

Interaction Of Components In Aquatic System With The Chlorates And Chlorides Calcium, Magnesium And Acetate monoethanol ammonium

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Abstract: *The solubility of the components in the system $\{84,3\% \Sigma [Ca(ClO_3)_2 + Mg(ClO_3)_2] + 15,7\% \Sigma [CaCl_2 + MgCl_2]\} - CH_3COOH \cdot NH_2C_2H_4OH - H_2O$ was studied by visually polythermal method. The system was studied using six internal sections, on the basis of which a polythermal solubility diagram of the system was constructed. The surface of the liquidus of the polythermal solubility diagram of the system is divided into the crystallization fields of ice, $[Ca(ClO_3)_2 \cdot Mg(ClO_3)_2]$, $[CaCl_2 \cdot MgCl_2]$, CH_3COOH , $CH_3COOH \cdot NH_2C_2H_4OH$ and a new compound of the composition $CaOHCLO_3 \cdot 2NH_2C_2H_4OH \cdot 2H_2O$. The above fields in the solubility diagram converge at four nodal non-invariant points. The compound was precipitated in the crystalline from the assumed area of its crystallization and identified by chemical, x-ray phase and thermogravimetric analysis methods. It was found that the largest volume in the solubility diagram belongs to the crystallization field $CaOHCLO_3 \cdot 2NH_2C_2H_4OH \cdot 2H_2O$ due to its low solubility in comparison with other components of the system. Analysis of the radiograph of the initial components and the synthesized complex based on them shows that diffraction reflexes differ from each other, both in the value of interplanar distances and in the intensity of diffraction lines. Thermal analysis also confirms the identity of the new compound. The obtained data on the solubility of components in the studied system can serve as a scientific basis for obtaining a new complex active preparation based on calcium-magnesium chlorate defoliant and monoethanol ammonium acetate.*

Keywords: *Physiological active substances, polytherma, solubility, crystallization area, double and triple main points, calcium and magnesium chlorates and chlorides.*

1. INTRODUCTION

Timely defoliation of cotton guarantees the production of high-quality raw cotton, its high yield and economic effect. Despite its low toxicity and low cost, the recommended for use defoliants do not fully comply with the modern requirements of agriculture and health authorities for chemical plant protection products. The existing assortment of chlorate-

containing defoliant from the point of view of production and use are the most low-toxic and cheap drugs. Chlorate preparations act hard on plants, thereby reducing the quality and productivity of the grown raw. An alternative is the use of chlorates together with ethylene-producing additives that improve the action of chlorates and lead to the rapid growth and development of crops [1-2].

2. OBJECTS AND RESEARCH METHODS

The objects of study are calcium chlorate-magnesium defoliant [3-4] and monoethanolammonium acetate, synthesized by reacting acetic acid with monoethanolamine, taken at a 1: 1 molar ratio and vigorous stirring.

When studying the system, the visual-polythermal method was used [5]. In quantitative chemical analysis, well-known methods of analytical chemistry were used, in particular: chlorate-ion was determined by the volumetric permeanganometric method [6]; calcium and magnesium were determined by the volumetric complexometric method [7]; the content of chlorine ion according to the method of Mohr [8].

Solid phases were identified by chemical and various methods of physicochemical analysis. Thermal analysis of the studied new phase was carried out on a Paulik-Paulik-Erdeyderivatograph. X-ray phase analysis was carried out on a Dron-3.0 diffractometer. The values of interplanar distances were found according to the reference manual [9-10] according to the angle of reflection, and the intensity of the diffraction lines was evaluated on a stobal scale.

3. RESULTS AND ITS DISCUSSION

The binary system $\text{NH}_2\text{C}_2\text{H}_4\text{OH}\cdot\text{CH}_3\text{COOH}\cdot\text{H}_2\text{O}$ [11] was studied in the temperature range from $-50,4$ to $78,0^\circ\text{C}$. The polythermal solubility diagram is characterized by the presence of ice crystallization branches, CH_3COOH and $\text{NH}_2\text{C}_2\text{H}_4\text{OH}\cdot\text{CH}_3\text{COOH}$, which intersect at two double points of the joint existence of two solid phases. The first double point corresponds to the joint crystallization of ice and acetic acid at a temperature of $-50,4^\circ\text{C}$ and a concentration of 55,6% $\text{NH}_2\text{C}_2\text{H}_4\text{OH}\cdot\text{CH}_3\text{COOH}$ and 44,4% H_2O . The second double point corresponds to the joint crystallization of acetic acid and monoethanolamine acetate at a temperature of $-26,0^\circ\text{C}$ and a concentration of monoethanolamine acetate of 78,0% and 22,0% of water (Fig. 1).

