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Studies for alternative anti-caking additives used in the production of ammonium nitrate

Burak Lok^a, Meric Gedikagaoglu^b, Cengiz Yenikaya^{*c}, Fatih Sen^{*d}

^aİGSAŞ Kütahya Factory R&D Center, Çalca Mh. Eskişehir Karayolu Bul No:89 43100, Kütahya, Türkiye, ORCID:0000-0002-1439-2805

^bİGSAŞ Kütahya Factory R&D Center, Çalca Mh. Eskişehir Karayolu Bul No:89 43100, Kütahya, Türkiye, ORCID:0000-0001-7503-3665

^cKütahya Dumlupınar University, Graduated Institute, Department of Chemistry, Kütahya, Türkiye, ORCID:0000-0002-5867-9146

^dKütahya Dumlupınar University, Graduated Institute, Department of Chemistry, Kütahya, Türkiye, ORCID:0000-0001-9929-9556

Abstract

In the production of ammonium nitrate, powdered, caking, and grain size to the desired standards cause great problems in prilling and granulation processes. In this study, the problems of caking were discussed in the final product in ammonium nitrate production. Additives are added at certain stages of production to reduce and eliminate the problems of caking. The product is usually passed through a drum where it is fed with anti-caking additives with the help of a dosing system before the packaging process. At the next stage, it is stored under appropriate conditions and placed on the market.

In this study, mixtures containing different components, petroleum-derived chemicals (liquid and solid paraffin), and inorganic salts were formed, and their physical properties were determined by standard analysis methods. A quick caking measurement test was performed by dosing operations providing ammonium nitrate product remained within the range standard specifications. For the ammonium nitrate product without anti-caking agent dosage, the caking percentage was determined as 68.27%. The commercial anti-caking agent is dosed at a rate of 0.05% and has 40.84%, a 0.10% caking ratio of 39.05%. In the final product, caking was reduced by 29.22%. Six prescriptions based on ANO, a petroleum-derived chemical, were prepared (R17-R22). Effective results were obtained in commercial product comparison in ANO mold caking performance tests. While the % caking ratio of R18 is 15.33 according to the 1:1000 dose amount, this value is 13.07% for the commercial anti-caking agent.

The study was completed by identifying the mixtures that give the best results.

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Keywords: ammonium nitrate, agglomeration, pollution, prilling process, granulation.

* Corresponding author. phone.: +90-5059184498

E-mail address: fatihsen1980@gmail.com, cengiz.yenikaya@dpu.edu.tr

1. Introduction

Ammonium nitrate is a chemical compound with the formula NH_4NO_3 . It is a white crystalline solid composed of ammonium and nitrate ions. Although it does not hydrate as a hygroscopic solid, it is very soluble in water. It is mainly used as a high-nitrogen fertilizer in agriculture. Another important use is as a component of explosives (ANFO) mixtures used in mining, quarrying, and building construction. ANFO is ammonium nitrate impregnated with fuel oil [1].

In our country, ammonium nitrate is produced in high capacities by companies such as İGSAŞ İstanbul Fertilizer Industry Inc., BAGFAŞ Bandırma Fertilizer Factories Inc., Toros Tarım Inc., and Gemlik Fertilizer Inc.

The raw material of ammonium nitrate is ammonia and nitric acid. In industry, nitric acid production begins with the combustion of ammonia over platinum-rhodium-palladium catalysts in ammonia combustion reactors to form nitrogen monoxide. At high temperatures, nitrogen monoxide gases from the ammonia combustion reactors first pass through the cascade heat exchangers. The next operation of the process is the oxidation stage. In the oxidation phase, nitrogen monoxide is oxidized by oxygen and converted to nitrogen dioxide. After the oxidation operation, nitrogen dioxide is absorbed with water, and nitric acid is produced. The production of ammonia, another raw material, starts with the reaction of natural gas in the steam reformer reactor, releasing hydrogen, carbon dioxide, carbon monoxide, hydrogen sulfide, and trace amounts of hydrocarbon gases ($\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$). Hydrogen sulfide is separated from the syngas by desulfurization. Carbon monoxide is oxidized to carbon dioxide. Carbon dioxide is sent to the urea plant for urea production. The remaining hydrogen is reacted with nitrogen from the air separation unit to produce ammonia.

