

Improving the properties of ammonium nitrate fertilizer using additives

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Ammonium nitrate fertilizer is a very hygroscopic material. Absorption of moisture by ammonium nitrate leads to a decrease in the mechanical strength of the granules, thus the chance of dust formation during storage is very high. This phenomena eventually leads to the caking of the fertilizer and its transformation to a solid lump accompanied by major economic losses. In this study attempts were made for the purpose of the prevention of caking and the reduction of dust formation of ammonium nitrate fertilizer during storage. This was achieved by coating the surface of the granules with urea lignosulfonate mixtures, which renders the surface of the granules hydrophobic. The best results obtained were: a urea lignosulfonate mixture containing 80% solids, a mixing ratio between urea and lignosulfonate not exceeding 1:2 and a % coating not more than 0.3%.

يهدف البحث الى دراسة احدي الطرق الأمنة المستخدمة في تقليل قابلية حبيبات سماد نترات الأمونيوم للتحجر و ذلك بواسطة تغطية سطح حبيبات السماد بخليط من مادتي اليوريا و اللجنوسلفونيات هذا الخليط يكون طبقة علي سطح حبيبات السماد تقلل من كمية الرطوبة التي يمكن ان تمتصها الحبيبات حيث ان امتصاص الرطوبة يعتبر من اهم العوامل الأساسية المسببة لتحجر السماد حيث انه يقلل من صلابة الحبيبات فتكون سهلة الكسر اثناء التخزين مما يؤدي الي تكوين حبيبات صغيرة لتساعد في عملية التحجر. و افضل النتائج التي تم الحصول عليها كانت عند الظروف الآتية: نسبة المواد الصلبة في الخليط في حدود ٨٠%. نسبة الخلط لا تزيد عن ٢:١ يوريا: اللجنوسلفونيات. نسبة التغليف لا تزيد عن ٠,٣%.

Keywords: Ammonium nitrate, Fertilizer, Anticaking, Urea lignosulfonate, Caking

1. Introduction

Ammonium nitrate fertilizer is one of the most widely used nitrogen fertilizers in the world. However between its production and final application to the soil, it must be stored in bags for periods that vary from less than a month to a year or more. During that time it is essential that the material remains completely free flowing. Unfortunately, ammonium nitrate has the disadvantage of being strongly hygroscopic, a phenomena which leads to caking, ie. The formation of big lumps of the fertilizer, accompanied by major economic losses [1, 2, 3, 4, 5, 6].

1.1. Causes of caking

Caking of a fertilizer is caused by the formation of contact points between the particles. These contact points differ in nature and basically have three mechanisms, namely phase contacts, adhesive contacts, and surface diffusion.

Phase contacts: are crystal bridges formed at the contact points between the fertilizer particles. The most troublesome caking of fertilizers is believed to be caused by crystal bridging. Crystal bridges develop during storage as a result of continuing internal chemical reactions, dissolution/ recrystallization processes and /or thermal effects.

Adhesive contacts: are formed as a result of molecular attraction between the surfaces in contact. The forces of attraction involved in this phenomena are known as van der waals forces, and are considered to be relatively weak. This type of contact is influenced mostly by the plasticity of the particles and the pressure exerted on the fertilizer material when it is stacked in bags, or piled in bulk. The material normally reverts to a free flowing form rather easily with a minimal amount of handling.

Surface diffusion: is a result of water- salt complexes consisting of pairs of hydrated ions that are transported within an adsorbed phase

and then form contacts with adjacent granules.

1.2. Factors influencing caking

1.2.1. Internal factors

- a. Chemical composition of the fertilizer
- b. The amount of moisture allowed to remain in a fertilizer at the time of its manufacture, which is found to have a great effect on its tendency to cake during storage.
- c. The size, shape, and structure of the particles
- d. The mechanical strength or hardness.

1.2.2. External factors

- a. The humidity of the surrounding atmosphere
- b. The storage temperature
- c. The length of the storage time
- d. The pressure exerted at the bottom of the pile.