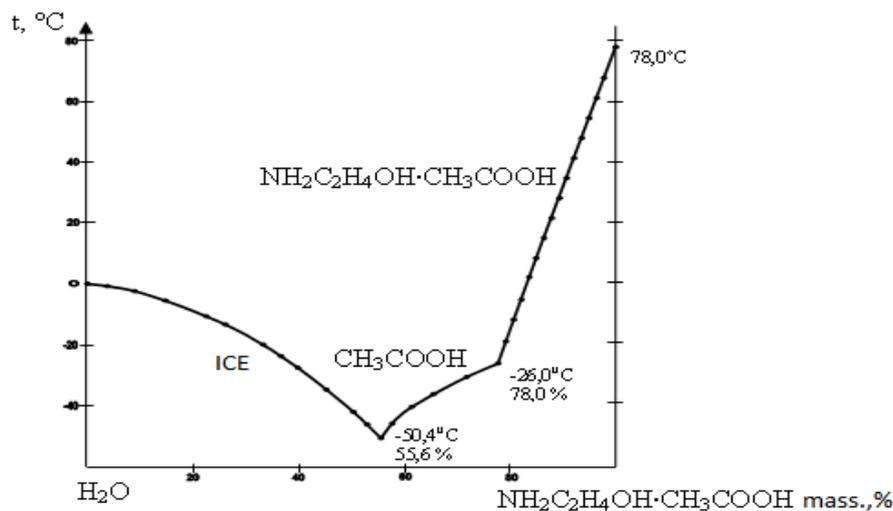


Fig. 1. The solubility diagram of the system $\text{NH}_2\text{C}_2\text{H}_4\text{OH}\cdot\text{CH}_3\text{COOH} - \text{H}_2\text{O}$

Studying the binary system $[22,52\%\text{Ca}(\text{ClO}_3)_2+17,51\%\text{Mg}(\text{ClO}_3)_2+4,33\%\text{CaCl}_2+3,12\%\text{MgCl}_2+52,52\%\text{H}_2\text{O}] - \text{H}_2\text{O}$ [12] showed that its polythermal solubility diagram revealed branches of ice crystallization and a mixture of salts $\{84,3\%\sum[\text{Ca}(\text{ClO}_3)_2+\text{Mg}(\text{ClO}_3)_2]+15,7\%\sum[\text{CaCl}_2+\text{MgCl}_2]\}$. Ice crystallization continues to 41,43% content $\{84,3\%\sum[\text{Ca}(\text{ClO}_3)_2+\text{Mg}(\text{ClO}_3)_2]+15,7\%\sum[\text{CaCl}_2+\text{MgCl}_2]\}$ at $-51,0^\circ\text{C}$. This point is the transition point where the crystallization branch begins $\{84,3\%\sum[\text{Ca}(\text{ClO}_3)_2+\text{Mg}(\text{ClO}_3)_2]+15,7\%\sum[\text{CaCl}_2+\text{MgCl}_2]\}$ (Fig.2.).

