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Anti-Caking Additives for NPK Fertilisers: A New Concept

J. RIAZA

Kao Corporation SA

Puig dels Tudons 10, Centro Industrial Santiga
Barbera del Valles, 08210 Barcelona, Spain

The term "NPK fertilisers" includes a broad range of products, which can be prepared in different ways, depending on the selection of available raw materials, to contain the nutrients in predetermined concentrations. In spite of this diversity, most types of granulated NPK fertiliser suffer from two basic problems: the tendency to cake (form clods) and dust formation. These result mainly from post-reactions, moisture absorption, irregular shape and heterogeneous mass.

Kao started to design anti-caking and anti-dusting additives for NPK fertilisers a long time ago. Until now, Kao has developed different additives for different NPK types depending, for example, on which nitrogen source they are based: ammonium nitrate, ammonium sulphate or urea.

Last Year Kao decided to develop new "all-purpose" additives for any type of granulated NPK fertilisers. To attain this objective, we studied mixtures of different surfactants that, on their own, are known to have suitable caking protection in specific fertilisers. We evaluated different ratios of these components in NPK fertilisers based on any of ammonium nitrate, ammonium sulphate and urea.

We present the stages of this study and the new additives proposed.

INTRODUCTION

NPK fertilisers encompass a broad range of chemical substances that can be made in different ways depending on the selected raw materials (ammonia, phosphate rock, potash), the required nutrient concentrations (% of N, P_2O_5, K_2O, MgO) and the required physical state of the product (crystal, granular, blend, liquid).

Kao Corporation has been working on fertilisers additives for more than 25 years and we have developed products for different proposals:

- Hydrophobic anti-caking and anti-dusting additives for granulated fertilisers
- Aqueous anti-caking additives for crystalline and prilled fertilisers.
- Processing agents for granulation.
- Agents for porous ammonium nitrate.
- Anti-foaming agents for wet acid attack of phosphate rock.
- Corrosion inhibitors for liquid fertilisers like UAN.

In this presentation we will focus on the first family: additives for granulated fertilisers.

MAIN TROUBLES OF GRANULATED NPK

There are two main troubles with granulated fertilisers: caking tendency and dust formation. These troubles are due to post-reactions, moisture absorption, irregular shape and heterogeneous mass.

Post-reactions are usually due to infelicitous mixtures of the components or a inadequate contact time between them during the granulation process. For whichever of these reasons, granular fertilisers undergo a period of curing after they are first manufactured in which self-heating, caking and dust formation phenomena may occur. Certain kinds of NPK are particularly susceptible. For instance, in an NPK based on ammonium sulfate and potassium chloride, these two materials interact to produce potassium sulfate and ammonium chloride or mixed ammonium-potassium salts.

$$(NH_4)_2SO_4 + 2KCl \rightarrow K_2SO_4 + 2NH_4Cl$$

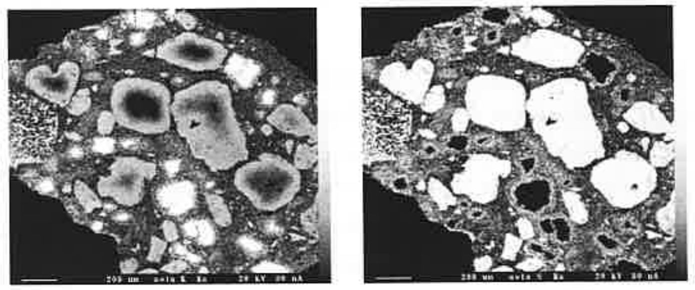
K  S

FIG. 1: X-RAY MAPPING OF POTASSIUM AND SULPHUR IN AN NPK GRANULE CONTAINING $(NH_4)_2SO_4$, MAP, DAP, KCL AND CLAY

In Fig. 1 we can observe the crystals of AS (the palest patches, which are in fact yellowish on the S map) that are becoming potassium sulfate in the external part of the particles: looking at the K map we can appreciate a yellowish part that corresponds to potassium sulfate. The dark area corresponds to the remaining ammonium sulfate.

In the same way we can observe the same phenomenon for chloride salts.

