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The Study of the Physic-Chemical Interaction of Components in the Calcium Chlorate - Urea Phosphate - Water System

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Abstract: *More than 20 million tons are annually produced in the world cotton fiber from plants occupying 30 million hectares of crops. The main factor in growing a high and high-quality crop yield is the use of chemicals: mineral fertilizers, stimulants, pesticides, as well as defoliants and desiccants. One of the important and topical issues in the field of chemistry of defoliant technology is the problem of obtaining complex defoliants containing nutritional and ethylene-producing components, in which good defoliation effects can be obtained.*

Keywords: *defoliant technology, monoammonium phosphate, Calcium Chlorate, urea phosphate.*

Introduction

In order to clarify the interaction of the initial components in their joint presence, the solubility of the calcium chlorate – urea phosphate – water system was studied by the visual-polythermal method [3] in a wide temperature and concentration range. Calcium chlorate and urea phosphate were used for the research. Urea phosphate was synthesized by the interaction of phosphoric acid with urea at a molar ratio of 1:1. Calcium chlorate was obtained by an exchange reaction between calcium chloride and sodium chlorate in an acetone medium [4,7].

The main part

The binary urea phosphate-water system that makes up this system is considered in [5]. The results obtained are in good agreement with the known ones. The $Ca(ClO_3)_2 – CO(NH_2)_2{\cdot}H_3PO_4 – H_2O$ system has been studied by ten internal sections from –40.3 to 70 °C. On its polythermal solubility diagram, the fields of crystallization of ice, urea phosphate, six-, four-, two aqueous calcium chlorate and a compound of the composition $Ca(H_2PO_4){\cdot}(ClO_3){\cdot}CO(NH_2)_2$ are delimited (Figure 3.21).

Four triple points of the system have been established, for which crystallization temperatures and compositions of equilibrium solutions have been determined[8]. System projections are shown in Fig.2.

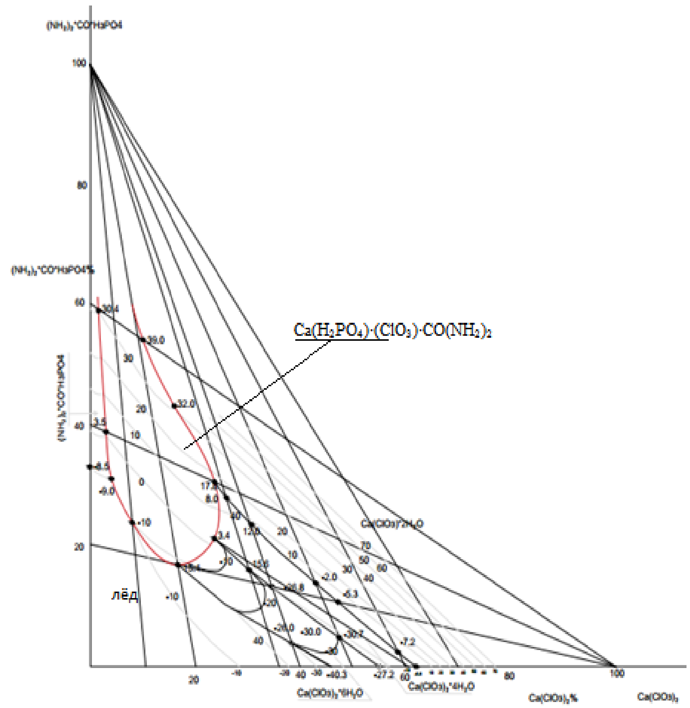


Figure 1. Polythermal diagram of the solubility of the $Ca(ClO_3)_2$– $CO(NH_2)_2 \cdot H_3PO_4$ – H_2O system