1.3. Solutions to alleviate caking

- a. Various drying processes to obtain a product with a low moisture content
- b. Various granulation, prilling and pelletizing processes to produce larger particles thereby decreasing the surface area and the number of contact points between particles.
- c. The use of screening equipment to obtain a more uniform particle size
- d. The control of storage conditions such as relative humidity, temperature, pile height, and storage time.
- e. Packing fertilizer products in moisture resistant bags.
- f. Addition of anticaking agents (conditioners)

1.4. Anti caking agents

An anti caking agent is a material added to a fertilizer to promote the maintenance of good physical flowability during storage and handling. Anti caking agents can be classified into two categories according to the method of application.

1.4.1. Coating agents

Coating agents are conditioning materials that are applied uniformly onto the surface of fertilizer particles. Most coating agents are very finely divided inert powders eg. Kaolin, clay, diatomaceous earth, talc that adhere to the particle surface. Coating agents could also be liquids that are sprayed onto the surface which function as hydrophobic barriers to inhibit moisture absorption. Examples of which are organic surface active agents, which may be anionic, cationic, or non ionic surfactants.

1.4.2. Internal or chemical conditioners

This type is added to the fertilizer during processing, they act internally usually as hardners, or crystal modifiers to improve storage properties.

1.5. Previous attempts

1.5.1. Internal conditioners

Eisen [7] cited that in order to improve the stability and transportability of ammonium nitrate fertilizer, molten ammonium nitrate should be mixed with 4-28.5% by weight finely ground clays having a particle size >100 μ m. Other studies showed that the addition of 0.25-0.5% $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$ [8] or ammonium polyphosphate [9] to ammonium nitrate melt, was found to decrease the caking tendency of ammonium nitrate fertilizer. However, the addition of silica gel [10] or 4-5% polygypsum [11] to ammonium nitrate melt before granulation, was found to increase the strength of ammonium nitrate granules and its resistance to modification transition. In another study carried out by Zurmendi et al. [12] it was found out that ammonium nitrate fertilizer when mixed with 0.1% triethanol ammonium dodecyl sulfate, sodium alkyl sulfate and ammonium alkyl sulfate, became completely free flowing. Another study showed that upon treating 83% ammonium nitrate solution with 0.4% ligonosulfonate a product having a higher crushing strength and hardness was obtained [13]. Addition of magnesium silicates [14], magnesium nitrate [15], a mixture of sodium silicate and calcined magnesite [16] or potassium sulfate [17] also imparts anticaking properties to ammonium nitrate fertilizer. It was also mentioned that a mixture of sodium

toluene sulfonate and mineral oil dosages of 0.04% and 0.05% [18] was comparable to universal anionic anticaking agents.

1.5.2. Substances applied to the surface of the granular fertilizer: (coating agents)

1.5.2.1. Action of amines on the caking

tendency. It was found out that the treatment of the ammonium nitrate granule surface with either aminotriazine derivatives [19], or a 0.005-0.3% solution of high molecular weight cationic surface active poly amino ester [20], or 0.01-0.1 % of aliphatic fatty amine [21] or 0.02-0.3% of a mixture of fatty acid amines [22], or 0.1%C11-24 aliphatic amines [23], results in decreasing caking.

1.5.2.2. *Action of oil /amine mixture on the caking tendency.* Several studies showed that ammonium nitrate flowing properties were improved and the caking tendency was decreased by treating the granule surface with either quaternary ammonium derivatives and fatty amine solution [24], or by the addition of 20-30% by weight peat wax to the repellent containing from 60 to 70% paraffin and from 5 to 15 weight % alkylamine [25], or by using a mixture of octadecyl amine and polyoxyalkylate with an oil containing aromatics 2%, naphthenic 45.5%, paraffinic hydrocarbons 52.5% [26], or by coating the surface with a mixture of 15% stearylamine, 42.5% mineral oil, 30.35% coarse crystal paraffin wax and 12.2% microcrystal paraffin wax [27], or by spraying the surface of the granule with 0.3% by weight 30% fatty amine C10-22 and 70% mineral oil mixture [28], or by using a mixture containing 30% tertiary aliphatic amines, 11%C12-18 fatty alcohols and 59 % mineral oils [29].

