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PRODUCT QUALITY REQUIREMENTS IN BULK SHIPMENT OF FERTILIZERS

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1. INTRODUCTION

Handling and distribution of fertilizers in bulk increase year by year at the same time as the size of the ocean-going bulk vessels also increases.

Use of large ships for transportation of bulk fertilizers usually leads to favourable freight rates, but the cost of lay time in port for this type of ship is high. This necessitates high load and discharge rates, in the order of 4-5 000 tonnes/day.

Norsk Hydro's export of fertilizers in bulk has increased substantially during the last years. This is largely due to the fact that this distribution system is more economical and requires less manpower than shipment in bags.

Successful bulk shipping requires that the fertilizers have good storage properties and good mechanical resistance to the stresses which usually occur during loading, transport and discharge.

Fertilizer producers have therefore found that bulk shipment leads to demands for higher quality with regard to physical properties than shipment of bagged fertilizer.

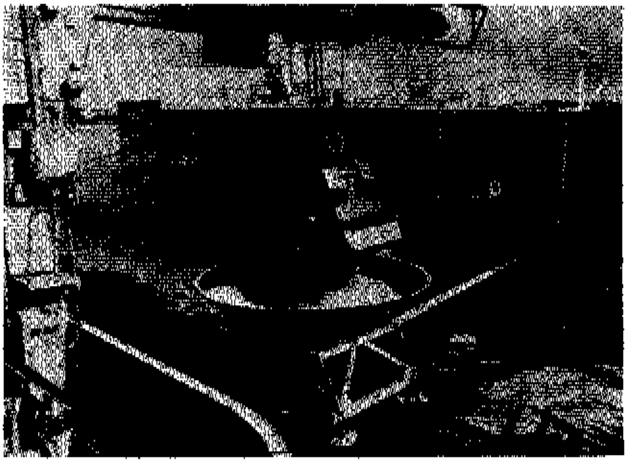
Demands for low dust emission necessitate use of good production equipment and methods. Use of anticaking agents possessing good adhesive properties is one important factor. In order to avoid excessive breakdown or degradation of fertilizer particles, great attention should be paid to the selection of the handling equipment.

2. NORSK HYDRO'S EXPERIENCE

Norsk Hydro has extensive experience in the shipping and handling of bulk materials. The first consignment of bulk urea was shipped to the U.S. West Coast as far back as 1960, since when most of our urea exports to the U.S. have been in bulk form. Up to 1972 consignments were shipped by liners. Cargoes were usually between 3,000 and 4,000 tons.

Since 1972 large bulk carriers have been used for shipping fertilizers to the U.S. West Coast. These carriers have seven holds and a capacity of 27,500 t.dw. The holds are 15 metres deep, which calls for high mechanical resistance of the fertilizer particles and good storage properties.

The hatches are large and allow for free digging in the holds. With one 10 m^3 grab in use the rate of discharge is about 5,000 t/d.



Photograph 2.1: Discharge of fertilizer by 10 m^3 grab.

In addition to urea we have also shipped calcium nitrate (CN) and various types of NP and NPK by these bulk carriers.

The same types of fertilizer have also been shipped to the U.S. East Coast over the years. Conventional ships of between 7,000 and 12,000 t. dw. have been employed, normally discharged by shore-based equipment.

Consignments are shipped to the U.S. the year round and are not restricted to favourable meteorological periods. During discharging it is not unusual for the air temperature to exceed 30°C and the humidity 80%.

We have also shipped bulk NPK to Danish ports for some years now. Last year, for example, 300,000 tons were consigned to Denmark.

Every year approx. 200,000 tons of bulk calcium nitrate are shipped to two Swedish ports from Norsk Hydro's plants in Glomfjord.

Carriers employed for bulk shipment to Sweden are now equipped with specially designed discharge equipment. Two of these carriers have a capacity of approx. 1,300 t. dw., while a third has a capacity of about 3,000 t. dw.

In recent years consignments of 5,000 to about 18,000 t NP have also been shipped to places like India, Thailand and El Salvador. In one case, due to special circumstances, transport from Norway to India took 5 months. Although the fertilizer - NP 23-10 - was exposed to vibration and relatively great fluctuations in temperature, the cargo was in good condition on arrival at its destination.

3. IMPORTANT PRODUCT PROPERTIES

In practice the following properties have proved to be of great importance when shipping fertilizers in bulk:

- Mechanical resistance
- Caking tendency
- Hygroscopicity
- Dusting tendency

This paper deals with some of the conditions which may influence these properties. Since the hygroscopicity of fertilizers will be treated in another paper at this conference, we will only deal with it briefly and show some examples of how a special coating can reduce the hygroscopicity of some fertilizers.

