Influence of Anti-Caking Agents on the Highly Effective Organic Coatings for Preventing the Caking of Ammonium Nitrate Fertilizers

Aleksandra Tyc 1,2*, Dominik Nieweś 1, Szymon Penkala 1, Ryszard Grzesik 2, Krystyna Hoffmann 3 and Józef Hoffmann 1,*

1 Department of Engineering and Technology of Chemical Processes, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland; aleksandra.tyc@pwr.edu.pl (A.T.); dominik.niewes@pwr.edu.pl (D.N.); 234184@student.pwr.edu.pl (S.P.)

2 Department of Research and Innovations, Grupa Azoty Zakłady Azotowe Kędzierzyn, S.A., Mostowa 30A, 47-220 Kędzierzyn-Koźle, Poland; ryszard.grzesik@grupaazoty.com

3 Department of Micro, Nano and Bioprocess Engineering, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland; kristyna.hoffmann@pwr.edu.pl

* Correspondence: jozef.hoffmann@pwr.edu.pl

Received: 25 October 2020; Accepted: 13 November 2020; Published: 15 November 2020

Abstract: Ammonium nitrate fertilizers have a tendency to cake during storage. The aim of this study was to examine the effectiveness of organic coatings for preventing the caking of ammonium nitrate fertilizers and to assess the influence of the composition and physicochemical properties of the anti-caking agents used as coatings for fertilizers on their effectiveness. CAN (calcium ammonium nitrate) and AN (ammonium nitrate) fertilizers were coated with three anti-caking agents. A GC–MS technique was used for the identification and quantitative determination of the composition of the organic coatings. The influence of the following physicochemical parameters of the preparations was assessed: density, viscosity, melting point, water content, and base number. The effectiveness of anti-caking agents was determined by measuring the force needed to crush the clumped uncoated and coated fertilizers, which were previously subjected to thermal cycles under load. Composition studies showed that all the tested preparations contained hexadecylamine and octadecylamine in comparable amounts and a slack wax. The results demonstrate that the key parameters of an effective anti-caking agent are low water content, appropriate viscosity, and appropriate content of fatty amines. This study can facilitate the development of innovative coatings with similar or higher efficiency, yet with a reduced negative impact on the environment.

Keywords: organic coatings; anti-caking agents; fertilizers; ammonium nitrate; GC–MS

1. Introduction

The global demand for mineral fertilizers, particularly those based on nitrogen, is constantly increasing due to the growing population and demand for food [1]. The most commonly used solid fertilizers based on ammonium nitrate are CAN (calcium ammonium nitrate) and AN (ammonium nitrate). The popularity of these fertilizers stems primarily from the possibility of obtaining high nitrogen content in the product. As nitrogen plays a very important role in the plant growth processes, there is a high demand for fertilizers containing this element in high concentration in granulate [2].

The physicochemical properties of ammonium nitrate include explosiveness, water solubility, and high hygroscopicity. Ammonium nitrate occurs in different phase variations, which affect the behavior of the fertilizers based on this compound during storage, particularly in conditions of
high humidity of both air and the product itself, as well as variable temperature. Such properties of ammonium nitrate contribute to the phenomenon of caking, an undesirable effect observed in nitrate fertilizers [3–5]. The phenomenon of granule caking of ammonium nitrate fertilizers is associated with the occurrence of cohesion, affected by the aforementioned physicochemical properties, as well as the storage conditions of the fertilizer. Another factor that determines the susceptibility of nitrogen fertilizers to the caking process is their composition. Furthermore, the shape and size of the granules in these fertilizers determine the tendency of caking, which is directly related to the contact surface between the granules during their transport and storage. As a consequence of caking, the performance of fertilizers deteriorates, rendering their storage difficult. In addition, caked fertilizers result in material loss and impose additional costs, because they cannot be equally dosed without additional works [5–7].

Modification of ammonium nitrate surface using coatings (chemical, physical, and encapsulation coating) may reduce hygroscopicity, as described in the literature [8].

