazole and its derivatives [4], 2-aminotriazole and disodium phosphate are being used to protect cooper and its alloys in aqueous glycol solutions.

Moreover, sodium nitrite, triethylammonium phosphate [1], benzolsulfamid, sodium arsenate Na_3AsO_3, alkylene polyamines (ethylene diamine, diethylene triamine, triethylene triamine and etc.), sodium tetraborate (meta) $NaBO_2$ and some others are effective inhibitors of the ferrous metal corrosion.

To decrease corrosion of structural aluminium and its alloy elements, water-soluble inorganic molybdates [5], silicates and nitrates of alkali and alkaline earth metals are applied and disodium tetraborate (borax) and sodium benzoate were used to decrease aggressive influence of aqueous glycol solutions on lead-tin alloys (solder).

Combinations of different inhibitors which properties ensure an effective anticorrosion protection of all structural materials in cooling systems [6] have been used in modern cooling liquids as the anticorrosion complexes.

The Main Part: This study shows the research data on efficiency of inhibiting complexes based on the salts of carboxylic acids for aqueous-glycol solutions. The sodium salts of benzoic, lauric, siccine, adipinic and sebacic acids in concentration 0,25-2,5% have been studied.

Table 2: Corrosion losses of metal in aqueous glycol solutions of sodium salts.

	Mass losses, mg					
Salt concentration %	Solder	Cooper	Brass	Aluminium	Steel	Cast iron
1	2	3	4	5	6	7
Sodium succinate						
0,25	10,7	7,1	5,8	5,0	2,2	3,1
0,5	4,1	7,0	2,6	5,1	1,7	2,6
0,75	3,2	4,4	2,5	4,9	0,5	1,1
1,0	2,8	4,1	2,4	5,2	0,4	0,9
1,5	2,0	2,4	2,5	5,5	0,3	0,2
2,0	1,7	2,2	2,4	5,9	0,1	0,1
2,5	1,6	1,5	1,9	6,1	0,0	G
Sodium adipate						
0,25	11,8	5,0	5,0	1,8	5,4	6,9
0,5	4,5	5,0	4,9	1,9	2,8	4,0
0,75	3,3	4,2	3,4	3,5	2,0	3,1
1,0	2,4	2,9	3,0	4,5	1,5	2,3
1,5	2,3	2,1	2,8	4,4	0,2	0,4
2,0	0,7	1,4	2,8	4,5	0,1	0,3
2,5	0,6	0,9	2,7	4,8	0,1	0,1
Sodium sebacinate						
0,25	7,4	5,4	5,2	4,0	6,9	4,1
0,5	7,0	4,2	2,9	4,5	6,8	4,0
0,75	4,6	3,2	2,7	5,9	5,7	2,9
1,0	2,7	0,8	1,4	6,8	3,2	2,6
1,5	0,7	0,1	0,1	7,4	0,1	1,2
2,0	0,6	0,1	0,1	8,2	0,1	1,2
2,5	0,5	0,0	0,0	8,8	0,1	0,9
Sodium laurinate						
0,25	16,9	6,0	5,5	5,4	18,8	20,5
0,5	12,4	6,0	5,1	5,4	9,0	10,7
0,75	7,2	4,9	4,6	4,9	8,2	10,2
1,0	4,7	4,6	2,3	4,2	6,6	6,8
1,5	2,4	3,3	2,3	3,5	4,7	6,8
2,0	2,1	3,0	2,2	3,3	4,6	6,7
2,5	2,0	2,9	2,2	2,9	4,4	6,2

Corrosion tests were undertaken in 50% vol. ethylene glycol aqueous solution by gravimetry [2] and galvanostatic metal dilution methods [7]. Corrosion aggression to the aluminium (type 3003); steel (SAE 1010), cooper (electrolytic); brass (Cu-70, Zn-30); cast iron; solder (Pb-70, Sn-30) was evaluated.

The data on corrosion losses of tested metals in various leaches are shown in Table 2.

It is well known that the carboxylate-anions of dibasic organic acids are effective complexing agents for wide variety of metals. Therefore, the protective activity of dicarboxylic acid salts is related to formation of sparingly soluble chelate compounds on the surface of all studied metals excluding aluminium and its alloys. Neutral octahedral aluminium complexes $\{[(CH2)nC2O4]^{3}Al\}^{3-}$ are water insoluble but easy soluble in most organic solvents including alcohols [4, 8]. Possibly, this characteristic limits the formation of effective protective films on the surface of aluminium and its alloys.

