THE NEW FERTILIZER "CALCOUREA"

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SUMMARY

The new product "calcourea" fits perfectly into the research strategies of Enichem Agricoltura whose aim is to prepare new methods to deal with the culture cycle. This aim may be reached through new products such as, "calcourea" and new technologies in cultivation that ensure optimum plant growth with minimum environmental damage.

The utilization rate of nitrogen in urea is unlikely to exceed 50-60%. In order to increase this rate of utilization, to agronomic and environmental advantage, Enichem Agricoltura has developed a fertilizer consisting of a urea - calcium nitrate compound: Calcourea 4 $CO(NH2)_2$ - $Ca(NO3)_2$ with the following properties:

N total = 33 - 34%, 7% of which is nitrate.

There are three reasons of interest in this new nitrogen fertilizer:

- the presence of different forms of nitrogen (nitrate and urea) at the same time

- the reduction of the phenomenon of volatilization of ammonia from the amide fraction

- calcium content

Moreover, from an agronomical point of view, the presence of both nitrate and urea nitrogen makes "calcourea" an ideal formula for spring fertilizing, and in the phase of summer crop, after transplanting and weeding.

However, this fertilizer undoubtedly reaches its maximum operative potential as top-dressing for cereals, field fodder and colza.

From an energy standpoint, the presence of nitrate and urea nitrogen and of calcium at the same time makes "calcourea" a high savings fertilizer. It can reduce ammonia losses to the air by as much as 50-60%, depending on soil quality-ranging from clayey to acid.

From an environmental point of view, the near absence of NH_3 losses to the air even in surface fertilizing makes it an ecological fertilizer.

CALCOUREA

Chemically, calcourea is a urea and calcium nitrate double salt. This product made its appearance in Germany during the Second World War under the name of CAL-UREA but was unsuccessful on account of its poor product quality (brittle and powdery) that made it unmarketable.

Terni Industrie Chimiche has carried out a long series of tests during the last years with modern technologies from:

GUTTA Company, Dutch, for crystallization
EIRICH Company, Germany, for agglomeration from dusts
NIRO Company, Danish, for granulation by spray dryers

These technologies did not make it possible to obtain a marketable product on account of its poor physical and morphological properties (very brittle crystals, irregular granulate, insufficient hardness). After these series of unsuccessful attempts, we resumed the experiments within our company together with local companies.

The new experiments lasted for about two years and ended positively with the construction of a pilot plant (with a potential of 500 kg/h) in which about 130 tons of calcourea were produced and with the publication of a patent (n° 19363, February 2nd, 1987) in which claims are made on three different production methods. (See enclosure n° 1)

CHEMICAL AND PHYSICAL PROPERTIES OF CALCOUREA

See enclosures n° 2 and n° 3.

SPECIAL PROPERTIES OF CALCOUREA

See enclosure n° 4.

REDUCTION OF AMMONIA LOSSES

Upon contact with soil, urea undergoes the well-known reaction of hydrolysis (see enclosure n° 5) releasing ammonia to the atmosphere, producing energy losses and air pollution. The levels of loss may be very high - up to 50% of the nitrogen applied - depending on the soil quality (see enclosure n° 6).

The reaction of calcourea in the soil (see enclosure n° 7) takes place without the release of ammonia and with the formation of ammonium nitrate and of calcium carbonate which precipitate displacing the equilibrium towards the right until complete transformation of the urea contained in the calcourea has taken place.

Enclosures n° 8 and 9 show diagrams of ammonia release from calcourea compared with urea and ammonium nitrate in different soil types.

AGRONOMICAL ADVANTAGES OF CALCOUREA DUE TO THE PRESENCE OF BOTH UREA AND NITRATE NITROGEN

The presence of 7% of the nitrogen in nitrate form in the product is agronomically favourable.

This makes the product effective both immediately as well as over time. When compared with ammonium nitrate, the latter has a higher titre and hence is more competitive with respect to the costs of handling and applying. From an agronomical point of view, the presence of both nitrate and urea nitrogen makes calcourea an ideal formula for spring fertilizing, in the phase of summer crop after transplanting and weeding. However, this fertilizer undoubtedly reaches its maximum operative potential as top-dressing on grass cereals. Unlike urea per se the association with calcium nitrate serves to reduce ammonia losses by volatilization to insignificant levels even when the product is distributed over the soil surface without being plowed in.

In order to emphasize the agronomical advantages derived from the presence of both types of nitrogen, the product has been given the commercial name of NITROSTAR (see enclosure n° 10).

The presence of both nitrogen makes NITROSTAR ideal for use during the phase of plant growth renewal, not necessarily in spring, to give this phase or renewal an "charge".