1.6. Action of lignosulfonate as dust control agents [30,31,32,33]

Lignosulfonates are broad class of wood based chemicals, made from the spent liquor generated in the sulfate pulping process. The functional groups of lignosulfonates include primary, and secondary hydroxyl, phenolic hydroxyl, methoxyl, ether groups, carbonyl, car-

boxyl, as well as sulfonate groups. This high content of different types of polar groups and the complex polymer structure make lignosulfonate completely insoluble in oil, whereas they are miscible in all proportions with water. Recent US patent number 4, 846, 871 claims that the caking tendency and dusting of inorganic fertilizers including phosphates and nitrates can be reduced by adding lignosulfonate during the granulation procedure. The use of lignosulfonate as an anti caking material was also carried out in several studies. Lefroy [34] used alkali metal lignosulfonate for coating fertilizer granules in which an adhesive material (alkali metal lignosulfonate) and additive material (nutrients, ion exchange agents or pesticides) are applied to the fertilizer granules by any method to evenly coat them without agglomeration. On the other hand, Rehberg [35] discussed the nondusting abrasion resistance of a fertilizer coated with a mixture of urea and lignosulfonate, while Detroit [13] found that a 83% ammonium nitrate solution when treated with 0.4% lignosulfonate followed by water evaporation and crystallization gave a product with a higher crushing strength and hardness than ammonium without lignosulfonate.

2. Experimental

2.1. Raw materials used

Ammonium nitrate (a product of Abu Qir fertilizer and chemical industries).

Calcium lignosulfonate (a product of Sika, Egypt Company).

Urea granules obtained from Abu Qir fertilizers and chemical industries.

2.2. Preparation of urea lignosulfonate mixtures

The aqueous urea lignosulfonate solution was prepared by dissolving urea in lignosulfonate solution.

2.3. Experimental procedure

100 grams of uncoated ammonium nitrate granules were weighed, screened and stored in a good sealed dry plastic bottle. Meanwhile

urea-lignosulfonate mixture was prepared in the required proportions in a plastic sprayer bottle immersed in water bath at 90° c until complete miscibility. The mixture was then sprayed over the granules. The coated granules were reweighed to obtain the percent coating. The plastic sprayer bottle was calibrated before use and it was found that each sprinkle is equivalent to 0.1 gm/100 gm of the granules.

2.4. The following variables were studied

1. % total solids 40%, 50%, 60%, 70%, and 80%
2. Mixing ratio {urea / lignosulphonate} 1:1, 1:2, 1:4, 1:6, 1:8, and 1:10.

3. Results and discussion

3.1. Effect of coating on the percentage free moisture content of the granules

As shown in figs. 1- 6, that as the percentage of coating increases the percentage of free moisture content increases. This was the case for different total solids and different mixing ratios. This phenomena may be due to the fact that the increase in the percentage of coating is accompanied with increase in water content of the urea lignosulfonate mixtures. It is also noticed that the percentage of free moisture decreases by increasing the percentage total solids of urea-lignosulfonate mixtures at the same percentage of coating. This is probably due to the fact that the water content of urea lignosulfonate mixtures decreases with increasing the percentage total solids. It is also observed that the change in the mixing ratio from 1:1 to 1:10 does not have a significant effect on the free moisture content for the same percentage of coating.

3.2. Effect of coating on the mechanical Strength of the granules

As shown in figs. 7-12, that as the percentage of coating increases the mechanical strength decreases for all different total solids. This is due to the increase in the percentage free moisture accompanying the increase in the % coating, has an adverse

effect on the mechanical strength. It can also be observed from the same set of figures that the mechanical strength of the granules increases with increasing the percentage total solids of urea lignosulfonate coating mixtures at the same percentage of coating. This can also be due to the reduction in the water content with increasing the percentage total solids.

Moreover, it is also obvious that the change of the mixing ratio from 1:1-1:10 does not have a significant effect on the mechanical strength for the same percentage of coating.

