

IFA Technical Conference

**Amman, Jordan
2-6 October 1994**

PROSPECTIVE METHODS OF PRODUCTION OF SLOW-RELEASE CAPSULATED FERTILIZERS WITH REGULABLE NUTRIENT RELEASE

V.M. Olevsky, M.K. Rustambekov

GIAP

A.L. Taran

Agrotekhnologiya

Russia

RESUME

L'augmentation de l'efficacité agronomique des engrais contenant de l'azote, la réduction des pertes à partir du sol et l'empêchement de l'accumulation des composés nitriques et nitreux dans les produits végétaux en croissance peuvent être obtenus en faisant varier le taux de dissolution des engrais et de leurs constituants.

Dans ce but, des polymères avec groupes de transport et additifs minéraux qui modifient le coefficient de perméabilité des capsules ont été introduits dans l'agent capsulant déposé sur les granules : on a obtenu des granules à multi-couches avec différentes concentrations en éléments nutritifs sur les couches et les capsules ayant différentes perméabilités entre les couches ; on a aussi contrôlé la vitesse de dissolution de l'engrais et de ses constituants au moyen d'une préparation de mélange de granules ayant différentes compositions et différentes perméabilités des capsules.

Une méthode d'évaluation de la qualité de l'encapsulation par des courbes en fonction de la fraction d'engrais passant à travers la capsule d'engrais à temps est proposée.

Il y a aussi certaines recommandations données sur les sujets ci-dessus pour différents types d'engrais y compris le nitrate d'ammonium.



INTRODUCTION

The losses of mineral nitrogen-containing fertilizers in soil by surface application in a zone of rain precipitation is about 50% due to leaching and nitrification (1). Apart from economics, this problem has an important ecological aspect connected with penetration of fertilizers to surface and ground waters and accumulation of nitrates and nitrites in plants because of their irrational nutrition at different growth phases. The ideal method of solution of the above problems is creation of the interconnected system "plant - source of nutrients (fertilizers and micronutrients)" which assures the nutrient release required for a plant. Such a system including e.g. an internal controlling action is the "hydroponics" technology widely used in cultivation of plants in a protected ground. A self-regulable system "plant - nutrient source" may be built if the system elements are separated by a selective membrane, i.e., particularly, while using slow-release granulated fertilizers capsulated with selective capsules (2,3,4). This approach (in contrast to other possible methods of creation of such systems, e.g. microbiological, biochemical, or chemical "delivery" of nutrients to the root system of plants) allows: firstly, granulated mineral fertilizers now commercially produced to be used, secondly, the losses of traditional nitrogen-containing fertilizers owing to nitrification, leaching, transportation, storage to be sharply cut, the probability of caking and dust formation in handling with fertilizer to be excluded, the production of agricultural wares with a diminished nitrate and nitrite content to be assured as well as the crop capacity to be increased at the same fertilizer application rates, thirdly, the possibility of fertilizer application once per season (particularly in intrasoil application) to be realized, which cuts the labour, technical/energy expenses and the soil load in cultivation of different crops.

In production of the fertilizers of this class, capsulation with thin polymeric waterproof coatings corresponding to the capsulant content of 1.5 to 5% as well as that with coatings which are nutrients or components structuring a soil is reported (2,3,4). As the studies carried out at the M.V.Lomonosov Moscow Institute of Fine Chemical Engineering and at GIAP during the last 20 years have shown (5), manufacturing high-quality capsulated fertilizers consists of a number of stages in each of which the appropriate requirements shall be fulfilled.