Similar reactions occur with several salts:

$$NH_4NO_3 + KCl \rightarrow KNO_3 + NH_4Cl$$
$$(NH_4)_2SO_4 + Ca(H_2PO_4)_2.H_2O + H_2O \rightarrow CaSO_4.2H_2O + 2(NH_4)H_2PO_4$$
$$(NH_4)_2SO_4 + CaSO_4 + H_2O \rightarrow (NH_4)_2SO_4.CaSO_4.H_2O$$
$$K_2SO_4 + CaSO_4 + H_2O \rightarrow K_2SO_4.CaSO_4.H_2O$$
$$4CO(NH_2)_2 + Ca(H_2PO_4)_2.H_2O \rightarrow Ca(H_2PO_4)_2.4CO(NH_2)_2 + H_2O$$
$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$$
$$(NH_4)_2HPO_4 + 2KCl \rightarrow 2NH_4Cl + K_2HPO_4$$
$$H_3PO_4 + (NH_4)_2HPO_4 \rightarrow 2(NH_4)H_2PO_4$$
$$Ca(H_2PO_4)_2 + NH_3 \rightarrow CaHPO_4 + (NH_4)H_2PO_4$$
$$NH_4H_2PO_4 + NH_3 + H_2O \rightarrow (NH_4)_2HPO_4 + H_2O$$

Moisture absorption is another big problem for certain NPKs in which the critical relative humidity of some components is very low. In this situation, the granules absorb large quantities of

moisture, and later the released moisture promotes caking and recrystallisation of the salts with dust formation. NPKs based on urea tend to have this trouble.

Irregular shape and **heterogeneous mass** of granules is another trouble that seems to appear when the liquid phase in the granulation is poor, as where a large quantity of the components is added in a solid state: powder, crystal or prill.

As we explained at the beginning of this chapter, a short period of contact and a bad mixture generates irregular surfaces, where the abrasion is very high. See Fig. 2.

FIG. 2: SURFACE OF THE GRANULES OF FIG. 1

KAO'S ADDITIVES FOR EACH NPK TYPE

Our company has developed anti-caking and anti-dusting additives for different types of NPK. We divided them into additives for NPK based on ammonium nitrate ***(NPK(AN))***, NPK based on ammonium sulfate ***(NPK(AS))***, NPK based on urea ***(NPK (Urea))*** and for NPK with low Nitrogen content ***(NPK (low N))***.

The additives were designed taking into consideration the mode of incorporation of the chemicals into the fertiliser composition and the nature of the salts present in the NPK. In addition, we considered also the physico-chemical parameters that define the granules' behaviour: moisture absorption, post-reaction and abrasion.

Following these principles we developed different additives, each one tailored for one or two types of NPK, as tabulated below.

NPK Type	SK Fert® FW5AG SK Fert® F50AG	SK Fert® FA-143	SK Fert® FA-62	SK Fert® FT200	SK Fert® FT500
NPK (AN)	X				
NPK (AS)		X	X		X
NPK (Urea)		X		X	
NPK (Low N)			X		X

In general, we can define our additives as a mixture of from one to several hydrocarbons (mineral oils, paraffin waxes) selected according to the worst characteristics of the specific fertiliser (high moisture absorption, abrasion, dust formation) and several crystal modifiers that act to prevent the caking.

"ALL-PURPOSE" ADDITIVES

Given the fact that the fertiliser industry tends to use different nitrogen sources at the same time and prefers only to keep one additive in stock, we decided to develop new, all-purpose additives for use with any type of granulated NPK fertiliser.

For this proposal, different crystal modifiers that are known for their good response in specific NPK types were selected. The goal was to find out the best combination of crystal modifiers to achieve good caking protection in any NPK type.

We used the ***Minitab®*** program to design experimental mixtures. Cake protection was evaluated by means of real accelerated caking tests done in our laboratory, using defined mixtures of these crystal modifiers in several NPK fertilisers of different types.