4. MECHANICAL RESISTANCE

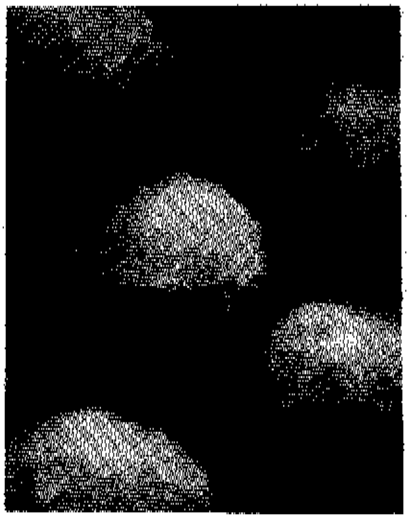
Mechanical resistance means the ability to resist the stresses to which the fertilizer particles are subjected during storage, loading, transport and discharge without being crushed into smaller particles or dust.

We have used various methods to test the mechanical resistance of the particles, but have found that measurement of the crushing strength or hardness of particles provides a sufficiently good characterization of this property. The method we use is identical with that described in TVA's Special Report No. S-444 dated September, 1970.

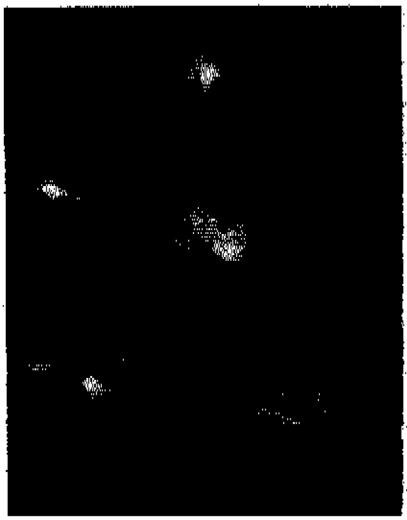
Our target is that the force required to crush our NP and NPK fertilizer particles, with a selected diameter of about 2.5 mm, should not be less than 3 kg. The force required to crush calcium nitrate and urea particles, with a selected diameter of 1.5 mm, is 1 kg and 0.7 kg respectively.

When the values of the crushing strength are lower than stated, we know from experience that the operational conditions in the prilling or granulating stages have not been normal. For example, insufficient quantity of seeds in the calcium nitrate melt will result in fissured particles, and therefore low resistance to crushing, while too high temperature in the NP melt will have the result, that the NP or NPK prills have gas-filled cavities and low resistance to crushing. (Examples are shown in photographs 4.1 and 4.2).

The crushing strength of NP and NPK prills varies according to the chemical composition. Typical values for fertilizers produced by Norsk Hydro's prilling process are shown in Table 4.1. It will be seen that NP prills have the highest strength, and that the particles of chloride-based types are weaker than those based on K_2SO_4 as potassium source. There is also a clear tendency toward reduced crushing strength the higher the content of nitrogen.



Photograph 4.1: Fissured calcium nitrate particles.



Photograph 4.2: NPK prills with gas-filled cavities.

Table 4.1: Particle strength of prilled fertilizers

Fertilizer	Crushing strength, kg		Remarks
	With normal moisture content	After about 1% moisture absorption	
NPK 16-7-13	6,3	4,9	KCl-based
" 20-5-9	5,6	4,4	
" 21-4-10	3,9	3,1	
" 25-3-9	3,2	3,1	
NPK 14-4-7	6,9	5,7	
" 15-6-12	7,0	6,3	
" 15-4-12	6,0	5,6	K_2SO_4-based
" 21-7-14	5,6	4,0	
" 23-3-7	3,5	2,9	
NP 20-9	8,2	8,2	
" 23-10	7,4	7,3	
" 26-6	6,0	6,0	
Urea	1,0	1,0	
CN	1,0	1,0	
CAN	3,0	0,5	

Measurements have shown that the crushing strength of NPK particles is reduced by 10 to 20% after absorption of about 1% moisture. This amount of moisture will have no noticeable effect on the strength of the NP particles, due to the fact that prilled NP consists of compact particles of low porosity and that the moisture does not penetrate into the particles but condenses on the surface.

Moisture absorption of about 3% results in a drastic reduction of the strength of NPK prills. The particles become soft and sticky, and quite unsuitable for handling.

Particles which repeatedly absorb and give off moisture also possess low crushing strength. The same is the case with particles containing NH_4NO_3 when exposed to temperature cycles around 32°C. This is due to the changes in the crystal lattice of the ammonium nitrate at this temperature.