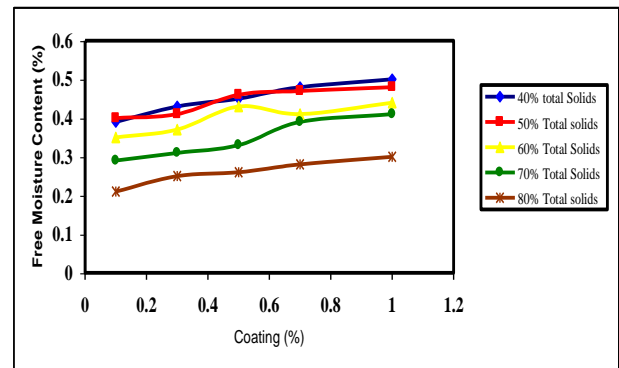


Fig. 1. Effect of coating ammonium nitrate granules with urea – lignosulfonate mixture on the free moisture content with different total solids at mixing ratio 1:1. Conditions : RH of air = 55% CRH of ammonium nitrate at 35 °C = 57% Storage time = 24 Hours.

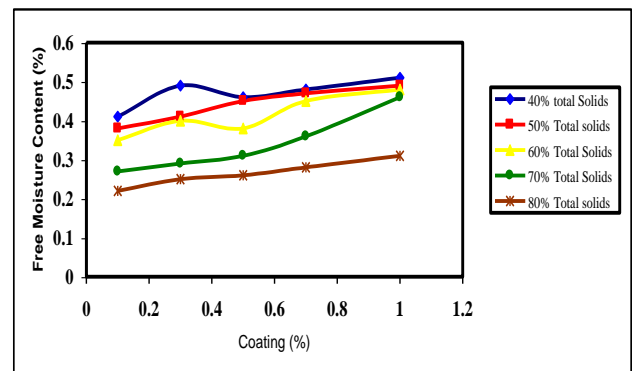


Fig. 2. Effect of coating ammonium nitrate granules with urea – lignosulfonate mixture on the free moisture content with different total solids at mixing ratio 1:2. Conditions : RH of air = 55% CRH of ammonium nitrate at 35 °C = 57% Storage time = 24 Hours.

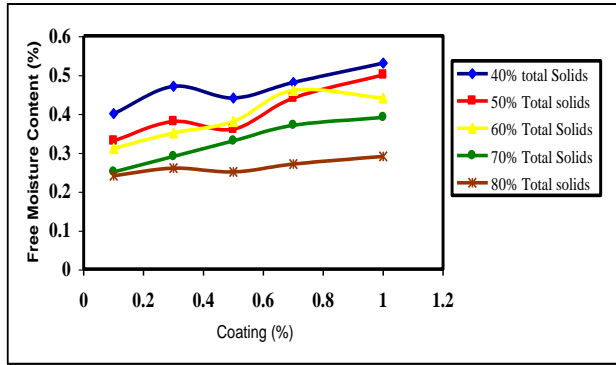


Fig. 3. Effect of coating ammonium nitrate granules with urea – lignosulfonate mixture on the free moisture content with different total solids at mixing ratio 1:4. Conditions : RH of air = 55% CRH of ammonium nitrate at 35 °C = 57% Storage time = 24 Hours.

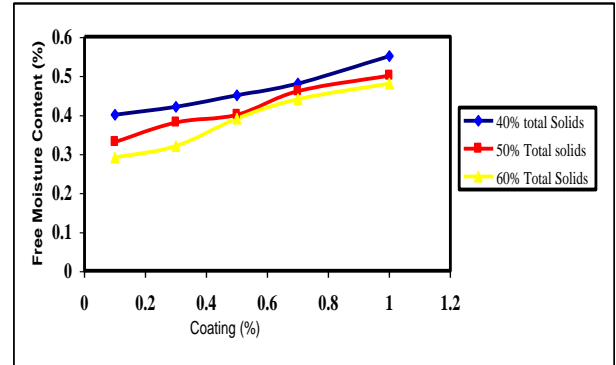


Fig. 6. Effect of coating ammonium nitrate granules with urea – lignosulfonate mixture on the free moisture content with different total solids at mixing ratio 1:10. Conditions : RH of air = 55% CRH of ammonium nitrate at 35 °C = 57% Storage time = 24 Hours.

