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## THE EFFECTS OF DE-ICING AGENTS ON AUTOMOBILE PARTS

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**Keywords:**

De-icing agents, technical salt, urea, sodium phormiate, electrochemical corrosion, underlying chemistry

**Abstract:** The paper examines the classification of de-icing agents and identifies the most commonly used additives in road maintenance. The article describes the mechanism for producing a combined acetate de-icing agent from sealant production wastes. Experiments shows total removing of ice by combined acetate reagent in 30 minutes. Also the study investigates the effect of de-icing agents on galvanised automobile parts. The interaction between the de-icing agent and the metal automobile parts proceeds through the anodic and cathodic oxidation-reduction reactions. The paper dwells on electrochemical corrosion underlying chemistry. In order to evaluate the effect of antifreeze additives on the electrochemical corrosion of zinc coating the authors present the results of the quantum-chemical calculations of zinc ions intermolecular complexes energies formations with water molecules and antifreeze additives. We made the conclusions by the results of the scientific work. According to the results, sodium phormiate can be classified as a gentle de-icing agent, characterising by low corrosive effect in a humid environment. The better result was shown by the combined de-icing agent in a dry environment. The maximum corrosion rate of the zinc coating in a wet environment is higher than in a dry one.

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### Introduction

In winter traffic conditions are unfavourable due to snow and ice crusts. Slippery roads reduce the traffic speed and increase the cost of transportation and the number of car accidents. The main objective of winter road maintenance is to carry out a range of measures to ensure continuous and safe traffic on the roads, including snow clearance and de-icing. The situation on the roads is particularly acute in winter with short periods of heavy snowfall, as in the winter periods of the last three years.



Falls are the second leading cause of accidents. The World Health Organisation (WHO) estimated there are 424,000 deaths from falls worldwide each year. The majority of falls occur in winter. The main reason is that the streets are not cleared of snow and ice. Winter injuries account for up to 18% of total temporary disability and cause 15-20% of disabilities. Falls in the street result in the following injuries: fractures and dislocations (65-72%), bruises and sprains (22-25%) and minor injuries (4-6%). Arms and legs are the most prone to injury - 83-85% of all cases.

In addition to injury, de-icing materials contain substances that are harmful to the environment. The current trend is to develop de-icing agents that meet all the requirements of the standard, including those with a minimal environmental impact [1-6].

The most popular method of de-icing in Russia is the treatment of road surfaces with chemical de-icing agents. De-icing materials include solid or liquid road maintenance materials used for de-icing of roads and streets [3, 7-9].

Fig. 1. The classification of de-icing agents.

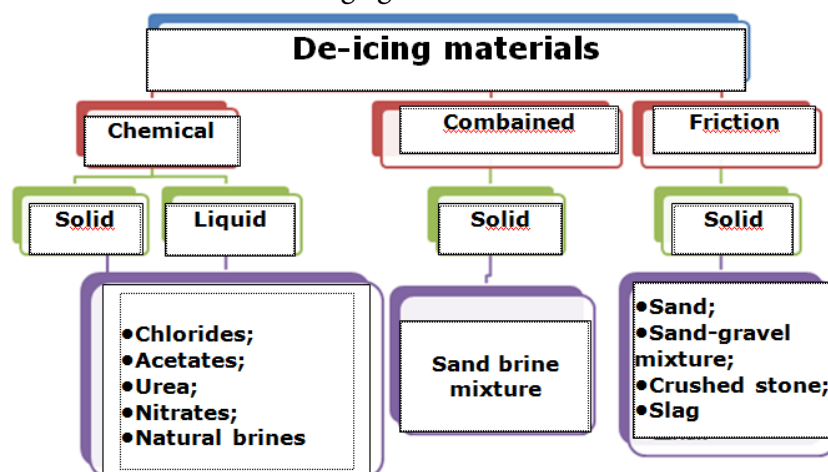


Fig. 1. The classification of de-icing agents

Urea and sodium phormiate based reagents (Bionord, Bionord-Avia, Biodor etc.) have recently become widespread for icing prevention. In addition, industrial salt is still used because of its low cost.