Caking can be prevented in several ways, yet the most common anti-caking method currently used involves coating the prepared granules with an anti-caking agent. In addition, caking increases the propensity of ammonium nitrate to explode when forced by external factors. Therefore, precautionary measures should be taken to reduce the possibility of the occurrence of these negative phenomena. By preventing caking, the quality of ammonium nitrate fertilizers as well as public safety can be improved [3]. A literature and patent overview showed that the composition of products such as fertilizers is carefully selected by their manufacturers depending on the properties and intended application [9].

Nowadays, polymer coatings are increasingly proposed, related to the production of slow-release fertilizers (SRFs) and controlled-release fertilizers (CRFs). Furthermore, the application of such coatings on nitrate fertilizer granules restricts their tendency of caking. Thus far, the effects of coatings composed of, among others, polysulphone, cellulose acetate, and polyacrylonitrile have been described. Polymer coatings were applied on fertilizer granules that represent three of the macro-nutrients, nitrogen, phosphorus, and potassium (NPK fertilizer), using the phase inversion method. It was determined that increased polymer contribution in the coating mixture reduces the coating porosity, which may be undesirable and highly hazardous due to the decomposition of ammonium nitrate. Therefore, only low amounts of the polymer can be used in the preparation of anti-caking coatings for nitrate fertilizers, while ensuring reduced contact between granules and maintaining appropriate coating porosity [10,11]. Research is underway on controlled-release coatings for urea, including particles with bio-based epoxy. The bio-based epoxy was fabricated with liquefied bagasse used as a green coating material for CRF [12]. In another study, urea with SRF was obtained by coating with polyurethane. Polyurethane was prepared from fully vegetable oil-based polyols and polymethylene polyphenylene isocyanate. The vegetable oil content was 70% in the polyurethane film of SRFs. Additionally, the films had excellent degradability [13].

However, fertilizers based on ammonium nitrate require slightly different coatings from those used for NPK fertilizers and urea, and several alternative additives have been successfully tested to prevent their caking. These additives include calcium trialkylamine, dimethyl decylamine, potassium dimethyloctylamine, and dimethyl laurylamine [14]. Other studies have shown that a mixture of mineral oil and slack wax together with high-molecular-weight polyisobutylene additives significantly reduces water absorption and the dust-generating tendency of ammonium nitrate fertilizers [15]. A reduction in moisture adsorption has also been noticed when additives such as potassium alkyl sulfate, sodium alkyl sulfate, and mono-, di-, and triethanolammonium alkyl sulfate were used for nitrate fertilizers [16]. In addition, it has been reported that coating of nitrogenous fertilizers with bitumen reduced the absorption of moisture by fertilizer granules [17]. Recently, research was carried out to minimize moisture absorption by ammonium nitrate-based fertilizers by introducing additives such as silicic acid, calcium lignosulphonate, and sodium silicate in a two-stage vacuum process used for the production of ammonium nitrate [18]. A patent review has shown that most of the anti-caking preparations have slack waxes in their composition.
The negative environmental impact of oil-derived polymeric materials and depletion of oil resources is currently a significant concern. This necessitates the replacement of oil-based polymeric materials with bio-based polymers obtained from abundant renewable materials and the replacement of petroleum-based raw materials with other more environmentally friendly substances [19,20].

The aim of this work was to demonstrate the influence of composition and physicochemical properties of the anti-caking agents commercially used as coatings for ammonium nitrate-based fertilizers on their effectiveness, in order to develop innovative organic coatings of similar or higher efficiency but with a reduced negative environmental impact.

2. Materials and Methods

2.1. Materials

Isopropanol, toluene, and hydrochloric acid were purchased from Sigma-Aldrich (St. Louis, MO, USA). Chloroform (CZDA) was acquired from POCH (Avantor Performance Materials Poland S.A., Gliwice, Poland). Karl Fischer reagent (Hydra-Point Composite 5) was procured from J.T. Baker (Thermo Fisher Scientific, Waltham, MA, USA). Standards used for gas chromatography–mass spectrometry (GC–MS) analysis were octadecylamine ($\geq 86.0\%$), hexadecylamine ($\geq 94.0\%$), and stearic acid ($\geq 97.0\%$) (Merck KGaA, Darmstadt, Germany). The anti-caking preparations were purchased from their producers. Two types of ammonium nitrate-based fertilizers were used to study the effect of individual anti-caking agents: AN (ammonium nitrate) and CAN (calcium ammonium nitrate). Physical and chemical parameters of the examined fertilizers are listed in Table 1. Fertilizers were obtained from their manufacturer (GA ZAK S.A., Kędzierzyn, Poland). All fertilizers were coated to the same rate with commercial anti-caking agents (1.15 g of preparation for 1 kg of fertilizer). Granules of tested fertilizers were sieved analyzed. Only a fraction of diameter between 3.15 and 4.00 mm was used for the coatings process and testing of anti-caking properties.

