# Development and evaluation of polymer coated urea as a potential slow-release urea supplement for ruminants.

by

**Erlanda Upton**

Thesis presented in partial fulfilment of the requirements for the degree

of

**Master of Agricultural Sciences (Animal Science)**
**at the University of Stellenbosch**



**SUPERVISOR:**

**J. Coetzee**, Ph.D. Agric.
Voermol Feeds
Stellenbosch

**CO-SUPERVISORS:**

**C.W. Cruywagen**, D.Sc.Agric.
Department of Animal Sciences
University of Stellenbosch

**R.D. Sanderson**, Ph.D. Polymer Science
Institute for Polymer Sciences
University of Stellenbosch

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**Stellenbosch**

# DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

Signature: Date:

# ABSTRACT

## Development and evaluation of polymer coated urea as a potential slow-release urea supplement for ruminants

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| | |
|---|---|
| **Supervisor:** | **Dr. J. Coetzee** |
| **Co-supervisor:** | **Dr. C.W. Cruywagen** |
| **Department:** | **Animal Sciences** |
| **Faculty:** | **Agricultural Sciences** |
| **University:** | **Stellenbosch** |
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The rate of hydrolysis of urea in the rumen of animals is a major limitation when considering the substitution of natural protein with urea in the formulation of rations. The aim of this study was to evaluate polymer coated urea prills with variable coating thickness and evaluate its potential as a slow-release NPN compound. A new slow-release urea compound, made by coating prilled feedgrade urea with a co-polymer of urea-formaldehyde resin and a castor-coconut alkyd was initially evaluated for urea-nitrogen concentration in distilled water in order to evaluate its potential as a slow-release urea product for ruminants. Amino/alkyd or polyester blends are among the cheapest of the modern synthetic systems and are considered because it is non-toxic, low-cost, biodegradable and easy to manufacture. A 2 x 2 x 2 x 2 factorial design was used and 16 individual products were made and evaluated. The Wurster method was used to encapsulate urea prills. The slopes of the urea release curves represented the release rate of the encapsulated products and were compared to identify the process variables, which had an effect on release rate. Two of the coating variables, coating weight and alkyd: resin ratio, had a major effect ($P = 0.0001$) on the release rate of urea. The crushing strength of encapsulated products was significantly ($P = 0.0001$) higher than that of untreated urea. Results motivated the evaluation of the products in the rumen of sheep in terms of rumen ammonia and blood urea N concentrations. Four slow-release products were made after interpreting results from the first study, and differed on account of the coating weight

and the composition of the co-polymer. Fifteen fistulated wethers were randomly allotted into 5 groups and intraruminally received an equivalent of 15g urea. Rumen ammonia and blood ammonia were taken at 0, 1, 2, 4, 6, 8, 12, 16, 20, 24, 36 and 48 h after administration of the various treatments. Slow release urea (SRU) resulted in significantly lower rumen ammonia peaks (P = 0.0001) than untreated urea, while the peaks were also significantly delayed. Untreated urea resulted in the maximum concentration at two hours after administration of the urea (P = 0.0685) while the SRU's reached a maximum at six hours after administration in the rumen. No significant differences between the four different SRU types were found. Responses in blood urea-N was similar to that observed for rumen ammonia nitrogen. The encapsulation was effective in decreasing the rate of ammonia release from the urea for up to six hours after administration. In a third trial four Dohne Merino wethers were used in a 2 x 2 Latin square design. They received a SRU product equivalent to 0.4 g urea per kg body weight orally. Rumen liquor and blood samples were taken at 0, 1, 2, 4, 6, 8, 12, 16, 20, 24, 36 and 48 h after intake. Difficulty was initially experienced with ingestion and palatability of the SRU products due to the strong formaldehyde and butanone odour present in the coating. The maximum rumen ammonia ($NH_3$) concentration for the SRU were lower than that of untreated urea (17.5 mg N/dl vs. 66.9 mg N/dl). The time to reach blood urea levels also differed considerably (6 h vs. 24 h for blood urea nitrogen) between treatments.

The encapsulation of urea prills shows potential solutions to reduce the solubility of urea and also reduce the hygroscopic nature of urea and improve the palatability and storage characteristics thereof.