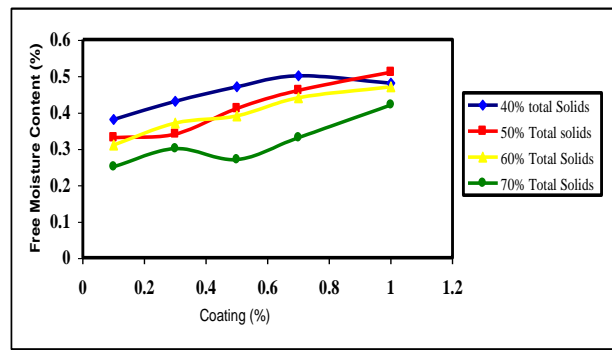


Fig. 4. Effect of coating ammonium nitrate granules with urea – lignosulfonate mixture on the free moisture content with different total solids at mixing ratio 1:6. Conditions : RH of air = 55% CRH of ammonium nitrate at 35 °C = 57% Storage time = 24 Hours.

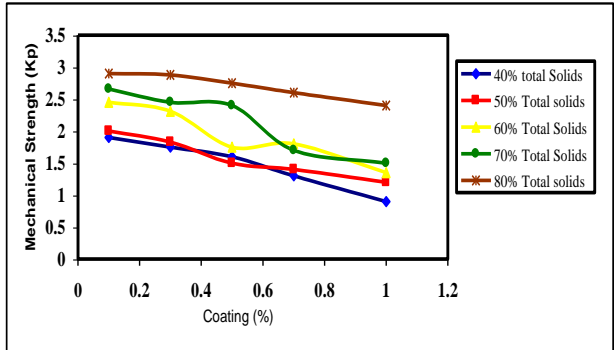


Fig. 7. Effect of coating ammonium nitrate granules with urea – lignosulfonate mixture on the mechanical strength with different total solids at mixing ratio 1:1. Conditions : RH of air = 55% CRH of ammonium nitrate at 35 °C = 57% Storage time = 24 Hours.

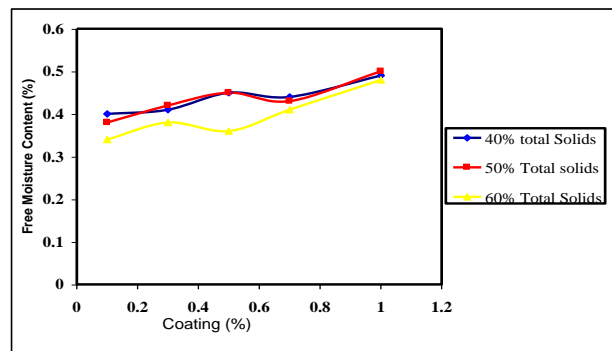


Fig. 5. Effect of coating ammonium nitrate granules with urea – lignosulfonate mixture on the free moisture content with different total solids at mixing ratio 1:8. Conditions : RH of air = 55%. CRH of ammonium nitrate at 35 °C = 57% Storage time = 24 Hours.

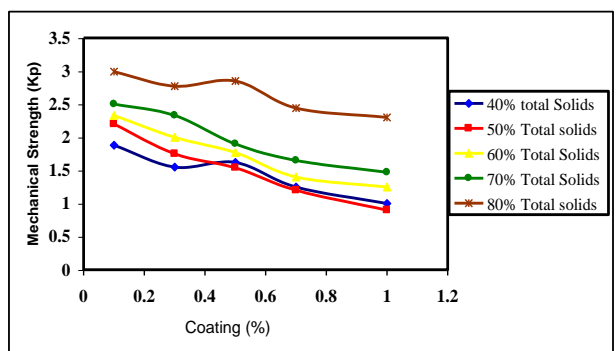


Fig. 8. Effect of coating ammonium nitrate granules with urea – lignosulfonate mixture on the mechanical strength with different total solids at mixing ratio 1:2. Conditions : RH of air = 55% CRH of ammonium nitrate at 35 °C = 57% Storage time = 24 Hours.