Table 1. Physical and chemical parameters of the examined ammonium nitrate fertilizers.

| Parameter                        | Unit   | AN  | CAN |
|----------------------------------|--------|-----|-----|
| Total nitrogen                   | % (w/w)| 32.0| 27.0|
| Nitric nitrogen                  | % (w/w)| 16.0| 13.5|
| Ammoniacal nitrogen              | % (w/w)| 16.0| 13.5|
| Total magnesium (MgO)            | % (w/w)| -   | 4.0 |
| Water-soluble calcium (CaO)      | % (w/w)| -   | 3.0 |
| Bulk density                     | g·cm$^{-3}$ | 0.96| 1.0 |
| Granule diameter                 | mm     | 2–5 | 2–5 |
| Grain class: content of 2–5 mm granules | % (w/w) | 95  | 95  |

2.2. Physical and Chemical Parameters of Anti-Caking Agents

The physicochemical properties of anti-caking agents such as density, viscosity, melting point, water content, and base number (BN) were determined using the methods described in the relevant standards. All samples were prepared and analyzed in triplicate. The results were presented as mean ± standard deviation (S.D.). The density of anti-caking agents was determined using the areometric method at 70 °C (PN-ISO 3675:2004). Viscosity was measured with an MCR 102 rheometer (Anton Paar GmbH, Graz, Austria) at 70 °C. The melting temperature tests of the anti-caking agents were performed with a differential scanning colorimeter (Mettler-Toledo International, Columbus, OH, USA) (PN 81/C-04513). Water content of the anti-caking agents was tested as specified by the standard (PN-81/C-04959). The testing method involved titration of a sample of anti-caking agents with Karl Fischer reagent and converting the volume of the titrant used for titration into water content in the anti-caking agents using Karl Fischer Automat 633 (Metrohm, Herisau, Switzerland). Characterization of BN was performed using the reference method (PN-ISO 6618:2011). The analysis of BN consisted of dissolving the tested product in a mixture of toluene and isopropyl alcohol containing 5% water. This was followed by hot titration of the obtained
solution with a mixture of isopropanol and hydrochloric acid (concentration of \( c(\text{HCl}) = 0.1 \text{ mol/L} \)) in the presence of bromocresol green for color change. BN is calculated using the formula:

\[
BN \ [\text{mg KOH/g}] = \frac{(V_2 - V_1) \cdot c \cdot 56.1}{m} \tag{1}
\]

where \( V_2 \) is the amount of hydrochloric acid used for the titration of the test sample [mL], \( V_1 \) is the amount of hydrochloric acid used for the titration of the blank sample [mL], \( c \) is the concentration of hydrochloric acid used [mol/L], 56.1 is the molecular weight of potassium hydroxide [g/mol], and \( m \) is the mass of the anti-caking sample [g].

2.3. GC–MS Analysis

Chromatography analysis was performed using a 7890 B GC system with simultaneous detection (splitter) in a flame ionization detector (FID; 5977 Mass Selective Detector, Agilent Technologies). The samples for analysis were prepared by dissolving 0.1 g of the preparation in chloroform (in a 50-mL flask) to record its whole content. Then, 1 \( \mu \)L of the sample was injected into a column (30 m \( \times \) 0.25 mm \( \times \) 0.25 \( \mu \)m, HP5 MS) with a 4:1 split (320 °C) at a constant flow rate of 3 mL/min. The temperature program was set as follows: 120 °C (3 min), 10 °C/min–210 °C (6 min), and 10 °C/min–300 °C (23 min). Assignments from main peaks were made using retention time data obtained for standard compounds and by using the NIST 14 MS library. The compounds were identified based on the chromatogram obtained from the mass detector. The mass spectra of the compounds were compared with the NIST 14 MS library base spectra. Compounds with an 80% match (or better) were recognized as positively identified, which was confirmed by performing a GC–MS/FID standards analysis. Quantitative analysis of the compounds was carried out based on the results obtained from the FID, using the simple normalization method.