Ammonium nitrate (AN) was first prepared in the 16th century. Its early industrial development was primarily for use in explosives. Its use as a fertilizer developed rapidly in the 1940s. Ammonium nitrate is mainly produced by the reaction of gaseous ammonia with aqueous nitric acid [2]. The production of ammonium nitrate begins with the formation of ammonium nitrate solution after 78 % conversion of ammonia and nitric acid in a 1:1 ratio in a stoichiometric reactor at a temperature of approximately 3.5 bar and 180 °C. Then, 78 % by mass of ammonium nitrate solution is sent to the first evaporation stage. In the first evaporation, 78 % by mass of ammonium nitrate is concentrated and increased to 95 % concentrations. In this process, waste steam from the reactors is fed to the evaporators. In the second evaporation, 95 % ammonium nitrate solution is concentrated and increased to 99 % concentration. 99 % ammonium nitrate solution is sent to the prill tower for prilling. The ammonium nitrate sprayed down from the tower takes the form of prill. Afterward, it is presented to the market by physical processes such as drying, cooling, dosing, and packaging.

Agglomeration occurs with the help of either natural forces or applied forces. For example, if it rains on a dusty road, the wet dust sticks together and then the dust stays stuck to each other even if the water evaporates and escapes from the environment. Here, water has created a natural agglomeration force [3].

The caking of ammonium nitrate fertilizer (ANG) is agglomeration and occurs with the effect of one or the other or both of the above two groups of forces [4]. The main ingredient used to make ammonium nitrate fertilizers is ammonium nitrate. However, at room temperature it exhibits some undesirable physicochemical properties, including hygroscopicity and phase change, resulting in an undesirable agglomeration phenomenon. Incineration changes the properties of the fertilizer, resulting in material loss. As a result, both the producer and the end customer suffer financial losses. Currently, anti-caking chemicals are the best approach to prevent fertilizers from clumping. Depending on the type of fertilizer and the anti-caking agent, the finished fertilizer granules are sprayed with the required amounts of these substances [5].

Most fertilizers tend to clump or clump (caking) during storage. The caking mechanism in fertilizers is mostly attributed to the formation of salt bridges and/or capillary adhesion. The severity of agglomeration can be affected by several factors including chemical composition, moisture content, particle structure, mechanical strength, hygroscopic properties, product temperature, ambient conditions, storage time, and storage pressure. Various methods of reducing or eliminating caking in fertilizers mainly involve process control, storage/packaging conditions, and/or the addition of anticaking agents [6].

The fact that fertilizers have a propensity to clump together while being transported and stored is one of the biggest issues facing the industry. Interaction between solid fertilizer particles at their places of contact leads to agglomeration. Certain fertilizer characteristics and environmental factors trigger these interactions, also known as contact mechanisms. An essential area of study that guarantees the use of the anti-caking mechanism while also having a direct impact on the end product's quality and financial worth [7].

To lessen hygroscopicity, a physical coating technique was created to replace the surface of ammonium nitrate particles with various surfactants. The surfactants that were employed were tetradecyl amine, dodecyl amine, tetradecanoyl, palmitic acid, lauric acid, stearic acid, and stearyl alcohol. Tests were conducted on the hygroscopicity of coated and uncoated ammonium nitrate [8].

Granular fertilizers have a tendency to clump when being stored, particularly those based on ammonium nitrate (AN). The goal was to create efficient anti-caking coatings for fertilizers containing ammonium nitrate while simultaneously enhancing fertilizer quality and perfecting the anti-caking coatings' composition. Response surface methodology (RSM) employing Box-Behnken design (BBD) was used to examine the impact of the manufactured organic coatings' composition on the anti-caking efficacy of fertilizers. Furthermore, the impact of the created anti-caking agents on the quality of the fertilizer was assessed by gauging the granules' crushing strength [9].

The flocculation of calcium ammonium nitrate (CAN) fertilizer, the flocculation mechanism, the factors causing caking, and remedial measures are discussed. The two theories regarding the aggregation mechanism are the capillary adhesion theory and the crystal bridging theory. Factors affecting caking are humidity, external humidity, the physical shape of the product, calcium nitrate formation, thermal shocks, heap height in storage, temperature fluctuation range, inefficient product conditioning, and seamless linings in bags. Anti-caking agents used to coat fertilizer particles to reduce caking are of two types: inert and active. The first includes finely divided powders such as clays or talc, and the second includes surfactants and water-resistant materials. Primary fatty amines play a key role in the anti-caking treatment of CAN [10].