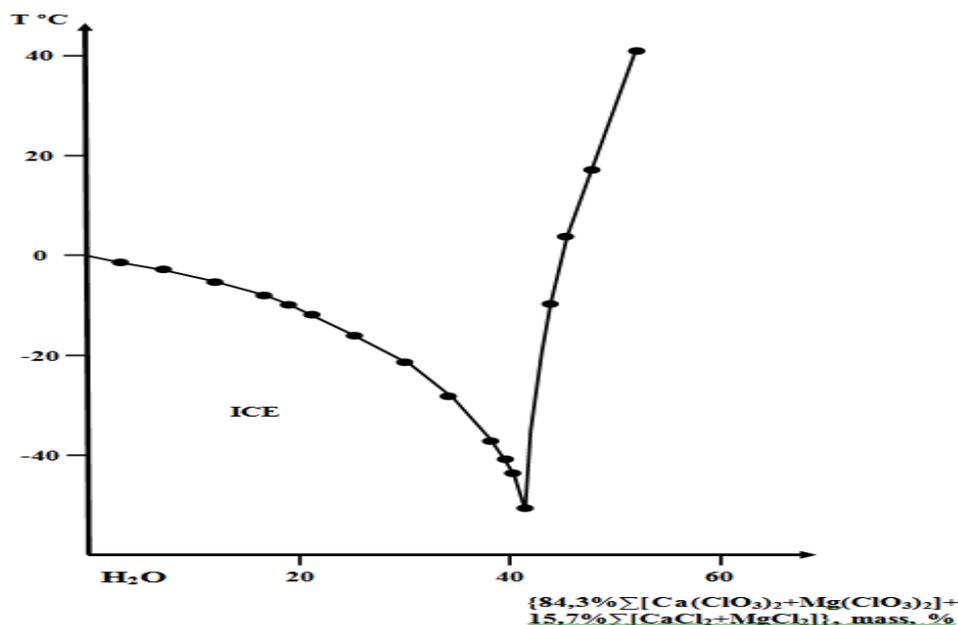


Fig. 2. The solubility diagram of the system $\{84,3\%\sum\text{Ca}(\text{ClO}_3)_2+\text{Mg}(\text{ClO}_3)_2+15,7\%\sum\text{CaCl}_2+\text{MgCl}_2\} - \text{H}_2\text{O}$

For the physicochemical substantiation of the process of obtaining a complex-acting defoliant based on the components of calcium-magnesium defoliant chlorate and ethylene producer - $\text{CH}_3\text{COOH}\cdot\text{NH}_2\text{C}_2\text{H}_4\text{OH}$, the solubility of the components in the system $\{84,3\%\Sigma[\text{Ca}(\text{ClO}_3)_2+\text{Mg}(\text{ClO}_3)_2]+15,7\%\Sigma[\text{CaCl}_2+\text{MgCl}_2]\} - \text{CH}_3\text{COOH}\cdot\text{NH}_2\text{C}_2\text{H}_4\text{OH} - \text{H}_2\text{O}$. The system was studied using six internal sections, on the basis of which a polythermal diagram of the solubility of the system was constructed (Fig. 3).

The liquidus surface of the polythermal solubility diagram of the system is divided into ice crystallization fields, $[\text{Ca}(\text{ClO}_3)_2 \text{ Mg}(\text{ClO}_3)_2]$, $[\text{CaCl}_2\cdot\text{MgCl}_2]$, CH_3COOH , $\text{CH}_3\text{COOH}\cdot\text{NH}_2\text{C}_2\text{H}_4\text{OH}$ and a new compound of the composition $\text{CaOHClO}_3\cdot 2\text{NH}_2\text{C}_2\text{H}_4\text{OH}\cdot 2\text{H}_2\text{O}$. The above fields on the solubility diagram converge into one nodal invariant point. It is known that calcium chlorate actively forms complex compounds with a number of organic compounds containing a hydroxyl group [13], which is also observed in this system.