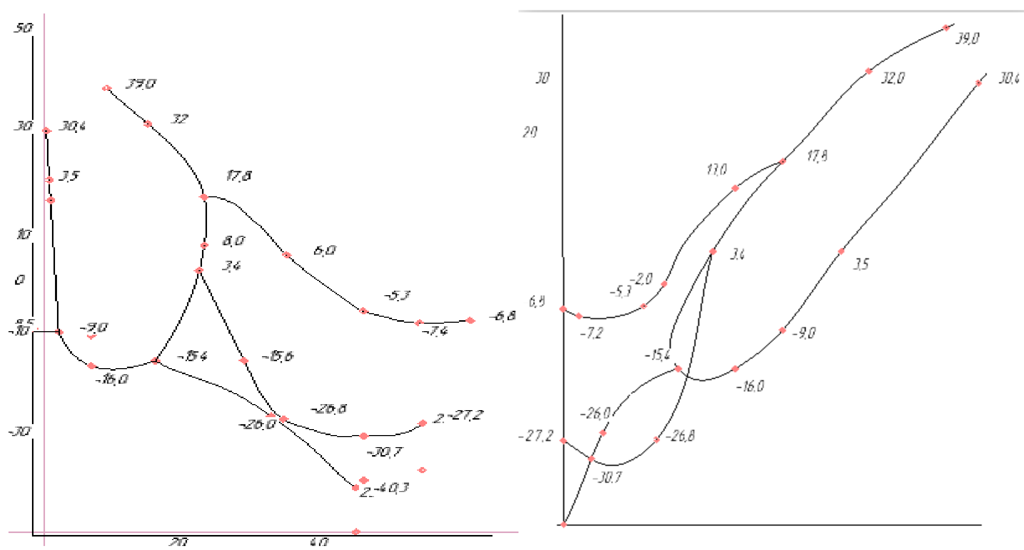


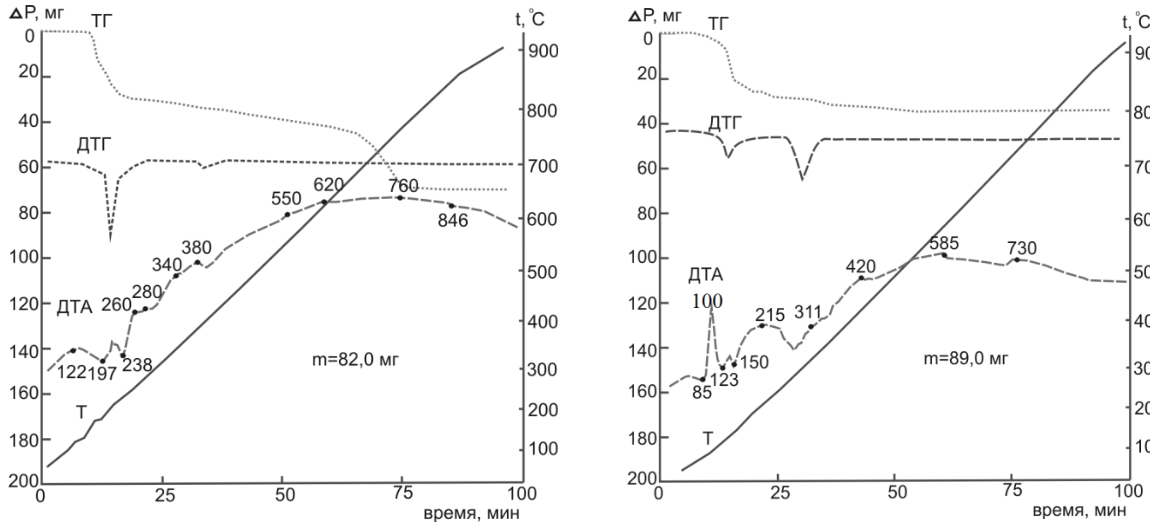
Figure 2. Polythermal projections of the $Ca(ClO_3)_2$–$CO(NH_2)_2 \cdot H_3PO_4$–H_2O system

It can be seen from the solubility diagrams of the system that a compound of the composition $Ca(H_2PO_4)(ClO_3) \cdot CO(NH_2)_2$ is formed in it as a new phase. It occupies a significant part of the liquidus surface of the solubility diagram, which indicates its lower solubility relative to other components of the systems.

