Studies on Process of Obtaining the Fertilizers based on Ammonium Phosphates with Addition of Boric Acid

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The paper presents studies about the process of obtaining the fertilizers based on ammonium phosphates $(NH_4)_2HPO_4$ and $NH_4H_2PO_4$ with boron added as micronutrient. As boron source was used boric acid, which has been introduced into the neutralization mass at various NH_3:H_3PO_4 molar ratio, in order to obtain thermal stable compounds, with a minimum loss of nutritional elements (N, P). The variation of pH, considered the process control parameter, as a function of NH_3:H_3PO_4 molar ratio was recorded during the neutralization.Specific analyses has been used in order to determine phosphorus, ammonia nitrogen and boron content in the obtained fertilizers. The thermal behaviour of the fertilizers was studied using TG and DTG. The lowest total mass loss was observed at a 1.5 NH_3:H_3PO_4 molar ratio.

Keywords: ammonium phosphates, boric acid, complex fertilizers, micronutrient

Recent research [1,2] showed that boron is involved in three main processes of plants normal growth: keeping cell wall structure, maintaining membrane function and supporting metabolic activities. Boric acid reacts with chemical compounds containing multiple hydroxil groups (polyols) with an important role in boron uptake and fixation in plants [3, 4].

Boron is essential for fruit set and seed development. Boron increases the content of sugar in fruit, sugar beet and melon, due to its role in translocation of sugars and starches. Both the quantity and the quality of the crops are improved by boron application. Boron deficiences occur over a much wider range of soil and crops than do deficiences of any other micronutrient. Normal plant growth requires a continuos supply of boron. Once boron is taken up in plants, it is not translocated from old to new tissues. This explains why boron deficiency symptoms often start with the youngest growing tissues. In boron deficient plants, growing tips may not develop properly, or they may die back while the older leaves remain green [5-12].

The object of the present work is the obtaining of fertilizers based on ammonium phosphates with boron. Boron has been added as solid boric acid at various ammonia/phosphoric acid molar ratio. The optimum conditions of obtaining thermal stable fertilizers of this class, with a minimum nitrogen loss during the technological process, have been established.

Experimental part

Fertilizers based on ammonium phosphate with boron as micronutrient were obtained by neutralization of defined volumes (50 mL) of phosphoric acid 43.5% P_2O_5 (Merck, minimum purity 99%) with 25% ammonia solution, under continuos stirring at room temperature, up to *p*H ~ 8.8. The solid boric acid was introduced into the reaction mass, in different stages of the neutralization, in a well defined quantity **(**1g boron in 100 g fertilizer).

During the neutralization of phosphoric acid with ammonia, and addition of boric acid, it was determined the dependence of the reaction mass *p*H on the molar ratio NH_3:H_3PO_4. The *p*H measurements were carried out by mean of a Denver instruments 250 pH-meter.

The obtained products, dried at 60°C, have been subjected to a complex study: chemical analysis and thermogravimetric analysis.

P_2O_5 content has been determined according to a gravimetric procedure [13], using a Denver analytical balance, with a maximum capacity of 110 g and a sensibility of 0.1 mg.

The ammonia nitrogen has been spectrophotometrically determined using the Nessler reagent (λ = 425nm) [14]. The boron content has been spectrophotometrically determined using the carminic method (λ = 630 nm) [15,16]. The absorbance of the solutions was measured with a Cary 50 spectrophotometer at 425nm.

The TG and DTG thermal curves have been registered using a NETZSCH TG 209 computer controlled system, with a K (Ni-Cr-Ni) thermocouple. The experiments have been performed in nitrogen medium, in controlled dynamic atmosphere (5mL/min flow rate), in the range of temperature 20-200°C, and using a 1K/min heating rate. Al_2O_3 crucibles were used.