The first stage is manufacturing a granulated kernel which contains the nutrients. In the commercial production of traditional fertilizers, the most widespread methods are granulation by crystallization of melt droplets in a coolant stream (e.g. prilling (6)), granulation by nodulating owing to a layer-by-layer application of crystallizing melt, dried solution, or a powdery material mortared by a binder onto germs growing because of it, granulation of melts, solutions, and powders with a binder in a fluidized bed in vessels with regulated and non-regulated movement of a dispersed phase (6,7). The granules suitable for effective capsulation with thin (1.5 to 5.0%) waterproof coatings shall be firm (with the static strength of not less than 1500 g/granule), stable to thermal cycles "heating - cooling $20 \leftrightarrow 60^{\circ}\text{C}$ ", big enough ($d_{gr} \geq 3$ to 5 mm), shall have a shape near to spheric one, and, above all, they shall have a smooth (with no defects and cracks) surface well wettable by melt (solution) of a capsulant. Each of the granulation methods used now in the mineral fertilizer industry does not assure in the full measure manufacturing granules suitable for effective capsulation with thin (see above) protective coatings (6,7,8). For example, in case of granulation by crystallization of melt droplets in a coolant stream (prilling), a channel connecting the shrinkage cavity with atmosphere is formed in a prill (9). This phenomenon has been analysed in detail experimentally and theoretically by the authors of this work (10-15) and by other investigators (9). A mathematic model has been developed to estimate the fraction of granules with no shrinkage channels on their surface, this model conforming satisfactorily to the experiment (16,17). Of the methods developed based on this analysis for obtaining an increased yield of prills with no shrinkage channels on their surface, let's mention only "physical activation" of additives insoluble in fertilizer melt which is based on "inoculation" of microcrystals of initial fertilizer into cracks on particles (1). Such an additive introduced into fertilizer melt upstream of prilling assures an intensive bulk crystallization of a melt droplet, which, in its turn, prevents formation of a shrinkage channel on the prill surface (16-18). At the same time, the size of a crystalline grain diminishes practically by an order, which increases the static strength of prills, the stability of NH_4NO_3 prills and fertilizers based on it to thermal cycles $20 \leftrightarrow 60^{\circ}\text{C}$ (19,20) as well as decreases the surface roughness. Since the process of heterogeneous nucleus formation (nucleation) is connected with the surface energy of additive particles, another proposed method of "activation" of additives insoluble in fertilizer melt (21) is based on treatment of their surface with surfactants, with "cold" plasma in an ultrahigh-frequency plasma generator etc. upstream of their introduction into the melt fed to prilling. A very effective method of increase of the nucleation rate is formation, as a result of an exchange chemical reaction, of additive particles insoluble in melt and of fertilizer particles inoculated in them (e.g., to prill NH_4NO_3 , such an additive may be obtained based on components $\text{Mg}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$, or $(\text{NH}_4)_2\text{SO}_4$ and $\text{Ca}(\text{NO}_3)_2$, etc., soluble in NH_4NO_3 melt, i.e. on components used now as commercial additives). A particle of such an additive is an ideal multipoint nucleation centre insoluble in superheated fertilizer melt (22). The above ways are a part of the methods proposed by the authors to increase the efficacy of action of the additives assuring the production of prills suitable for capsulation.

The commercial production of such prills is assured by introduction of such additives into melt upstream of prilling while using the technology of prilling or upstream of treatment of the granule surface obtained by nodulating in plate, drum granulators, spherodizers, etc., as well as treatment in fluidized-bed vessels of growing granules or in granulators with mechanical suspended bed, and others (6,7) with melt with the above additives while nodulating. In this case, the fraction of the melt with additives applied in the last stage of obtaining granules suitable for effective capsulation shall be not less than 10 to 30% by mass (depending on the surface quality of initial granules) (23).

Table 1 shows a part of the experimental data obtained by the authors to illustrate that the granules suitable for effective capsulation shall meet the above requirements and that the methods proposed by us (18, 21-23) assure the fulfilment of these requirements. The data indicated the manufacturing characteristic of a slow-release capsulated urea and a waterproof ammonium nitrate used by technical users. Capsulation carried out under the same conditions with granules obtained by prilling, nodulating on a plate granulator from powdered product, and by granulation in a cylindrical vessel with a gushing "fluidized" bed without utilization of the above ways of treatment of additives and of preparation of granules and with their utilization. Before capsulation using the standardized methods used at GIAP (24), the physico-mechanical properties of granules were determined (Table 1). The analysis of the dissolution curves for samples of capsulated granules with the mass of 5 g in 250 ml of distilled water in a non-flowable cell shows: firstly, a substantially smaller dissolution rate of capsulated products manufactured from the granules obtained with utilization of the proposed (18, 21-23) and above described ways. Secondly, processing the dissolution curves by the method described in (25) shows that in this case the distribution function of effective diffusion coefficients in the mass of granules is substantially less polydisperse. In other words, the fraction of the granules coated badly (with defects in the capsulating coating) is substantially lower.

