

# ISMA\* Technical Conference

Sandefjord, Norway  
8-11 September 1970

*\*In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

## USE OF AMINES AGAINST CAKING OF FERTILISERS

---

By :

J. Breiss  
Azote et Produits Chimiques S.A.  
France

Treatment of fertilisers with a view to avoiding caking is assuming today an increasing importance. The development of production plant size on one hand, and the seasonal character of sales on the other, entail the necessity of stocking large quantities over more or less prolonged periods. Furthermore, there is the need to produce fertilisers of high concentration, especially complex fertilisers - fertilisers whose tendency to lumping increases with the concentration of nutrients - and there is also the need to offer fertilisers which are easy to handle and easy to spread. Thus an anti-caking treatment is indispensable in spite of all the precautions taken by the manufacturers during production and storage.

Amongst several methods studied and proposed, the fatty amines occupy a predominant place and have proved useful in the most difficult cases because of their effectiveness and ease of use.

In our Company, Azote et Produits Chimiques S.A. - which is both a producer of fertilisers and of fatty amines, the problem of anti-caking using amines has been under consideration for a long time, and the amines have given a satisfactory solution.

This paper concerns the application of amines in the anti-caking treatment of fertilisers, and in particular of complex fertilisers.

### CAUSES OF CAKING

Before considering treatment, it is necessary to review briefly the principal causes of caking, which will allow a better understanding of the fatty amines.

Without going into detail to try to explain the precise mechanism of caking, a very complex phenomenon, principal causes can be listed :

#### - Chemical causes

Chemical composition plays a role, as well as the reactions which may take place in storage.

### - Physical Causes

Such as ;

- hygroscopic variations in storage atmosphere and/or transfer of humidity from the inside to the outside of the fertiliser granules
- temperature variations
- pressures to which the granules are submitted at the base of the silos and in the lower sacks in the storage heaps.
- size and shape of the granules.

Some factors can be controlled to some extent, while for others this control is practically impossible.

Amongst all these causes, the variations of humidity and temperature undoubtedly play a preponderant role. They cause physical transformations on the surface of the granules as a result of the phenomena of solution and re-crystallisation, which bring about the establishment of crystalline bridges binding the granules together, and this results in caking. It is therefore these variations in humidity which one must seek to control. The fatty amines, by their constitution, offer the means of doing this, especially in association with inert mineral charges which allow completion of the treatment.

### CHARACTERISTICS OF FATTY AMINES

There are several types of amines differentiated by their chemical character and their composition. Those which interest us here from the point of view of chemical activity are the mono-amines.

The fatty amines of the general formula  $R-NH_2$  are molecules having a long hydrocarbon chain and a residual  $NH_2$ . They are obtained from natural fatty acids by ammoniation, dehydration and hydrogenation in a series of chemical transformations.

The hydrocarbon chain, which is characterised by the number of carbon atoms present, may be saturated or not. In general, the fatty amines which have been commercialised do not form a chemical entity, but are a mixture of amines with chains of different lengths. They depend on the nature of the starting material, that is to say the natural fatty acid which itself is composed of several different acids.

The chains which one normally meets are chains of :

- C 16 generally saturated (palmatic)
- C 18 saturated (stearic)
- and C 18 non-saturated (oleic)

But besides these, the amines also include derivatives of C 12 and C 14.

The fatty amines manufactured by the A.P.C. Company are called STERONIA. We shall consider their properties later.

### SURFACE-ACTIVE PROPERTIES OF AMINES

The hydrocarbon chain is of an apolar hydrophobic character whilst the  $\text{NH}_2$  group is of a polar cationic character.

The molecule as a whole has a polar-apolar character, which results in the fatty amines being cationic surface-active.

### MODE OF ACTION OF THE AMINES

This particular characteristic explains the action of fatty amines in the caking of fertilisers.

When the fatty amine molecule approaches a negatively charged surface, which is the case for most fertilisers, the amino residual with the cationic character is fixed on this whilst the apolar and hydrophobic hydrocarbon chain is orientated perpendicularly.

Because of the properties of fatty amines it is possible to coat the fertiliser granules with a hydrophobic film which will protect them from humidity.

### APPLICATION OF AMINES IN THE ANTI-CAKING TREATMENT OF COMPLEX FERTILISERS

After having briefly reviewed the causes of caking and the properties of amines, we shall now describe their use as anti-caking agents. Several methods are possible and are used in practice ;

- use of the amine alone which is sprayed onto the fertiliser in a molten state or in solution
- use of the amine in aminated charges, that is to say mineral charges treated beforehand with amines,
- and finally, treatment in two steps comprising the spraying of the amines and a subsequent coating with an inert mineral charge.

It is this last method which will be examined in detail. From the point of view of effectiveness it gives excellent results and, in certain difficult cases, results superior to aminated charges.

## 1. Spraying of the amine

### a) Application of the amine, physical form, nature of the amine.

In order that the amine may be sprayed onto the fertiliser, it is necessary to have it in a sufficiently fluid liquid form.

If the amine is liquid by nature, it can be used as it is ; but this is rarely the case.

If it is in a solid or paste form, it can be completely fused (by raising the temperature) and spraying of the molten amine is possible.

In most cases, solutions of one or several amines are used, i.e. amine formulations. These formulations have the advantage of being ready-to-use products and thus very convenient.

Before considering the different products used and recommended, it is necessary to say a few words about possible solvents :

- water need not to be considered except for amine salts, for example the acetates. However, since their solubility is normally very low, it is possible to make only very weak solutions.