Caking of Ammonium Nitrate Fertilizer (ANG); It is an agglomeration event caused by some factors, especially humidity, temperature, and pressure, from time to time in factory and customer warehouses.

This fertilizer; is produced as granules (grain) for reasons such as storage, filling, transportation, and agricultural application convenience, prevention of deterioration, and keeping waste at a low level. It has long been known to the research bodies of the manufacturing companies that caking shows some differences depending on whether the filler is limestone dolomite or another inert material. Many research attempts to eliminate petrification have either been hidden as private secrets of the relevant factories or have been patented and both legally secured and turned into a means of earning for the relevant organization.

It can be said that studies on this subject continue even today. For this reason, it is a research principle to always try to achieve better results with good results. The subject of this article is a new-generation product development study to be used in the anti-cake dosing process, which is a physical operation. Organic and inorganic materials were used in the studies. Anti-caking agent mixtures were formed with paraffin forms, which are organic substances.

Finally, samples made with a mixture of commercial product ANO, stearic acid, and naphthalene derivative chemicals (SNS) were applied to ammonium nitrate and effective results were observed. Istanbul Fertilizer Industry Inc. The commercial anticaking agent used in the ammonium nitrate plant and the samples made in the study were compared.

2. Experimental Studies

In this study, mixtures containing different components preventing the caking of ANG were formed from petroleum-derived chemicals (liquid and solid paraffin) and mixtures containing inorganic salts under laboratory conditions.

Experimental studies consist of five main steps;
Prescription Preparation Phases
Physical Determination and Comparison Studies

Suggestion and Preparation of New Prescriptions
 Application of Appropriate Prescription
 Measuring Cake Performance in the Final Product

2.1. Materials and methods

Anti-caking chemicals [11] used during the studies were provided in analytical and technical purity. Anti-caking mixtures were prepared by using these chemicals in different ratios. The commercial anti-caking agent used in the Ky 230 Fertilizer Plant was analyzed (Table 2.1). It was tried to find the product closest to the physical properties of the commercial product from the anti-cake agent mixtures with appropriate content prepared in the studies.

Table 2.1. Commercial Product Properties Used as Anti-Caking Agent.

Ingredients	Color	Density(g/cm ³)	Pour Point °C ASTM D97	Melting Point °C ASTM D127	Viscosity cSt ASTM D721	Oil Content % ASTM D127
Commercial Anticaking Agent	Dark Brown	0.83	38-41	66-77	Max 30	-

2.1.1. Chemicals

2.1.1.1. Ammonium nitrate

The ammonium nitrate used in the experiments and produced in our facility was taken from the dryer trammel outlet of the production. The reason why it is taken from this stage is that anti-caking agent dosing has not been performed yet. The product temperature is high at this point (90-110 °C). In the experiments, the product was used for cooling.

2.1.1.2. Solid paraffin

Paraffin wax (or petroleum wax) is a soft, colorless solid obtained from petroleum, coal, or oily things, consisting of a mixture of hydrocarbon molecules containing 20 to 40 carbon atoms. It is solid at room temperature and begins to melt above about 37 °C (99 °F) [12]. It differs from kerosene and other petroleum products, sometimes called paraffin [13]. The solid paraffin product obtained from Merck in granular form was used at high rates in the prepared mixtures. For this alkane with a high carbon number, a melting process was applied in the experiments.

2.1.1.3. Liquid paraffin

Liquid paraffin, also known as paraffin oil, liquid paraffin oil, or Russian mineral oil, is a highly refined mineral oil used in cosmetics and medicine. Cosmetic or medical liquid paraffin should not be confused with paraffin (ie kerosene) used as a fuel. The generic meaning of paraffin, meaning alkane, has led to regional differences in the meanings of both paraffin and paraffin oil. It is a transparent, colorless, almost odorless, and oily liquid consisting of saturated hydrocarbons derived from petroleum. This product, which is supplied by Merck in liquid form, has been used at a high rate in the prepared mixtures. No melting process was applied for this alkane with a low carbon number.

2.1.1.4. ANO material

ANO material, which is a commercial product, is the material that has the closest physical properties to the anti-caking agent product and liquid paraffin applied in the enterprise. Its pour point is 40 °C, flash point is 200 °C.