Improvement of wettability of a granule with capsulant melt (solution) and increase of its adhesion with the granule surface are important for an effective capsulation of the surface of granules. For this purpose, the granule surface was preliminarily treated with solution of a surfactant or it was introduced in the quantity of 1 to 3% by mass into the capsulant solution applied onto the granule surface. Table 2 shows the data for the half-dissolution time of a sample of urea granules capsulated with and without a surfactant of 1% by mass of dodecyl alcohol. The known fact (2,3) of a more effective capsulation of granules by multilayer coating while nodulating compared to single-layer coating (e.g. in granulation of fertilizer melt droplets in capsulant melt (solution) or during "flight" of granules through a capsulant film) indirectly confirms the above considerations.

OBJECTIVES OF THE STUDY

- a) to develop the technologies and to select the composition of capsulants which ensure the minimum dissolution rate in water of the encapsulated nutrient. The control of the dissolution rate of the encapsulated component in water and soil is related to the thickness of the capsulant.
- b) to study technology of capsulation which affects a regulable release of nutrients from multicomponent capsulated granules.

RESULTS AND DISCUSSION

During the studies, joint processes of granulation and capsulation were examined. In the first case, a fertilizer melt was dispersed into droplets crystallizing in a stream of a liquid coolant. As such, a capsulant solution (melt) was used. The granules obtained were separated in the vessel bottom from capsulant (in this case the granules occupied 3 to 6% by mass of liquid coolant). The partially capsulated granules went into a drum vessel where the capsulation process came to an end and where the falling quantity of capsulant was fed (26, 27). In the second case, the melt droplets fell in a stream of dropwise capsulant dispersed by injectors, and in the column bottom the capsulation process was terminated and while nodulating the granules formed (28). The schemes proposed (26-28) are particularly effective in capsulation with solutions of capsulants. In this case the solvent evaporation was realized mainly at the expense of the heat of crystallizing melt droplets with practically no external heat-transfer agent. The solvent was caught by condensation of its vapour and returned to dissolve new portions of capsulant. Polyolefines and other polymers were used as capsulants (26, 27, 28).

A substantial (30 to 40% by mass) decrease of the capsulant consumption may be achieved if after the primary capsulation (at the stage of combination of the granulation and capsulation processes) the granules with an "island-wise" coating with capsulant are subjected to radiation (or another initiated) polymerization from the vapour phase (29). The latter method allows thin even high-quality coatings to be obtained, but it is very long and requires considerable energy consumption. In the method proposed (29), not more than 5% of the surface of granules is coated by radiation polymerization, which substantially improves the economic indices of the method. At the same time, the possibility appears to "close up" the finest defects of the coating surface (29). This ensures a high water resistance of a coating at its minimum thickness.

An increase in the diameter of granules at the same film thickness allows the specific capsulant consumption by volume to be substantially diminished without affecting the water resistance of granules (Table 3). Therefore, the feasibility to produce enlarged ($d_{gr} = 5$ to 7 mm) capsulated waterproof granules for intrasoil application can now be realized. In addition, this will allow the production losses of 10 to 15% owing to an uneven surface application of a fertilizer 10 to 15% to be excluded (1).