2.4. Effectiveness of Anti-Caking Agents

The effectiveness of anti-caking agents was examined on a thermostatic device. The appliance consisted of 24 closed, cylindric compartments, into which the fertilizer to be tested was added. Samples were subjected to seven thermal cycles. One thermal cycle involved holding the sample for 1 h at 40 °C and then for 1 h at 20 °C. After thermostating, the obtained fertilizer block was measured for the force needed to crush it using a vertical automatic crusher (IMADA). The efficacy of anti-caking agents was determined by conducting a force test on both cylindric agglomerates, which were created after the process for uncoated and coated fertilizers and was calculated based on the following formula [21]:

\[
R [\%] = \frac{(M_p - M_{ot})}{M_p} \cdot 100\% \tag{2}
\]

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].

All measurements were made after the granulation process and after 10 and 30 days of storage. All samples were prepared and analyzed in triplicate. The results were presented as mean ± S.D.

Coated fertilizer was obtained by spraying the raw one on a laboratory scale with an anti-caking agent in a rotary drum with inner vanes. Briefly, 2.3 g of anti-caking agent dissolved in 10 mL of chloroform was applied per 2 kg of raw fertilizer so that the coverage was 1.15 g of anti-caking agent for 1 kg of fertilizer. To spray the solution to cover the fertilizer granules, a sprinkler was used with a connected air supply hose to obtain a slight mist and direct the spray to the interior of the running drum with the fertilizer placed inside.
3. Results and Discussion

3.1. Physical and Chemical Parameters of Anti-Caking Agents

Table 2 presents the determined physical and chemical parameters of anti-caking agents. The parameters of each formulation were analyzed to investigate the relationship between their physical and chemical characteristics and their effectiveness to prevent the caking of ammonium nitrate-based fertilizers. The water content of the anti-caking agents can directly increase the water content in the granules of the fertilizers they cover. Taking into account the hygroscopicity of ammonium nitrate fertilizers, and thus their tendency of caking, it is necessary to maintain a low water content in the final fertilizer product. This is therefore a test parameter and is likely to have a large impact on the anti-caking effect in fertilizers. The A2 preparation contained the least water content (0.04%). The anti-caking agents A1 and A2 had a similar density, melting point, and BN. However, they differed significantly in viscosity. The lowest viscosity was found in preparation A2 (8.0 mPa·s) and the highest in A3 (17.0 mPa·s). BN is the amount of potassium hydroxide (in milligrams) determined as equivalent in terms of the acid neutralization capacity of alkaline additives contained in 1 g of anti-caking preparations and was used to assess the content of alkaline additives in the test preparations. The results obtained showed that A3 had a lower BN (18.8 mg KOH/g) than the other anti-caking agents (22.8 and 22.2 mg KOH/g).

Table 2. Physical and chemical parameters of anti-caking agents.

| Parameters             | Unit     | Anti-Caking Agent |
|------------------------|----------|-------------------|
|                        |          | A1     | A2     | A3     |
| Density (70˚C)         | g/cm³    | 0.816 ± 0.001 | 0.813 ± 0.001 | 0.867 ± 0.001 |
| Viscosity (70˚C)       | mPa·s    | 10.3 ± 0.1   | 8.0 ± 0.1   | 17.0 ± 0.2   |
| Water content          | % m/m    | 0.08 ± 0.01  | 0.04 ± 0.01  | 0.10 ± 0.01  |
| Melting point          | ºC       | 70.3 ± 0.3   | 69.2 ± 0.4   | 64.6 ± 0.2   |
| BN                     | mg KOH/g | 22.8 ± 0.4   | 22.2 ± 0.3   | 18.8 ± 0.3   |

Values are expressed as mean ± S.D. of triplicate samples.

