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THERMAL ANALYSIS OF MIXED FERTILIZERS

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ABSTRACT

Thermal analysis, and in particular DSC, constitutes a very valuable technique for investigating fertilizers. In this paper a survey is given of the potential of this technique in the field of fertilizers.

First, it is demonstrated that DSC may serve as an aid in process control. In particular, differences between first and second heating curves give valuable information on the nature and efficiency of the production process.

Secondly, major parts of the complex phasediagrams of NPK-type fertilizers may be unravelled with DSC. In this way insight in the thermal behaviour of such a fertilizer is obtained.

Finally, it is shown that with DSC a rapid (semi-) quantitative analysis of a fertilizer may be performed.

INTRODUCTION

Mixed fertilizers may donate nitrogen, phosphorus and potassium to the soil and therefore enjoy widespread use in agriculture. They are frequently termed NPK-type fertilizers. They are composed of such substances as NH_4NO_3, KNO_3, NH_4Cl, K_2SO_4, $NH_4(H_2PO_4)$, $(NH_4)_2SO_4$, etc., with NPK ratios varying in a wide range, dependent on their specific application.

On heating, these fertilizers show complex thermal behaviour. Not only are several phase transitions possible; a number of reactions between the constituents may also occur. As a result, the DSC curve of an NPK-type fertilizer is very complex.

In literature little information is available on the thermal analysis of mixed fertilizers (1,2). A study has therefore been performed on the potential of thermal analysis, and in particular DSC, for investigating fertilizers.

In this paper a survey is given.

EXPERIMENTS

All DSC curves were measured with a Maple Instruments Model 42 DSC unit. The measurements were performed in a dynamic nitrogen atmosphere (3 l/hr) using a sample weight of about 12 mg. and a heating rate of 10 ^{o}C/min. in the temperature range between ambient and 200 ^{o}C. The commercial NPK fertilizers, as well as the basic constituents, were all obtained from Windmill Holland b.v.

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RESULTS AND DISCUSSION

A DSC curve of an NPK-type fertilizer depends not only on the mixture itself; additionally, the production process has a distinct influence on the curve. As a consequence, the curve reveals information on the nature and efficiency of the production process. In this way DSC may serve as an aid in process control.

Two main processes exist for the production of these fertilizers. In the first process, the components are dissolved in an ammoniumnitrate melt, after which granulation or prilling follows. As the temperature of the system is rather high (approx. 170 °C) several reactions proceed. Some examples are :

$NH_4NO_3 + KCl \rightarrow KNO_3 + NH_4Cl$ (1) $NH_4NO_3 + K_2SO_4 \rightarrow KNO_3 + KNH_4SO_4$

$KNO_3 + NH_4H_2PO_4 \rightarrow KH_2PO_4 + NH_4NO_3$ (1) $KCL + NH_4H_2PO_4 \rightarrow KH_2PO_4 + NH_4Cl$

$(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + NH_3$ (4)

Because of the high temperature, equilibrium is reached and the resulting fertilizer is thermally stable.

In the other process, the constituents are mixed in a granulator operating at much lower temperatures (100-140 °C).Here, equilibrium is not reached and the fertilizer is thermally reactive. The differences between the two processes are clearly expressed in the DSC curve. In particular, the differences between the first and second heating curves give valuable information on the nature and efficiency of the process. Two examples are given in Figures 1 and 2.

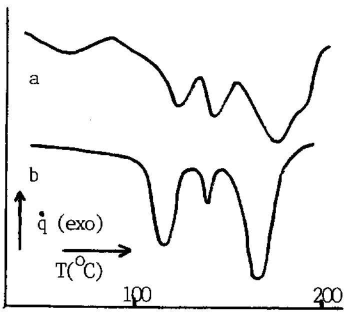

fig. 1 a,b NPK 17-17-17 (Windmill)

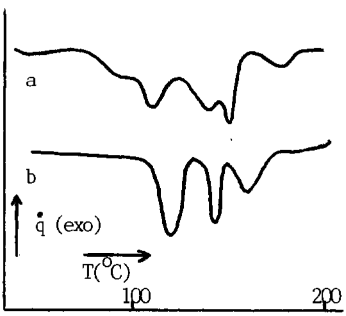

fig. 2 a,b NPK 17-17-17 (UKF)

Fig. 1.a.b. shows the first and second heating curves of an NPK 17-17-17 fertilizer produced according to the ammonium nitrate meltprocess (source : Windmill). It can easily be seen that the differences between the curves are small, indicating that all reactions between the components have been completed.

Fig. 2.a.b. gives the first and second heating curves of an NPK 17-17-17 fertilizer produced according to the granulation process (source : UKF). Here the differences between a and b are much larger, indicating that the reactions described have by no means proceeded to completion. Due to different ratios between the respective constituents, the intensities of the peaks in Fig. 1b also differ. In this way a DSC curve may also serve as a fingerprint of a given fertilizer.