*Keywords: Slow-release urea, encapsulate, copolymer, urea formaldehyde rumen ammonia, blood urea nitrogen, solubility, palatability, storage characteristics.*

# SAMEVATTING

## Ontwikkeling en evaluering van polimeer bedekte ureum as 'n potentiële stadig vrystellende ureum supplement vir herkouers

deur

**Erlanda Upton**

| | |
|---|---|
| **Studieleier:** | **Dr. J. Coetzee** |
| **Mede-studieleier:** | **Dr. C.W. Cruywagen** |
| **Departement:** | **Veekundige Wetenskappe** |
| **Fakulteit:** | **Landbouwetenskappe** |
| **Universiteit:** | **Stellenbosch** |
| **Graad:** | **M.Sc.Agric** |

Die vinnige tempo waarteen ureum in die rumen na ammoniak omgesit word, is die grootste beperking in die optimale benutting van ureum, as vervanging van natuurlike protein in herkouerrantsoene. Die doel van hierdie studie was om 'n stadig vrystellende ureumproduk te ontwikkel wat die rumenammoniakvlak gedurende 'n aansienlike periode van die dag bokant 'n sekere vlak kan hou. 'n Nuwe stadig vrystellende ureumproduk, vervaardig deur ureumkorrels met 'n kopolimeer van ureum-formaldehiedhars en 'n kastor-en klapperalkied te bedek, is geëvalueer om die potentiaal as stadig vrystellende nie-protein stikstof (NPN)-produk vir herkouers te ondersoek. Die veiligheid, biodegradeerbaarheid, lae koste en maklike vervaardiging van amino/alkied-kopolimere maak dit een van die goedkoopste sintetiese sisteme om vir stadig vrystellende sisteme te oorweeg. 'n 2 x 2 x 2 x 2 Faktoriale ontwerp is gebruik om 16 individuele produkte te vervaardig. Die Wurster-metode is gebruik om individuele korrels te enkapsuleer met die polimeer en die potentiaal van die produkte is aanvanklik geëvalueer deur die ureumstikstofvrystelling in gedistilleerde water te meet. Die hellings van die vrystellingsgrafieke is vergelyk om die veranderlikes te bepaal wat die grootste invloed op die vrystellingstempo van ureum uit die geïnkapsuleerde produkte het. Resultate dui dat twee verandelikes 'n betekenisvolle effek het op die

vrystellingstempo, nl. dikte van die omhulsel, en die samestelling van die kopolimeer (P = 0.0001 en P = 0.0135, onderskeidelik) het. Die samedrukbaarheid van die geïnkapsuleerde produkte was ook betekenisvol hoër (P = 0.0001) as díe van onbehandelde ureumkorrels, wat lei tot verbeterde bergings- en hanteringseienskappe. Interpetering van resultate lei tot die vorming van vier stadig vrystellende produkte. Vyf groepe van 3 volwasse rumengefistuleerde Dohnemerinohamels is in 'n proef gebruik om die potentiaal van die produkte verder te ondersoek. 'n Ekwivalent van 15 g ureum is direk in die rumen van elke dier geplaas en ammoniak-en bloed monsters is 0, 1, 2, 4, 6, 8, 12, 16, 20, 24, 36 & 48 ure na dosering geneem. Die stadig vrystellende ureumprodukte het 'n betekenisvol laer maksimum waardes vir beide ammoniak-en bloedstikstofureum getoon (P = 0.0001). Onbehandelde ureum het 'n maksimum rumenammoniakstikstof konsentrasie reeds twee ure na toediening bereik in vergelyking met ses ure vir die stadig vrysellende produkte. Geen betekenisvolle verskille in hierdie parameters is tussen die geïnkapsuleerde produkte gevind nie, terwyl geen interaksie is tussen hoofeffekte voorgekom het nie. In 'n derde proef is vier Dohnemerinohamels gebruik om die vrystellingstempos, in terme van rumenammoniak-en bloedureumstikstof te bepaal waar die stadig vrystellende produk en onbehandelde ureum direk aan die diere gevoer is. 'n Ekwivalent van 0.4 g ureum/kg liggaamsmassa is gevoer. Aanvanklik is inname- en smaakliksheidprobleme ondervind, moontlik as gevolg van die sterk butanoon-en formaldehiedreuk van die omhulsel. Die rumenammoniakstikstof het 'n laer maksimum (17.5 vs. 66.9 mg N/100 ml) as die van onbehandelde ureum gehad terwyl die tyd wanneer maksimum konsentrasie bereik word ook aansienlik later was. Die polimeer inkapsulering van ureumkorrels toon potensiaal as 'n stadig vrystellende ureumproduk deurdat dit die oplosbaarheid van ureum in die rumen verlaag. Bykomende voordele is dat die omhulsel die higroskopisiteit verlaag en die samedrukbaarheid verhoog, beide eienskappe wat die hantering-en bergingseienskappe bevorder.

