Aleksandra TYC[1], Szymon PENKALA[1], Marcin BIEGUN[1],
Dominik NIEWEŚ[1], Marta HUCULAK-MĄCZKA[1]
and Krystyna HOFFMANN[1*]

THE EFFECTIVENESS OF COMMERCIAL ANTICAKING AGENTS FOR AMMONIUM NITRATE FERTILIZERS

SKUTECZNOŚĆ DZIAŁANIA HANDLOWYCH ANTYZBRYLACZY NA NAWOZY SALETRZANE

Abstract: Ammonium nitrate is the primary component used in the production of ammonium nitrate fertilizers. However, it has certain undesirable physicochemical properties such as hygroscopicity and phase transition at room temperature, which results in an undesirable phenomenon of caking. Caking changes the properties of the fertilizer thereby contributing to material loss. This, in turn, causes economic losses to both the manufacturer and the end-user. Anticaking agents are currently the most effective way to prevent fertilizers from caking. Finished granules of fertilizer are sprayed with anticaking agents in appropriate quantities, depending on the type of fertilizer and the anticaking agent. Therefore, in this study, we aimed to evaluate the effectiveness of commercial anticaking agents for use with ammonium nitrate fertilizers (Salmag® and ZAKsan®) and to evaluate the compressive strength of fertilizer granules coated with the anticaking agent. We evaluated a method to test the effectiveness of anticaking agents, which enables the effective selection of appropriate anticaking agents for various types of fertilizers.

Keywords: anticaking agents, ammonium nitrate, fertilizers

Introduction

Ammonium nitrate is a colorless crystalline chemical compound, which is primarily used in the making of fertilizers and explosives [1]. The application of ammonium nitrate in fertilizers results from its physicochemical properties. Among the mass-produced nitrogen compounds with yield-forming effect, ammonium nitrate stands out, which, if used skillfully, gives high and good quality yields with relatively low environmental damage. In Poland, ammonium nitrate fertilizers are produced by Grupa

[1] Department of Technology and Chemical Processes, Faculty of Chemistry, Wroclaw University of Science and Technology, ul. M. Smoluchowskiego 25, 50-372 Wrocław, Poland, phone: +48 71 320 62 93, fax: 71 328 04 25.

* Corresponding author: krystyna.hoffmann@pwr.edu.pl

Azoty Kędzierzyn (ZAK S.A.), Grupa Azoty Puławy (ZAP S.A.), Grupa Azoty S.A. located in the district of Mościce (Tarnów), and by Anwil S.A. located in Włocławek. Grupa Azoty is the leader in the production of mineral fertilizers on the Polish market. Table 1 shows the names of fertilizers based on ammonium nitrate that are produced in Poland.

Table 1

Fertilizers based on ammonium nitrate produced in Poland

Company	Product	Nitrogen content [%]
Grupa Azoty ZAK S.A.	ZAKsan®	32
	ZAKsan® 33	33
	Salmag®	27
	Salmag with boron®	27
	Salmag with sulfur®	27
	Salmag® 20 Mg plus	20
Grupa Azoty ZAP S.A.	PULAN®	34.5
Grupa Azoty S.A. with location Tarnów-Mościce	Saletrzak 27 standard	27
	Saletrzak 27 standard with born	27
	Ammonium nitrate 32	32
	Saletrosan® 26	26
	Saletrosan® 30	30
Anwil S.A.	Ammonium nitrate	34
	CANWIL S with sulfur	27
	CANWIL with magnesium	27

Ammonium nitrate has the following physicochemical properties: hygroscopicity and phase transition occurring at room temperature, which results in an undesirable phenomenon of caking. Caking changes the properties of the fertilizer thereby contributing to material loss. This, in turn, leads to economic losses to both the manufacturer and the end-user. The agglomeration of the fertilizer is also affected by the storage conditions, which include air temperature and humidity, storage time, and methods of storage [2]. The phenomenon of caking due to phase transition of ammonium nitrate can be described as follows: during the transformation phase IV→III which takes place at 32 °C, the volume of the granules increases, which in turn increases the pressure between the granules of the fertilizer. This increased pressure causes deformation in the structure of the granules which in turn increases the contact area between the granules. Individual granules are joined to each other via "crystalline bridges," because water participates during the process of phase IV→III transformation. When the temperature falls, the reversible phase transition from III→IV takes place. At this point, the volume of the fertilizer reduces again. However, the granules will still be joined together, which results in cracks.