CAN should also be mentioned. The particles have a strength of about 3 kg. Absorption of only 0.2% - 0.3% moisture noticeably reduces particle strength. Absorption of 1% moisture reduces particle resistance to about 0.5 kg.

Correct handling at all stages from producer to consumer has proved that all the fertilizers mentioned in Table 4.1 have adequate particle strength to permit bulk shipment and handling. However, in order to prevent the formation of large amounts of undersizes and dust it is important to employ a system which handles the product gently.

Products of low particle strength such as urea and CN must be handled with particular care. Rapidly moving bucket conveyors with centrifugal discharge cause considerable crushing. If it is necessary to lift the product, inclined conveyors should be used. Failing this, slow-moving bucket conveyors may be used.

5. CAKING

Fertilizers to be shipped in bulk must not only be able to stand up to the mechanical strains to which they will be subjected during loading and discharging. Storage properties must also be such that they do not cake during transportation to their port of destination. Particularly good storage properties are necessary if bulk material is to be shipped over long distances and by large carriers in which the depth of holds is often 15 metres or more.

Caking has undoubtedly been, and still is, the problem with which fertilizer producers are most concerned. Considerable research has been devoted to solving the caking problem. We will not deal with the bonds which are formed between fertilizer particles during the caking process, but merely emphasize that humidity, temperature, pressure during storage and contact between particles are the main factors in this process.

Apart from dust, caking is without doubt the biggest problem in bulk fertilizer shipment.

If the fertilizer is hard on arrival at its destination, it can be a difficult and time-consuming operation to unload the cargo. It is not unusual for the rate of discharge in such cases to be reduced to 1/3 of the rate normal for freeflowing fertilizer. As an example, a cargo of 15,000 tons for which the charterparty states an agreed discharge rate of 3,000 tons per day, the discharge of freeflowing material will take 5 days. If the material is hard the same operation will take 15 days. If we include a demurrage rate of $ 0,40 per ton and day, the 10 extra days will increase discharge costs by $ 60.000.-, or $ 4.- per ton. Thus a considerable portion of the profit normally obtained by bulk shipping compared with shipping in bags, will be lost because of the poor storage properties of the fertilizer.

When the material is hard, it is customary to use bulldozers to break and move it to the hatch opening so the grab can reach it. We know from experience that the use of bulldozers results in considerable crushing of the particles and that further handling causes excessive dust.

Photograph 5.1: Caked fertilizer being handled by bulldozer.

Fertilizer which has hardened in the ship's hold will be almost sure to cake soon after being deposited in the distributor's terminal. The producer is undoubtedly familiar with the reaction of distributors and customers.

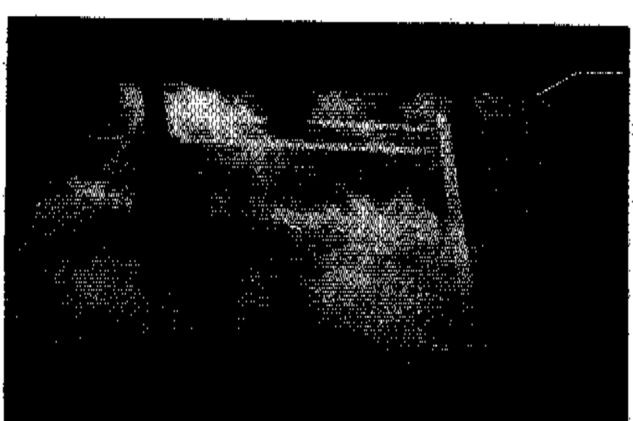
Most commercial fertilizers have a tendency to cake during storage, and in order to minimize this tendency the particles must be treated with anti-caking agents. These agents must not cause permanent harm to plants, the soil or human beings.

5.1. Fine powder as anti-caking agents

Until a few years ago it was customary to use fine powders such as kieselguhr, kaolin, talc, calcium carbonate and metal stearates as anti-caking agents.

These powders act primarily as parting agents, i.e. they prevent direct contact between water-soluble salts on the surface of the particles.

The amount of additives varies from 0.2% to over 2%, depending on the tendency of the fertilizer to cake and the anti-caking effect of the additives. The storage properties of a number of fertilizers are improved by the use of these additives, but the amount of dust when the product is handled is often unpleasantly high, because of the poor ability of the additives to adhere to the surface of the granules.



Photograph 5.1.1: Handling of dusty fertilizers.

The loading, discharging and handling of bulk fertilizers subject the particles to great mechanical strain. The additives used must have good adhesive properties in order to retain the anti-caking effect and to prevent pollution of the surroundings.

In order to test conditions which can influence the adhesive properties and the ability of each anti-caking agent to adhere to the fertilizer particles, Norsk Hydro uses a special de-dusting bed. This and the testing procedure are described in Appendix 1.