The technology of application of waterproof coatings from solution and melt of capsulant has been studied experimentally. In application of coatings from solution, polyolefine coatings (e.g. 3 to 5% solution of high-pressure polyethylene) and composition based on alkyd resins are the most promising (30). For example, in the case of production of ammonium nitrate as 2.5 to 3 mm dia. granules capsulated with low-pressure polyethylene (with polyethylene glycol as a plasticizer) at 5.5% by mass, the quantity of ammonium nitrate released from granules in a non-flowable cell for 180 days was practically equal to zero. But when the coating mass was 2.5 to 3% by mass, the half-dissolution time of ammonium nitrate and urea as 3 mm dia. granules was equal to not less than 80 to 100 days. The dynamics of release of the encapsulated components was near to linear (30). Based on the studies carried out, a plant has been built for production of waterproof urea granules for agriculture and NH_4NO_3 for technical use. It produces by capsulation from solution (particularly, from 3 to 5% by mass solution of low-pressure polyethylene) and has a capacity of 9 t/hour. A substantial disadvantage of the above capsulation method is the necessity for the regeneration of the solvent in a closed cycle with its return to the capsulant dissolution stage.

The above disadvantage is prevented by capsulation of granules with melts forming watertight envelopes. The low-molecular polyethylenes (waxes) with 2 to 5% powdery low-pressure polyethylene plasticized with polyethylene glycols are considered the most promising (31). These envelopes completely decompose in soil in one year. When the granule diameter is 3 to 5 mm and the capsulating coating mass is 3 to 6% by mass, the granules will dissolve in the soil for 45 to 60 days at a near linear release of the encapsulated component (31).

The inclusion of bactericide soil conditioners to the envelopes of the slow-release fertilizers is found to be promising (3,4). As applied to the production of slow-release urea, NK, NP, and NPK fertilizers, the process of their capsulation with sulphur melt has been studied. But, in contrast to slow-release urea produced particularly by ICI and its subsidiaries with the trade-mark "Gold N", capsulation was carried out with sulphur melt at elevated, up to 30 to 40% by mass stabilized polymeric sulphur content. This allowed the urea dissolution rate in water and in soil to be diminished 2 to 3 times or, respectively, the sulphur content of capsulated granules to be cut down to 6 to 8% by mass. One succeeded to achieve an additional (3 to 4 times) decrease of the dissolution rate of the aim component (e.g. urea) by water-repellency treatment of the sulphur envelope (6% by mass) with the above compositions based on melts of low-molecular polyolefine waxes or alkyd resins at 2 to 2.5% by mass.

The half-dissolution time of 3 to 5 mm dia. urea granules capsulated with 6% by mass of sulphur with the stabilized polymeric sulphur content of about 40% and water-repellency treated with 2% by mass of polyethylene wax with addition of polyethylene glycol and powdery low-pressure polyethylene in the quantity of about 5% by mass is equal to 35 to 40 days. Their dissolution dynamics is nearly linear (31). One may control the duration and dynamics of dissolution of the encapsulated component (urea, NK, NP, NPK fertilizers) by varying the thickness and ratio of the two-layer capsulating coating (31).

The slow-release ammonium nitrate for agriculture was obtained by capsulation of granules with inorganic water-insoluble powders of calcium and magnesium phosphates or with ground phosphate rock (from phosphate rocks of the Karatau and Oshurkov deposits) utilizing as a binder potassium silicate solution with the modulus of 2.5 to 3.2. But the half-dissolution time of capsulated granules of $d_{gr} = 3$ to 5 mm did not exceed 6 hours. The water-repellency treatment of the surface of the capsulating coating with 0.2% by mass of petrolatum or polyethylene wax plasticized with polyethylene glycol increases the half-dissolution time of granules in a non-flowable cell 2 to 2.5 times.