Another reason for the caking of ammonium nitrate fertilizers is the presence of admixtures, hygroscopicity, and physical water content in the fertilizer. These factors are strongly related to each other. A certain amount of water contained in the granules creates hydrates while part of the water affects the formation of a thin layer of saturated solution on the surface of the fertilizer. Concentration of this saturated solution depends on the temperature. The higher the temperature, the higher the amount of ammonium nitrate that dissolves. Then, when the temperature decreases, part of the ammonium nitrate contained in the solution becomes crystallized. This phenomenon (dissolution and crystallization) also occurs when there is a change in the humidity in the air. Moreover, surface tension causes the granules of ammonium nitrate to travels toward the contact points between the granules to form liquid bridges, which after evaporation becomes crystalline bridges. This results in caking of the fertilizer (Fig. 1).

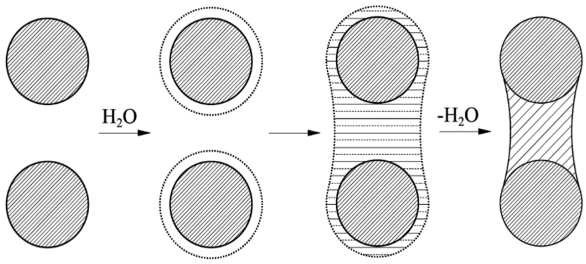

Fig. 1. Mechanism of caking of fertilizer granules [3]

Nowadays, caking is most commonly prevented by adding inorganic salts or stabilizers during the production of the fertilizer and or by spraying the finished product with a mixture consisting mainly of petroleum raw material and surfactants [4]. Such a mixture is called an anticaking agent and its main purpose is to prevent the clumping of the fertilizer. The surfactant in the anticaking agent plays an important role. It reduces adhesion between the granules of the fertilizer, increases hydrophobicity, and improves the coverage of granules with a conditioning agent. Fatty amines are very effective surfactants used as anticaking agents. They are particularly effective when it comes to ammonium nitrate fertilizers. Aliphatic amines reduce the interfacial energy on the crystal-solution boundary, and if the reduction of this energy is greater than the energy of crystallization, then crystallization is inhibited thereby blocking crystal surfaces. Aliphatic amines also cause the surface of the fertilizer to change from hydrophilic to hydrophobic state, which changes the adsorption properties of the surface of the fertilizer. This makes fertilizers less susceptible to moisture absorption from the atmosphere, which also prevents clumping. However, each fertilizer must be studied individually for all these changes in the properties after the addition of an anticaking agent. In addition, it is also very important to test the type of fillers or additives to be used, the method of producing the fertilizer, the chemical composition of the fertilizer, and the impurities contained in it. The amount of anticaking agents to be used for spraying the fertilizer granules is another important parameter in the evaluation of the effectiveness of anticaking agents, as a high quantity can lead to water-insoluble fertilizer [5–7].

Therefore, in this study, we aimed to evaluate the effectiveness of commercial anticaking agents in the production of ammonium nitrate fertilizers (Salmag® and

ZAKsan®) and to evaluate the compressive strength of fertilizer granules coated with the tested anticaking agents. We also present a method to evaluate the effectiveness of anticaking agents, which enables the effective selection of appropriate anticaking agents for various types of fertilizers.

Materials and methods

We tested the compressive strength of fertilizer granules with anticaking agents and the effectiveness of anticaking agents. Two types of fertilizers (Salmag® and ZAKsan®) were studied. Six commercially available anticaking agents (Amigos, Fluidiram, JRCH Ansol, F-21D (Kao), FW5AG (Kao), and 2060 (NovoFlow)) were analyzed.

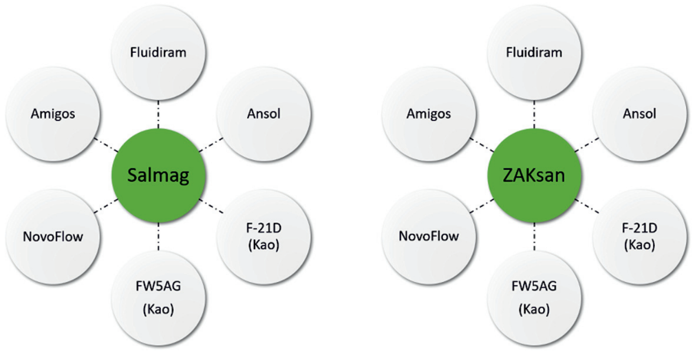

Fig. 2. Tested fertilizers and commercial anticaking agents

Fig. 3. Erweka GmbH for measuring the compressive strength of fertilizer granules