Conditions of the experiments

The selected crystal modifiers were

Crystal modifier	Usual NPK type
Cationic mixture 1	NPK (AS/Urea)
Cationic mixture 2	NPK (AN)
Anionic mixture	NPK (Urea)

The total formula contained 14% of the crystal modifier mixture in a specific mineral oil. Only one hydrocarbon base was used in this screening stage. Later on, when the mixture of crystal modifiers was defined, the optimal hydrocarbon base would be proposed according to the main problems with the specific NPK (moisture absorption, abrasion)

Following the Minitab® option: DOE/Mixtures/Simplex centroid, an experimental design of three components (A,B,C) with 10 points was chosen. See Fig. 3.

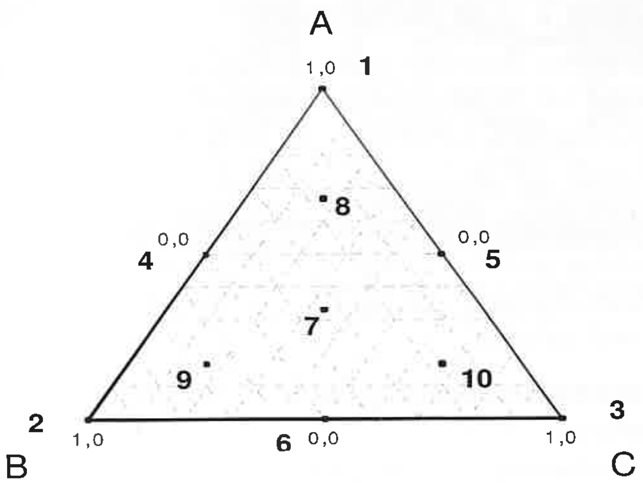


FIG. 3: COMPOSITIONS OF TEN EXPERIMENTAL MIXTURES

The proportion of the three components was selected in the following way:

Component	Crystal modifier	Range
A	Cationic mixture 1	5 - 14
B	Cationic mixture 2	0 - 9
C	Anionic mixture	0 - 9

The selected NPK were:

NPK Type	Fertilisers	Main components (By X- Ray diffraction)
NPK (AN)	NPK 15.15.15 (A)	$K_{0.333}(NH_4)_{0.667}NO_3$, $CaHPO_4$, $Ca(SO_4).0.5H_2O$, $NH_4H_2PO_4$, K_2HPO_4, NH_4Cl, KCl
	NPK 15.15.15 (B)	$K_{0.333}(NH_4)_{0.667}NO_3$, $(NH_4)_2SO_4$,$NH_4H_2PO_4$, NH_4Cl, KCl, SiO_2, $Ca(Fe,Mg)(CO_3)_2$, $CaMg(CO_3)_2$, $CaSO_4.0.67H_2O$
	NPK 15.15.15 (C)	$K_{0.333}(NH_4)_{0.667}NO_3$, $K(NH_4)_3(NO_3)_2SO_4$,K_2SO_4, $NH_4H_2PO_4$, NH_4Cl, KCl, SiO_2
NPK (AS)	NPK 15.15.15	$(NH_4)_2SO_4$, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, K_2HPO_4, NH_4Cl, KCl, K_2SO_4, SiO_2
NPK (AS/urea)	NPK 15.15.15	$(NH_4)_2SO_4$, $CO(NH_2)_2$ *, KNO_3, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, KCl, $Ca(SO_4)$, SiO_2, Fe_2O_3
NPK (Urea/AS)	NPK 18.12.8	$CO(NH_2)_2$, $(NH_4)_2SO_4$*, KNO_3, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, KCl, $Ca(SO_4)$, SiO_2, Fe_2O_3
NPK (Low N)	NPK 8.24.8	$NH_4H_2PO_4$, $(NH_4)_2HPO_4$, NH_4Cl, KCl,$CaMg(CO_3)_2$, SiO_2

* *Minor quantity*

The climatic conditions of the accelerated caking test were:

