Department of Technology and Chemical Processes
Chemistry Faculty, Wrocław University of Science and Technology

Doctoral thesis

„Kinetics of physicochemical changes in nitrogen fertilizer compounds for assessing their quality and technical safety"

Author: Dariusz Popławski, MSc, Eng

Supervisor: Józef Hoffmann, Professor, PhD, DSc

SUMMARY

Ammonium nitrate is a major and indispensable component of nitrogen fertilizers, produced on an industrial scale in very large quantities. Some of its properties may, however, adversely affect the safety and quality of fertilizer products. Ammonium nitrate can undergo rapid decomposition and even detonation, under the influence of high temperature or mechanical impact, which results in the need to properly stabilize the mixtures containing this compound. One of the common additives used for this purpose are various fillers, containing calcium carbonate and magnesium carbonate. Their main sources are usually mineral materials, such as dolomite and limestone. Properly selected carbonate fillers can react with ammonium nitrate at elevated temperature, and as a result, a significant portion of it, instead of decomposing, is converted to more thermally stable calcium and magnesium nitrates. At the same time, evolved ammonia strongly inhibits the decomposition of the remaining ammonium nitrate in the mixture, and the exothermic effect associated with this process can be compensated due to the endothermic nature of the reaction with carbonates. In the selection of effective fillers, positively influencing the thermal stability of fertilizer mixtures, the reactivity of the carbonate raw material to ammonium nitrate is crucial.

The work has evaluated the safety and quality of nitrogen fertilizers produced on the basis of ammonium nitrate. For this purpose, the results of the kinetics analysis of physicochemical changes occurring in mixtures of ammonium nitrate with selected carbonate raw materials of different composition were used. Thermal stability studies of the mixtures were performed using differential thermal analysis (DSC) and differential scanning calorimetry (DSC), coupled with thermogravimetry (TG) and mass spectrometry (MS). A simplified 3-step mechanism of observed changes was proposed, taking into account: endothermic dissociation of ammonium nitrate into ammonia and nitric acid, exothermic

secondary reactions between dissociation products, reactions between ammonium nitrate and carbonates. A suitable model was chosen for the description of each step and the values of kinetic parameters were determined. For this purpose, a model fitting method based on nonlinear regression was used, which was preceded by an analysis of experimental data using isoconversional methods.

Based on the values of the kinetic parameters determined for each model, the rates of the individual steps were calculated. It was found that for all of the examined carbonate fillers, their addition caused a 1.5 to 3.5-fold reduction in the rate constant for the exothermic decomposition of ammonium nitrate. This is a direct confirmation of the positive effect of examined carbonate raw materials on the thermal stability of ammonium nitrate.

The obtained kinetic data was used to compare the reactivity of the investigated fillers. The higher the ratio of the rate constant for the reaction of ammonium nitrate with carbonates with respect to the constant for its decomposition reaction, the more effective the filler should be. For slightly calcitic dolomite (32.7% CaO by mass) the ratio of both constants was close to 14. For other fillers with a CaO content of 30-39% by mass, at a temperature of 250^{o}C the value of the rate constant for reactions with carbonates was at least six times higher than the constant for the decomposition of ammonium nitrate, which should allow to fully compensate the undesirable exothermic effect. It was also observed that the reactivity of the filler is primarily dependent on the content of calcium carbonate in the raw material. Additives containing more $CaCO_3$, interacting with ammonium nitrate at lower temperatures, are characterized by a lower intensity of these changes. Much faster are the reactions of ammonium nitrate with carbonates contained in fillers with a CaO content in the range of 31-33% by mass, occurring in higher temperatures.

Characterization of reactivity of carbonate raw materials dependence on their composition, based on suitably performed measurements and kinetic analysis, can be used to select fillers, positively influencing the safety of production, storage, transportation and use of nitrogen fertilizers based on ammonium nitrate, while ensuring the intended quality and composition of the product. Carbonate raw materials with a positive effect on the properties of nitrogen fertilizers should contain 30-40% CaO by mass. From this range, slightly calcitic dolomites containing 31-33% CaO by mass, appear to have a particularly beneficial effect.