In contrast, application of sodium laurinate as corrosion inhibitor caused significant decrease of corrosion losses of aluminium that possibly related to formation of aluminium laurinate on the surface which insoluble in aqueous glycol solution.

The tested salts of carboxylic acids can be arranged within the following rows according to efficiency of corrosion inhibition on tested metals in aqueous glycolic solution:

Table 3: Corrosion activity of metals in 2% aqueous glycol solutions of the mixtures of dicarboxylic acids in ratio 1:1.

	Mass losses, mg					
Salt of dicarboxylic acid	Solder	Cooper	Brass	Aluminum	Steel	Cast iron
Sodium succinate Sodium adipate	1,9 1,5; 0,7	1,7 2,4; 1,4	2,2 2,4; 2,8	4,4 5,9; 4,5	0,1 0,1; 0,1	0,1 0,1; 0,3
Sodium succinate Sodium sebacinate	1,1 1,5; 0,7	0,5 2,4; 0,7	2,2 2,4; 0,1	4,7 5,9; 8,2	0,1 0,1; 0,1	0,6 0,1; 1,2
Sodium adipate Sodium sebacinate	1,4 1,5; 0,7	1,5 1,4; 0,1	0,5 2,8; 0,1	6,4 4,5; 8,2	0,3 0.1; 0,1	0,7 0,3; 1,2

*- a lower row indicates the data of metal losses caused by corrosion in 2% solutions of individual salts.

Table 4: The rates of metal corrosion in contact systems in aqueous-glycolic solutions of sodium salts of dicarboxylic acids.

	Corrosion rate, mg								
	Solder			Cooper			Brass		
Concentration of sodium salts	Succ.	Adip.	Seb.	Succ.	Adip.	Seb.	Succ.	Adip.	Seb.
1	2	3	4	5	6	7	8	9	10
				Solder-cooper-brass system					
0	0,435*			0,080			0,085		
0,25	0,288	0,290	0,185	0,178	0,125	0,135	0.14	0,125	0,130
0,5	0,105	0,112	0,130	0,175	0,125	0,105	0,065	0,092	0,073
1	2	3	4	5	6	7	8	9	10
0,75	0,080	0,083	0,105	0,110	0,105	0,080	0,063	0,085	0,068
1,0	0,070	0,060	0,068	0,100	0,073	0,020	0,060	0,075	0,035
1,5	0,050	0,057	0,018	0,061	0,053	0,005	0,063	0,070	0,005
2,0	0,043	0,018	0,015	0,055	0,035	0,004	0,060	0,070	0,003
2,5	0,040	0,015	0,013	0,038	0,022	0,000	0,056	0,066	0,000
Aluminium-steel-cast iron system	Aluminium			Steel			Cast iron		
0	0,108			0,553			0,865		
0,25	0,125	0,045	0,100	0,055	0,135	0,175	0,075	0,173	0,103
0,5	0,128	0,048	0,112	0,043	0,070	0,170	0,065	0,100	0,100
0,75	0,123	0,088	0,148	0,013	0,050	0,145	0,028	0,078	0,073
1,0	0,130	0,113	0,170	0,010	0,038	0,080	0,023	0,058	0,065
1,5	0,138	0,110	0,185	0,007	0,005	0,002	0,005	0,010	0,030
2,0	0,148	0,113	0,205	0,002	0,002	0,002	0,002	0,008	0,030
2,5	0,150	0,117	0,220	0,000	0,002	0,002	0,000	0,002	0,022

* - the metal corrosion rate which are not corresponding to GOST 28084 standards (a standard of metal corrosion losses according to GOST 28084: for solder is 0,2 mg and for other metals is 0,1 mg).

for non-ferrous metals (solder, cooper, brass)
sebacinate > adipate > succinate > laurinate
for ferrous metals (steel, cast iron)
succinate > adipate > sebacinate > laurinate for aluminum
laurinate > adipate > succinate > sebacinate

Table 1 indicates that elongation of hydrocarbon chain in dicarboxylic acids results in an increase of protective activity of their salts regards to non-ferrous metals and decrease to ferrous metals (cast iron). Protection degree for solder, cooper and brass is 96-97% (for succinate is 91% in case of solder and 25-30% for cooper and brass) in aqueous-glycolic solutions containing 2,0% sodium sebacinate and for similar solutions of sodium succinate, the protection degree of cast iron is 99,7% (for sebacinate-96,5%).