Table 1. Double and triple points of the $Ca(ClO_3)_2$– $CO(NH_2)_2{\cdot}H_3PO_4$ – H_2O system

Liquid phase composition,%			Temp-ra crystal, ^0C	Solid phase
$Ca(ClO_3)_2$	$CO(NH_2)_2{\cdot}H_3PO_4$	H_2O		
62,0	-	38,0	-6,8	$Ca(ClO_3)_2{\cdot}4H_2O$+$Ca(ClO_3)_2{\cdot}$ 2 H_2O
55,0	4,7	40,3	-7,4	$Ca(ClO_3)_2{\cdot}4H_2O$+ $Ca(ClO_3)_2{\cdot}$ 2 H_2O
47,0	10,8	42,2	-5,3	$Ca(ClO_3)_2{\cdot}4H_2O$+ $Ca(ClO_3)_2{\cdot}$ 2 H_2O
36,0	19,2	44,8	6,0	$Ca(ClO_3)_2{\cdot}4H_2O$+ $Ca(ClO_3)_2{\cdot}$ 2 H_2O
25,9	28,2	45,9	16,9	$Ca(ClO_3)_2{\cdot}4H_2O$+ $Ca(ClO_3)_2{\cdot}$ 2 H_2O
24,0	30,5	45,5	17,8	$Ca(ClO_3)_2{\cdot}4H_2O$+ $Ca(ClO_3)_2{\cdot}$ 2 H_2O + $Ca(H_2PO_4){\cdot}(ClO_3){\cdot}CO(NH_2)_2$
16,0	43,8	40,2	32,0	$Ca(ClO_3)_2{\cdot}$ 2 H_2O + $Ca(H_2PO_4){\cdot}(ClO_3){\cdot}CO(NH_2)_2$
10,0	54,0	36,0	39,0	$Ca(ClO_3)_2{\cdot}$ 2 H_2O + $Ca(H_2PO_4){\cdot}(ClO_3){\cdot}CO(NH_2)_2$
55,0	-	45,0	-27,2	$Ca(ClO_3)_2{\cdot}4H_2O$+$Ca(ClO_3)_2{\cdot}6H_2O$
47,2	5,2	47,6	-30,7	$Ca(ClO_3)_2{\cdot}6H_2O$+$Ca(ClO_3)_2{\cdot}4H_2O$
35,4	13,0	51,6	-26,8	$Ca(ClO_3)_2{\cdot}6H_2O$+$Ca(ClO_3)_2{\cdot}4H_2O$
30,0	17,0	53,0	-15,6	$Ca(ClO_3)_2{\cdot}6H_2O$+$Ca(ClO_3)_2{\cdot}4H_2O$
23,8	21,2	55,0	3,4	$Ca(ClO_3)_2{\cdot}6H_2O$+$Ca(ClO_3)_2{\cdot}4H_2O$+ $Ca(H_2PO_4){\cdot}(ClO_3){\cdot}CO(NH_2)_2$
24,2	22,8	53,0	8,0	$Ca(ClO_3)_2{\cdot}4H_2O$+ $Ca(H_2PO_4){\cdot}(ClO_3){\cdot}CO(NH_2)_2$
46,0	-	54,0	-40,3	Ice + $Ca(ClO_3)_2{\cdot}6H_2O$
33,8	6,4	59,8	-26,0	Ice + $Ca(ClO_3)_2{\cdot}6H_2O$
16,8	16,5	66,7	-15,4	Ice + $Ca(ClO_3)_2{\cdot}6H_2O$+ $Ca(H_2PO_4){\cdot}(ClO_3){\cdot}CO(NH_2)_2$
8,0	24,0	68,0	-10,6	Ice + $Ca(H_2PO_4){\cdot}(ClO_3){\cdot}CO(NH_2)_2$
4,5	28,4	67,1	-8,7	Ice + $Ca(H_2PO_4){\cdot}(ClO_3){\cdot}CO(NH_2)_2$
3,5	32,0	64,5	-9,0	Ice + $Ca(H_2PO_4){\cdot}(ClO_3){\cdot}CO(NH_2)_2$+ $CO(NH_2)_2{\cdot}H_3PO_4$
3,2	38,5	58,3	3,5	$Ca(H_2PO_4){\cdot}(ClO_3){\cdot}CO(NH_2)_2$+ $CO(NH_2)_2{\cdot}H_3PO_4$
2,4	50,5	47,1	21,0	$Ca(H_2PO_4){\cdot}(ClO_3){\cdot}CO(NH_2)_2$+ $CO(NH_2)_2{\cdot}H_3PO_4$
1,9	59,0	39,1	30,4	$Ca(H_2PO_4){\cdot}(ClO_3){\cdot}CO(NH_2)_2$+ $CO(NH_2)_2{\cdot}H_3PO_4$
-	33,0	67,0	-8,5	Ice + $CO(NH_2)_2{\cdot}H_3PO_4$