NPK type	Conditions
NPK (**AN**)	6 - 15 h at 20°C/ 80% R.H. + 3 days at 40°C/ 20% R.H. 15 days at 20°C/ 60% R.H.
NPK (**AS**)	24 h at 20°C/ 80% R.H. + 3 days at 40°C/ 20 % R.H.
NPK (**AS**/Urea)	24 h at 20°C/ 80% R.H. + 3 days at 40°C/ 20 % R.H.
NPK (**Urea**/AS)	24 h at 20°C/ 60% R.H. + 3 days at 40°C/ 20 % R.H.
NPK (**Low N**)	24 h at 20°C/ 80% R.H. + 3 days at 40°C/ 20 % R.H. (Low caking tendency, more interesting for the dust formation)

The crushing strength of the caked sample was evaluated and the percentage of caking protection was calculated, using the crushing strength of the uncoated samples as a reference. The dosage of additives was 0.1% w/w.

Caking results

In a first step, the evaluation of the ten defined formulas started with four fertilisers:

NPK Type	Specific fertilisers
NPK (**AN**)	NPK 15.15.15 (B)
NPK (**AS**)	NPK 15.15.15
NPK (**AS**/Urea)	NPK 15.15.15
NPK (**Urea**/AS)	NPK 18.12.8

The obtained caking protections were presented in Fig. 4 in an overlaid contour plot of the four fertilisers. Where the best formulas were located in a new triangular area, that appeared inside the original one.

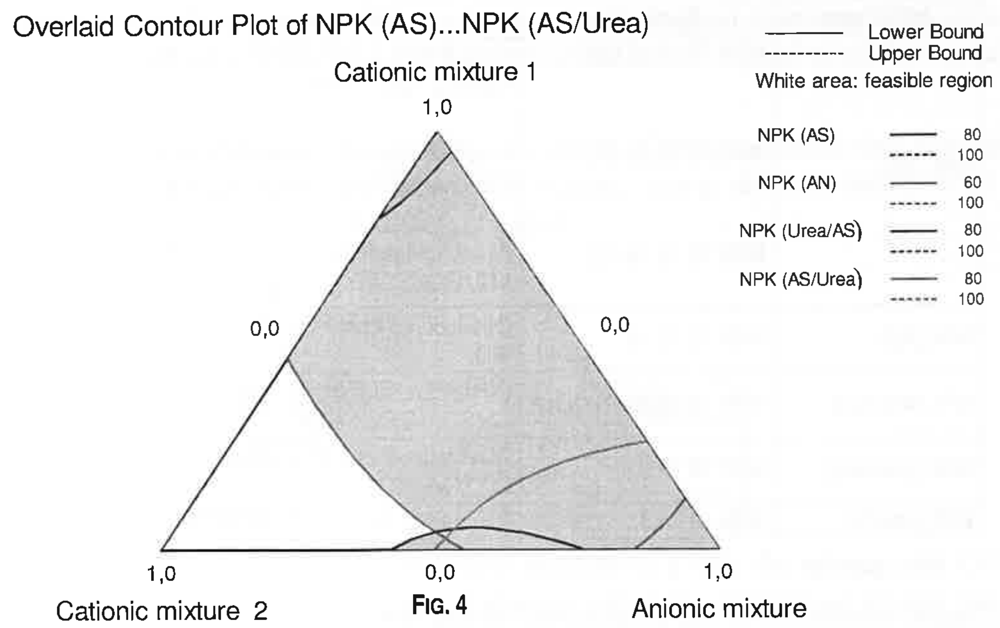


FIG. 4

Then, as a second step, the new area was considered a new triangle of mixtures with the three components (A,B,C). Ten additional points were chosen.

The new proportion ranges of the three components were:

Component	Crystal modifier	Range
A	Cationic mixture 1	5.0 – 9.5
B	Cationic mixture 2	4.5 – 9.0
C	Anionic mixture	0.0 – 4.5

The new NPK selection was:

NPK type	Specific fertilisers
NPK (**AN**)	NPK 15.15.15 (A) NPK 15.15.15 (C)
NPK (**AS**)	NPK 15.15.15
NPK (**Urea**/AS)	NPK 18.12.8
NPK (**Low N**) (1)	NPK 8.24.8

(1) The blank crushed at an average value of 22.3 kgf, but the treated samples didn't form a complete cake in any case

The new caking protections were presented in the new triangle, in an overlaid contour plot of five caking tests. See **Graphic 3**.