3.2. GC–MS Analysis

Chromatographic analysis was performed on the three commercial anti-caking agents dedicated to ammonium nitrate fertilizers. The spectra of these preparations are shown in Figure 1. It can be seen that all three anti-caking agents were relatively similar. Preparation A1 had most of the peaks with a retention time of 5–15 min. In this area, all preparations had several characteristic peaks with the same retention time but with different signal intensities. Additionally, a wide band with a retention time of 20–30 min can be found for all compounds. On the basis of the MS library database, three compounds were identified in the tested preparations and their samples were purchased. GC–MS analysis was also performed for these compounds to confirm their presence and determine their content in the individual studied anti-caking agents. Table 3 shows the compounds identified based on the MS library database in particular anti-caking agents.
Figure 1. Chromatograms of commercial anti-caking preparations (A1, A2, A3).

Table 3. Compounds identified in the tested anti-caking agents based on the NIST 14 MS library.

| Identified Compounds     | Time [Min] |         |         |
|--------------------------|------------|---------|---------|
|                          | A1         | A2      | A3      |
| Octadecylamine           | 13.69      | 13.68   | 13.69   |
| Hexadecylamine           | 11.46      | 11.46   | 11.46   |
| Stearic acid             | 15.07      | 15.10   | 15.09   |

Figure 2 shows the chromatograms of the standard compounds. Their concentrations were adjusted to be comparable with those of specific compounds in the initial preparations. The obtained chromatograms confirmed the presence of compounds identified based on MS in the commercial anti-caking agents.
Figure 2. Chromatograms of the standards.

A wide range of peaks with a retention time of 20–30 min probably resulted from slack wax. Therefore, a GC–MS/FID analysis of slack wax of hydrocarbons C16–C48 (Figure 3) was conducted. Table 4 presents the quantitative analysis results of the identified compounds in mass %.

Table 4. Composition of commercial anti-caking agents determined using GC–MS.

| Parameter       | wt % | A1  | A2  | A3  |
|-----------------|------|-----|-----|-----|
| Octadecylamine  | 6.95 | 5.91| 5.81|     |
| Hexadecylamine  | 3.56 | 3.36| 2.80|     |
| Stearic acid    | 2.11 | 0.79| 0.32|     |
| Slack wax       | 74.52| 86.87| 86.20|     |
| Other           | 12.86| 3.07| 4.87|     |

The composition analysis results of the commercial anti-caking agents showed that all the tested preparations contained hexadecylamine and octadecylamine in comparable amounts. Only in
preparation A1, there were more unidentified compounds and a high amount of stearic acid. A less amount of hydrocarbon base was present in this agent. Hexadecylamine and octadecylamine probably originated from the commercial fatty amine with the hydrocarbon chain C16–C18, and additionally identified compounds, such as stearic acid, were also included (at least in some amount) in the commercial fatty amines used.

3.3. Effectiveness of Anti-Caking Agents

All anti-caking agents were found to be very effective in protecting the granules of AN fertilizers against clumping. Effectiveness of anti-caking agents are listed in Table 5. A2 turned out to be the best (for both AN and CAN), but the differences were very small. In addition, it should be noted that all three commercial anti-caking agents protected AN very well against clumping, but CAN very poorly. This is due to the fact that CAN has a lower critical humidity value, which resulted in higher clumping of this fertilizer. Therefore, it is probably very difficult to choose the right coating to prevent caking. This confirms that not only the anti-caking agent but also the quality and composition of the fertilizer are of key importance. After 10 days of storage, the effectiveness of anti-caking agents decreased and then increased after 1 month of storage. Similar conclusions were drawn from earlier studies [21].

Table 5. Effectiveness of anti-caking agents.

| Storage Period | Effectiveness of Anti-Caking Agent [%] |
|----------------|--------------------------------------|
|                | CAN | A1 | A2 | A3 |
|                | AN  | A1 | A2 | A3 |
| 10 days        |     | 76.4 ± 1.2 | 77.0 ± 0.8 | 62.3 ± 0.9 | 95.9 ± 0.7 | 100 ± 0 | 95.1 ± 0.7 |
| 30 days        |     | 63.2 ± 1.4 | 68.1 ± 1.0 | 60.0 ± 1.5 | 94.8 ± 1.1 | 97.9 ± 0.3 | 93.9 ± 0.6 |
| 30 days        |     | 93.4 ± 1.1 | 94.3 ± 0.6 | 91.2 ± 1.3 | 100 ± 0 | 100 ± 0 | 100 ± 0 |

Values are expressed as mean ± S.D. of triplicate samples.