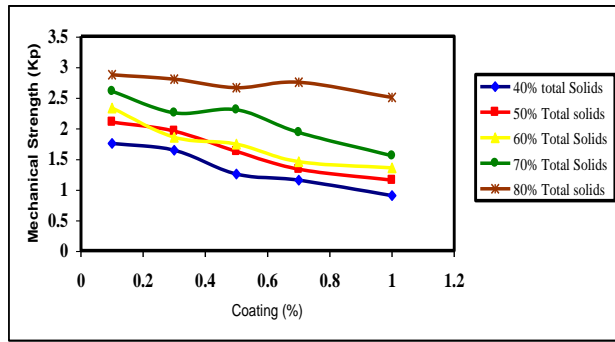


Fig. 9. Effect of coating ammonium nitrate granules with urea – lignosulfonate mixture on the mechanical strength with different total solids at mixing ratio 1:4. Conditions : RH of air = 55% CRH of ammonium nitrate at 35 °C = 57% Storage time = 24 Hours.

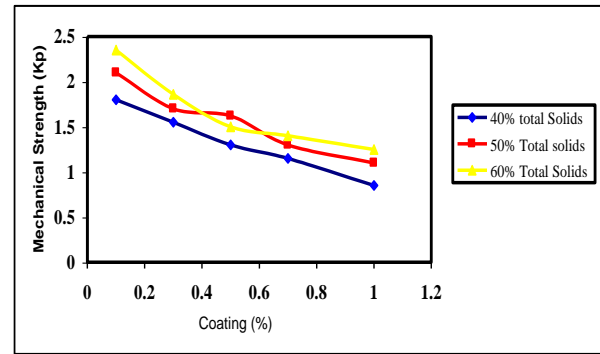


Fig. 12. Effect of coating ammonium nitrate granules with urea – lignosulfonate mixture on the mechanical strength with different total solids at mixing ratio 1:10. Conditions : RH of air = 55% CRH of ammonium nitrate at 35 °C = 57% Storage time = 24 Hours.

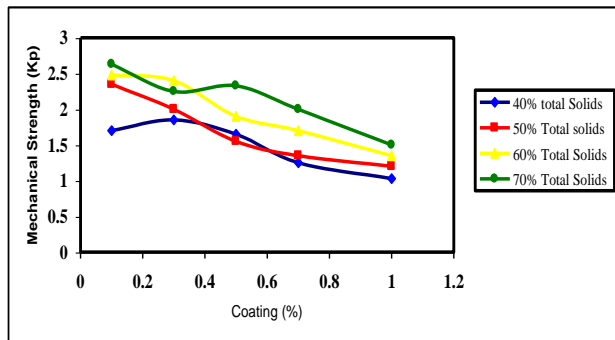


Fig. 10. Effect of coating ammonium nitrate granules with urea – lignosulfonate mixture on the mechanical strength with different total solids at mixing ratio 1:6. Conditions : RH of air = 55% CRH of ammonium nitrate at 35 °C = 57% Storage time = 24 Hours.

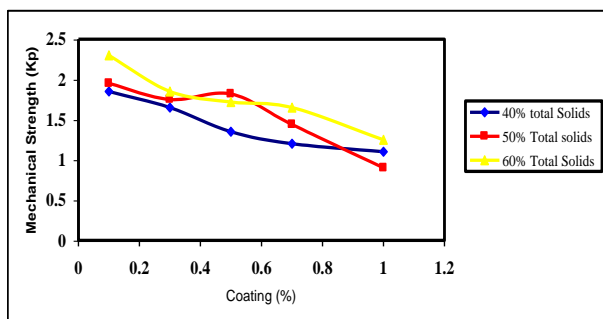


Fig. 11. Effect of coating ammonium nitrate granules with urea – lignosulfonate mixture on the mechanical strength with different total solids at mixing ratio 1:8. Conditions : RH of air = 55% CRH of ammonium nitrate at 35 °C = 57% Storage time = 24 Hours.

3.3. Effect of coating on the particle size distribution

As shown in figs. 13-18 that as the percentage of coating increases the percentage of the fine particles (less than 2mm) decreases from 1.5%- 1.3%, in the initial samples of uncoated ammonium nitrate granules to values ranging from 0.2% to zero. On the other hand, the percentage of the over size particles (more than 4mm) increases from 8% or 9% in the initial uncoated ammonium nitrate samples to values ranging from 15% to 20% for a percentage of coating approaching 1%. This can be explained as follows; The surfactant nature of the lignosulfonate salt solution causes dust particles to adhere to granules or to agglomerate and thus not to become air borne during handling.