Erweka GmbH was used to measure the compressive strength of 20 randomly selected granules. We tested the fertilizer caking resistance (effectiveness of anticaking agents) on a thermostatic device. The device consists of 12 places into which the fertilizer under test was poured. Samples were loaded and subjected to 7 thermal cycles. One thermal cycle involved holding the sample for 1 h at 45 °C and then for 1 h at 20 °C. After thermostating, the obtained fertilizer block was measured for the force needed to crush it. In order to determine the effectiveness of anticaking agents, a force test was conducted for both uncoated and coated fertilizers. The effectiveness of anticaking agents, *R,* was calculated based on the formula below [8]. All measurements were made immediately after the granulation process and after 3, 10, and 30 days of storage.

$$R = \frac{M_p - M_{ot}}{M_p} \cdot 100 \quad [\%]$$

where M_p is the force needed to crush the uncoated fertilizer [N] and M_{ot} is the force needed to crush the coated fertilizer [N].

Results

In this study, we aimed to evaluate the effectiveness of commercial anticaking agents for ammonium nitrate fertilizers and to evaluate the compressive strength of fertilizer granules coated with anticaking agents. Resistance to caking allows to assess the susceptibility of a given fertilizer to lumping and/or in order to determine the effectiveness of the applied anticaking agent. This research will allow for the effective selection of anticaking preparations for various types of fertilizers.

Effectiveness tests of anticaking preparations (Figs. 4 and 5) showed that F-21D and FW5AG were appropriate for the production of Salmag fertilizer. Their efficiency was low for ZAKsan. Amigos preparation for ZAKsan fertilizers showed initial effectiveness of 55.0 %, which increased after 30 days of storage to 96.8 %. In the case of Fluidiram, the values increased from 77.2 % to 94.3 % after 30 days of storage. Therefore, Fluidiram was found to be appropriate for ZAKsan, but it did not prevent Salmag granules from caking. NovoFlow prevented the clumping of Salmag very well. After 3 days of storage, the effectiveness was 100.0 %. After 30 days of storage, NovoFlow prevented the clumping of ZAKsan-type fertilizers ranging from 89.9 % (without storage period) to 100.0 %. The effectiveness of JRCH Ansol in preventing the

