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# International Journal of Engineering Technologies and Management Research

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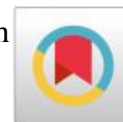


## ANTI-ICE REAGENT ON THE BASIS OF DOLOMITE, NITROGEN ACID AND CARBAMIDE

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### Abstract:

*For the safe operation of pavements in the cold season, especially in mountainous areas, anti-icing means are required. The task was to develop the technology of their production from local raw materials. A domestic anti-icing reagent, from unbaked dolomite from Dekhkanabad deposit of Uzbekistan was offered, consisting of calcium, magnesium nitrates and carbamide. Standard chemical-analytical methods for investigating raw materials, laboratory technological methods, enlarged pilot-industrial approaches to the methods of its processing, followed by the development of technology for obtaining the required dolomite's derivatives, as well as its implementation at JSC "Maxam-Chirchik" were used. Sulfur-hydrochloric acid's processing of dolomite provided bischofite's obtaining in industrial reactors. As the result, optimal conditions for obtaining anti-ice reagent were selected for its industrial production.*

**Keywords:** Dolomite; Calcium Nitrate; Magnesium-Containing Compounds; Anti-Ice Reagent.

**Cite This Article:** Mansur E. Akhmedov, Abdulla T. Dadakhodzhaev, and Vitaliy P. Guro. (2018). "ANTI-ICE REAGENT ON THE BASIS OF DOLOMITE, NITROGEN ACID AND CARBAMIDE." *International Journal of Engineering Technologies and Management Research*, 5(10), 45-52. DOI: <https://doi.org/10.29121/ijetmr.v5.i10.2018.301>.

### 1. Introduction

Anti-ice reagent is applied to fight ice on roads, aprons and airfields. The reagent should have a high melting capacity to ice, be effective down to -20 °C, as well as against metals corrosion activity, at the level of rainwater.

To combat icing the following substances are used: sand, salt, ash, scattering them on the surface of the ice, allowing to make the surface less slippery. However, salt mixtures, aggressive to metals, ferro-concrete, also have a negative impact on the environment. In addition, a number of anti-glazed reagents of softer action are known [1]. They gradually melt the ice, forming a reagent solution, which subsequently freezes at a lower temperature than water: i.e. they not only eliminate ice, but also partially prevent its appearance in the future [2].

The most common are three types of icing: rolled snow crust; ice, formed due to freezing of thin layers of water (atmospheric precipitation, surface runoff); black ice (freezing on coatings of supercooled water) (**Table 1**).

Table 1: The physical and operational properties of icing

Indicators	Types of Icing		
	Rolled Snow Crust	Ice	Black Ice
The thickness of the layer, cm	>2	2.0-0.5	0.5-0.1
Density, g /cm <sup>3</sup>	0.3-0.5	0.8-0.9	0.5-0.9
Coefficient of traction of the tire with a coating	0.20-0.30	0.10-0.20	0.05-0.15
Rate of ice formation	Small	Medium	Large

In Europe, the use of chlorides began in Sweden since 1947, in the UK - since 1960. In Russia, anti-icing salts were first used in 1966: sodium and calcium chlorides were added to the sand in an amount of 2% by weight. Until the mid-1960s on the territory of former USSR, the use of pure salts on roads was almost never practiced. In winter, only friction materials were used in a mixture with or without salt. The ice was partially flooded, and the rest of the ice cover lost its slipping property, as a result of which the roads remained in relative operational condition. It was quite simple and quite cheap, so it was used everywhere, from small towns to Soviet megacities. However, such a mixture, which, frankly speaking, was not an anti-ice reagent in the modern sense of the term, had a lot of shortcomings. So, sand heavily hammered storm drains, and it took a lot of time and money to clean the drains. Clogged sewerage reduced the effectiveness of such anti-ice reagent: during the daytime melting of ice, the water collected on the roads, but did not go to the sewers, and on the night of the sixth road covered a new layer of ice, on top of the sand, and everything had to be done first. The amount of sand began to be reduced. At the same time, the share of technical salt (NaCl - tech.) began to increase. After several tens of years, the first "fruits" appeared: as a result of the widespread use of salt, the soil seriously changed its composition, which affected the health and development of plants. If you take into account that in Europe or the USA the salt is strictly dosed - no more than 30 grams per square meter of the roadway, in Russia the norm was exceeded several times, spreading the salt exactly the same as before - the sand and salt mix.

It came to that snow with ice descended, and the road remained white - from salt. This overuse of salt led to the fact that the salt began to corrode not only ice, but also the wheels and car bodies, pedestrian shoes and even trolley bus networks and trams. Gradually salt from the means of fighting ice itself became a problem. Public transportation suffered to a great extent - couples of salt corroded the electric wires, so the drivers of trolley buses had to stop constantly to toss the rod of the current collector into entire sections of the wires, which could not but lead to congestion. As a result of too much salt in the soil, green plantings began to die. It was decided to use more advanced means, which are not so destructive for the environment. At the same time, neutrality became the main criterion in selecting a reagent to fight ice, that is, it had to interact only with ice, without touching anything more - no metal, no plastic, no rubber, no other materials [2-4].