Results and discussions

The process of obtaining ammonium phosphates take place according to the following main reactions [17-20]:

$$H_3PO_4[l] + NH_3[aq] = NH_4H_2PO_4[s] \quad (1)$$

$$H_3PO_4[s] + 2\,NH_3[aq] = (NH_4)_2HPO_4[s] \quad (2)$$

$$NH_4H_2PO_4\,[s] + NH_3[aq] = (NH_4)_2HPO_4[s] \quad (3)$$

The dependence of the reactive mixture pH on the NH_3:H_3PO_4 molar ratio

The experimental data concerning the dependence of the reaction mass *p*H on the NH_3: H_3PO_4 ratio is presented in figure 1.

The *p*H variation of the reaction mass with the NH_3:H_3PO_4 molar ratio was studied for the obtained fertilizers in comparison with the same variation for the fertilizer whithout boron. The curves representing the *p*H variation of the reaction mass versus the NH_3: H_3PO_4 molar ratio present two inflection points, which correspond to the end of the formation of monoammonium phosphate, respectively diammonium phosphate. The *p*H, respectively

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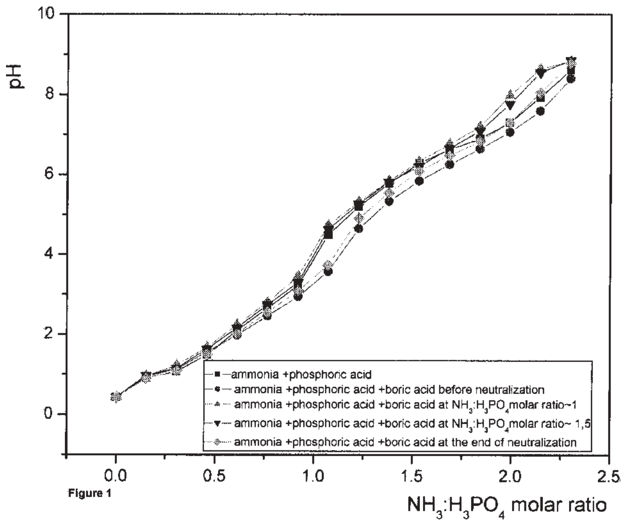


Fig. 1. The dependence of the reactive mixture *p*H on the NH_3:H_3PO_4 ratio at the neutralization of phosphoric acid with ammonia and boric acid addition

NH_3:H_3PO_4 molar ratio values, corresponding to the inflexion points of the curves, are presented in table1.

One can observe that regardless the NH_3:H_3PO_4 molar ratio at which boric acid was added, both the pH and the NH_3:H_3PO_4 molar ratio corresponding to the first inflection point have about the same value. The *p*H and the NH_3:H_3PO_4 molar ratio values corresponding to the second inflection point have also close values, excepting the product obtained by the addition of boric acid into the reaction mass at the NH_3: H_3PO_4 molar ratio ~ 1, when the *p*H has a slightly higher value.

There is a well defined dependence between the pH of the reaction mixture, and the NH_3:H_3PO_4 molar ratio, specific to each product. The shape of the curves is generally similar for all the obtained products.The inflections of the curves appear in limited *p*H ranges, and are specific to each product. The *p*H values at the same NH_3:H_3PO_4 molar ratio vary in a limited field, depending on the way boric acid is added into the process.

One can consider that the control parameter of the obtaining process of complex fertilizers with boron, based on ammonium phosphates, is the *p*H of the reaction mixture, which allows to control in optimum conditions the neutralization of phosphoric acid with ammonia and boric acid addition.

The experimental data regarding the chemical composition of the obtained products are presented in table 2.

The experimental data show that regardless the NH_3:H_3PO_4 molar ratio at which boric acid was added, the massic ratio N:P_2O_5 belongs to the range 0.37-0.38, which shows the obtaining of a $(NH_4)_2HPO_4$ and $NH_4H_2PO_4$ mixture, concordantly to some data from literature [17-20]. The boron concentration is in the limits of the initial chosen concentration.