In the capsulation of multicomponent granules, it is often necessary to control the selective release of components into an aqueous solution. Within the bounds of this task, a technology of obtaining a slowly acting NK fertilizer with the composition of $(N_2:K_2O = 1: 1.6$ by moles) was developed (32) for a protected ground based on NH_4NO_3 and K_2SO_4 and for an open ground which is used in cultivation of vegetable crops (cucumbers, tomatoes, etc.) based on urea and K_2SO_4 . In this case, besides the requirement of complete dissolution in the ground for 60 to 65 days and an approximative constant release rate of components, it was necessary to ensure a more rapid release of potassium compared to nitrogen. Several versions of production technology of NK fertilizer have been developed which meet the above requirements. The first version consists of a granule which contains the whole set of nutrients in the indicated ratio. For this purpose, one took prilled NH_4NO_3 as granulation nuclei and applied on it by nodulating fine-crystalline K_2SO_4 with utilization as a binder NH_4NO_3 melt or saturated boiling K_2SO_4 solution. In obtaining NK fertilizer granules based on urea, one may use both the above technologies and obtaining granules by crystallization of NK fertilizer melt suspension droplets in a coolant stream (e.g. prilling). The NK fertilizer granules (prills) obtained were capsulated with selective waterproof coatings which assure a better penetration of K ions (32). To achieve this, finely dispersed ($d = 20$ to $40 \mu m$) particles of inorganic fillers were introduced in the capsulant solution (melt), the coating selectivity being controlled by the filler concentration. The filler of finely dispersed ground phosphate rock introduced in the quantity of 10 to 50% of the capsulating coating mass proved to be the most suitable for practical utilization. Somewhat worse results are given by utilization of phosphogypsum and calcium phosphate (Table 4). A remarkably greater selectivity is achieved in case of pretreatment of filler particles with "cold" plasma (780 to $950^\circ C$) in a superhigh-frequency plasma generator and introduction of freshly ground (with the holding time of about 1 min) particles (Table 4). As capsulating polymers, the above compositions may be used most expediently.

The possibility of obtaining a selective envelope owing to "facilitated transport" of the ions required has been considered. For this purpose, caprolactam derivatives were introduced in the capsulant polymeric matrix.

Another method of flexible control of the release rate of nutrients was creation of multilayer granules in which the layers are separated from each other by capsulating envelopes (32). In this case, the change in the envelope thickness and the combination of capsulant types ensure a wide range of flexibility in the change of the release rates of nutrients (32). A number of examples is given in Table 4.

The same effect may be achieved by production of NK fertilizer granules of different composition with a different thickness of the capsulating coating and, hence, with a different dissolution rate and by their subsequent mechanical mixing in a proper ratio (32).

To carry out necessary calculations, a body of mathematics may be used which has been developed by us to estimate the capsulation quality (25). Its essence is that the quality of the coating which capsulates a granule is estimated by the effective diffusion coefficient of the encapsulated component. The quality of the capsulating coating depends on the capsulant water resistance and on the capsulation quality. The capsulation quality is different in the mass of granules and may be characterized by the function of distribution of the effective diffusion coefficient in the mass of granules. The capsulant quality is determined by the minimum value of the effective diffusion coefficient or indirectly by the most probable value of the effective diffusion coefficient of the aim component. As a result of experiments for study of the dissolution rate of capsulated granules, one obtains the change of the fraction of dissolving aim component in time. In work (25), an algorithm was proposed and realized for obtaining the distribution function of the effective diffusion coefficient in mass according to these data. The shape of the distribution function allows the capsulation quality and the capsulant "water resistance" to be estimated (25). The same algorithm may be used for solution of the reverse task of "composition of the mixture of granules with different effective diffusion coefficients" to assure the necessary arbitrary law of release of the aim component (25).

In 1989 to 1991, agrochemical tests of capsulated urea were carried out with the polymer coating content equal to 2, 4, and 6% of the granule weight.

All the tests with vegetable crops - tomatoes, cucumbers, cabbage, marrow squashes - showed decrease of the nitrate content of the commodity output 2 to 3 times compared with the maximum allowable concentration (Table 5).

A growth of the total crop capacity and the output of additional product from the unit area were observed nearly always. The maximum effectiveness was noticed in the case of urea with the coating content of 4% (Table 6).

An increase in crop capacity and quality of agricultural products was observed also in the case of application of capsulated urea for flax, perennial herbs, barley.

In the latter case, the harvest increased about twice compared with usual urea.

It should be noted that although the technology of obtaining capsulated urea increases the fertilizer cost by about 25%, it is more than compensated by the increase in the harvest of the cultivated crops.