Table 5.1.1 shows the results of such a test. Newly produced, prilled and dust-free NPK was treated with 0.4% and 0.8% of some of the more common anti-caking powders. With calcium nitrate 0.2% and 0.4% were used.

Table 5.1.1

Powder	Dust - mg per kg NPK	
	Quantity 0.4%	Quantity 0.8%
Amorphous SiO_2	64	356
Kaolin	1790	5000
Kieselguhr	2730	5080
Talc 0000	1700	6550
Danish powdering chalk	1627	2135
Attacote	2680	4120
Ca-stearate (OB)[x)]	1400	2000

x) 0.2% and 0.4%

From observations made in the production plant, transport channels and warehouses, we have found that tests of the product in the de-dusting bed must not give more than 200 mg dust per kg fertilizer. As Table 5.1.1 shows, only the test in which 0.4% amorphous SiO_2 was used, satisfied this requirement. The adhesive ability of the other agents was too poor which will result in excessive amounts of dust when the fertilizer is handled.

5.2 Surface active anti-caking agents

The use of surface active organic chemicals as anti-caking agents for fertilizers has become more and more common in recent years. These chemicals change the wetting properties of the liquid phase which can form on the surface of the fertilizer particles.

Surface active anti-caking agents are used either alone or in combination with a parting agent, i.e. a fine powder.

The effect of various surface active anti-caking agents has been tested at Norsk Hydro's Research Centre. In the case of urea prills we have found that small quantities, i.e. about 0.01%, of an anionic surfactant normally reduce somewhat the caking tendency of the product. However, the effect is not sufficient to provide a product quality which does not give rise to caking problems when transported in bulk over long distances. In addition the content of moisture and dust must be kept low.

With respect to prilled and granulated NPK and prilled AN we found that surface active chemicals alone have very little anti-caking effect. On the other hand a good effect is achieved if these products are treated with cationic surfactants in addition to powder. Where products have a strong tendency to cake, it may be necessary to use this combination to ensure that the fertilizer particles remain freeflowing after long sea transport by bulk carriers.

Table 5.2.1 shows typical values of caking indices for a fertilizer product treated with different anti-caking agents.

Table 5.2.1: Caking Index for NPK with 0.5% H_2O.

Anti-caking agent	Caking Index
Untreated product	1000
0.5% fatty amine	950
0.4% Kieselguhr	650
0.4% Kieselguhr + 0.05% fatty amine	300
0.4% Amorphous SiO_2	360
0.4% Amorphous SiO_2+0.05% fatty amine	170
0.2% Ca stearate	460

5.3 Caking of newly produced NPK

The fertilizer is most vulnerable to caking in the first period after production, mainly because it is still warm and because postreactions are taking place.

We have found that a bulk product which is freeflowing after 3 to 4 week storage in the producer's storehouse very rarely becomes hard during transport and subsequent storage in the consignee's warehouse. Thus the condition of the fertilizer when removed from the producer's storage, in many cases provides a good basis for evaluating the ability of a product to withstand the strains of bulk shipment.

5.4 Particularly hygroscopic and humidity-sensitive fertilizers

Most fertilizers are hygroscopic and readily absorb moisture from the air. This is an important property which is necessary if the particles are to dissolve rapidly and thus ensure plants of nutrients shortly after the fertilizer is applied.

However, the absorption of moisture during storage is detrimental. As already mentioned, the absorption of moisture has a negative effect on the storage and handling properties of fertilizers.

Some fertilizers are so hygroscopic or so sensitive to moisture absorption that they cannot be handled in bulk form unless special precautions are taken. If they are loaded or discharged under very humid weather conditions, wet and slippery conveyors will cause problems. The particles become moist and sticky and tend to form lumps. The floors in the warehouse and the handling equipment will remain wet for a greater part of the year, and a thick crust will rapidly form on the fertilizer surface. Such products also result in a higher percentage of waste than other, less hygroscopic fertilizers.

Of the hygroscopic products with which we are most familiar, it is the NP fertilizers with a high content of NH_4NO_3, and calcium nitrate which have created the greatest problems in bulk handling and shipping.

Normally NP particles have a higher mechanical strength, better storage properties, a lower rate of moisture absorption and a higher CRH at 25°C than, for example, most NPK fertilizers. Thus even under the most unfavourable climatic conditions one should expect NP-products to be very suitable for bulk handling and shipping. The reason that this is not always the case, is that most NP fertilizers consist of hard particles with a compact surface and low porosity. If these fertilizers are exposed to humid air, most of the moisture absorbed will condense on the surface of the particles. A low degree of absorption, which normally is not noticeable in the case of particles which have greater absorption ability, may result in wet and sticky particles with poor flow properties. This tendency will increase with increasing NH_4NO_3 content, temperature and humidity. This is due to the high solubility of NH_4NO_3.