It should be mentioned that the reduction in the percentage of fine particles in ammonium nitrate fertilizer is considered an important factor in improving the physical properties of the granules and reducing its caking tendency, since in this case the specific surface area of the granules is reduced, and consequently, the forces of attraction and points of contacts between the adjacent particles are also reduced.

3.4. Effect of coating on caking tendency

Several samples of ammonium nitrate granules coated with urea lignosulfonate mixtures having different % total solids and

different mixing ratios were selected on the following basis:

1. It fulfills at least 75% of the initial mechanical strength of uncoated granules before storage.
2. The coating mixture has low total solids
3. A low % of coating.

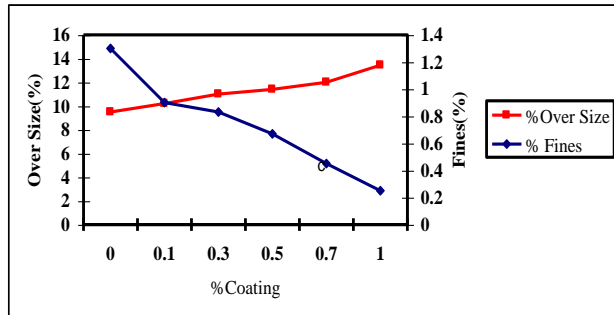


Fig. 13. Effect of coating ammonium nitrate granules with urea lignosulfonate mixture (40% total solids and mixing ratio 1:1) on particle size distribution.

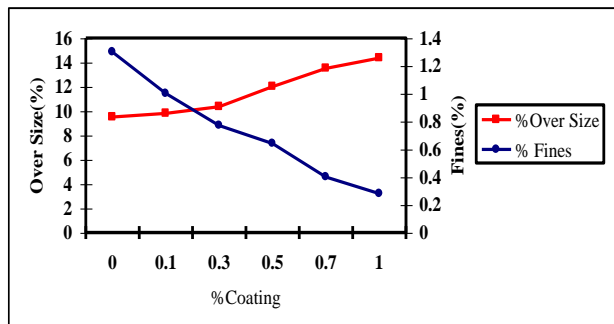


Fig. 14. Effect of coating ammonium nitrate granules with urea lignosulfonate mixture (40% total solids and mixing ratio 1:2) on particle size distribution.

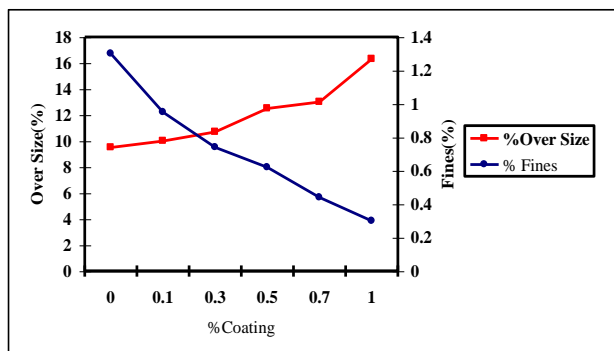


Fig. 15. Effect of coating ammonium nitrate granules with urea lignosulfonate mixture (40% total solids and mixing ratio 1:4) on particle size distribution.

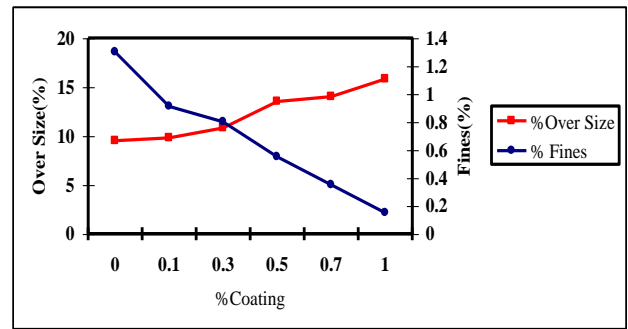


Fig. 16. Effect of coating ammonium nitrate granules with urea lignosulfonate mixture (40% total solids and mixing ratio 1:6) on particle size distribution.