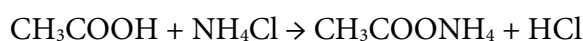
## Results and Discussion

The purpose of this work is to determine the effect of de-icing agents on galvanized automobile body parts.

The objects of the study are de-icing agents currently used in Russia: technical salt, urea, sodium phormiate and combined de-icing agent (CDA).

The combined reagent was produced at the Department of Labour and Nature Protection at Yaroslavl State Technical University (YSTU) from sealant production waste. About 24 tonnes of these waste is accumulated in Ratmirovo village, the Moscow region, Russia. The waste consists of 25% ammonium chloride and 45% acetic acid. The rest is water.

When acetic acid reacts with ammonium chloride, ammonium acetate is produced:





The reaction is reversible. Ammonium acetate is a preservative and widely used as a food additive known as E264. In addition, the substance is also used in the production of de-icing agents used to treat motorways.

Acetates have the ability to stay on the road even after it has been mechanically cleaned. In favourable weather conditions, such reagents can retain their protective properties for more than four days without the need for re-treatment. Acetate-based de-icing agents have a high environmental safety rating of Hazard Class IV. Acetate reagents are safe for humans, the groundwater system, animals and plants. Acetates undergo complete biodegradation in aquatic systems for a limited period of time without creating an oxygen deficiency problem for aquatic organisms. In addition, acetate de-icing agents do not undergo degradation with the formation of ammonium and are therefore not toxic to fish.

They have good biodegradation properties with less oxygen demand than any other de-icing agent. By replacing the chlorides, urea and glycols used in other de-icing chemicals, all the problems associated with chloride and nitrate contamination of wastewater are eliminated. Using acetates eliminates the need to collect and treat wastewater from the effects of the reagent.

However, acetate-based de-icing agents are only used in well ventilated areas (bridges, overpasses, or airfields). They should not be used in cities, as there is a distinctive vinegar odour during the use.

Fig. 2. A flowchart of the production of an anti-icing agent from sealant waste.

To obtain de-icing agent (CDA), the waste was evaporated to dryness, then ground to a mineral particle dispersion of no more than 1 mm. After grinding, the powder samples were tested as an anti-icing agent on a 1m<sup>2</sup> ice surface. The results of the experiment showed that the de-icing agent, obtained from sealant production waste, started working after just a couple of minutes, and after 30 minutes the ice was completely gone.

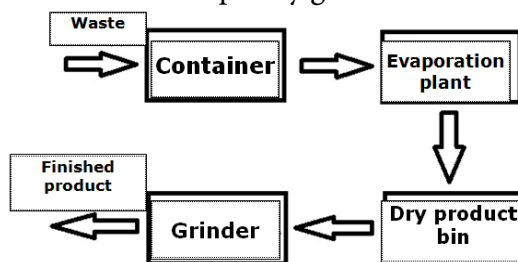


Fig. 2. Scheme for producing a combined de-icing agent

A working group determined the phytotoxicity parameters of de-icing agents [10-12].

In this work we studied the effect of de-icing agents (sodium phormiate, urea, sodium chloride, combined de-icing agent) on the automobile parts.

The experiment was conducted in a dry air in a humid media. Water was used as a control. To obtain data in a humid media, the sample was placed in solution and in a dry media, the sample was suspended over the solution.

The mass loss per unit surface area  $\Delta m$ , kg/m<sup>2</sup>, is calculated according to the formula

$$\Delta m = \frac{m_0 - m_1}{S},$$

where  $m_0$  is the mass of the sample before the testing, kg,

$m_1$  - mass of the sample after testing and removal of corrosion products, kg,

$S$  - the surface area of the sample, m<sup>2</sup>.