- organic solvents

Methanol is an excellent solvent, but its volatility and its inflammability make its use difficult and dangerous. Hydro-alcoholic solvents may possibly be used.

In this category there are other solvents which give satisfactory results. Thus fuel, naphtha and paraffin oils can be used.

The base amines for anti-caking treatment are the following :

- STERONIA SO, a primary non-saturated amine which is in the form of a paste at the ambient temperature, its melting point being 30-40° C, its density at 60° C in relation to water at 4° C being 0.8 and its iodine value 40-50.
- STERONIA SS, a saturated primary amine, a paste, melting point 47-55° C,  $d_4^{60}$  0.795, iodine value 2-5.
- ASTERONIA SS, Steronia SS acetate, solid, melting point 65-70°C.

#### Formulations :

- Fuel-Steronia mixture SO 70/30 at 30% active product which is liquid at the ambient temperature, but must be heated at lower temperatures to be liquified.

- Flonia 380 based on a primary amine in an oil with 50% active product, clouding point 46-50° C (= saturation temperature),  $d_4^{20}$  0.826.

Other mixtures are possible.

b) Choice of amine - dosage - laboratory method.

In order to determine the amine which is most suitable for the type of fertiliser which one wishes to treat, appropriate laboratory tests are carried out with the fertiliser in question and different types of amines or formulations.

For this test it is necessary to take a sample of fertiliser from a production batch.

The fertiliser (100 gm) is coated with the desired quantity of anti-caking agent in a stopped flask and agitated by turning at a temperature of 80-85° C for 5 minutes.

4 to 6 cylindrical test-tubes of fertiliser are then prepared and are submitted to a constant pressure (1.425 bar). These test-tubes, kept under pressure, are placed in a variable climate oven with a programmed cycle. The test tubes are thus exposed to two types of storage conditions : a warm and humid climate (30° C with a relative humidity of 66%) and a cold and dry climate (15° C at a relative humidity of 34%). Each cycle lasts 6 hours and there are four cycles per day, the total duration being 48 hours. After a drying phase of 48 hours at 30° C and 27% relative humidity the resistance of the test tubes to crushing is measured and the mean calculated.

This method has only a relative validity and it is necessary to determine the resistance to crushing of a test tube made up from the same but untreated fertiliser - the control test tube - in order to be able to assess the effectiveness.

This method allows, by means of systematic tests, the most appropriate amine for anti-caking treatment of the fertiliser to be determined, and the effect of the quantity of amines used to be studied. Thus one arrives at the dose necessary for effective treatment.

This dose is generally very low and is about 0.2 - 0.3% of 100% amine relative to the weight of fertiliser, which involves the use of 0.2 - 0.3 kg of amine per ton of fertiliser to be treated.

With a formulation containing 30% of active product, 0.7 - 1 kg of product per ton of fertiliser is sprayed, and with a formulation of 50% (Flonia 380), 0.4 - 0.6 kg.

These relatively low doses are sufficient to ensure a high level of effectiveness due to the film-forming property of surface-active cationics. Once the granules are coated with a film of monomolecular amine, the desired effect is achieved and any excess anti-caking agent is lost and could even be detrimental and have an adverse effect.

### c) Temperature of use

In order to be able to spray these formulations it is necessary to heat to a temperature of 80-90° C, whilst the fertiliser to be treated is at a temperature of about 35° C. The working temperature is an important parameter for the success of regular coating of the granules with an homogenous cover of the anti-caking agent on their surface. It is particularly necessary to avoid solidification of the reagent in contact with the grains but to allow it time to move about and spread uniformly.

## 2. Coating with a mineral charge

Once the fertiliser granules are treated with the amine, the next step is coating with an inert mineral charge such as clay, kaolin kieselguhr, talc, chalk etc.

In general the size of the charge used in relation to the weight of fertiliser treated is of the order of 0.8 to 1%.

### Points at which treatment is carried out

#### Spraying and coating.

Various spraying treatment points are possible in the course of manufacture. Complex fertilisers, which are now all granulated, may be treated after screening and calibration and before cooling. It is at this point that it seems most rational to locate spraying : it is useless to treat granules which will be recycled again. This would lead to a loss of anti-caking agent.

The spraying may be done on the fertiliser when it is being carried on a transporting belt, whilst in a chute, or at the entrance to a drum coater when the spraying is carried out at the inlet and the mineral charge added in the drum itself, the granules remaining there being for about 3 to 4 minutes.

## APPARATUS

The spraying apparatus comprises :

- A storage vessel for the amine solution or for the fused amines with heating facilities, the vessel being provided

with thermic insulation.

- A dosing pump which sends the anti-caking agent round a closed circuit with a double cover to maintain its temperature. The liquid pumped from the vessel returns to the same vessel.
- Part of the flow is taken from the general circuit and led into a diversion provided with a spraying nozzle. The quantity thus removed is in general small in relation to the flow effected by the dosing pump. This method enables a constant spraying quantity to be ensured. The quantity must obviously be adjusted according to the delivery rate of the fertiliser to be treated.

For coating with the inert charge, it suffices to have an apparatus giving continuous and regular addition.

### CONCLUSIONS

The fatty amines constitute an effective means for treatment of complex fertilisers to avoid caking and are easy to apply. They confer on the fertilisers a durable effect and thousands of tons of fertilisers are treated each year.