Once a mixture has reacted completely, the peaks in a DSC heatingcurve result from the various phase transitions in the fertilizer, and by studying them a proper understanding of the thermal behaviour of the fertilizer may be obtained. The mixture is of course very complex, so complete unravelling of the phase diagram is not possible with DSC alone. Some parts of it may be understood, however. For this purpose, two modes of investigation are available :

. Starting from the basic binary system, followed by stepwise addition of the remaining component(s).

. Stepwise increase of the concentration of a component in the actual fertilizer. After each step the resulting DSC curve is measured.

In Fig. 3 a DSC curve is given of NP 23-23-0. The composition of this mixture is : 48% wt. NH_4NO_3 41% wt. $NH_4H_2PO_4$ 11% wt. $(NH_4)_2SO_4$

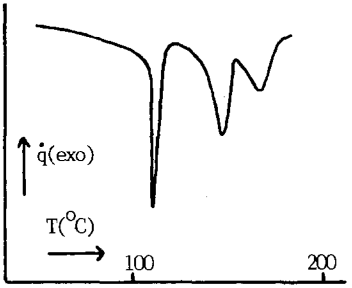

fig. 3 NP 23-23-0

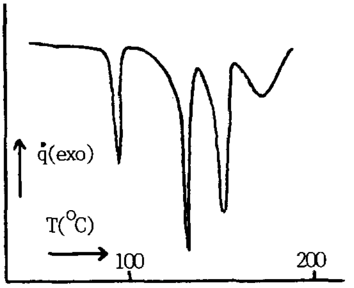

fig. 4 NH_4NO_3 / $NH_4H_2PO_4$ mixture

To determine the origin of the peaks in Fig 3, the binary mixture $NH_4NO_3/NH_4H_2PO_4$ (in the same ratio) was measured. This curve is shown in Fig. 4.

In fig. 4, it can easily be seen that the peak at 95 °C is due to a perturbed 3-2 transition of the NH_4NO_3 phase. Phase 2 often remains metastable even at low temperatures, so the absence of this peak in Fig. 3 is not unusual. The peaks at temperatures higher than 140 °C nicely compare in Figs. 3 and 4 and represent an eutectic melt at about 150 °C followed by dissolution of the remaining solid phase. It could be shown that by adding $(NH_4)_2SO_4$ the 2-1 transition of the NH_4NO_3 phase (130 °C in Fig. 4) shifts to a lower temperature (112 °C in Fig 3).

The NPK 17-17-17 also forms a illustrative example (Fig. 5.a.).This fertilizer is composed of 40% NH_4NO_3 28% $NH_4H_2PO_4$ and 27% KCl. (besides 5% other material). Here, the KCl is transformed to KNO_3 according to the reaction :

NH_4NO_3 + KCl -- KNO_3 + NH_4Cl

An increase of the KCl concentration gives rise to an increase of the peak at 140 °C and a decrease of the peak at 117 °C, as Fig. 5.b. shows. It can easily be seen that these peaks originate from a perturbed KNO_3 and NH_4NO_3 transition. When the amount of $NH_4H_2PO_4$ is increased the peak at 167 °C strongly increases, while the intensity of the other peaks remains almost constant (Fig. 5.c.). Pure $NH_4H_2PO_4$ melts at approx. 190 °C.

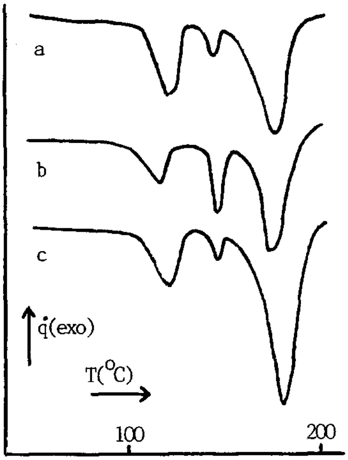

fig. 5 a,b,c NPK 17-17-17

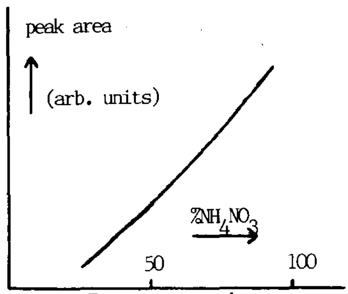

fig. 6 %NH_4NO_3 vs. peak area

The existence of peaks in the DSC curve, which can be attributed to a (perturbed) transition of (a single) component in the mixture, enables (semi-) quantitative analysis of the fertilizer to be readilly performed. For example, in virtually all NPK's the peak at 117 °C is present, originating from a 2-1 NH_4NO_3 phase transition. The area of this peak is dependent on the NH_4NO_3 concentration, as is shown in Fig.6. for the NPK 17-17-17. In this way, DSC may serve as a rapid check on the composition of a given fertilizer.

CONCLUSIONS

- Mixed fertilizers exhibit very complex thermal behaviour, which cannot fully be understood using thermal analysis alone. Major aspects of it may be well understood however.
- In the fertilizer industry, DSC may serve as a very valuable technique in process control.
- As each fertilizer has its specific DSC curve, these can be used as a fingerprint of the fertilizer.
- A good correlation between peak area and concentration of a distinct component (especially NH_4NO_3) can often be found, enabling for rapid (semi-) quantitative analysis of the fertilizer.

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