The decrease in effectiveness is due to the presence of water in the granule. The water concentration at the surface of the granule is different than that on the inside. During storage, water is evenly distributed in the whole granule, and then it is partly evaporated in the storehouse and partly bound in the hydrates. During the storage of fertilizer granules, some reactions take place, which are related to dolomite contamination, migration of the solvent (water), and the action of a strong oxidant (ammonium nitrate). In addition, if such a granule was coated with an anti-caking agent, changes occur in the chemical activity of the components used for its composition. Hence, after a few days, the effectiveness of anti-caking agents decreases compared to that observed immediately after coating the granules. However, after a month, the effectiveness increases and becomes higher than that observed immediately after granule coating.

A very similar composition of the preparations indicates that the key compounds in them are fatty amines and hydrocarbon base, which is the main component by mass. This was already confirmed by the patent review.

The A2 preparation, which was found to be the best, had the lowest viscosity (8.0 mPa-s) and the lowest water content (0.04%). Water content is crucial for a preparation to have good effectiveness as water is involved in the process of granule clumping. The remaining parameters of all preparations were comparable. A significant difference was observed between the preparations in viscosity (8.0–17.0 mPa-s). The research shows that the most optimal viscosity for the tested preparations is about 8 mPa-s.

4. Conclusions

The aim of this work was to examine the composition and physicochemical parameters of commercial anti-caking preparations and to determine the effectiveness of these anti-caking agents in preventing the caking of fertilizers (AN, CAN) coated with them. The study also determined the influence of particular parameters and composition on the effectiveness of protecting fertilizers based
on ammonium nitrate against caking. The research was intended to create innovative formulations of anti-caking agents using more environmentally friendly raw materials. Moreover, by preventing the caking of ammonium nitrate fertilizers, it is possible to reduce the propensity of ammonium nitrate to explode when forced by external factors. The conducted research confirmed the data on the composition indicated by the patent review. It was found that the tested anti-caking agents contained hexadecylamine, octadecylamine, and stearic acid, which are the compounds likely to be a part (at least in some amount) of the commercial C16–C18 fatty amines used. The largest part of the preparations was the hydrocarbon base from slack waxes. The composition and physicochemical parameters of the anti-caking preparations showed that their effectiveness in protecting caking was greatly influenced by the water content, appropriate viscosity and appropriate content of fatty amines in them, and the quality and type of fertilizer. Fat amines are a crucial component in anti-caking preparations for ammonium nitrate fertilizers due to their amphiphilic character.

The tests carried out allowed the parameters that influenced the effectiveness of the anti-caking preparations to be determined. The presented results will help to develop new coatings for more environmentally friendly fertilizers based on ammonium nitrate.

Author Contributions: Conceptualization, A.T.; methodology, A.T. and R.G.; formal analysis, A.T., D.N. and S.P.; investigation, A.T.; resources, J.H.; writing—original draft preparation, A.T.; writing—review and editing, D.N. and K.H.; visualization, A.T.; supervision, K.H.; project administration, K.H. and J.H.; funding acquisition, J.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Science and Higher Education of Poland within a frame of science subsidy for 2020 which was realized in the Department of Engineering and Technology of Chemical Processes, Wroclaw University of Science and Technology (No. 8201003902-K24W03D05).

Conflicts of Interest: The authors declare no conflict of interest.