The urea phosphate heating curve (Fig. 1) shows four endothermic effects at 122, 197, 238, 846 °C and seven exothermic effects at 260, 280, 340, 380, 550, 620 and 760 °C. The total weight loss in the temperature range 60-900 °C according to the derivatogram curve is 89.63%. On the differential heating curve, the melting process corresponds to an endothermic effect in the range of 110-130 °C. With further heating, decomposition of the substance is observed, which is accompanied by the release of heat. In the range 260-760 °C, phosphoric acid is neutralized with ammonia with the formation of monoammonium phosphate, which then goes into pyro and metaphosphates of ammonium.



(1) (2)

Figure 3. Derivatograms: CO(NH2)2·H3PO4 (1), Ca(H2PO4)·(ClO3)·CO(NH2)2 (2)

On the heating curve of a compound of the composition $Ca(H_2PO_4)\cdot(ClO_3)\cdot CO(NH_2)_2$, the following exothermic effects are observed at 100, 215, 311, 420, 585 and 730 °C, as well as endothermic effects at 85, 123, 150 °C. Thermal effects at 85-100 °C correspond to the release of the products of the chlorate fragment, in which the weight loss is 28-30%. Effects at 215-311°C is characteristic of the decomposition of bound carbamide with the release of ammonia and carbon dioxide. With further heating, a stepwise decomposition of $Ca(H_2PO_4)_2$ and the combustion of thermolysis products occur, as evidenced by thermal effects above 420 °C. The total weight loss along the TG curve is 43.26%. To establish the place and methods of coordination of the molecules of the isolated compound, its IR spectra were studied (Fig. 3.1). The IR spectra of carbamide phosphate and calcium chlorate contain all their inherent valence and deformation vibrations, which are consistent with the literature data [6].

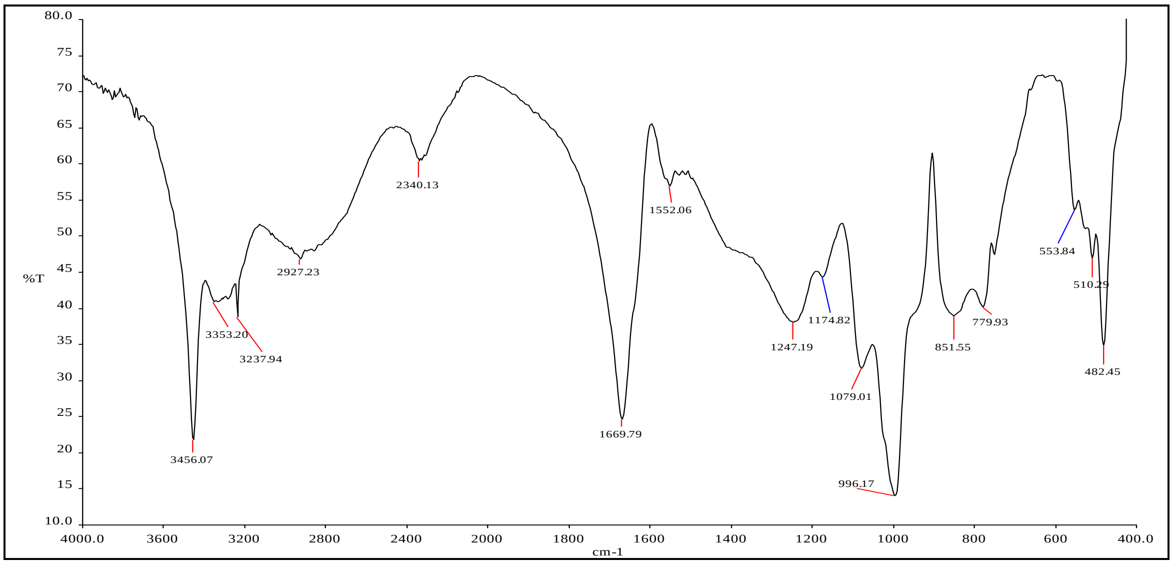
There are several absorption bands in the frequency range of the valence oscillations of the P-H and NH_2 bond. The high-frequency oscillations in the spectrum of urea phosphate 3456-3238 cm^{-1} are attributed to the valence vibrations of the NH_2 group bound by hydrogen bonds, and the frequency with a maximum of 2340 cm^{-1} to the valence vibrations of P-H bonds. The band 1669-1552 cm^{-1} is caused by deformation fluctuations of the N-H bond. The band 1174-996 cm^{-1} belongs to the valence symmetric and asymmetric vibrations of $H_2PO_4^-$.