If solid corrosion products are difficult to remove, or if their removal is impractical, solid corrosion is quantified by the mass increasing. The mass increasing per unit of surface area is calculated by the difference in mass of the sample before and after the test referred to the unit surface area of the sample. In order to calculate the metal mass loss by the increase in sample mass, it is necessary to know the composition of the corrosion products.

During [13, 14] the electrochemical corrosion zinc coatings protect steel both mechanically and electrochemically in places, where the coatings are damaged and in pores, where zinc forms a galvanic pair with steel by shielding it from the media. At the same time, short-circuited micro-galvanic elements appear in the system located in the electrolyte, due to the separation of the surface into cathode and anode sections as a result of mechanical damage. The anode for these elements is zinc, and the cathode is iron. The process of electrochemical corrosion is a combination of two reactions occurring on the surface of metals: anodic, in which zinc atoms oxidise to form ions which pass into solution, and cathodic, which is accompanied by the reduction of the oxidant (depolariser).

The oxidation of zinc at the anode end produces zinc ions which form intermolecular complexes with water molecules and the de-icing agent and pass into the solution. This process can be represented as



As S may be water molecules as well as de-icing additives. The released electrons pass from the anode to the cathode surface, where they combine with the hydrogen ions in the solution, releasing hydrogen:



This process is called hydrogen depolarisation. In presence of oxygen in air the reaction of the oxygen depolarisation can also take place to form hydroxyl ions:



For theoretical estimation of the antifreeze additives effect on electrochemical corrosion of zinc coating we provide the quantum-chemical calculations of energies of formation of intermolecular complexes [15] of zinc ions with water molecules and antifreeze additives on reaction (2), as well as complexes with hydroxyl ions:



The calculations were performed by the DFT B3LYP/6-311G\*\* density functional method using the ORCA quantum chemical package [16, 17]. The total electron energies of the components of the reactions in aqueous medium were calculated within the CPCM solvation model. The energies of intermolecular  $E_{\text{imi}}$  complexes formation were calculated similarly [15, 18-20] as the difference of the total electronic energies of the reaction products and the starting substances in the solvating medium. The values obtained are shown in Table 1.

**Table 1.**  $E_{\text{imi}}$  formation energies (kJ/mol) of intermolecular complexes of water and de-icing molecules with zinc ions and hydroxyl ions

Substrate	Ion	
	$\text{Zn}^{2+}$	OH
Water	-71.04	15.74
Urea	-82.65	-412.34
Sodium phormiate	-501.08	-412.34
Sodium chloride	-138.50	-134.50
Ammonium acetate	-309.69	-233.55

The molecules of all presented types of anti-icing coatings form complexes with zinc ions and hydroxyl ions exceeding the energy of formation of the corresponding complexes with water molecules, which confirms their potential corrosive activity. However, it is not possible to compare the corrosion activity of different types of coatings on the basis of these data, because it depends on many factors, such as the degree of dissociation of the electrolyte in solution, concentration, interaction with zinc oxide, solubility of the resulting salts, etc. In this regard, experimental studies have been carried out on the corrosion activity of different de-icing agents.

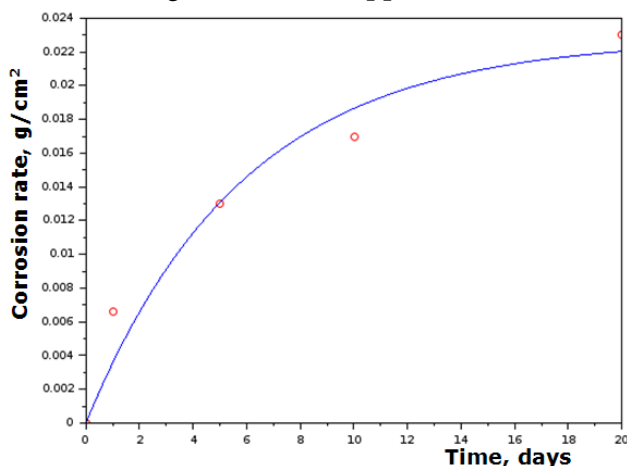
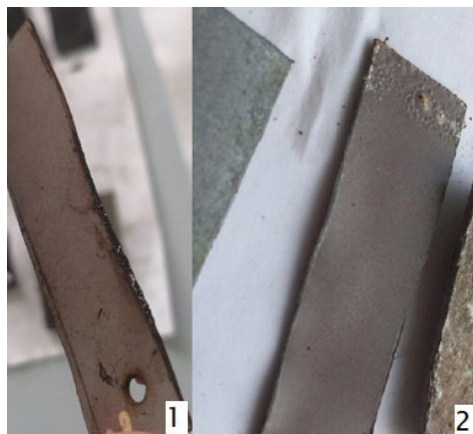
By the experiments, the corrosion rate ( $C$ ) versus time ( $t$ ) is a curve with saturation, which is approximated by a regression equation of the form