*Sleutelwoorde: Stadig vrystellende ureum, enkapsulering, kopolimeer, ureum-formaldehied, rumenammoniak, bloed ureum stikstof, oplosbaarheid, smaaklikheid, bergingseienskappe..*

*"Surely, there can be no greater contribution to ruminant nutrition than for scientists to define in the future the conditions under which NPN utilization can be maximized."*

Johnson, 1976.

# INDEX

# ACKNOWLEDGEMENTS

This thesis completes a chapter of my life, academically yes, but mainly personally. I will look back at the last few years with mixed feelings and emotions, but know that in the end, only the highlights of the journey will remain. I thank the following people and institutions, for making this an unforgettable experience.

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# Chapter One

## 1 General Introduction - Literature review

### 1.1 Non protein Nitrogen (NPN)

It has been known for almost a century that ruminant animals have the unique ability to convert NPN to protein. As early as 1879, Weiske *et al.* have used NPN compounds as protein substitutes in ruminant rations. Non protein nitrogen (NPN) includes any compound that contains nitrogen (N) but are not present in the polypeptide form of protein which can be precipitated from a solution (Church, 1991). The use of NPN- supplements depends on the ability of the rumen to utilise micro-organisms in the synthesis of their own cellular tissues. They are thus able to satisfy the microbial portion of the animal's demand for nitrogen and, by way of the microbial protein, supply at least part of its nitrogen demand at tissue level (McDonald *et al.*, 1988).

The earliest practical use of NPN in the form of urea in feeds for farm livestock was probably that of Morgen (1911), who had convincingly shown that a significant percentage of protein in rations for sheep could be replaced by urea. A comprehensive literature review was published in the same year by Armsby of the U.S. Department of Agriculture in which he concluded that microbial protein formed from urea or related compounds was not inferior to other forms of protein and that the limiting factor in the use of these NPN compounds as dietary protein replacements was simply the rate at which these compounds could be converted to microbial protein within the intestines. In this study, urea, based on the consideration of price, convenience, palatability and toxicity, the most widely used and investigated non-protein compound, will be used.

## 1.2 Nitrogen metabolism

Relationships between ingested nitrogen and its degradation and synthesis of microbial protein (MP) by rumen bacteria have been extensively researched and reported by numerous workers (see reviews in Annison, 1956; Leng & Nolan, 1984; Armstrong, 1993) and quantitative models of nitrogen metabolism in ruminants have been published (Nolan, 1975). The flow diagram on Figure 1 summarises the major nitrogen transactions in the rumen. Important pools and flows into and out of those pools of nitrogenous materials are described.