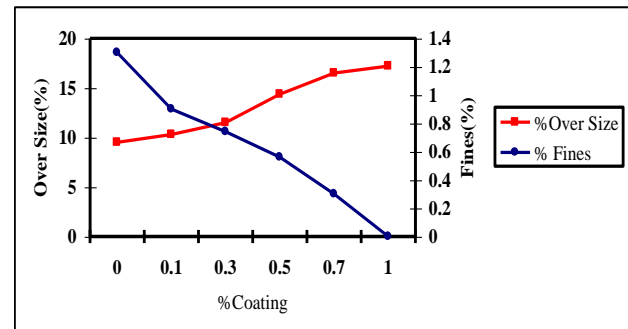


Fig. 17. Effect of coating ammonium nitrate granules with urea lignosulfonate mixture (40% total solids and mixing ratio 1:8) on particle size distribution.

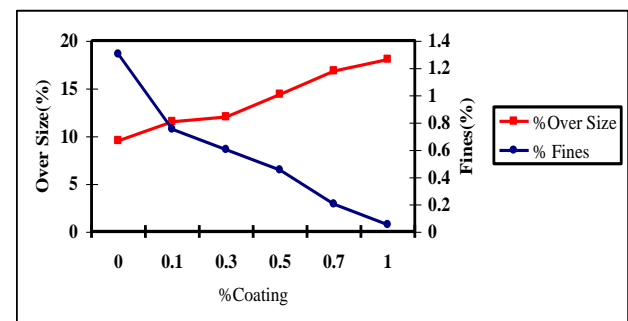


Fig. 18. Effect of coating ammonium nitrate granules with urea lignosulfonate mixture (40% total solids and mixing ratio 1:10) on particle size distribution.

An accelerated caking test (the load applied in the accelerated test equals 0.83 kg/cm² which is equivalent to a load of 66 bags 50 kg each, stacked vertically) was performed on each of these samples and the results were tabulated in table 1.

Table 1.
Results of accelerated caking test

Mixing ratio	Coating %	Total solid%	Mechanical strength (kPa)	Free moisture content	Caking force kPa	% Fine
1:1	0.1	60%	2.54	0.35	1.3	2.1
	0.1	70%	2.66	0.29	0	0.1
	0.3	70%	2.45	0.31	1.4	2.0
	0.5	70%	2.4	0.33	1.4	0.88
	0.1	80%	2.9	0.21	0	0
	0.3	80%	2.88	0.25	0	0
	0.5	80%	1.75	0.26	0	0.4
1:2	0.1	60%	3.33	0.35	1.9	2
	0.1	70%	2.5	0.27	1.2	1.5
	0.3	70%	2.33	0.29	1.8	2.2
	0.1	80%	2.91	0.22	0	0
	0.3	80%	2.71	0.25	0	0.3
	0.5	80%	2.85	0.26	0	0
1:4	0.1	60%	2.33	0.31	1.8	1.6
	0.1	70%	2.6	0.25	0	0.7
	0.1	80%	2.87	0.24	0	0.1
	0.3	80%	2.8	0.26	0	0.2
	0.5	80%	2.66	0.25	0	0.4
1:6	0.1	50%	2.35	0.33	1.8	1.8
	0.1	60%	2.48	0.31	1.3	2.3
	0.1	70%	2.63	0.25	0	0.6
1:8	0.1	60%	2.3	0.34	1.9	1.7
1:10	0.1	60%	2.35	0.29	1.9	1.5
Uncoated sample	-	-	1.3	0.48	6.75	Big lump

From the results it is observed that the caking force (force required for breaking the formed cake) required for all samples coated with urea ligonosulfonate mixtures having 80% total solids were zero, and for the other samples the caking force varied from zero to 1.9 kPa.

4. Conclusions

Ammonium nitrate fertilizer is highly hygroscopic material. Absorption of moisture by ammonium nitrate leads to a decrease in the mechanical strength of the granules, a phenomenon which eventually leads to caking of the fertilizer. In this study however, it was found out that upon coating the ammonium nitrate granules with urea ligonosulfonate mixtures under recommended conditions

which are: a % total solids of 80%, a mixing ratio of 1:1 to 1:2 and a % coating of 0.1% to 0.3%, the coated granules kept their free flowing properties and showed a good stability against caking when subjected to accelerated caking test. In this case no force is required to break the formed cake, and the percentage of dust was in the range of 0% to 0.3%.

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