The hygroscopicity of calcium nitrate is the main reason for difficult product handling. The hygroscopicity is determined by the chemical composition of the product:

$$85\% \quad NH_4NO_3 \cdot 5Ca(NO_3)_2 \cdot 10H_2O$$

and $$15\% \quad Ca(NO_3)_2 \cdot xH_2O$$

Measurements have shown that the water vapour pressure, which is a good characteristic of the hygroscopicity of a salt, is very low over CN particles. For example, at 20°C the water vapour pressure is about 3.5 mm Hg, which corresponds to a dewpoint of minus 4°C or a relative humidity of 20%.

Thus calcium nitrate begins to absorb moisture when the humidity exceeds 20% at 20°C, if the temperatures of the air and the particles are the same. Owing to the content of $Ca(NO_3)_2$ and the ability of this component to bind moisture in the form of water of crystallisation, the absorption of moisture, which results in breakdown of particle strength and formation of a liquid phase, will not occur until the particles are exposed to air having more than 39% RH (25°). When the humidity of the air exceeds this figure, the calcium nitrate particles absorb a high percentage of moisture and rapidly disintegrate.

In order to bulk handle and ship fertilizers which are particularly sensitive to moisture, Norsk Hydro's Research Centre has developed a hydrofob coating which makes the surface of particles resistant to water so that the rate of moisture absorption is considerably reduced.

Figure 5.4.1 shows how much moisture absorption by CN - measured after 6 hours' exposure to an air temperature of 25°C and 70% RH - is reduced by the use of varying thicknesses of coating. It will be seen that 0.05% of coating reduces moisture absorption by 70%. Figure 5.4.2 shows the percentage of moisture absorption as a function of exposure time at a temperature of 25°C and 70% RH in CN samples with and without coating. Figure 5.4.3 shows corresponding data at 35°C and 50% RH for uncoated samples and samples coated with a thickness of 0.08%.

The use of this coating on CN and NP fertilizers enables them to be shipped in bulk without difficulty, even to very hot and humid areas.

Fig. 5.4.1

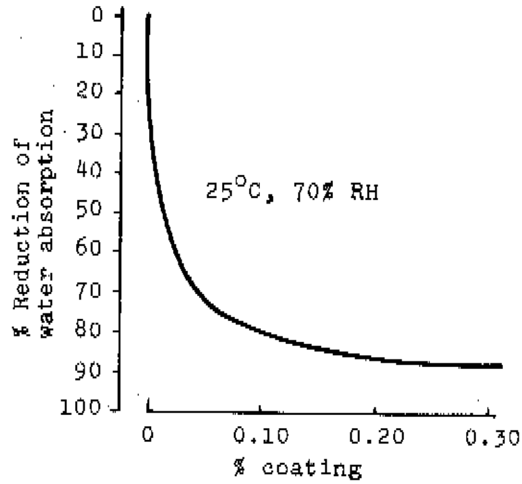


Fig. 5.4.2

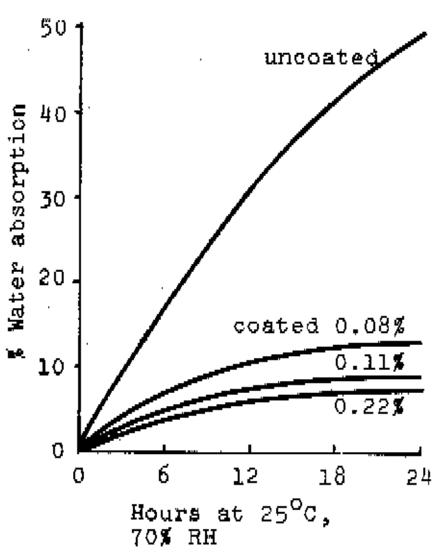
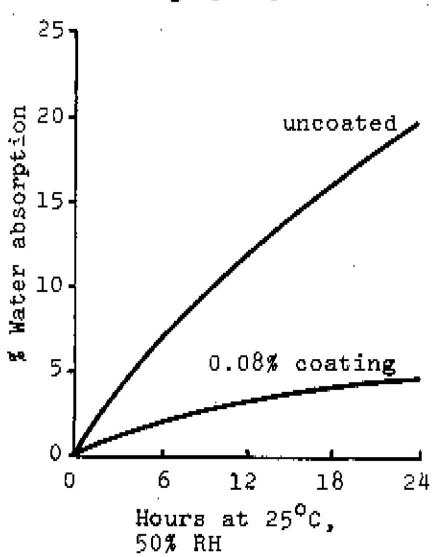