In the world and national practice, the tasks that are aimed at protecting the environment and human health remain urgent, and scientific research aimed at developing and improving technologies for the use of anti-ice reagents is conducted [5]. Large-scale application of technical

salt in the 70s - 90s of the XX century was one of the acute environmental and hygienic problems of Moscow and other large cities of Russia. Its use entailed not only corrosion of metal structures, transport, engineering networks, destruction of foundations, but also partial destruction of lawns, green plantations [6,7].

Table 2: Physicochemical characteristics of the reagent

Nr	The name of the indicator, units of measurement	Norm
1	Appearance	Granules of white, yellowish or gray
2	Mass fraction of calcium nitrate $\text{Ca}(\text{NO}_3)_2$ , %	37.5 – 40.6
3	The ratio of the mass fraction of carbamide to the mass fraction of calcium nitrate	1.38 – 1.58
4	Mass fraction of moisture,%, not more than	0.80
5	Mass fraction of ammonium nitrate, $(\text{NH}_4\text{NO}_3)$ , %, no more than	0.5
6	Mass fraction of insoluble impurities,%, not more: Including, calcium carbonate $(\text{CaCO}_3)$ , %, not more: surfactants (neonol), %, not more:	0.70 0.45 1.5 – 3.0
7	Grading: Mass fraction of granules is less than 1 mm, %, not more than Mass fraction of granules is 1-4 mm,%, not less than Mass fraction of granules is more than 4 mm,%, not more than	5 93 2
8	Friability, %	100

Elimination of the ice crust on road surfaces is possible in various ways - mechanical, physicochemical, thermal and chemical. The use of one or another method depends on the conditions of the ice formation, the thickness of the crust, the type of coating etc. Anti-ice reagents are liquid, solid and granulated, sand-salt mixture and they all have one common property - to lower the melting point of snow.

To date, there are the following anti-ice means. Anti-ice reagent - anti-ice, non-corrosive solution (ANS), Standard TU U6-13441912.001-1997 (**Table 2**).

It is a complex compound of calcium nitrate and carbamide with the addition of a surfactant. One ton of ANS is sufficient for processing 8500 m<sup>2</sup> of treated surface, with an ice thickness of 1 mm, at minus 4 °C. The ANS reagent under normal conditions is non-combustible, fire and explosion-proof, resistant in the temperature range from -60 °C up to +155 °C. Confidently clears from icing all kinds of road surfaces, at a low temperature regime, down to -15 °C. In the absence of salts, does not have a corrosive effect on steel, plastic, rubber.

Having unique properties, when hit on the soil, is still a fertilizer for plants. The products are used by airports in Central Asia, Europe, operational services of sea and railway ports.

Beginning in the winter of 2001/2002, the authorities of large cities, as well as private organizations, began to abandon traditional salt in favor of more effective environmentally friendly and more technologically advanced anti-ice reagents (PGR) of the new generation. As the main reagents began to use solid "Biomag" and HCF (calcium chloride inhibited by phosphates), liquid

HCM (calcium chloride modified) and "Nordex". These drugs were recognized as environmentally safe and sufficiently effective deicers. But at the same time, they found the property of creating an "oil film" on the road.

Due to the restriction of the use of technical salt in the city, metropolitan utilities began using more expensive anti-ice reagents HCMC (calcium chloride modified), HCNM (calcium chloride sodium modified) or granite chips, as well as their analogues.

Since the winter of 2005, the Moscow authorities have abandoned the use of magnesium chloride ("Biomag") due to trends in the accumulation of magnesium anion in soils and natural waters. For technical salt it is necessary to comply with the dosage 10 g/m<sup>2</sup>.

At present time, a number of [8-15] anti-ice-cold reagents of softer action are known. They contain CaCl<sub>2</sub>, calcium nitrite, urea (NKMM), reagent HCNM being a mixture of NaCl and CaCl<sub>2</sub>, reagent CMA (a mixture of Ca, Mg, dolomitic lime and acetic acid salts), NCMM reagent (a mixture of Ca, Mg, carbamide and surfactant) etc.