2.1.1.5. SNS material

For this naphthalene-derived chemical, which is used as a porous agent in the production of PPAN (Prill Porous Ammonium Nitrate), data on reducing caking were obtained in previous GPAN (Granular Porous Ammonium Nitrate) studies. Since it is an organic substance, it can be easily dissolved in ANO and paraffin substances.

2.1.1.6. Stearic acid

Stearic acid is obtained from fats and oils by saponification of triglycerides using hot water (approximately 100 °C). The resulting mixture is then distilled [14]. Commercial stearic acid is usually a mixture of stearic and palmitic acids, although purified stearic acid is available. Commercially, oleic acid found in dates and soybeans can be hydrogenated to yield stearic acid. Stearic acid, a plasticizer, has been used for pour point adjustment in studies.

2.1.1.7. Other inorganic salts

Both by powdering and before the prilling phase, they are added to the ammonium nitrate solution and added to the prepared anti-caking agent mixtures at certain rates, since they increase the strength of the product. These chemical salts; are sodium bisulfite, potassium sulfate, potassium hydroxide, ammonium sulfate, sodium phosphate, calcium nitrate, magnesium nitrate, and magnesium oxide.

2.1.2. Methods

In the preparation phase of anti-sealing agent mixtures with different compositions, a magnetic heater mixer with a digital display was used. A kinematic viscosity bath, oil content solvent extraction tester in waxes drop melting point tester, and internally cooled pour point tester were used to be used in physical determinations. Air spray guns and pipette, spray nozzles were used in spray experiments. A pilot drum with speed and angle adjustment was used to simulate the anti-slip drum used in the enterprise. Finally, a caking oven was used for caking performance measurements.

2.2. Experimental methods

Physical determinations in the studies were made according to ASTM standards. After the appropriate products were prepared, a certain amount of ammonium nitrate without additives was placed in the pilot drum (trammel), which simulates the operation in the enterprise, and the dosing process was carried out with the help of a spray gun and pipette. Finally, the caking performance of the ammonium nitrate samples, which were coated with an anticaking agent, was measured by using a caking oven and by applying the rapid caking method.

2.3. Rapid cake tests method

The rapid caking test method is a method used in IGSAŞ Central Laboratory. The sample is taken 300 grams in special stainless-steel containers. The lid of the stainless-steel container is closed. 300 grams of mass is put on it. It is then placed in the caking oven. The caking oven starts its process cycle at 15 °C, the temperature rises to 40 °C within 1 hour. The temperature drops again from 40 °C to 15 °C and thus the oven has made 1 cycle. 1 cycle is about 2.4 hours. By making 10 cycles in one day, the sample is quickly caked. At the end of 1 day, the sample is taken out

of the oven. The caking mass is weighed. The caking percentage is calculated. In cases where caking is not observed, the processes are repeated.

2.4. Recipe preparation

In the study, 22 different prescriptions were created. 8 of them are based on solid paraffin, 8 are based on liquid paraffin, and 6 are based on ANO. In the tables (2.2-2.4), recipe contents are given as percent by mass.

Table 2.2. Solid paraffin-based Recipes (R1 – R8)

Recipe No	Physical Appearance	Solid Paraffin %	Stearic Acid %	Sodium bi sulfide %	Potassium Sulfate %	Potassium Hydroxide %	Ammonium Sulfate %	Sodium Phosphate %	Calcium Nitrate %	Magnesium Nitrate %	Magnesium Oxide %	SNS %	Total %
R1	Solid	60	30	10	-	-	-	-	-	-	-	-	100
R2	Solid	60	20	10	10	-	-	-	-	-	-	-	100
R3	Solid	60	10	10	10	10	-	-	-	-	-	-	100
R4	Solid	60	5	10	10	10	5	-	-	-	-	-	100
R5	Solid	60	-	-	-	-	30	10	-	-	-	-	100
R6	Solid	60	-	-	-	-	20	10	10	-	-	-	100
R7	Solid	60	-	-	-	-	10	10	10	10	-	-	100
R8	Solid	60	-	-	-	-	5	10	10	10	5	5	100