Fig. 5.4.3



6. DUST PROBLEMS

Little is known or published about the physiological effects of most of the substances contained in fertilizers. Only for a few of them do threshold limit values exist. However, investigations indicate that the dust particles released, when handling fertilizers, have little or no injurious effect on health as long as the dust concentration in the air is kept at a reasonable level. For the time beeing, therefore, we have decided to regard fertilizer dust as an "inert" or nuisance dust. The threshold limit value for this kind of dust is in Norway, as well as in many other countries, 10 mg/m^3 air.

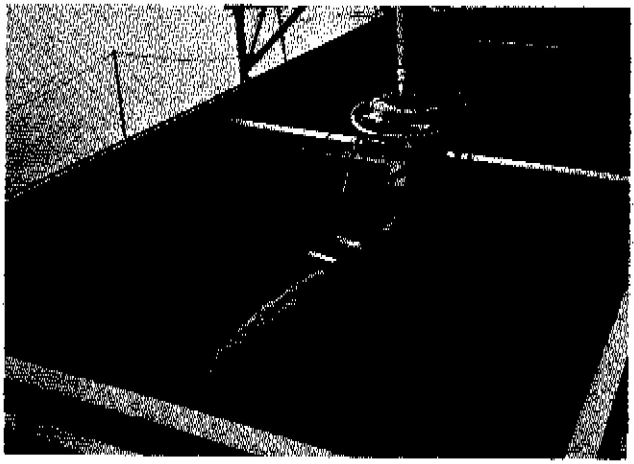
Even though, we know at present of no harmful effects of fertilizer dust, it is clear that it does cause discomfort and reduces work satisfaction. It is also obvious that fertilizer dust combined with moisture causes corrosion to metal structures, electrical plant, etc.

Fine dust can arise at all stages of bulk handling. Particularly when screening, transferring from one conveyor to another and at other stages in the handling system where fertilizer particles fall freely, the fine dust will be transported by air currents and thus pollute the atmosphere.

Today many port authorities permit only the minimum of dust when bulk products are loaded and discharged, and therefore, in recent years a great deal of work has been devoted to reducing the dust content of fertilizers. This has been necessary both in order to ensure a cleaner atmosphere in our plants, and in order to meet the requirements and wishes of consumers.

It has been necessary to improve the industrial processes so that fertilizers produce a minimum of dust when bulkhandled. Transport equipment has been replaced or improved. De-dusting equipment has been developed and later incorporated into the loading systems.

Further, a great deal of work has been devoted to finding effective dust suppressants.

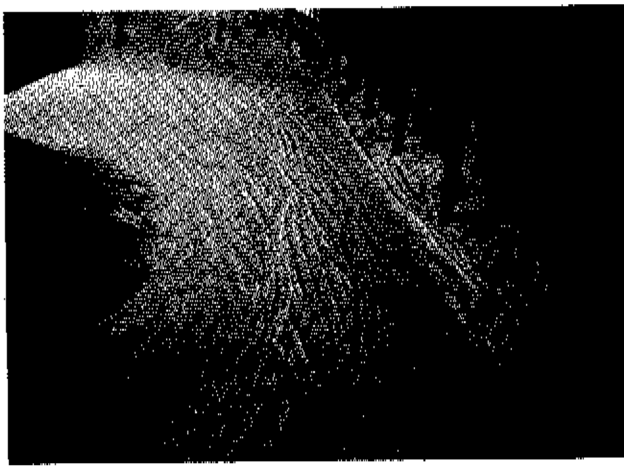


Photograph 6.1: Loading NPK treated with a dust suppressant.

6.1 Examples of dust formation

The use of large quantities of parting agent or agents having poor adhesive properties, results in very dusty fertilizer. The equipment used for removing fertilizers from the storage, and especially the manner in which it is used, has proved to be of decisive importance for the dust content of a fertilizer. For example, careless operation of payloaders in a bulk storage, will result in excessive amounts of dust. A very great amount of dust will be formed when material is removed from caked stock piles.

Payloaders are used for moving bulk fertilizer in most of Norsk Hydro's storages. In order to avoid excessive crushing and dust formation, we have found it necessary to hold instruction courses regularly for payloader operators. It is also important that payloaders are operated in accordance with regulations and that frequent checks are made to ensure that this is being done.



Photograph 6.1.1: Excessive quantities of crushed urea on the storage floor as a result of incorrect payloader operation.