ACKNOWLEDGEMENTS

The authors wish to express profound gratitude to R.P. Basova, T.V. Guryeva, and S.L. Shmelev for their active participation in carrying out experiments and preparation of this report.

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Table 1 - Qualitative indices of slowly-release capsulated fertilizers granulated by different methods

Composition of initial granules	Granulation method	Capsulant is numerator, volume of coating applied in % vol. is denominator	Size of initial granules mm	Static strength, g/granule	Fraction of granules without shrinkage channels on surface, %	Maximum size of surface roughness of granules, μm	Half-dissolution time of granules in H_2O , days
$\text{NH}_4\text{NO}_3 + 0.35\% \text{Mg}(\text{NO}_3)_2$	prilling	<u>polyethylene</u> 2.0	2.5	1300±200	35±3	< 10	1.5±0.2
$\text{NH}_4\text{NO}_3 + 1\% \text{MgO} + 1\% \text{NH}_4\text{NO}_3$ in combined mixing	prilling	<u>polyethylene</u> 2.0	2.5	3600±300	89±5	< 10	42±4
$\text{NH}_4\text{NO}_3 + 1\% \text{MgO} + 0.1\% (\text{NH}_4)_2\text{SO}_4$	prilling	<u>polyethylene</u> 2.0	2.5	3300±200	85±5	< 10	36±6
$\text{NH}_4\text{NO}_3 + 1\%$ mixture of $\text{Mg}(\text{NO}_3)_2 + (\text{NH}_4)_2\text{SO}_4$	prilling	<u>polyethylene</u> 2.0	2.5	3800±300	92±5	< 10	45±4
$\text{NH}_4\text{NO}_3 + 0.35\% \text{Mg}(\text{NO}_3)_2$	nodulating on plate granulator	<u>polyethylene</u> 2.0	3.5	2500±300	100	about 200	23±2
$\text{NH}_4\text{NO}_3 + 20\%$ mixture ($\text{NH}_4\text{NO}_3 + 1\% \text{MgO}$) + 1% NH_4NO_3 at joint mixing	nodulating on plate granulator	<u>polyethylene</u> 2.0	3.5	4500±400	100	< 10	55±5
$\text{NH}_4\text{NH}_3 + 0.35\% \text{Mg}(\text{NO}_3)_2$	granulation in a fluidized bed	<u>polyethylene</u> 2.0	3.5	2000±200	100	about 500	2.5±0.3

(to be continued)

Table 1 (cont'd)

Composition of initial granules	Granulation method	Capsulant is numerator, volume of coating applied in % vol. is denominator	Size of initial granules mm	Static strength, g/granule	Fraction of granules without shrinkage channels on surface, %	Maximum size of surface roughness of granules, μm	Half-dissolution time of granules in H_2O , days
NH_4NO_3 + 20% mixture (NH_4NO_3 + 1% MgO) + 1% NH_4NO_3 at joint mixing	granulation in a fluidized bed	<u>polyethylene</u> 2.0	3.5	4000 \pm 400	100	< 10	45 \pm 4
NH_4NO_3 + 20% mixture (NH_4NO_3 + 1% mixture of $\text{Mg}(\text{NO}_3)_2$ + $(\text{NH}_4)_2\text{SO}_4$)	granulation in a fluidized bed	<u>polyethylene</u> 2.0	3.5	4100 \pm 40	100	< 10	42 \pm 4
urea	prilling	<u>sulphur + polyethylene wax = 3:1 by mass</u> 6.0	2.5	890 \pm 100	55 \pm 3	< 10	1.2 \pm 0.2
urea + 1% mixture $\{(\text{NH}_4)_2\text{SO}_4$ + 1% urea (at joint grinding) $\}$	prilling	ditto	2.5	1400 \pm 200	90 \pm 5	< 10	14 \pm 1
urea + 1% mixture (urea + 1% allyl alcohol)	prilling	ditto	2.5	1500 \pm 200	93 \pm 5	< 10	16 \pm 1
urea	nodulating on plate granulator	ditto	3.5	2600 \pm 300	100	about 200	5.6 \pm 0.5