The pyramidal ClO_3^- ion has four fundamental oscillations active in the IR spectrum [3]. Symmetric valence oscillations of ClO_3^- ion on the IR spectrum of the initial two-water calcium chlorate were detected by us in the frequency range of 985-955 cm^{-1}, and asymmetric valence oscillations of this ion in the region of 1025 cm^{-1}. The deformation vibrations of the ClO_3^- ion correspond to frequencies of 630.498 cm^{-1}. The absorption bands observed in the frequency range 3420, 3190 and 1645 cm^{-1} are caused by asymmetric, symmetric valence and deformation vibrations of crystallization water.

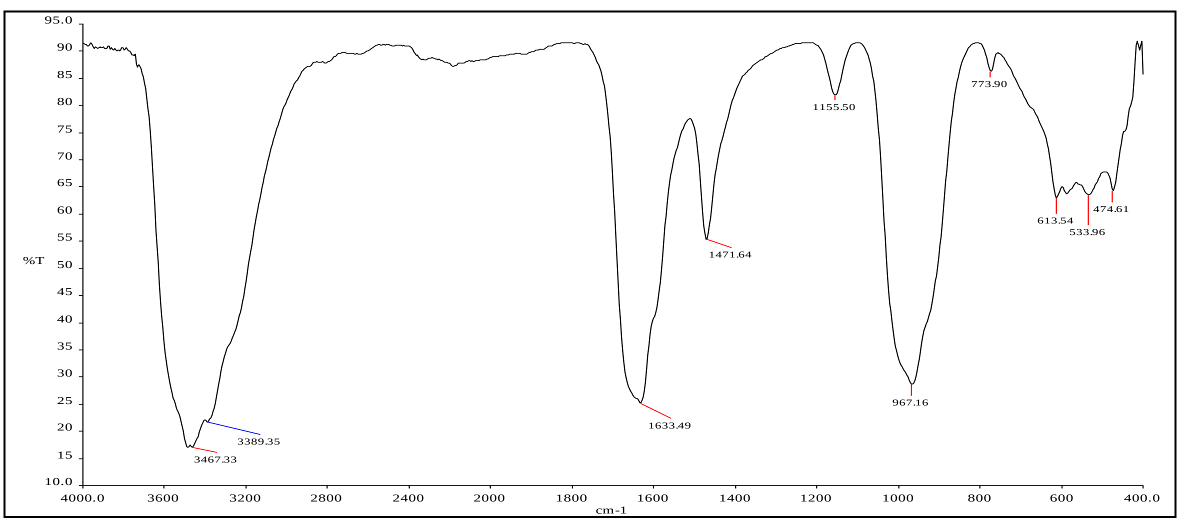
The IR spectrum of sodium dicarbamidochlorate is characterized by the presence of $\gamma_s(NH_2^+)$ and $\gamma_{as}(NH_2^+)$ at 3389 and 3467 cm^{-1}. The bands at 1633 and 773 cm^{-1} correspond to the valence and deformation vibrations of the CO group. Bending vibrations of the NH_2 group are observed at 1471 cm^{-1}. The bands at 1155, 967, 613-474 cm^{-1} correspond to the valence asymmetric, symmetric and deformation vibrations of the (ClO_3^-) group [3-10].