Depending on the prescriptions, some inferences were made based on the observations made during the preparation phase. For example, NH₃ output in R5 and R6 was sensed by smell. The reason for this is thought to be the degradation of ammonium sulphate with sodium phosphate. Since the ammonium sulphate ratio is low in R7 and R8, even if NH₃ was formed, its smell was not felt. In recipe 6, calcium nitrate was not homogenized in solid paraffin. Non-homogenized mixtures are also not very suitable for spraying. However, these products were subjected to physical determinations (pour point, melting point, oil content, density, and viscosity) in subsequent studies. In these mixtures with a high solid paraffin ratio, (R1-R8) samples with a melting point around solid paraffin (80°C) (Table 2.5) are not considered suitable for spraying applications, which is the third phase of the trials. The reason for this is that in the application of these recipes as anti-caking agents, the operating cost for the industrial facility will be higher than the commercial anti-caking agent and other recipes. At the same time, there is a homogenization problem in these recipes. The melting points of the products were determined qualitatively based on observations and measurements (Table 2.5). As a result, R1-R8 prescriptions were not found suitable.

Recipes (R9-R16) prepared with liquid paraffin and related components are given in Table 2.3.

Table 2.3. Liquid paraffin-based Recipes (R9 – R16)

Recipe No	Physical Appearance	Liquid Paraffin %	Stearic Acid %	Sodium bi sulfide %	Potassium Sulfate %	Potassium Hydroxide %	Ammonium Sulfate %	Sodium Phosphate %	Calcium Nitrate %	Magnesium Nitrate %	Magnesium Oxide %	SNS %	Total %
R9	Solid	60	30	10	-	-	-	-	-	-	-	-	100
R10	Solid	60	20	10	10	-	-	-	-	-	-	-	100
R11	Liquid	60	10	10	10	10	-	-	-	-	-	-	100

R12	Liquid	60	30	-	-	-	-	-	-	-	-	10	100
R13	Liquid	60	20	-	-	-	-	-	-	-	-	20	100
R13.1	Liquid	60	25	-	-	-	-	-	-	-	-	15	100
R14	Liquid	60	10	-	-	-	-	-	-	-	-	30	100
R15	Liquid	60	-	-	-	-	-	-	-	-	-	40	100
R16	Solid	50	30	-	-	-	-	-	-	-	-	20	100

2.5. Physical Determination and Comparison Studies

Physical determinations were performed on the prepared recipes according to ASTM standards. Viscosity determinations were determined according to the ASTM D445 standard [15]. Density determinations were measured in g/cm^3 with the help of a simple measuring tape.

Melting point determinations were determined with the help of a drop melting point test device according to ASTM D127 standards [16].

Pour point determinations were made with a pour point tester by ASTM D97 standard [17].

Table 2.4. Physical Properties of Anticaking Agents.

Ingredients	Physical Appearance	Color	Density(g/cm^3)	Pour Point °C ASTM D97	Melting Point °C ASTM D127	Viscosity cSt ASTM D721	Oil Content % ASTM D127
Commercial Anticaking Agent	Liquid	Dark Brown	0.83	38-41	66-77	Max 30	-
R1	Solid	White	0.50	47-50	51-57	-	-
R2	Solid	White	0.55	49-52	54-61	-	-
R3	Solid	White	0.55	52-55	58-62	-	-
R4	Solid	White	0.62	54-57	58-62	-	-
R5	Solid	White	0.59	53-56	56-61	-	-
R6	Solid	White	0.49	51-54	54-58	-	-
R7	Solid	White	-	-	-	-	-
R8	Solid	White	0.80	54-57	57-61	-	-
R9	Liquid	White	0.72	54-57	-	-	-
R10	Liquid	White	0.82	55-58	-	-	-
R11	Liquid	Light Brown	-	-	-	-	-
R12	Liquid	Light Brown	0.88	52-55	-	-	-
R13	Liquid	Light Brown	0.76	50-53	-	-	-
R13.1	Liquid	Light Brown	0.81	38-41	-	-	-
R14	Liquid	Light Brown	0.89	33-36	-	-	-
R15	Liquid	Light Brown	0.94	-7—4	-	-	-
R16	Solid	Light Brown	0.93	8-10	-	-	-
R17	Solid	Dark Brown	1.06	50	50-55	-	-
R18	Liquid	Dark Brown	1.00	35	-	-	-
R19	Liquid	Dark Brown	0.91	36	-	-	-
R20	Liquid	Dark Brown	0.89	38	-	-	-
R21	Liquid	Dark Brown	0.89	40	-	-	-
R22	Liquid	Dark Brown	0.88	41	-	-	-