Studies on the thermal behaviour of the neutralization products

In order to determine the thermal stability of the products with minimum ammonia loss during the process thermoanalytical methods (TG and DTG) were used. One can observe (fig. 2) the following: the neutralization product of phosphoric acid with ammonia (I) is stable up to 65°C. The mass loss takes place in two stages. In the first stage, between 65 and 144°C the product undergoes a mass loss

Table1

THE INFLECTION POINTS OF THE *p*H VARIATION WITH THE NH_3:H_3PO_4 RATIO AT THE NEUTRALIZATION OF PHOSPHORIC ACID WITH AMMONIA

Product	Inflection point 1		Inflection point 2	
	Molar ratio NH_3:H_3PO_4	pH	Molar ratio NH_3:H_3PO_4	pH
Reaction mass without boron (I)	1.0	3.91	1.8	6.94
Reaction mass with boric acid added at the beginning of neutralization(II)	1.1	3.92	1.9	6.77
Reaction mass with boric acid added at NH_3:H_3PO_4 molar ratio~1 (III)	1.0	3.93	1.9	7.61
Reaction mass with boric acid added at NH_3:H_3PO_4 molar ratio~1,5 (IV)	1.0	3.98	1.9	7.32
Reaction mass with boric acid added at the end of neutralization (V)	1.0	4.0	1.8	6.86

Table 2

THE CHEMICAL COMPOSITION OF THE NEUTRALIZATION

Product	P_2O_5, %	N-NH_4, %	Massic ratio N/P_2O_5	Boron, %
I	51.3	19	0.37	-
II	51.5	19.8	0.38	0.8
III	51.4	19.1	0.37	1.1
IV	51.1	19.1	0.37	1
V	51	18.7	0.37	1

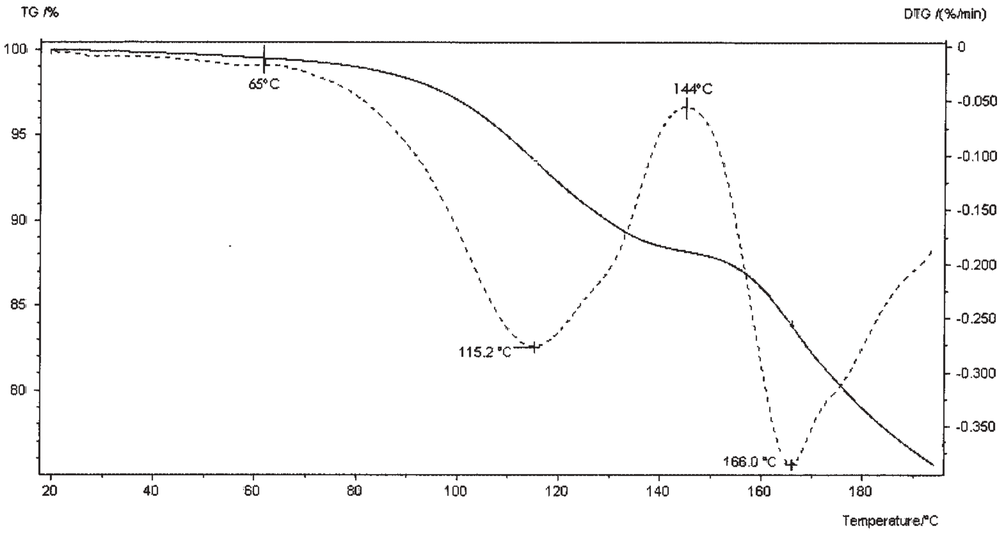


Fig. 2. TG and DTG curves of the neutralization product of phosphoric acid with ammonia (I)