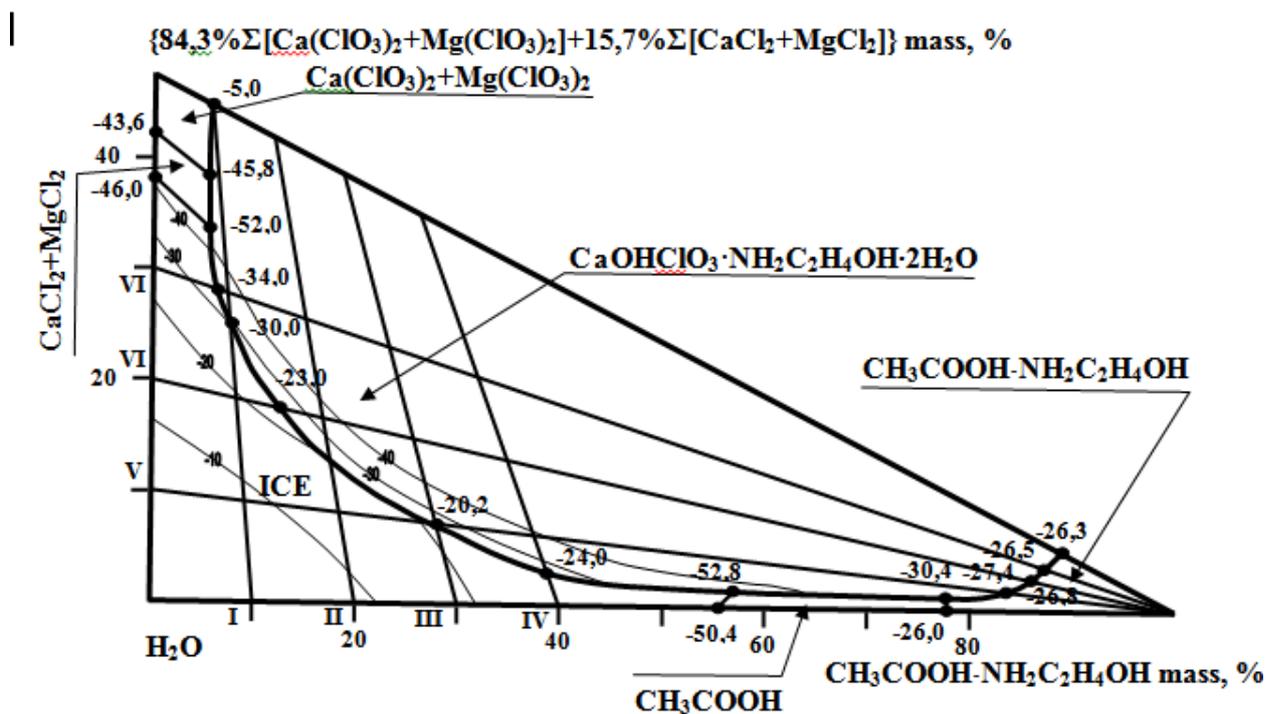


Fig. 3. Polythermal solubility diagram of the system $\{84,3\%\Sigma[\text{Ca}(\text{ClO}_3)_2+\text{Mg}(\text{ClO}_3)_2]+15,7\%\Sigma[\text{CaCl}_2+\text{MgCl}_2]\} - \text{CH}_3\text{COOH}\cdot\text{NH}_2\text{C}_2\text{H}_4\text{OH} - \text{H}_2\text{O}$

The compound formed in the studied system is isolated in crystalline form and identified by chemical, x-ray phase and thermal analysis methods.

According to chemical analysis for $\text{CaOHClO}_3\cdot\text{NH}_2\text{C}_2\text{H}_4\text{OH}\cdot 2\text{H}_2\text{O}$:

Found wt.%: C = 10,2; H = 5,10; N = 5,92; Ca = 16,95; ClO_3 = 35,41; H_2O = 15,11.

Calculated mass%: C = 10,105; H = 5,053; N = 5,89; Ca = 16,84; ClO_3 = 35,158; H_2O = 15,158.

The formation of $\text{CaOHClO}_3 \cdot \text{NH}_2\text{C}_2\text{H}_4\text{OH} \cdot 2\text{H}_2\text{O}$ is confirmed by X-ray phase analysis. Comparison of diffractograms and the corresponding values of the interplanar spacings of the compound and its components showed that this compound is individual, with its inherent structure of the crystal lattice (Fig.4.).

Table. Double and triple nodal points of the system $\{84,3\% \sum[\text{Ca}(\text{ClO}_3)_2 + \text{Mg}(\text{ClO}_3)_2] + 15,7\% \sum[\text{CaCl}_2 + \text{MgCl}_2]\} - \text{CH}_3\text{COOH} \cdot \text{NH}_2\text{C}_2\text{H}_4\text{OH} - \text{H}_2\text{O}$