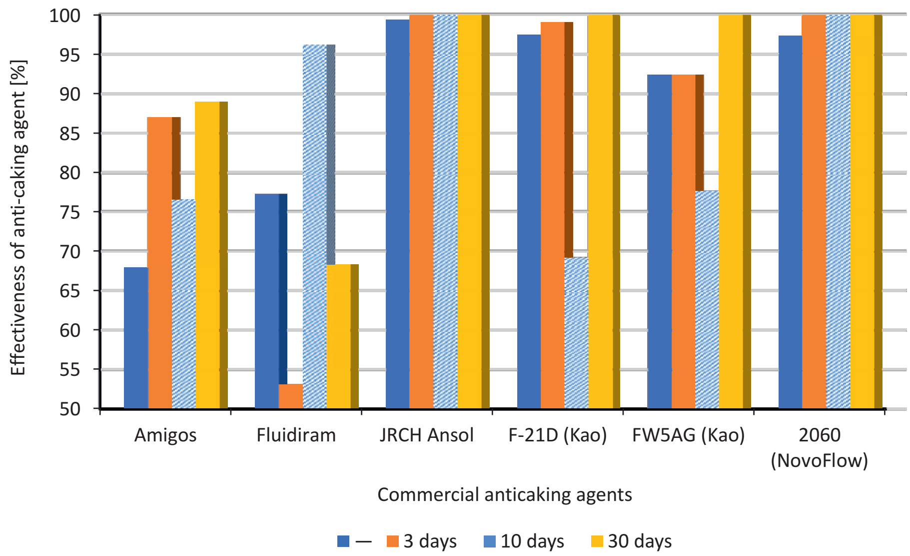

Fig. 4. Resistance to caking (anticaking effectiveness) for Salmag®

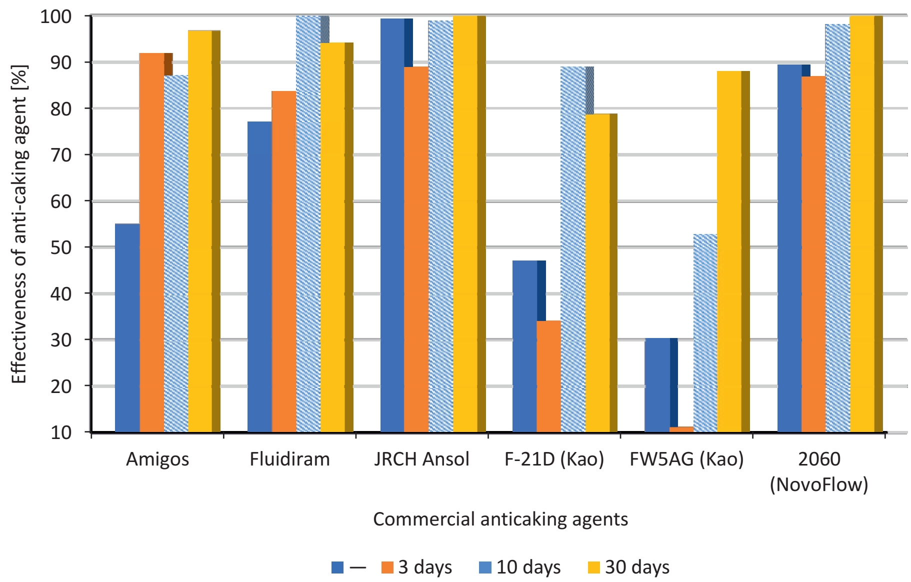

Fig. 5. Resistance to caking (anticaking effectiveness) for ZAKsan®

clumping of Salmag and ZAKsan granules was 91.4 % and 94.3 %, respectively, which increased to 100.0 % after 3 days of storage. The same values (100.0 %) were observed after 10 and 30 days of storage for both fertilizers.

The resistance of granules to compression is one of the important parameters used to assess the quality of granulated fertilizers. When testing the strength (hardness) of the granules, we can predict the behavior of the fertilizer during storage, transport, or during application. Tables 2 and 3 show the results of the compressive strength of the granulated fertilizer. According to the results, the use of Amigos caused an increase in the physical resistance of ZAKsan granules and a decrease in the compression resistance of Salmag granules. ZAKsan coated with NovoFlow showed a higher crushing resistance than that of uncoated fertilizer. The value after 30 days of storage increased from 43.33 N to 44.82 N. For comparison, the sample of uncoated fertilizer increased from only 41.15 N to 41.46 N. However, NovoFlow, like Amigos, did not improve the compressive strength of granulated Salmag. Salmag coated with Fluidiram provided the following results: coated fertilizer showed an increase in resistance from 45.23 N to 50.50 N, whereas uncoated fertilizer showed resistance from 46.83 N to 56.69 N. Fluidiram reduced the compression strength of ZAKsan. Kao anticaking agents (F-21D and FW5AG) reduced the physical resistance of granulated ZAKsan and Salmag. ZAKsan coated with JRCH Ansol showed a higher crushing strength than that of uncoated fertilizer only when the product is not subjected to a storage test. The use of this preparation caused a decrease in the physical resistance of ZAKsan. However, freshly coated Salmag with JRCH Ansol showed lower resistance to crushing than that of fertilizer without coating. However, after 3 and 10 days of storage, it showed greater value than that of uncoated fertilizer. However, after 30 days of storage, this preparation caused a decrease in the physical resistance of Salmag granules.

Table 2

Compressive strength of fertilizer granules for Salmag®

Storage period	Medium compressive strength [N]					
	without agent	Amigos	without agent	Fluidiram	without agent	JRCH Ansol
—	46.40	45.72	46.83	45.23	54.54	55.54
3 days	48.95	46.71	45.03	46.05	59.94	66.94
10 days	51.40	48.00	45.24	46.88	63.88	68.01
30 days	50.10	52.04	56.69	50.50	83.18	67.64
Storage period	without agent	F-21D (Kao)	without agent	FW5AG (Kao)	without agent	2060 (NovoFlow)
—	58.75	57.41	58.75	59.59	58.03	56.88
3 days	58.98	58.84	58.98	55.61	60.79	58.66
10 days	78.39	64.81	78.39	59.28	71.10	59.80
30 days	73.29	59.94	73.29	55.99	82.11	67.82

Table 3

Compressive strength of fertilizer granules for ZAKsan®

Storage period	Medium compressive strength [N]					
	without agent	Amigos	without agent	Fluidiram	without agent	JRCH Ansol
—	44.98	46.18	47.21	44.18	54.09	58.36
3 days	49.66	44.52	46.19	43.87	59.88	65.69
10 days	47.08	50.08	44.17	44.50	63.50	65.05
30 days	49.88	50.18	62.91	58.81	69.63	65.87
Storage period	without agent	F-21D (Kao)	without agent	FW5AG (Kao)	without agent	2060 (NovoFlow)
—	47.04	42.95	47.04	45.37	41.15	43.33
3 days	38.03	46.51	38.03	45.66	34.49	34.05
10 days	58.01	55.80	58.01	54.26	42.58	46.86
30 days	64.74	56.48	64.74	54.98	41.46	44.82