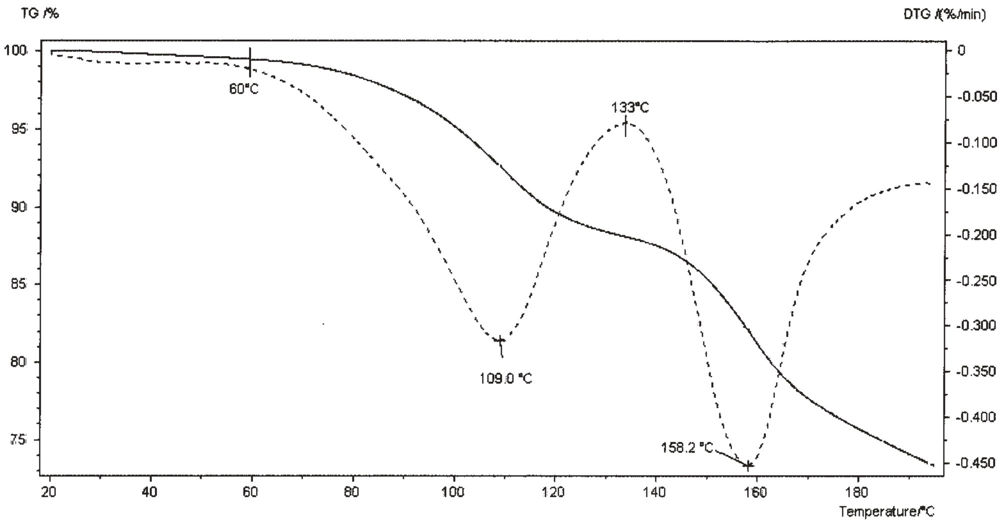


Fig. 3. TG and DTG curves of the neutralization product of phosphoric acid with ammonia with boric acid added at the beginning of neutralization (II)

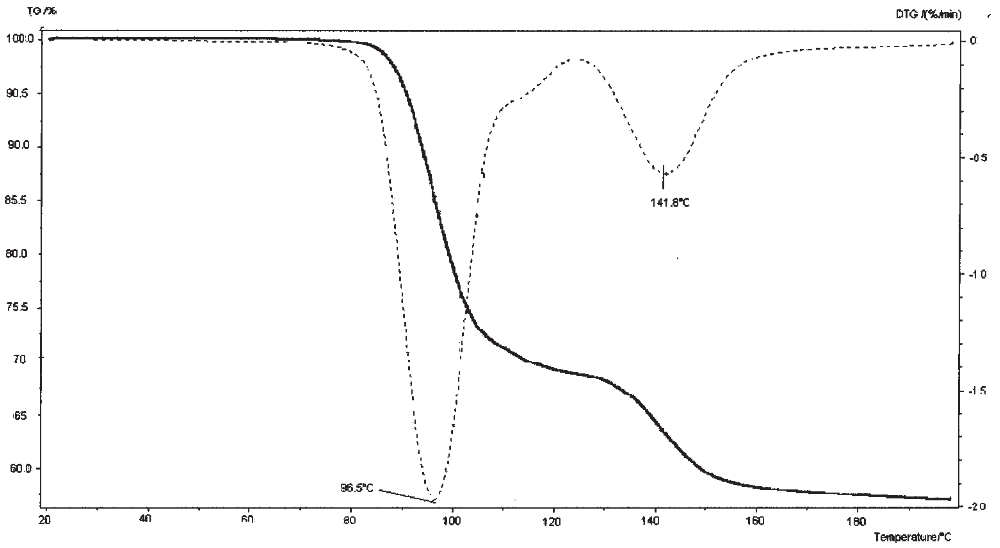


Fig. 4. TG and DTG curves of boric acid

of 11.2% with a maximum rate at 115°C. This loss is close to the theoretical one, according to the reaction:

$$(NH_4)_2HPO_4 \rightarrow NH_4H_2PO_4 + NH_3 \qquad (4)$$

In the second thermal decomposition stage (144-190°C), the mass loss is 12.9% with a maximum rate at 166°C, corresponding to the complex decomposition of monoammonium phosphate.

The analysis of TG and DTG curves of the product II (fig. 3) shows that a mass loss of 11.3%, with a maximum rate at 109°C takes place in the temperature range of 60°C - 133°C, due to the loss of a mole of ammonia from diammonium phosphate (reaction 4). In this temperature range boric acid also begins to lose water (reaction 5), as shown in figure 4.

$$H_3BO_3 \rightarrow HBO_2 + H_2O \qquad (5)$$

In the temperature range 133°-190°C the mass loss is 13.5%, with a maximum rate at 158°C, when complex thermal decomposition of monoammonium phosphate is combined with the further loss of water from the boric acid.