Liquidphase, %			$t_{cr},$ °C	Solidphase
$\{84,3\% \sum[\text{Ca}(\text{ClO}_3)_2 + \text{Mg}(\text{ClO}_3)_2] + 15,7\% \sum[\text{CaCl}_2 + \text{MgCl}_2]\}$	$\text{CH}_3\text{COOH} \cdot \text{NH}_2\text{C}_2\text{H}_4\text{OH}$	H_2O		
44,8	6,0	49,2	-5,0	$\text{Ca}(\text{ClO}_3)_2 \cdot \text{Mg}(\text{ClO}_3)_2 + \text{CaOHClO}_3 \cdot 2\text{NH}_2\text{C}_2\text{H}_4\text{OH} \cdot 2\text{H}_2\text{O}$
38,4	5,4	56,2	-45,8	$\text{Ca}(\text{ClO}_3)_2 \cdot \text{Mg}(\text{ClO}_3)_2 + \text{CaCl}_2 \cdot \text{MgCl}_2 + \text{CaOHClO}_3 \cdot 2\text{NH}_2\text{C}_2\text{H}_4\text{OH} \cdot 2\text{H}_2\text{O}$
33,7	5,5	60,8	-52,0	Ice + $\text{CaOHClO}_3 \cdot 2\text{NH}_2\text{C}_2\text{H}_4\text{OH} \cdot 2\text{H}_2\text{O}$
28,0	6,0	66,0	-34,0	То же
25,0	7,9	67,1	-30,0	-/-
17,7	12,3	70,0	-23,0	-/-
7,4	27,9	64,7	-20,2	-/-
3,0	38,9	58,1	-24,0	-/-
1,7	57,0	41,3	-52,8	Ice + $\text{CaOHClO}_3 \cdot 2\text{NH}_2\text{C}_2\text{H}_4\text{OH} \cdot 2\text{H}_2\text{O} + \text{CH}_3\text{COOH}$
1,0	77,8	21,2	-30,4	$\text{CaOHClO}_3 \cdot 2\text{NH}_2\text{C}_2\text{H}_4\text{OH} \cdot 2\text{H}_2\text{O} + \text{CH}_3\text{COOH} + \text{CH}_3\text{COOH} \cdot \text{NH}_2\text{C}_2\text{H}_4\text{OH}$
1,8	83,9	14,3	-27,4	$\text{CaOHClO}_3 \cdot 2\text{NH}_2\text{C}_2\text{H}_4\text{OH} \cdot 2\text{H}_2\text{O} + \text{CH}_3\text{COOH} \cdot \text{NH}_2\text{C}_2\text{H}_4\text{OH}$
3,0	86,0	11,0	-26,8	То же
3,9	87,3	8,8	-26,5	-/-
5,7	89,0	5,3	-26,3	-/-
-	78,0	22,0	-26,0	$\text{CH}_3\text{COOH} + \text{CH}_3\text{COOH} \cdot \text{NH}_2\text{C}_2\text{H}_4\text{OH}$
-	55,6	44,4	-50,4	Ice + CH_3COOH
42,2	-	57,8	-43,6	$\text{Ca}(\text{ClO}_3)_2 \cdot \text{Mg}(\text{ClO}_3)_2 + \text{CaCl}_2 \cdot \text{MgCl}_2$
38,0	-	62,0	-46,0	Ice + $\text{CaCl}_2 \cdot \text{MgCl}_2$

Three endothermic effects at 170, 225, 282 and three exothermic effects at 310, 545, and 690°C were found on the heating curve of the $\text{CaOHClO}_3 \cdot \text{NH}_2\text{C}_2\text{H}_4\text{OH} \cdot 2\text{H}_2\text{O}$ sample. The nature of the endothermic effects is due to the removal of water and the onset of decomposition of the complex. Intensive exothermic effect at 310°C occurs with a strong

explosion of the product. This process proceeds in the temperature range of 300-320°C. The nature of the two subsequent exothermic effects is due to the completion of the decomposition of the thermolysis of the product. In composition, the final decomposition product is calcium oxide (Fig.5.).