The study of the metal corrosion in mixed solutions of sodium salts of dicarboxylic acids (Table 3) revealed the significant positive synergetic effect in regards to all tested metals during test of the mixture of sodium succinate and sodium sebacinate. The study of other compounds has showed that metal corrosion losses in these mixtures are lower then in solutions of individual salts with same concentration.

The cooling systems of combustion engine are polymetal contact systems composed of aluminum-steel-cast iron and cooper-brass-solder [9, 10]. A the result, the influence of aqueous glycol solutions of sodium salts of dicarboxylic acids on corrosion process in metals were studied in polymetal contact systems. Table 4 shows the results of corrosion tests.

The salts of dicarboxylic acids in concentrations 0,5-0,75% significantly prevented the corrosion of solder, brass and cast iron and concentration increase up to 1,0% for cooper and steel. These also initiate aluminium corrosion excluding sodium adipate which slightly decreases corrosion losses of the metal in concentrations 0,25-0,75%. An increase of sodium succinate concentration (sodium salt of siccine acid) from 1,5 to 2,5% insignificantly influence the ferrous metal corrosion losses while implementation of sodium adipate in similar concentrations significantly decreases cooper and solder corrosion rates (approximately by four times). Sodium sebacinate completely suppresses cooper and brass corrosion (protection degree is 100%) and significantly suppresses solder (97%). An increase of salt concentration in aqueous glycolic solution up to 2,0% sufficiently prevents steel corrosion (99,7%). The protection degree for cast iron using sodium succinate was 99,8% and for sodium adipate and sodium sebacinate were-99,1 and 96,5%, respectively. Further increase of dicarboxylic acid salts insignificantly influenced the metal corrosion losses.

CONCLUSION

Thus, we have identified the corrosion effect of aqueous-glycolic solutions of sodium salts of dicarboxylic acids on tested materials and determined that anticorrosion complexes with sodium succinate and sodium sebacinate are most efficient.

Comparison of the test data obtained in the experiments on investigation of protective properties of corrosion inhibitors in aqueous-glycolic solutions has revealed that anticorrosion complexes based on carboxylic and dicarboxylic acids possess the high protective properties for all tested metals and can be used in mixtures with coolants.

ACKNOWLEDGEMENT

This work was financially supported by the Russian Ministry of Education and Science and performed within the integrated programs implemented according to Russian Federation governmental resolution no. 218.

REFERENCES

1. Skorchelletti, V.V., 1973. Theoretical Principles of Metal Corrosion. Leningrad: Khimiya, pp: 264.
2. GOST no. 28084-89: Low-Freezing Liquids. General Technical Conditions.
3. Sladovskaya, O.Y.U. and S.A. Chupakhina, 2008. Synthesis of inhibiting additives for modern coolants. In Republican concourse of student and postgraduate student’s scientific works for a grant of N. I. Lobachevskiy, Kazan, 3: 402-404.
4. Kuznetsov, YU.I., 1996. Organic Inhibitors of Corrosion of Metals. New York: Plenum Press, pp: 283.
5. Lukovits, I., E. Dalman and G. Palikas, 1995. Nonlinear Group-Contribution Models of Corrosion Inhibition. Corrosion, 51: 201-206.
6. Esenin, V.N. and L.I. Denisovich, 2008. Stability of Metallic in Aqueous and Aqueous-Glycol Solutions. Russian Journal of Applied Chemistry, 81(11): 1890-1894.
7. Esenin, V.N., A.A. Stepanov and L.I. Denisovich, 2006. Electrochemical Procedure for Express Evaluation of the Corrosion Effect of Aqueous Glycol Solution on Metals. Russian Journal of Applied Chemistry, 79(12): 1957-1963.
8. Esenin, V.N., L.I. Denisovich and B.L. Zhuravlev, 2006. Corrosion of Multielectrode Systems in Aqueous-Glycol Solution. Vestnik Kazanskogo Gosudarstvennogo Tekhnologicheskogo Universiteta, 3: 125-130.
9. Esenin, V.N., B.L. Zhuravlev, A.A. Stepanov and L.I. Denisovich, 2006. Assessment of Corrosion Effect of Aqueous Glycol Solutions on the Metals in Cooling Systems. Butlerovskie Soobshcheniya, 8(3): 33-35.
10. Esenin, V.N. and L.I. Denisovich, 2008. Contact Corrosion of Metals in Aqueous and Aqueous-Glycol Solutions. Russian Journal of Applied Chemistry, 81(10): 1796-1802.