AGRONOMICAL ADVANTAGES DUE TO THE PRESENCE OF SOLUBLE CALCIUM

The presence of calcium (about 14% CaO) causes this product, characterized by a neutral pH, to have a slightly alkaline physiological effect on the soil, corresponding to the alkalinity induced by about 35 kg of $CaCO_3$ for every 100 kg of fertilizer applied.

For this reason, the new fertilizer has an especially favourable action in all those conditions where the use of average to high levels of nitrogen fertilizing must match the need to respect the natural soil pH (corn, sugar beet, rice, peach, strawberries and other market garden species).

Very often problems of poor substratum structure, of excessively slow humification of organic matter, of rapid deactivation of weed killers and difficulties in plant mineral uptake, especially in the case of phosphates and microelements (with corresponding problems for crop production quality and quantity) are due to calcium deficiencies and consequent abnormal soil pH values.

Calcium is a source of flocculate cations. It alleviates the formation of a surface crust which is due to the rapid alternation of rain and dry cycles, and which impede efficient water and gas exchanges and create a mechanical barrier to emerging crops like sugar beets, sunflower and corn.

The properties of NITROSTAR are in enclosure n° 11.

OPTIMUM AGRONOMICAL USES OF NITROSTAR

This product is primarily designed for use after planting without plowing in, as top-dressing for autumn and winter cereals, for colza which is an emerging crop used especially in calcareous soils and for field fodder (alfalfa and gramineous fodder).

Other excellent uses are in after-planting and weeding of crops such as corn, sugar beet, sunflower, field crop, glasshouse crop, and peach.

As can be seen, calcourea can be used in an extremely broad range of crops (see enclosures n° 12 and n° 13).

The tests and agronomical evaluation were carried out by Prof. Miele of the Faculty of Agriculture of the University of Pisa.

REFERENCES

MC VICKAR M.H., BRIDGER G.L., NELSON L.B., ed.: Fertilizer Technology and Usage; SSSA, Madison, 1963, p 464.

NFDC & TVA: New Developments in Fertilizer Technology; 12th Demonstr., Bull. Y-136, 1978.

WHITE W.C., COLLINS D.N., ed.: The Fertilizer Handbook; TFI, Washington D.C., 1982, p. 274.

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Enclosure 1

PROCESSES FOR THE PRODUCTION OF CALCOUREA

- "dry" process

  (a) Dehydration of calcium nitrate to bring the water content from 15% to 0.1%

  (b) Dissolution - reaction of anhydrous calcium nitrate in the melted urea

  (c) Granulation

- slurry process

  (a) Direct mixture of the calcium nitrate solution at 15% H_2O with melted urea

  (b) Addition of 4% dolomite as hardener

  (c) Granulation - drying

- intermediate process

  (a) Partial dehydration of calcium nitrate

  (b) Mixing - reaction with melted urea

  (c) Granulation - drying

Enclosure 2

C A L C O U R E A

Chemical properties

Reaction $4CO(NH2)_2 + Ca(NO3)_2$ ----------> $4CO(NH2)_2.Ca(NO_3)_2$ 0.18 Kcal.

	Urea	**Calcium Nitrate**	**Calcourea**
Formula	$CO(NH2)_2$	$Ca(NO_3)_2.0.15NH_4NO_3.1.5H_2O$	$4CO(NH_2)_2.Ca(NO_3)_2$
N total %	46	15 - 16	33 - 34
N urea%	45	0	26 - 27
N nitrate%	0	15 - 16	7
CaO%	0	27	14
pH sol. 10%	9.5 - 10	5.5	7.3

Note with regard to the new fertilizer that:

- urea and nitrate nitrogen are present together

- soluble CaO is present

- the aqueous solutions are neutral

C A L C O U R E A

Physical properties

	Urea	Calcium Nitrate	Calcourea
melting point °C	132	95	155
melting λ cal/gr.	58	26	30
specific heat cal/gr °C	0.43	0.35	0.44
specific weight of solid at 20°C kg/dm^3	1.3	2.0	1.6
specific weight of liquid kg/dm^3	1.23 (138°C)	1.95 (130°C)	1.46 (160°C)
saturated vapor tension at 100°C mm Hg	255	137	237
μ Cps	2.4 (135°C)	314 (130°C)	23 - 32 (160°C)
critical moisture	75	20	40*

*) Note the lower deliquescence of calcourea with respect to calcium nitrate

Enclosure 4

PROPERTIES OF CALCOUREA

1) REDUCTION OF NH_3 LOSSES TO THE ATMOSPHERE ESPECIALLY IN SURFACE SPREADING

2) PRESENCE OF BOTH UREA AND NITRATE NITROGEN

3) PRESENCE OF SOLUBLE CaO

4) NEUTRAL pH OF THE AQUEOUS SOLUTION

Enclosure 5

UREA REACTION IN THE SOIL

$$CO(NH_2)_2 \xrightarrow{2H_2O} (NH_4)_2CO_3 \longrightarrow H_2O + CO_2 + NH_3$$