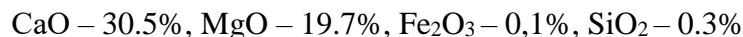
Known ways to produce NKMM are distinguished by raw materials used. Thus, in [9], CaO, HNO<sub>3</sub>, a solution of magnesium nitrate or magnesite, urea, surfactant (neonol, sulfonol, etc.) were used as raw materials for the preparation of a composition. The burnt dolomite is also used as a raw material [10] for the production of NKMM, with a corrosion inhibitor. An anti-ice composition [11] including calcium nitrate, magnesium nitrate, carbamide and surfactant is obtained from calcined dolomite. The Republic of Uzbekistan needs such an effective domestic anti-ice reagent. Its production is included in the "Localization program for the production of finished products, components and materials for 2015-2019." And approved by the Decree of the President of the Uzbekistan Republic No. PP-2298, dated Febr, 11, 2018.

## 2. Materials and Methods

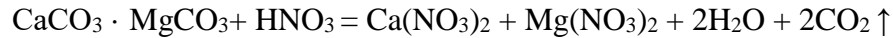
The object of the study was the dolomite of the Dekhkanabad deposit of the Uzbekistan Republic. Standard laboratory chemical-analytical methods for investigating raw materials, laboratory technological methods, enlarged pilot-industrial approaches to the methods of its processing, followed by the development of technology for obtaining the required derivatives from dolomite, as well as its implementation at JSC "Maxam-Chirchik" (Uzbekistan) were used.

## 3. Results and Discussions

For laboratory experiments, the Dekhkanabad dolomite was used for the composition:



From pulverized dolomite, a pulp with water was prepared in accordance with T:M=1:2. A solution of nitric acid with a mass fraction of 30% was fed into the pulp portionwise for the complete dissolution of dolomite and a decrease in the volume of the reaction mass due to the release of CO<sub>2</sub>. The termination of the decomposition of dolomite was judged by the termination of the increase in the reaction mass. The process of decomposition of dolomite with nitric acid occurs according to the reaction:



The resulting solution of a mixture of calcium and magnesium nitrates (a nitric acid solution) was separated from the mechanical impurities by filtration. In the solutions obtained, the mass concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions was calculated in terms of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Mg}(\text{NO}_3)_2$ . In the process of obtaining anti-ice reagent in the laboratory conditions, optimal conditions and reagent ratios were selected. The ground carbamide was first introduced into the nitric acid solution evaporated to 1/2 of its original volume. With continuous mixing, a thick suspension formed, with further evaporation to complete removal of moisture, an odor of ammonia appeared, indicating a partial decomposition of the carbamide.

In subsequent experiments, the nitric acid solution was evaporated to a melt state at a temperature of (85-90) °C and crushed carbamide was added in portions. Then the smelting of the melt was carried out with continuous stirring until a uniform thick oily mass was obtained. The resulting mass was separated from the mother liquor residues on a vacuum filter and dried at room temperature for 24 hours, then transferred to a dry container with a hermetically sealed closure. The finished crystalline antifoaming agent and the mother liquor were analyzed for the content of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in terms of  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$  and carbamide. The results of the analyses are shown in the **Table 3**.

Table 3: Results of analyses of anti-icing agent's composition and mother liquor

Nr	Volume of the solution, cm <sup>3</sup>	The total mass of calcium and magnesium nitrates, g	Mass of carbamide, g	The evaporation temperature, °C	Mass of the reagent, g	Mass fraction of components in the end product, %			The volume of the mother liquor, cm <sup>3</sup>	Mass concentration of components in the mother liquor, g/dm <sup>3</sup>		
						Ca(NO <sub>3</sub> ) <sub>2</sub>	Mg(NO <sub>3</sub> ) <sub>2</sub>	(NH <sub>2</sub> ) <sub>2</sub> CO		Ca(NO <sub>3</sub> ) <sub>2</sub>	Mg(NO <sub>3</sub> ) <sub>2</sub>	(NH <sub>2</sub> ) <sub>2</sub> CO
1	500	144.65	250	85	275	24.60	22.50	49.1	65.0	65.7	37.4	490
2	500	144.65	250	90	300	22.50	18.76	46.8	50.0	65.6	41.0	498
3	250	72.33	150	90	150	22.50	29.75	50.0	45.0	38.3	32.8	500
4	250	72.33	125	85	140	24.50	22.20	46.8	45.0	55.3	34.9	500
5	250	72.33	135	85	155	24.60	21.08	47.1	-	-	-	-

**Notes:**

- 1) Nitric acid solution obtained from dolomite had the following composition:  $\text{Ca}(\text{NO}_3)_2$  - 153.75 g/dm<sup>3</sup>,  $\text{Mg}(\text{NO}_3)_2$  - 131.54 g/dm<sup>3</sup>; The pH of the solution is 4.0. If the pH of the nitric acid solution is 1, then when the carbamide is added to the melt in a ratio of 2: 1, the medium becomes neutral (pH 7).
- 2) The pH of the 10% solution of the anti-ice reagent is 7.0.
- 3) The bulk density of the reagent is 0.96 kg/m<sup>3</sup>.