The results of the effectiveness of the anticaking agents and the compression strength of the fertilizer granules in some cases decrease after 3 or 10 days of storage and then increase again. To clarify this, it is important to remember that the storage behaviour of the fertilisers strongly depends on the composition of the anticaking agent and the organic compounds used, but also on the amount of water in the granule. The water concentration at the surface of the granule (after drying and cooling processes in dry air) is different than in the inside. Then, during the storage process, the water is evenly distributed in the whole granule and next partly is bound in the hydrates and partly is evaporated in the warehouse. Storage of fertilizer granules, cause some chemical transformations and reactions take place, related to dolomite contamination, to the migration of the solvent (water) and to the action of a strong oxidant, which is ammonium nitrate. If we cover such a granule with an anticaking agent (a mixture of organic substances), a lot depends on the chemical activity of the components used for its composition.

The greatest fluctuations in the results of anticaking effectiveness and compressive resistance of fertilizer granules during storage were recorded for Kao preparations (F-21D, FW5AG). Kao preparations probably contain more active organic compounds than other tested products. This results in greater decomposition of ammonium nitrate at the point of contact between the granule and the anticaking agent and the production of water. Created water weakens the hardness of the granule and gradually penetrates inside the granule at the same time being a solvent for other micro-scale chemical processes resulting from the chemical substances contained in the dolomite. After some time, chemical processes involving water and other compounds are stopped and stabilization takes place.

Conclusion

The results of this study conducted to test the effectiveness of anticaking agents under laboratory conditions showed that JRCH Ansol and NovoFlow were the most effective anticaking agents for Salmag® fertilizer. However, JRCH Ansol was found to be the most effective anticaking agent for ZAKsan® fertilizer. A standard product should be 100 % effective throughout the test period.

Our results show that the compressive strength of coated and uncoated fertilizers differed significantly. A standard anticaking agent should increase the force needed to crush the granules during the storage period (0–30 days). The decreased compressive strength is due to the decomposition reactions of ammonium nitrate at the contact surface between the anticaking agent and the granule. Nevertheless, the effectiveness of anticaking agents is related to the quality of the fertilizer, which results from the quality of the raw materials used in their production (e.g. dolomite quality – calcium, magnesium, and content of impurities), the raw material load of the installation (e.g. the degree of packing of granule changes), and the season of production (external temperature and humidity conditions).

In summary, this study was conducted to show the effect of selected anticaking agents on caking phenomena of specific types of fertilizers, which differ in terms of the content of ammonium nitrate.

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SKUTECZNOŚĆ DZIAŁANIA HANDLOWYCH ANTYZBRYLACZY NA NAWOZY SALETRZANE

Zakład Technologii i Procesów Chemicznych
Wydział Chemiczny, Politechnika Wrocławska, Wrocław

Abstrakt: Azotan amonu to główny związek do produkcji nawozów saletrzanych. Azotan amonu posiada jednak pewne właściwości fizykochemiczne takie jak: higroskopijność, rozpuszczalność w wodzie czy zachodzące w nim przemiany fazowe, które wpływają na to, że nawozy saletrzane ulegają niepożądanemu zjawisku zbrylania. Skutkuje to zmianą właściwości użytkowych nawozów i przyczynia się do strat materiałowych. To z kolei prowadzi do dodatkowych, niepotrzebnych kosztów zarówno u producenta, jak i końcowego odbiorcy. Antyzbrylacze są obecnie najskuteczniejszym sposobem przeciwdziałania zbrylaniu nawozów. Gotowe granule nawozu natryskuje się antyzbrylaczami w odpowiedniej ilości w zależności od typu nawozu jak i od konkretnego antyzbrylacza. Celem przeprowadzonych badań była ocena skuteczności przeciwdziałania zbrylaniu sześciu handlowych antyzbrylaczy dla nawozów saletrzanych (Salmag® i ZAKsan®) oraz ocena odporności na ściskanie granul badanych nawozów pokrytych testowanymi antyzbrylaczami. W pracy przedstawiono metodę oceny skuteczności przeciwdziałania zbrylaniu nawozów, która umożliwia skuteczny dobór odpowiednich antyzbrylaczy dla różnych typów nawozów.

Słowa kluczowe: antyzbrylacze, azotan amonu, nawozy