The IR spectrum of the compound shows absorption bands at 2324, 1635, 1466, 1239, 1152, 1091, 970, 862-619, 567 and 491 cm^{-1}. The bands at 1635 and 567 cm^{-1} correspond to ν(CO) and δ(CO), and the bands at 1466 cm^{-1} and 670-619 cm^{-1} correspond to the vibrations of the δ (NH_2 $^{+}$) group. The band at 1091 cm^{-1} is assigned to γ_{as}($H_2PO_4^-$). To valence symmetric, asymmetric and deformational vibrations of ClO_3^- include bands at 970, 1152 and 491 cm^{-1}. Compared with the initial substance, the disappearance of bands at 3456-2927, 553-510, 851-779 см$^{-1}$ corresponding to ν(NH), ν(P=O) is observed, and the appearance of new ones at 862-619, 567 cm^{-1}. In the spectrum of the compound, there is a shift of the bands ν(P-H) by 16 cm^{-1} to the low-frequency region, and deformation vibrations δ (NH_2) in the frequency range of 1635.38 cm -1 and 1466 cm-1 by 34 and 86 cm-1. The vibrations of δ (P-OH) and δ (ClO_3) in the spectrum of the compound were assigned absorption bands at 1239.88 and 491.84 cm^{-1}.

The bands at 1152.44, 1091.80, and 862.83 cm^{-1} correspond to γ_{as}($H_2PO_4^-$), γ_s($H_2PO_4^-$), γ(P=O), which are shifted to the low-frequency region by 18 and 26 cm^{-1} respectively. Changes are observed in the absorption band δ(ClO_3), which is shifted by 25.84 cm^{-1} into the long-wavelength region compared to the IR spectra of calcium chlorate.



(1)



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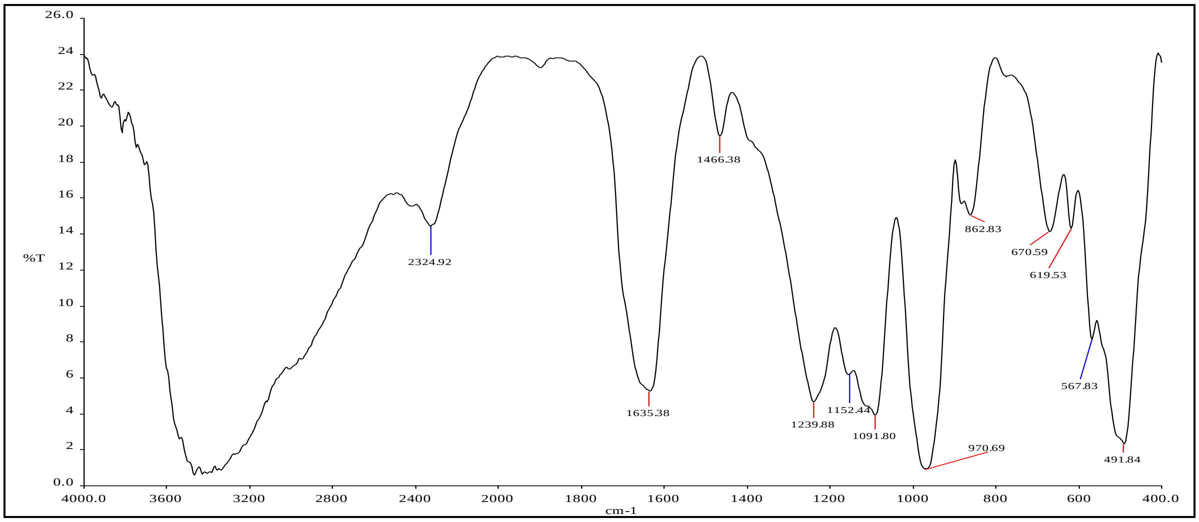

(3)

Figure 4. IR spectra: $CO(NH_2)_2 \cdot H_3PO_4$ (1), $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$ (2), $Ca(H_2PO_4)(ClO_3) \cdot CO(NH_2)_2$ (3)

Thus, in the IR spectrum of the compound relative to the spectra of the initial components, there are shifts of the bands characterizing the P-O-H, CO, NH_2^+ and ClO_3^- groups, which apparently indicates the participation of these groups in the formation of coordination bonds of the complex.

Conclusion

Analyzing the polythermal diagrams of the solubility of the systems under consideration, it should be noted that the components of the systems have a mutual salting-out and salting-out effect on each other. We have established the temperature and concentration limits for the formation of the initial components of the studied systems and the resulting new complex compound. Data on the physicochemical study of the interaction of components in systems with the participation of calcium chlorate, urea phosphate serve as the basis for further development of technology for the production of a new calcium chlorate-containing complex-acting defoliant, as well as reference data for scientists (postgraduate doctoral students) in the field of physical and chemical analysis, graphical analysis according to systems, and university students performing scientific research.

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