If the fertilizer particles absorb moisture, a film of salt-containing liquid will form on the surface. When the water later evaporates, or is absorbed by the particles, small crystals will form which adhere poorly to the particle surface. This effect, which can be studied under the microscope, will contribute to increasing the dust content of a product. A great amount of dust may also result if particles are stored under conditions where alternative wetting and drying occur. These conditions exist for example in most bulk storage buildings, as a result of natural climatic changes during day and night.

Our studies of dust-formation mechanisms have proved that the crystal growth, and thus also dust formation after moisture absorption and subsequent drying, are much greater in cases where fertilizer particles have been treated with both a parting agent and a surfactant than in cases where particles have only been treated with a parting agent as an anticaking agent.

Photographs 6.1.2 and 6.1.3 clearly show the difference in the crystal growth on the surface of particles treated with a parting agent and particles treated with both a parting agent and a surfactant. In both cases the particles have first absorbed and then later slowly given off about 1% moisture.

An example of how the dust content can increase when surfactants are used as anti-caking agents is shown in Fig. 6.1.1. Here particles treated with 0.4% parting agent with and

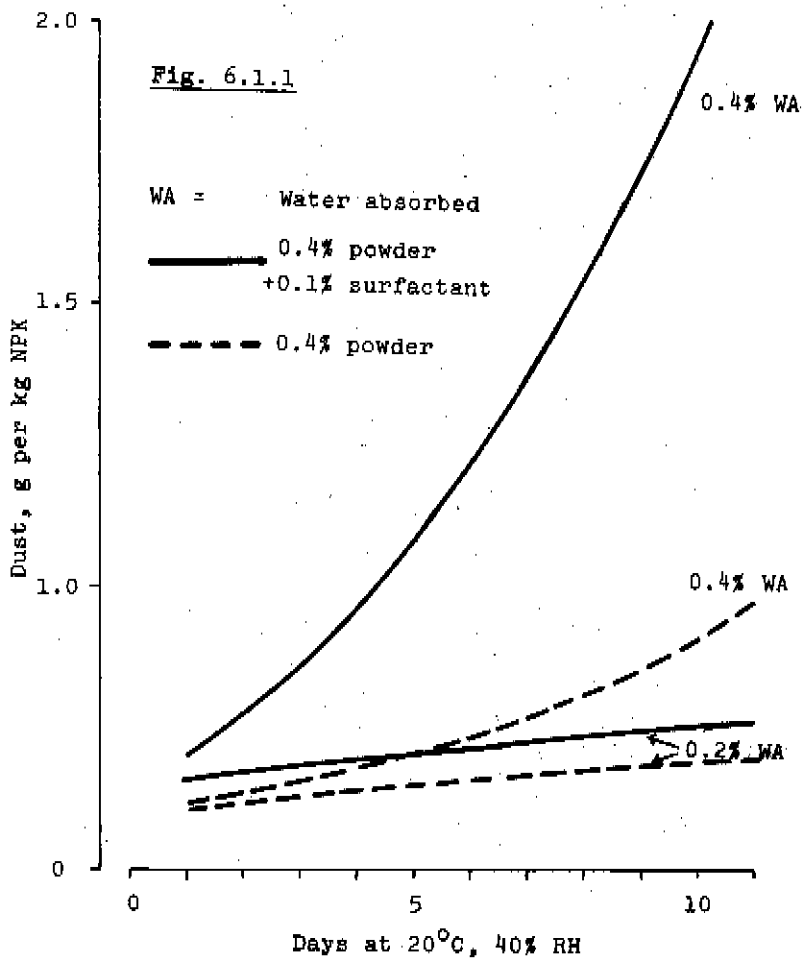
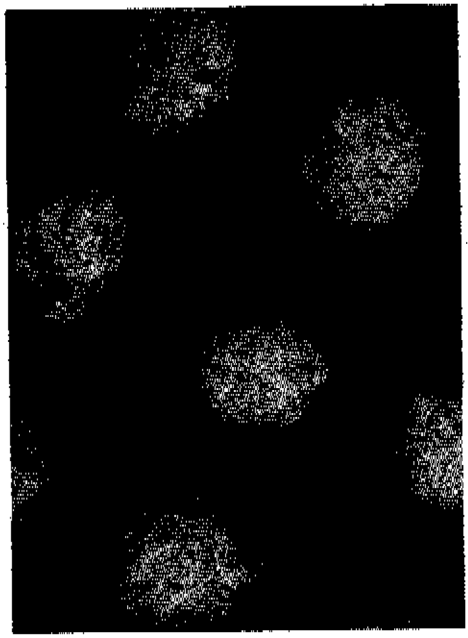
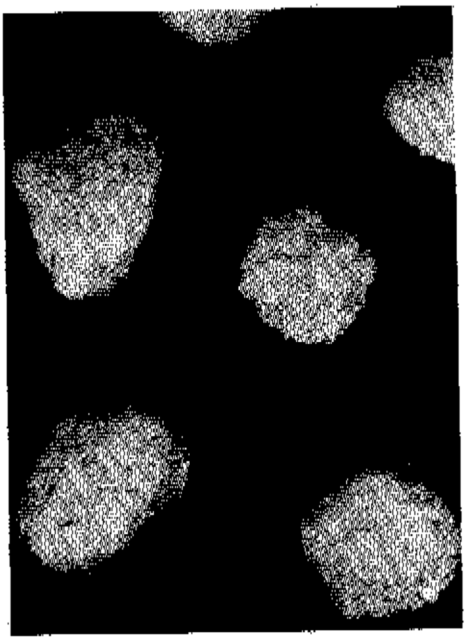