From the figures 3 and 5-7 one can observe that the TG curves have the same shape as the curve in figure 2, with

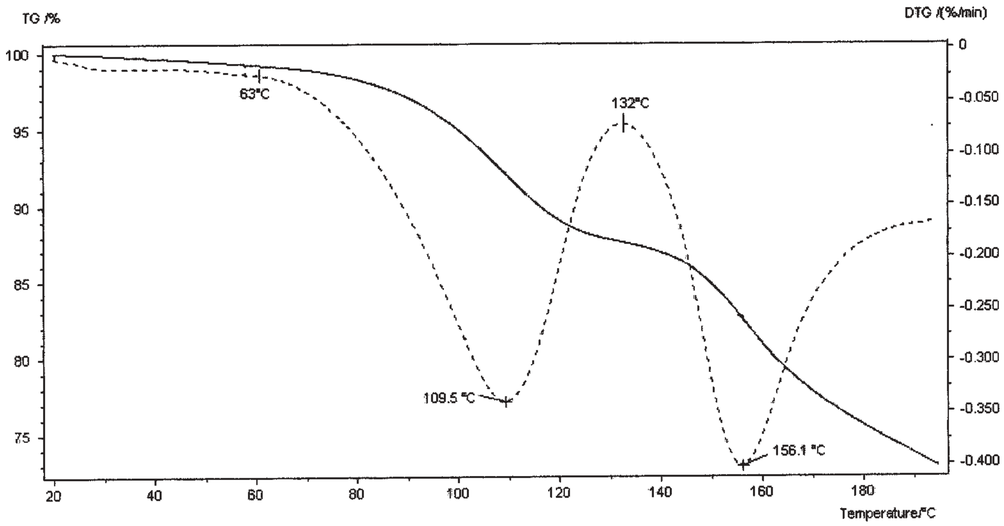
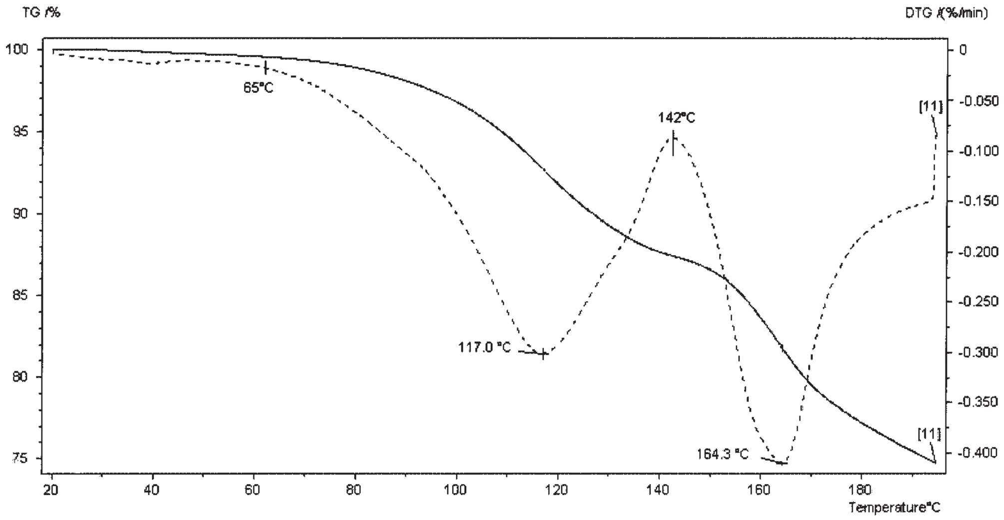


Fig. 5. TG and DTG curves of the neutralization product of phosphoric acid with ammonia with boric acid added at the NH_3:H_3PO_4 molar ratio ~1.0 (III)



Figu. 6. TG and DTG curves of the neutralization product of phosphoric acid with ammonia with boric acid added at the NH_3:H_3PO_4 molar ratio ~ 1.5 (IV)