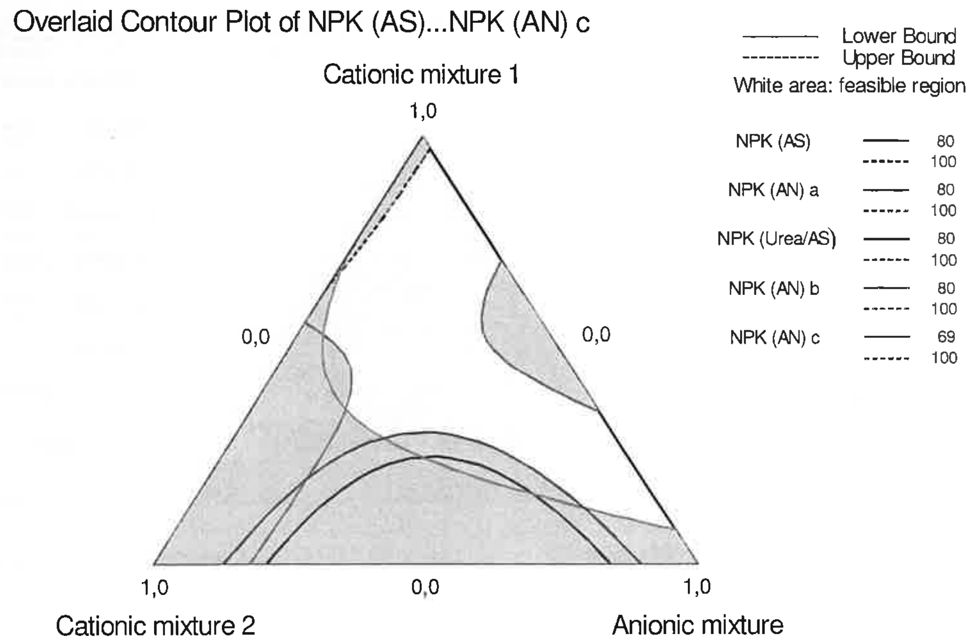


FIG. 5

A big area was obtained, considering minimal protections of 80% in four caking tests and 69% in one specific test.

In order to decide the optimal mixture, we considered in addition, the melting point variation inside the triangle. The melting point of the ten formulas was measured by Differential Scanning Calorimetry (D.S.C.) and they were presented in a Mixture Contour Plot. See Fig. 6.

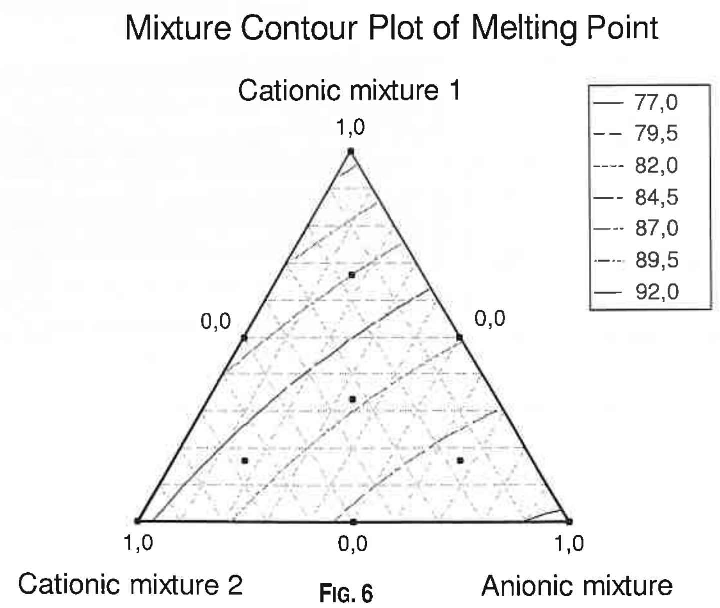


FIG. 6

Matching Figs 5 and 6, a new area was obtained, considering m.p.≤ 80°C. See Fig. 7.