Fig. 6.1.1: Dust-forming effect of surfactant.



Photograph 6.1.2: NPK-particles treated with parting agent.



Photograph 6.1.3: NPK-particles treated with parting agent and surfactant.

without 0.1% of a surfactant have been slowly moistened, thereby increasing the water content by 0.2% and 0.4% respectively. These particles have then been exposed to an air temperature of 20°C and 40% RH. After varying periods in this environment, samples were taken to measure the dust content. This was measured in the same apparatus as described and shown in Enclosure 1.

It may be necessary, particularly for bulk shipments of fertilizers with a strong tendency to cake, to use surfactants to ensure that they remain freeflowing. However, it will be seen from the aforementioned how important it is that the fertilizers are protected against the absorption of moisture.

6.2 Measurement of the dusting tendency of a product

When carrying out studies on reducing the dusting tendency of fertilizers, it is necessary to have a simple and suitable method for measuring this tendency. The dust particles which create problems in bulk-handling are so fine and adhere so firmly to the fertilizer particles that only a very limited amount can be separated by ordinary laboratory screens.

In our studies of the dust problems, we have derived great benefit from the apparatus shown in Appendix 1. Visual observations during loading, and determination of the dust content in representative samples from these cargoes, have established a useful correlation between analysis figures and observed dust level when loading. On this basis the values in Table 6.2.1. have been obtained.

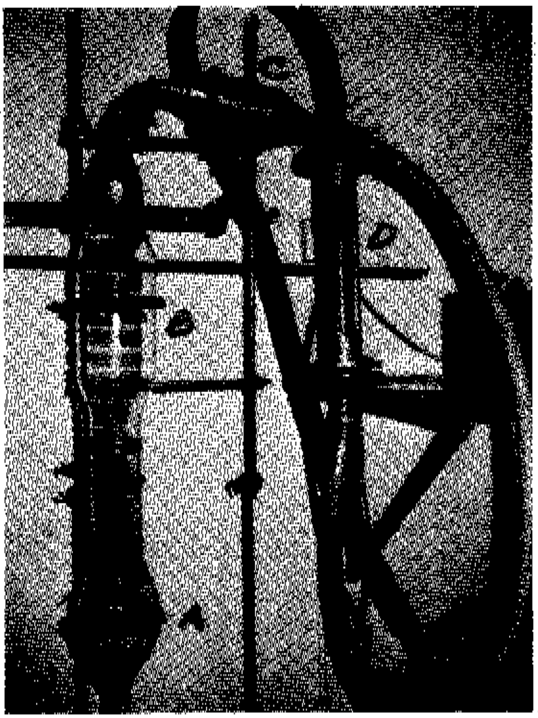
Table 6.2.1: Correlation between analyzed values and dust level observed when loading NPK fertilizer.

Analyzed values, mg/kg	Observed dust level
200	Little dust emission
200-500	Some " "
500-1000	High " "
1000-2000	Very high " "
2000	Extremely high " "

Method for determining the amount of dust in fertilizers

A weighed sample corresponding to 1.2 litre fertilizer is treated for 2 minutes in a spouting bed - see Photograph A 1. The liberated dust particles are collected in a preweighed filter bag held in a holder C. The dust in the filter bag is weighed and calculated as mg per kg fertilizer.

An ordinary vacuum cleaner is used as a means of suction. The air is regulated by means of a flowmeter - D - so that its velocity in the separator corresponds to the terminal falling velocity of the largest particles to be removed.
Air at the rate of 67,5 m^3 per hour, which equals an air velocity of 1.3 m/sec. is used to measure the dust content in NPK fertilizer. Microscopic examination shows that at this velocity particles up to 200 microns can be removed.



Photograph A 1: Dedusting apparatus.