References
1. World Fertilizer Trends and Outlook to 2022; Food and Agriculture Organization of the United Nations: Rome, Italy, 2019; Available online: http://www.fao.org/3/ca6746en/CA6746EN.pdf?eloutlink=imf2fao (accessed on 23 October 2020).
2. Gezerman, A.O.; Corbacioglu, B.D. Effects of sodium silicate, calcium carbonate, and silicic acid on ammonium nitrate degradation, and analytical investigations of the degradation process on an industrial scale. Chem. Ind. Chem. Eng. Q. 2015, 21, 359–367. [CrossRef]
3. Tyc, A.; Hoffmann, J.; Biskupski, A. Anti-caking agents for ammonium nitrate fertilizers. Part 1. Caking phenomenon. Przem. Chem. 2019, 98, 771–776. [CrossRef]
4. Gezerman, A.O.; Corbacioglu, B.D.; Cevik, H. Improvement of surface features of nitrogenous fertilisers and influence of surfactant composition on fertiliser surface. Int. J. Chem. 2011, 3, 201–209. [CrossRef]
5. Rutland, D.W. Fertilizer caking: Mechanisms, influential factors and method of prevention. Fertil. Res. 1991, 30, 99–114. [CrossRef]
6. Diwani, G.E.; Hawash, S.; Ibiari, N.E.; Imam, I. Treatment of ammonium nitrate fertilizer for cake prevention. Ind. Eng. Chem. Res. 1994, 33, 1620–1622. [CrossRef]
7. Chen, M.; Wu, S.; Xu, S.; Yu, B.; Shihibayeh, M.; Liu, Y.; Zhu, X.; Wang, J.; Gong, J. Caking of crystals: Characterization, mechanisms and prevention. Powder Technol. 2018, 337, 51–67. [CrossRef]
8. Elzaki, B.I.; Zhang, Y.J. Coating Methods for Surface Modification of Ammonium Nitrate: A Mini-Review. Materials 2016, 9, 502. [CrossRef] [PubMed]
9. Tyc, A.; Hoffmann, J.; Biskupski, A. Anti-caking agents for ammonium nitrate fertilizers. Part 2. Commercial products. Przem. Chem. 2019, 98, 948–952. [CrossRef]
10. Tomaszewska, M.; Jarosiewicz, A.; Karakulski, K. Physical and chemical characteristics of polymer coatings in CRF formulation. Desalination 2002, 146, 319–323. [CrossRef]
11. Tomaszewska, M.; Jarosiewicz, A. Polysulfone coating with starch addition in CRF formulation. Desalination 2004, 163, 247–252. [CrossRef]
12. Li, Y.; Jia, C.; Zhang, X.; Jiang, Y.; Zhang, M.; Lu, P.; Chen, H. Synthesis and performance of bio-based epoxy coated urea as controlled release fertilizer. Prog. Org. Coat. 2018, 119, 50–56. [CrossRef]
13. Feng, G.; Ma, Y.; Zhang, M.; Jia, P.; Hu, L.; Liu, C.; Zhou, Y. Polyurethane-coated urea using fully vegetable oil-based polyols: Design, nutrient release and degradation. **Prog. Org. Coat.** 2019, 133, 267–275. [CrossRef]

14. Martinez, J.A.R.; Fajardo, M.R. Anti-Caking Compositions for Fertilizers. U.S. Patent No. 8,932,490, 13 January 2015.

15. Obrestad, T.; Terje, T. Conditioning Agent for a Particulate Fertilizer for Reducing Hygroscopicity and Dust Formation. U.S. Patent No. 10,294,170, 21 May 2019.

16. Zurimendi, J. Anti-Caking Composition. U.S. Patent No. 4,772,308, 20 September 1988.

17. Ogzewalla, M.B.; Archimedo, M.C.; Barnat, J.J. Dust and Anticaking Resistant Fertilizer. U.S. Patent Application No. 15/404,348, 20 July 2017.

18. Gezerman, A.O. A novel industrial-scale strategy to prevent degradation and caking of ammonium nitrate. **Heliyon** 2020, 6, 1–9. [CrossRef] [PubMed]

19. Gandini, A.; Lacerda, T.M.; Carvalho, A.J.F.; Trovatti, E. Progress of Polymers from Renewable Resources: Furans, Vegetable Oils, and Polysaccharides. **Chem. Rev.** 2016, 116, 1637–1669. [CrossRef] [PubMed]

20. Xiao, X.; Yu, L.; Xie, F.; Bao, X.; Liu, H.; Ji, Z.; Chen, L. One-step method to prepare starch-based superabsorbent polymer for slow release of fertilizer. **Chem. Eng. J.** 2017, 309, 607–616. [CrossRef]

21. Tyc, A.; Penkala, S.; Biegun, M.; Nieweś, D.; Huculak-Mączka, M.; Hoffmann, K. The Effectiveness of Commercial Anticaking Agents for Ammonium Nitrate Fertilizers. **Ecol. Chem. Eng. A** 2019, 26, 127–135. [CrossRef]

**Publisher’s Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).