(to be continued)

Table 1 (cont'd)

Composition of initial granules	Granulation method	Capsulant is numerator, volume of coating applied in % vol. is denominator	Size of initial granules mm	Static strength, g/granule	Fraction of granules without shrinkage channels on surface, %	Maximum size of surface roughness of granules, μm	Half-dissolution time of granules in H_2O , days
urea + 20% mixture (urea + 1% $(\text{NH}_4)_2\text{SO}_4$ + 1% urea at mixing)	ditto	ditto	3.5	3100±300	100	< 10	16±1
urea + 20% mixture (urea + 1% allyl alcohol)	ditto	ditto	3.5	3000±300	100	< 10	15±1
urea	granulation in a fluidized bed	ditto	3.5	3000±200	100	about 500	1.4±0.2
urea + 20% mixture (urea + 1% $(\text{NH}_4)_2\text{SO}_4$ + 1% urea at joint grinding)	ditto	ditto	3.5	3000±300	100	< 10	
urea + 20% mixture (urea + 1% allyl alcohol)							

Table 2 - Influence of treatment of granule surface with surfactant before capsulation on the granule quality of slow-release fertilizers

Composition of initial granules	Granulation method	Capsulant is numerator, applied coating volume in % vol. is denominator	Granule size, mm	Static strength of granules, g/granule	Fraction of granules with no shrinkage channels on surface, %	Maximum size of roughnesses on granule surface, μm	Half-dissolution time of granules in H_2O , days
urea	prilling	sulphur + polyethylene wax = 3:1 by mass ----- 6.0	2.5	890 \pm 1	55 \pm 3	< 10	1.2 \pm 0.2
urea	prilling	sulphur + polyethylene wax + dodecyl alcohol = 3:1:0.04 by mass ----- 6.0	2.5	890 \pm 1	55 \pm 3	< 10	4.6 \pm 0.2
urea + 20% mixture (urea + 1% $(\text{NH}_4)_2\text{SO}_4$ + 1% urea at joint grinding)	nodulating on plate granulator	sulphur + polyethylene wax = 3:1 by mass ----- 6.0	3.5	3100 \pm 300	100	< 10	16 \pm 1
ditto	ditto	sulphur + polyethylene wax + dodecyl alcohol = 3:1:0.04 by mass	3.5	3100 \pm 300	100	< 10	20 \pm 2

Table 3 - Influence of granule size on the quality of capsulated granules of slow-release fertilizers

Composition of initial granules	Granulation method	Capsulant is numerator, applied coating volume in % vol. is denominator	Granule size, mm	Static strength of granules, g/granule	Fraction of granules with no shrinkage channels on surface, %	Maximum size of rough surface of granules, μm	Half-dissolution time in water, days
urea+20% mixture (urea + 1% $(\text{NH}_4)_2\text{SO}_4$ +1% urea at joint grinding)	nodulizing on plate granulator	$\frac{\text{sulphur+polyethylene wax}}{6.0} = 3:1 \text{ by mass}$	3.5	3100 \pm 300	100	10	16 \pm 1
ditto	ditto	ditto	5	4500 \pm 400	100	10	23 \pm 2
ditto	ditto	ditto	10	5600 \pm 500	100	10	56 \pm 5

Table 4 - Qualitative indices of slow-release NK fertilizer granules

Composition of initial granules	Granulation method	Capsulant is numerator, volume of coating applied in % vol. is denominator	Granule size, mm	Static strength, g/granule	Fraction of granules with no shrinkage channels on surface, %	Maximum size of surface roughnesses, μm	Half-dissolution time of nitrogen component of NK fertilizer, days	Half-dissolution time of potassium component of NK fertilizer, days
$\text{NH}_4\text{NO}_3 + \text{K}_2\text{SO}_4$	nodulating with K_2SO_4 solution	polyethylene ----- 2	4.5 ± 0.5	2900 ± 200	100	about 100	38 ± 4	46 ± 5
$\text{NH}_4\text{NO}_3 + \text{K}_2\text{SO}_4$	nodulating with K_2SO_4 solution	S+polyethylene wax ----- 8	4.5 ± 0.5	2900 ± 200	100	about 100	14 ± 2	18 ± 3
$\text{NH}_4\text{NO}_3 + \text{K}_2\text{SO}_4$	ditto	polyethylene+ ground phosphate rock=1:1 by mass ----- 4	4.5 ± 0.5	2900 ± 200	100	about 100	34 ± 4	26 ± 3
$\text{NH}_4\text{NO}_3 + \text{K}_2\text{SO}_4$	ditto	S+polyethylene wax + ground phosphate rock =1:1 by mass ----- 12	4.5 ± 0.5	2900 ± 200	100	about 100	12 ± 2	7 ± 1.5