UREA	AMMONIUM CARBONATE	WATER	CARBON DIOXIDE	AMMONIA

Enclosure 6

MEASURE OF N LOSSES DUE TO VOLATILIZATION FROM UREA

AVERAGE VALUE	10 - 30%
MAXIMUM VALUES	> 50%

(HAUCK, 1983)

Enclosure 7

CALCOUREA REACTION IN THE SOIL

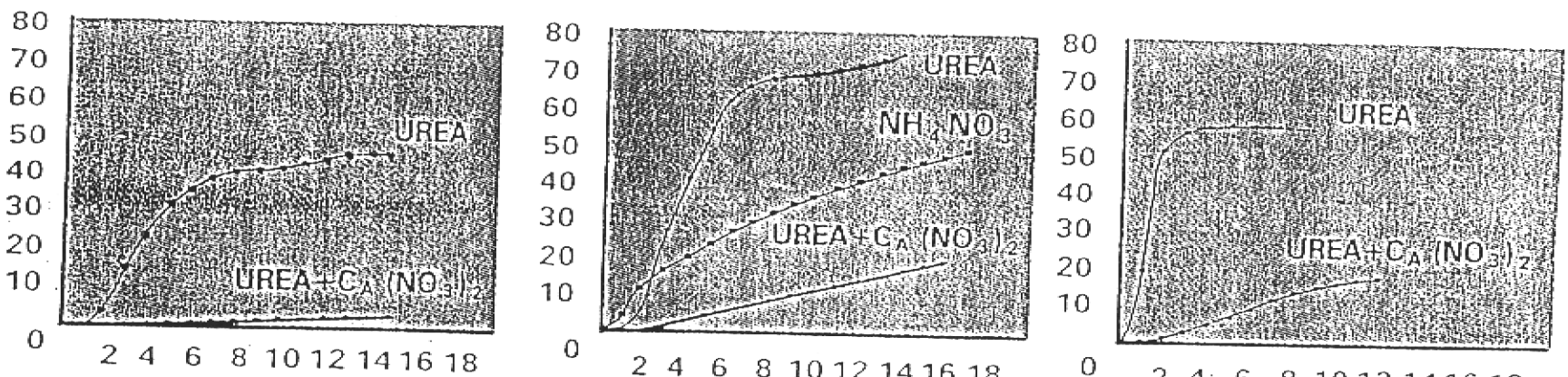
$$CO(NH_2)_2 \xrightarrow{2H_2O} (NH_4)_2CO_3 + Ca(NO_3)_2 \longrightarrow NH_4NO_3 + CaCO_3$$

UREA	AMMONIUM CARBONATE CALCIUM NITRATE	AMMONIUM NITRATE	CALCIUM CARBONATE

(FENNET ET AL 1973)

CALCIUM NITRATE REDUCES VOLATILIZATION OF NH_3 FROM UREA (FENNET ET AL. 1981)

AMMONIA LOSSES FROM UREA DISTRIBUTED OVER THE SURFACE ON THE Y-AXIS AND % N-NH_3 LOSSES ON THE X-AXIS - TIME EXPRESSSED IN DAYS



CLAYEY SOIL

CALCAREOUS SOIL

ACID SOIL

Enclosure 9

NITROGEN LOSSES AT 20° C (%)

SOIL	UREA	NITROSTAR	%
SANDY	0.60	3.50	-63
CLAYEY-SANDY	0.80	0.45	-44
CLAYEY	1.23	0.65	-47

Enclosure 10

N I T R O S T A R

UREA - CALCIUM NITRATE COMPOUND

($4\ CO(NH_2)_2 \cdot Ca\ (NO_3)_2$)

4 UREA + 1 CALCIUM NITRATE

Enclosure 11

- ECOLOGICAL FERTILIZER

- ENERGY SAVING FERTILIZER

LAW n°. 308/82 - SUBSIDIES FOR THE CREATION OF AN INNOVATIVE 400 T/D PLANT TO GRANULATE CALCOUREA, UREA AND CALCIUM NITRATE

Enclosure 12

OPTIMUM USES FOR NITROSTAR

* AFTER-PLANTING WITHOUT PLOWING IN

- AUTUMN AND WINTER CEREALS

- COLZA

- FIELD FODDER

Enclosure 13

OPTIMUM USES FOR NITROSTAR

* AFTER PLANTING ON WEEDING

- CORN

- BEETS

- SUNFLOWER

- FIELD CROP AND GREEN HOUSE CROP

- PEACH