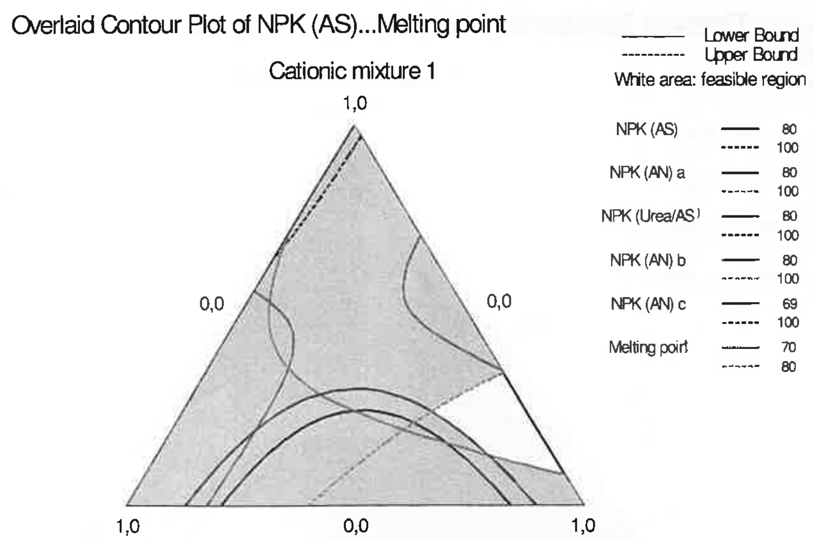


FIG. 7

The optimal mixture of crystal modifiers was:

Crystal modifier	Point in the triangle	%
Cationic mixture 1	0.22	6.0
Cationic mixture 2	0.00	4.5
Anionic mixture	0.78	3.5

This mixture with the hydrocarbon base has a complete m.p. of 78°C. If lower melting points were necessary for some specific application, it could be decreased by varying slightly the cationic mixture 1 and 2.

The concrete results obtained with this optimal formula were:

NPK Type	Specific fertilisers	% Protection
NPK (**AN**)	NPK 15.15.15 (A) (20°C/ 80% R.H...) NPK 15.15.15 (A) (20°C/60% R.H....) NPK 15.15.15 (C)	82.6 84.2 72.3
NPK (**AS**)	NPK 15.15.15	96.6
NPK (**Urea**/AS)	NPK 18.12.8	83.3
NPK (**Low N**)	NPK 8.24.8	100.0

Of course, increasing the crystal modifier content from 14% to higher values, the present protection values can be still improved.

In addition, as has been explained previously, the optimal formula was generated with only one hydrocarbon base. At that point, with the mixture of crystal modifiers already defined, the optimal hydrocarbon base would be proposed according to the nature of the main troubles to be solved for any specific NPK. Two main parameters were fixed: moisture absorption and dust release.

Selection of the best hydrocarbon base

The goal was to find out the best base for NPK fertilisers with **high moisture absorption** and the best one for NPK fertilisers with **high dust release** (by post-reaction, surface recrystallisation or abrasion).

Four bases were selected for this study in order to prepare the optimal formula with Cationic mixture 1, Cationic mixture 2 and Anionic mixture (6 / 4.5 / 3.5 %, respectively):

Hydrocarbon base	Characteristics
O	Mineral oil. The base used in the definition of the best crystal modifiers mixture. Optimal handling temperature: ≥60°C.
P	Paraffin. Optimal handling temperature: ≥40°C.
M-1	Mixture of paraffin and mineral oil. Optimal handling temperature: ≥60°C.
M-2	Mixture of paraffin and mineral oil. Optimal handling temperature: ≥60°C.

Two evaluation tests were performed:

Test	Fertiliser	Dosage	Conditions
Moisture absorption	NPK(Urea/AS)	1 kg/t	72 h at 20°C/ 80% R.H. Control of the weight increase
Dust releasing	NPK (Low N)	2 kg/t	15 days at 40°C/ 20% R.H. Sieving at 0.5 mm, 10 min.

Moisture absorption test

The lowest values of moisture absorption were obtained with hydrocarbon **base P** followed by **base M-2**. See Fig. 8.