Table 4 ...(cont'd)

Composition of initial granules	Granulation method	Capsulant is numerator, volume of coating applied in % vol. is denominator	Granule size, mm	Static strength, g/granule	Fraction of granules with no shrinkage channels on surface, %	Maximum size of surface roughnesses, μm	Half-dissolution time of nitrogen component of NK fertilizer, days	Half-dissolution time of potassium component of NK fertilizer, days
$\text{NH}_4\text{NO}_3 + \text{K}_2\text{SO}_4 =$ 1:0.1 by mass is nucleus; K_2SO_4 0.9% by mass is external layer	nodulizing with formation of 2-layer granules	polyethylene wax is <hr/> 4 the first layer S+ polyethylene wax is 4 the external layer	4.5 \pm 0.5	2300 \pm 200	100	about 150	19 \pm 3	10 \pm 1.5
ditto	ditto	polyethylene wax <hr/> is 6 the 1st layer S+ polyethylene wax <hr/> is 2 the external layer	4.5 \pm 0.5	2300 \pm 200	100	about 150	45 \pm 3	2.5 \pm 0.5

(to be continued)

Table 4...(cont'd)

Composition of initial granules	Granulation method	Capsulant is numerator, volume of coating applied in % vol. is denominator	Granule size, mm	Static strength, g/granule	Fraction of granules with no shrinkage channels on surface, %	Maximum size of surface roughnesses, μm	Half-dissolution time of nitrogen component of NK fertilizer, days	Half-dissolution time of potassium component of NK fertilizer, days
ditto	ditto	$\frac{\text{polyethylene}}{2}$ is the 1st layer S+polyethylene wax is $\frac{6}{2}$ the external layer	4.5±0.5	2300±200	100	about 150	45±4	12±2
$\text{NH}_4\text{NO}_3 + \text{K}_2\text{SO}_4$	nodulating with K_2SO_4 solution	$\frac{\text{polyethylene} + \text{caprolactam derivative} = 1:0.05}{2}$ by mass	4.5±0.1	2900±200	100	about 100	32±4	16±2
$\text{NH}_4\text{NO}_3 + \text{K}_2\text{SO}_4$	ditto	$\frac{\text{polyethylene wax} + \text{caprolactam derivative} = 1:0.05}{8}$ by mass	4.5±0.5	2900±200	100	about 100	14±2	8±1

Table 5 - Nitrate Content

Nos.	Crops	Control	Urea	GIAP slow-release urea
1.	Marrow squashes	600.7 mg/kg	688.9 mg/kg	478.0 mg/kg
2.	Cucumber	202.2 mg/kg	319.8 mg/kg	189.2 mg/kg
3.	Carrot	328.0 mg/kg	342.0 mg/kg	181.0 mg/kg
4.	Tomato	42 mg/kg	85 mg/kg	65 mg/kg

Table 6 - Crop Yield

Nos.	Crops	Control	Urea	GIAP slow-release urea
1.	Cabbage	121.4 t/ha	123.0 t/ha	147.0 t/ha
2.	Carrot	100.0 kg/ha	114.0 kg/ha	122.6 kg/ha
3.	Long-fibred flax K-6	23.6 q/ha	24.5 q/ha	31.9 q/ha *
4.	Tomato	381 g/vessel	755 g/vessel	873 g/vessel

* q = metric center (100 kg)