During the decomposition of dolomite with a solution of nitric acid, a solution with a mass concentration of calcium nitrate  $\text{Ca}(\text{NO}_3)_2$  -  $153.75 \text{ g/dm}^3$  and magnesium nitrate  $\text{Mg}(\text{NO}_3)_2$  -  $131.54 \text{ g/dm}^3$  was obtained.

Five experiments were carried out to obtain an anti-ice reagent. In the first two experiments  $0.5 \text{ m}^3$  of nitric acid solution was taken and, after evaporation, urea was introduced in such an amount that the ratio of carbamide and salts of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Mg}(\text{NO}_3)_2$  was 1.70: 1. The weight of the finished product was from 275 to 300 g. The product was a creamy white color, easily soluble in water.

In the following three experiments  $0.250 \text{ dm}^3$  of nitric acid solution was taken, carbamide was added in such quantities that its ratio to the mixture of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Mg}(\text{NO}_3)_2$  salts was  $(1.74 \div 2.08):1$ . The weight of the finished product was  $(140 \div 155) \text{ g}$ .

In the obtained product, the content of  $\text{Ca}(\text{NO}_3)_2$  was  $(22.50 \div 24.60)\%$ ;  $\text{Mg}(\text{NO}_3)_2$  -  $(18,76 \div 22,50)\%$ , carbamide -  $(47.1 \div 50.0)\%$ . The volume of the mother liquor was from  $45.0$  to  $65.0 \text{ cm}^3$ . The mass concentration of  $\text{Ca}(\text{NO}_3)_2$  in the mother liquor is  $(38.30 \div 65.75) \text{ g/dm}^3$ ,  $\text{Mg}(\text{NO}_3)_2$  - from  $(32.80 \div 41.04) \text{ g/dm}^3$ ; carbamide -  $(490.0 \div 500.0) \text{ g/dm}^3$  (see the table).

The most optimal conditions were selected in experiment No. 3 with a ratio of carbamide to a mixture of calcium nitrate and magnesium 2.08: 1. The yield of the finished product was 150 g; mass fraction of  $\text{Ca}(\text{NO}_3)_2$ -22.50%,  $\text{Mg}(\text{NO}_3)_2$  - 20.75%,  $\text{CO}(\text{NH}_2)$  2-50%. The product after separation of the mother liquor was practically dry.

The anti-icing agent should be stored in a closed container, as the product is hygroscopic. In the future it is planned to test the anti-ice reagent on the melting capacity with respect to ice and corrosion activity with respect to ferrous and non-ferrous metals.

#### 4. Conclusions and Recommendations

Work has been carried out to obtain an anti-ice reagent based on a solution of a mixture of calcium and magnesium nitrates and carbamide. A solution of a mixture of calcium and magnesium nitrates was obtained by decomposition of dolomite with a solution of nitric acid with a mass fraction of 30%.

Optimal conditions for obtaining anti-ice reagent are selected:

- evaporation of nitric acid solution to the state of melt;
- introduction into the fusion of pre-crushed urea;
- the ratio of carbamide to a mixture of calcium nitrates and magnesium 2:1.
- douparivanie melt at a temperature of  $85 \text{ }^\circ\text{C}$  and with continuous stirring to obtain a homogeneous wet mass;
- separation of residual mother liquor by filtration under vacuum;
- drying the product at room temperature.

In the finished anti-icicle reagent, the content of  $\text{Ca}(\text{NO}_3)_2$  was from 22.50% to 24.60%,  $\text{Mg}(\text{NO}_3)_2$  - from 18.76% to 22.50%, carbamide - from 47.1% to 50.0% %.



In the mother liquor, the mass concentration of  $\text{Ca}(\text{NO}_3)_2$  was from 38.30 to 65.75 g/dm<sup>3</sup>,  $\text{Mg}(\text{NO}_3)_2$  from 32.80 to 41.04 g/dm<sup>3</sup>. The mother liquor can be returned to the production process of the anti-ice reagent.

We have developed a technology for obtaining a liquid and granulated anti-ice reagent from unbaked dolomite and granulated urea, neutralizing the solution to  $\text{pH} \geq 7$  ammonia.

According to the developed recommendations of the Scientific Research Institute "Uzavtoyul", the liquid reagent can be used to eliminate ice from the roadway at temperatures up to  $-32^\circ \text{C}$ . The rate of consumption of the reagent to remove loose snow at a temperature of  $(15-20)^\circ \text{C}$  is  $(0.2 \div 0.5)$  g/m<sup>2</sup>, to remove ice thickness up to 1 mm -  $(0.6 \div 1.5)$  g/m<sup>2</sup>.

The reagent is not corrosively aggressive, which is confirmed by the result of studying the effect of the reagent on strength parameters of samples from cement and sand. It has been successfully tested on the roads, with a snowfall on the Kamchik Pass (Uzbekistan), and is recommended for serial production.

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