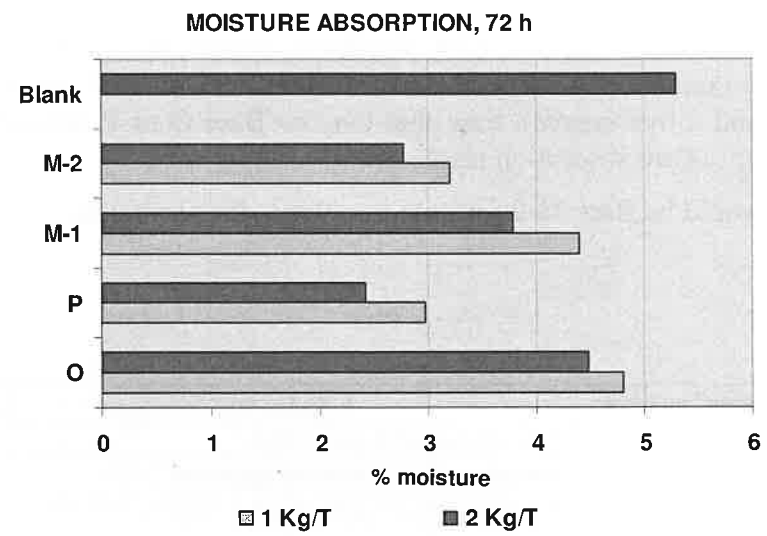


FIG. 8

Dust release test

The lowest values of dust release were obtained with hydrocarbon **base O** followed by **base M-2 and M-1**. See Fig. 9.

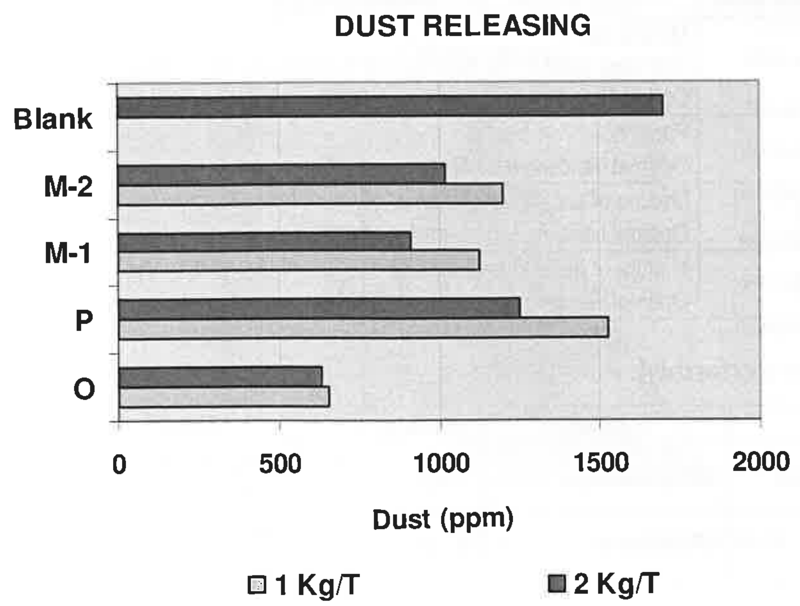


FIG. 9

CONCLUSIONS

Given the fact that in the fertiliser industry there is a tendency to use different nitrogen sources at the same time and a preference for only storing one additive, we developed new additives for application on any type of granulated NPK fertiliser.

These additives, useful in a broad range of NPK fertilisers, consist in a mixture of three crystal modifiers with a minimal content of 14%: 6% Cationic mixture 1, 4.5% Cationic mixture 2 and 3.5% Anionic mixture. And a hydrocarbon base that may be Base O or P depending on the main trouble: dust releasing or moisture absorption respectively.

A compromise proposal would be Base M-2 for both troubles at the same time.

As a summary:

"All Purpose" additives	Focused on:
Optimal - O	Anti-caking effect & dust control
Optimal - P	Anti-caking effect & moisture absorption
Optimal - M2	Anti-caking effect & dust control & moisture absorption