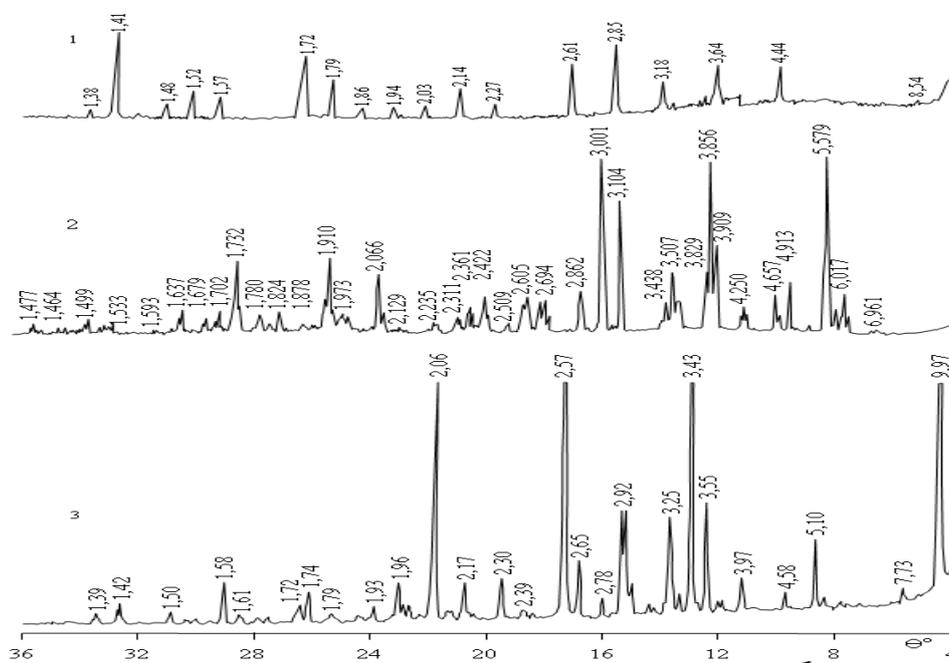


Fig. 4. Radiograph of $\{84,3\% \sum [\text{Ca}(\text{ClO}_3)_2 + \text{Mg}(\text{ClO}_3)_2] + 15,7\% \sum [\text{CaCl}_2 + \text{MgCl}_2]\}$ (1), $\text{CH}_3\text{COOH} \cdot \text{NH}_2\text{C}_2\text{H}_4\text{OH}$ (2) and compounds $\text{CaOHClO}_3 \cdot \text{NH}_2\text{C}_2\text{H}_4\text{OH} \cdot 2\text{H}_2\text{O}$

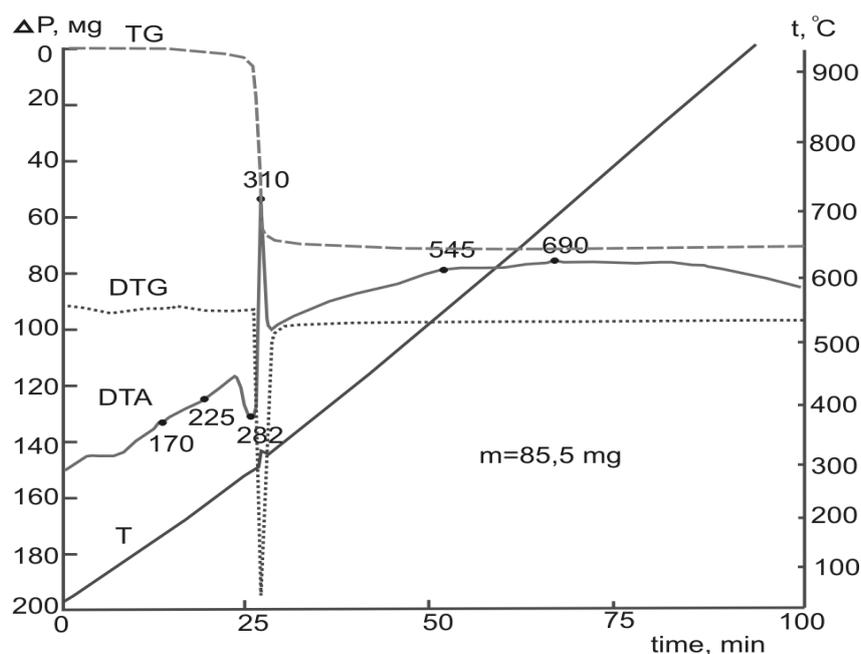


Fig.5. Thermogravimetric of $\text{CaOHClO}_3 \cdot \text{NH}_2\text{C}_2\text{H}_4\text{OH} \cdot 2\text{H}_2\text{O}$

4. CONCLUSION

Thus, the obtained data on the solubility of the components in the studied system by the visual polythermal method [22,52%Ca(ClO₃)₂+17,51% Mg(ClO₃)₂+4,33%CaCl₂+3,12%MgCl₂+52,52%H₂O] - CaOHClO₃·NH₂C₂H₄OH - H₂O can serve as a scientific basis for the preparation of a new complex-acting preparation based on calcium chlorate-magnesium defoliant and monoethanolammonium acetate. The formation of the compound CaOHClO₃·NH₂C₂H₄OH·2H₂O was established in the system. The compound is identified by chemical, thermal and x-ray phase analysis methods. To preserve the physiological activity of the synthesized preparation during defoliation, the necessary interval of the starting components should not exceed 39,2 – 39,7% chlorate, 0,72 – 2,00% monoethanolammonium acetate.

5. REFERENCES

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