2.6. Suggestion and preparation of new prescriptions

Depending on the prescriptions, some inferences were made based on the observations made during the

preparation phase. After prescriptions 9,10,11, the contents of the prescription were evaluated. By selecting the key compounds in the commercial product, recipes 13-22 were prepared with three components (ANO, Stearic acid, SNS). As a result of the trials on liquid paraffin and ANO-based recipes, products physically close to the commercial product were obtained. It was decided that the fourth component could be urea in terms of providing the ammine requirement. For color compatibility, the possibility of the fifth component being molasses was considered. A recipe containing molasses and urea was prepared. However, since homogenization could not be achieved, it was removed, and the use of molasses was abandoned.

Commercial product ANO material with the same properties was used instead of liquid paraffin. Recipes were prepared with ANO substance, stearic acid, and SNS. ANO-based prescriptions are given in Table 2.5.

Table 2.5. ANO based Recipes (R17-R22).

Recipe No	Physical Appearance	ANO %	Stearic Acid %	Sodium bi sulfide %	Potassium Sulfate %	Potassium Hydroxide %	Ammonium Sulfate %	Sodium Phosphate %	Calcium Nitrate %	Magnesium Nitrate %	Magnesium Oxide %	SNS %	Total %
R17	Solid	60	35	-	-	-	-	-	-	-	-	5	100
R18	Liquid	60	30	-	-	-	-	-	-	-	-	10	100
R19	Liquid	60	25	-	-	-	-	-	-	-	-	15	100
R20	Liquid	60	20	-	-	-	-	-	-	-	-	20	100
R21	Liquid	60	15	-	-	-	-	-	-	-	-	25	100
R22	Liquid	60	10	-	-	-	-	-	-	-	-	30	100

2.6. Application of appropriate prescriptions

22 samples (solid paraffin-based, liquid paraffin-based, ANO-based) prepared in section 2.4 were applied on ammonium nitrate by the operating dosing amounts (400 L/min) in this section. A pilot drum device was used in the experiments.

A pilot drum device was specially manufactured for these trials. This device is the prototype of the Anti-cake trammel at the Ky-230 Plant. The pilot drum device has features such as speed adjustment, direction adjustment, and angle adjustment. The pilot drum device is made of 316 L stainless steel considering the corrosive properties of ammonium nitrate.

Ammonium nitrate product without any additive applied after the dryer equipment of the Ky-230 Plant was used in the experiments for the application of appropriate recipes. In these studies, 5000 grams of ammonium nitrate without anti-caking was weighed and placed in the pilot drum device. The device was operated by adjusting the speed and angle settings. After 15 minutes, approximately 100 grams of samples are taken from the samples, brought to the appropriate dosing temperature under operating conditions (80 °C), and ammonium nitrate is placed in the pilot drum with an automatic pipette at the rates determined according to the operating conditions (these rates are in the form of the amount of anticaking agent/amount of AN, gram Doses applied in /gram were 1/1000 (0.1%), 2.5/1000 (0.25%) and 5/1000 (0.5%) sprayed. Trials were completed for all samples by providing a homogeneous mixture. Antique ammonium nitrate samples were taken and tested for caking performance in the final product.

2.7. Measuring cake performance in the final product

In this part of the study, caking performances for all samples are shown in Section 2.3. It was determined with the

help of the Rapid Stuttering Test Method in The caking performance measurements for R13.1 and R18-22 recipes are given in Tables 2.6 and 2.7, respectively

Table 2.6. Caking Performance for Recipe 13.1

Sample Dozing (%)	Caking Material (g)	Caking Percent (%)
0	204.80	68.27
0.05	122.52	40.84
0.10	117.14	39.05

Table 2.7. Caking Performance Results for ANO-based materials, Commercial Anticaking Agents and Ammonium Nitrate