$$C = C_{\text{max}}(1 - e^{-kt}), \quad (6)$$

where  $C_{\text{max}}$  is the maximum achievable corrosion rate under experimental conditions,

$k$  is the process rate constant.

The parameters  $C_{\text{max}}$  and  $k$  of the experimental data were calculated by the least-squares method using a non-linear estimation procedure [21]. Fig. 3 is an example of a kinetic corrosion curve in a humid media in the presence of urea. The experimental dots of the approximation were made. Fig. 4 shows the appearance of the corroded samples.

**Fig. 3.** Corrosion rate versus time in a humid environment in the presence of urea: dots - experiment, curve - calculation using function (6)**Fig. 4.** Galvanisation sample appearance after the experiment: 1 - urea sample, 2 - technical salt vapour sample

By Table 2 the kinetic parameters of the test samples corrosion in different media calculated by the experimental data.

**Table 2.** Calculated kinetic parameters of the test samples corrosion in different media

Substrate	C, g/cm <sup>2</sup>	k, days <sup>-1</sup>	Adequacy dispersion
Corrosion in the humid			
Water	0.00023	0.6762	1,15·10 <sup>-9</sup>
Sodium phormiate	0.00049	0.1960	1,77·10 <sup>-9</sup>
Sodium chloride	0.00427	1.9173	1,16·10 <sup>-8</sup>
Combined CDA	0.00807	0.0654	2,5·10 <sup>-8</sup>
Urea	0.02279	0.1707	3,2·10 <sup>-6</sup>
Corrosion in the air			
Combined CDA	0.00001	2.4946	1,01·10 <sup>-12</sup>
Water	0.00020	0.0791	7,79·10 <sup>-11</sup>
Sodium phormiate	0.00046	0.1230	8,39·10 <sup>-11</sup>
Urea	0.00049	0.2270	2,87·10 <sup>-9</sup>
Sodium chloride	0.00419	0.0632	6,73·10 <sup>-10</sup>

By the results, the rate constant is in approximately an antibactic relationship to the maximum corrosion rate. When corroding in a humid environment, urea has the maximum corrosion rate, while in a dry environment, sodium chloride has the maximum corrosion rate. However, sodium phormiate is a relatively mild corrosive agent in both dry and humid media. The combined de-icing agent exhibits almost no corrosive properties in a dry environment, but is a relatively active corrosive agent in a humid one.

### Conclusions

This paper investigates the corrosion protection properties of the most common de-icing agents in relation to galvanised iron, which is widely used in the automotive industry. According to the results, sodium phormiate can be classified as a gentle de-icing agent, characterising by low corrosive effect in a humid media. The better result was shown by the combined de-icing agent in a dry media. The maximum corrosion rate of the zinc coating in a wet media is higher than in a dry one. There is no correlation between the formation energy of the intermolecular complex with zinc ions and hydroxyl ion and the maximum corrosion rate of the respective substrate. This seems to be due to the fact that the corrosion rate of zinc is mainly determined by the ability of the substrate to interact with the zinc oxide.

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