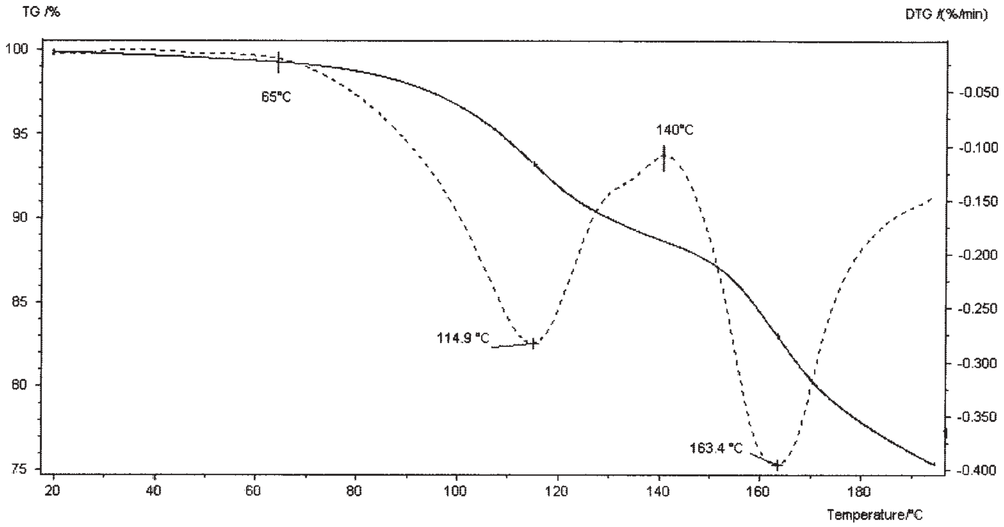


Fig. 7 . TG and DTG curves of the neutralization product of phosphoric acid with ammonia with boric acid added at the end of neutralization(V).

Table 3
MASS LOSS AT THERMAL DECOMPOSITION OF THE NEUTRALIZATION PRODUCTS (I-V)

Product	Stage I			Stage II			Total
	Temp. range/°C	Max. rate temp /°C	Mass loss/%	Temp. range/°C	Max. rate temp /°C	Mass loss/%	mass loss/%
(I)	65 - 144	115.2	11.18	144-190	166	11.96	23.14
(II)	60 - 133	109	11.30	133-190	158.2	14.05	25.35
(III)	63 - 132	109.5	11.49	132-190	156.1	13.89	25.38
(IV)	65 - 142	117	12.00	142-190	164.3	12.00	24.00
(V)	65 - 140	114.9	10.45	140-190	163.4	12.71	23.16

some changes of the temperature ranges in which mass loss takes place.

The mass loss of the obtained products and the corresponding temperature ranges are presented in table 3.

From the data presented in table 3 one can observe that boric acid introduced at the beginning of neutralization, respectively at the NH_3:H_3PO_4 molar ratio ~ 1 determines a higher total mass loss in the temperature range 65-190°C, comparatively to the mass loss, in the same temperature range, of the product without boron. The products IV and V present a mass loss close to the product I in the same temperature range and smaller than the products II and III. One can also observe that the second thermal decomposition stage starts at a higher temperature for the products IV and V, close to that one of the product I. The conclusions based on the experimental data recommend the addition of the boric acid into the reaction mixture at the NH_3:H_3PO_4 molar ratio ~ 1.5.

Conclusions

In the process of obtaining fertilizers based on ammonium phosphates the addition of boric acid at various NH_3:H_3PO_4 molar ratio does not influence the N:P_2O_5 massic ratio of the final product, in all cases a phosphates mixture is obtained.

Regardless the NH_3:H_3PO_4 molar ratio at which boric acid was added, there is a well defined dependency of the reaction mass *p*H on the NH_3:H_3PO_4 molar ratio, typical for each product. Therefore, the reaction mass *p*H is a control parameter for the obtaining process of the complex fertilizers based on ammonium phosphate with boron with minimum ammonia loss.

The neutralization products obtained by introducing the boric acid at a NH_3:H_3PO_4 molar ratio of 1.5, respectively at the end of neutralization, heated up to 190°C undergoes the minimum ammonia loss. The thermal analysis of the neutralization products shows that the second stage of thermal decomposition begins at a higher temperature that in case of products IV and V, close to the one of product I. The conclusions based on the experimental data recommend the addition of the boric into the reaction mixture at the NH_3:H_3PO_4 molar ratio ~ 1.5.

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