No	Name and No	Dosage Amount (%)	Caking Material (g)	Caking Percent (%)
-	Ammonium Nitrate	-	204.80	68.27
-	Ammonium Nitrate	-	211.60	70.53
-	Ammonium Nitrate	-	209.84	69.95
-	Commercial Anticaking Agent	0.10	39.20	13.07
-	Commercial Anticaking Agent	0.25	38.12	12.71
-	Commercial Anticaking Agent	0.50	37.22	12.41
R18	Sample 18	0.10	45.98	15.33
R18	Sample 18	0.25	35.84	11.95
R18	Sample 18	0.50	28.20	9.41
R19	Sample 19	0.10	64.69	21.56
R19	Sample 19	0.25	64.15	21.38
R19	Sample 19	0.50	54.37	18.12
R20	Sample 20	0.10	51.59	17.20
R20	Sample 20	0.25	42.42	14.14
R20	Sample 20	0.50	32.32	10.77
R21	Sample 21	0.10	54.94	18.31
R21	Sample 21	0.25	47.56	15.85
R21	Sample 21	0.50	26.70	8.90
R22	Sample 22	0.10	73.26	24.42
R22	Sample 22	0.25	92.78	30.93
R22	Sample 22	0.50	92.46	30.82

3. Conclusions and Suggestions

In this study, alternative mixtures were prepared to eliminate caking, which is an important problem in ammonium nitrate production. Physical analyses were made for the anticaking agent currently used in the Ky-230 Fertilizer Plant. By carrying out literature studies [18] and reverse engineering studies, anti-caking agent mixtures were formed in appropriate compositions.

In the light of physical determinations, the density of the prescriptions made with solid paraffin material is lower than the anti-caking agent currently used. While the density for the currently used anticaking agent is 0.83 g/cm³, the

density in the recipes prepared with solid paraffin remained in the range of 0.49-0.62 g/cm³. Melting points are not at the desired level. For the existing anticaking agent, which is in the range of 66-77 °C, this value remained in the range of 51-62 °C in recipes prepared with solid paraffin. At the same time, the pour points are higher than the commercial anticaking agent (47°C-54°C) according to the pour point determinations made according to the ASTM D97 standard. The anticaking agent pour point value is in the range of 38 °C-41 °C. Table 2.2 Samples prepared with solid paraffin were not applied to ammonium nitrate as they did not have the desired properties as a result of physical analysis.

Density values for the samples prepared with liquid paraffin were close to the anticaking agent used in the enterprise (0.88-0.94 g/cm³). The pour point value varied according to the stearic acid ratio in the samples prepared with liquid paraffin. As the stearic acid ratio increased on the samples, the pour point also increased (Table 2.4). The caking performance test was applied for recipe 13.1, whose physical properties were closest to the commercial product (Table 2.6).

According to the values in the table, while the percentage of caking was 68.27 % for the undosed ammonium nitrate product, 40.84 % caking was observed at a 0.05 % dosage rate and 39.05 % at the rate of 0.10 %. The caking was reduced by 29.22 %.

Six recipes based on ANO were prepared (R17-R22). Physical determinations were applied to the samples. Their densities are close to 0.88-1.00 g/cm³ of commercial product. The R17 is in solid physical appearance. The caking test was not applied due to commercial concerns. R18-22 is in the liquid phase. For R18-22, caking performance tests were performed for the available commercial anticaking agent and ant exhaust ammonium nitrate (Table 2.7).

ANO-based samples gave effective results in caking performance tests compared to the commercial product. While the % caking rate of R18 is 15.33 according to 1/1000 dosage amount, this value is 13.07% for commercial anti-caking agents. As the dosage amount increased, caking decreased in the ammonium nitrate sample applied to recipe 18. It gave more effective results than the commercial product. In the ammonium nitrate product, the dosing standard is a maximum of 0.125 % under operating conditions. Doses applied above this value deteriorate the product specifications (moisture, density, etc.) of the ammonium nitrate product supplied to the market. However, despite this, the reason for applying high dosages in this study is to observe the effect of samples on ammonium nitrate caking in wide ranges. Much research has been done on Ammonium Nitrate caking. The different aspect of this study is that all of the experiments covering the study were carried out in the factory that produces ammonium nitrate. The products have been tested in laboratory and production applications, and by obtaining effective results, contributions have been made to the literature and the archives of the institution.

Conflict of Interest

The authors declare that they have no conflict of interest.

Author Contributions

Conceptualization, B.L., and M.G., and F.S.; formal analysis, B.L., M.G., C.Y., and F.S.; investigation, B.L., and M.G; resources, B.L., and F.S., writing-original draft preparation, C.Y., and F.S.; writing-review and editing, C.Y., and F.S.; supervision. All authors have read and agreed to the published version of the manuscript.

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References

[1] Z. Karl-Heinz, W. Karl-Heinz, S. Manfred, S. Kimihiko, S. Herbert, Z. Werner, C. Ruthild and L. Herbert., "Ammonium Compounds," in

Ullmann's Encyclopedia of Industrial Chemistry, Wiley, 2000. doi: 10.1002/14356007.a02_243

[2] "Ammonium Nitrate," in *Synthetic Nitrogen Products*, Boston: Kluwer Academic Publishers, pp. 251–265.

[3] F. Patat, "Ullmanns Enzyklopädie der technischen Chemie," *Zeitschrift für Elektrochemie, Berichte der Bunsengesellschaft für Phys. Chemie*, vol. 60, no. 9–10, pp. 1207–1208, Nov. 1956, doi: 10.1002/bbpc.19560600957.

[4] Kirk Othmer, *Encyclopedia of Chemical Technology*, vol. 22. 2004.

[5] A. Tyc, S. Penkala, Ma. Biegun, and D. Niewes, "The effectiveness of commercial anticaking agents for ammonium nitrate fertilizers," *Ecol Chem Eng A.*, vol. 26, no. (1-2), pp. 127–135, 2019, doi: 10.2428/ecea.2019.26(1-2)11.

[6] D. W. Rutland, "Fertilizer caking: Mechanisms, influential factors, and methods of prevention," *Fertil. Res.*, vol. 30, no. 1, pp. 99–114, Oct. 1991, doi: 10.1007/BF01048832.

[7] A. Ulusal and C. Avsar, "Understanding Caking Phenomena in Industrial Fertilizers," *Chem. Biochem. Eng. Q.*, vol. 34, no. 4, pp. 209–222, 2021, doi: 10.15255/CABEQ.2020.1866.

[8] B. I. Elzaki and Y. J. Zhang, "Surface modification of ammonium nitrate by coating with surfactant materials to reduce hygroscopicity," *Def. Technol.*, vol. 15, no. 4, pp. 615–620, Aug. 2019, doi: 10.1016/j.dt.2019.01.004.

[9] A. Tyc, D. Nieweś, E. Pankalla, M. Huculak-Mączka, K. Hoffmann, and J. Hoffmann, "Anti-Caking Coatings for Improving the Useful Properties of Ammonium Nitrate Fertilizers with Composition Modeling Using Box–Behnken Design," *Materials (Basel)*, vol. 14, no. 19, p. 5761, Oct. 2021, doi: 10.3390/ma14195761.

[10] M. Ahmed, "Caking of CAN fertilizer & its prevention.," *J. Technol. Dev.*, vol. 15, no. 1, pp. 75–84, 1990.

[11] K. PI, "Non-Caking Fertilizers from Ammonium Nitrate and Supplementary Nutrients," *J. Univ. Chem. Technol. Metall.*, vol. 40, no. 3, pp. 209–212, 2005.

[12] M. Freund, R. Csikós, S. Keszthelyi, and G. Y. Mózes, "Paraffin Products Properties, Technologies, Applications," *Paraffin Prod. Technol. Appl.*, vol. Volume 14, p. 337, 1982.

[13] C. B. Willingham, W. J. Taylor, J. M. Pignocco, and F. D. Rossini, "Vapor pressures and boiling points of some paraffin, alkylcyclopentane, alkylcyclohexane, and alkylbenzene hydrocarbons," *J. Res. Natl. Bur. Stand. (1934)*, vol. 35, no. 3, p. 219, Sep. 1945, doi: 10.6028/jres.035.009.

[14] F. Sharif, E. Crushell, K. O'Driscoll, and B. Bourke, "Liquid paraffin: a reappraisal of its role in the treatment of constipation," *Arch. Dis. Child.*, vol. 85, no. 2, pp. 121–124, Aug. 2001, doi: 10.1136/adc.85.2.121.

[15] Anonim, "ASTM D445-19 Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)," 2021.

[16] ASTM D127-08 - Standard Test Method for Drop Melting Point of Petroleum Wax, Including Petrolatum. 2021.

[17] ASTM D97-11 - Standard Test Method for Pour Point of Petroleum Products. 2021.

[18] Anonim, *TÜGSAŞ İşletme Bültenleri*. 1964.