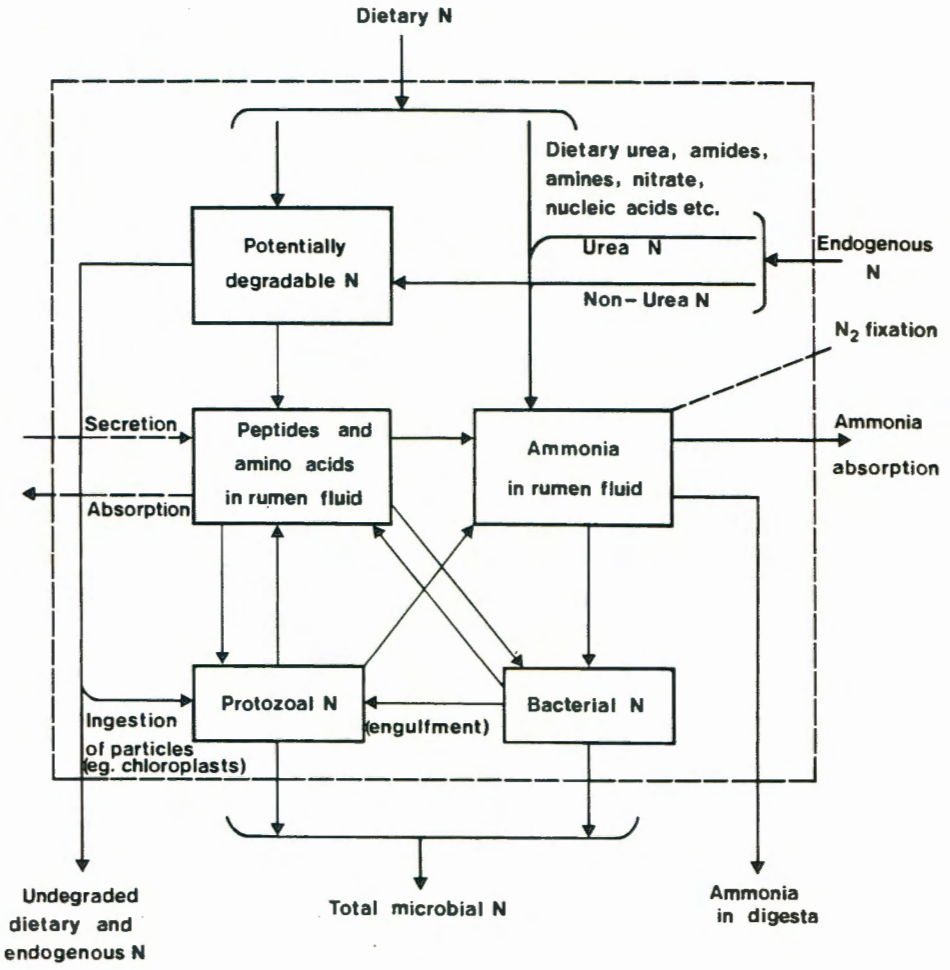



**Figure 1 Flow diagram of the major nitrogen transactions in the rumen (Leng & Nolan, 1984).**

## 1.3 NPN Supplementation

### *1.3.1 The role of NPN on the utilisation of low-quality pasture*

Low-quality forages are defined as forages which are less than 55 % digestible and are deficient in true protein (less than 80 g/kg crude protein) and low in soluble sugars and starches (less than 100 g/kg) (Dann *et al.,* 1987). The ability of ruminants to digest cellulose and other structural polysaccharides of plants has caused man for many years to consider the possibilities of using ruminants to convert high fibre waste materials into commodities such as meat, milk, wool and hides (Coombe, 1981). Grazing lands provide most of the feed to livestock, and the cheapest forms of animal production are based on grazing. As human population pressures grow and food suitable for humans become less available for animals, grazing will become increasingly important (Morley, 1981).

A climatic characteristic of many tropical and sub-tropical areas of the world, is the strong seasonality of rainfall with a consequent long dry season during which the pasture grasses mature and are poor in quality (Romero *et al.,* 1990). There is ample evidence that most plant residues constitute only sub-maintenance rations for ruminants, and that during a period each year, pasture severely limits the production of grazing animals. This is important, because areas affected by seasonal patterns of pasture growth and senescence represent a considerable proportion of the earth's surface, and carry large numbers of domestic animals (Coombe, 1981). In South Africa cattle grazing sourveld pastures during the 6 - 8 months winterperiod, may lose 25 - 30 % of their maximum summer liveweight. Beef production becomes uneconomic as a consequence of this alternating weight gain-loss pattern (Van Niekerk, 1975).

Probably the major limitation is that such feedstuffs are low in digestibility, but also that they are digested slowly in the rumen (Church, 1991). According to Allden (1981) the lower digestibility of matured plants is associated with a concurrent reduction in protein or nitrogen content. Studies done with animals under pen conditions showed that when ruminants consume herbage of low protein content the rate of digestion and intake of forage may be depressed. Allden (1981) suggests

that this could be due to a lower activity of the micro-organisms in the reticulo-rumen, since shortages of nutrients essential to the maintenance of high micro-organism activity are likely to be reflected in a lower rate of digestion in the rumen. The organisms responsible for fibre digestion in the rumen are bacteria, protozoa, and fungi. The actual and relative biomasses of each group are a function of the availability of fermentable N, soluble sugars or starch in the diet (Armstrong & Smithard, 1979).

Low-quality roughage diets were found to require a minimum of 2 g available nitrogen per 100 g OMD for efficient microbial production of protein (McMeniman & Armstrong, 1977 cited by Shirley, 1986). Herbages, which contain low proportions of available protein, may have insufficient N to meet the needs of the microbial population, thereby inducing an energy deficiency, and the nutrition of the host may be affected (Several authors, compiled by Allden, 1981). In South Africa Leng (1988) found that the intake of low-quality hay and body weight gains of cattle increased when supplemented with urea or biuret in comparison with unsupplemented cattle. Several authors (compiled by Allden, 1981) found that when protein was added to a roughage of low N content it improved the digestibility of the dry matter, rumen bacteria numbers and dry matter intake were improved. Coombe & Tribe (1962) found that increased straw intake with urea supplementation by sheep was associated with an increased rate of cellulose digestion in the rumen, and reduced retention times of undigested particles in the rumen and whole alimentary tract.

Although however, these results have not always been consistent, Allden (1981) suggests that it could be the result of the difference in the nitrogen content of the roughage and to the conflicting influences of starch and protein when fed together. With ruminants fed low-quality forages or pastures, the main aims of supplementation are to correct deficiencies in the diet that may occur at rumen level or animal level or both, and to increase the intake of the pasture. The recognition and correction of deficiencies of dietary N in herbage is dependent on a knowledge of what the animal is eating and how much dietary nitrogen is needed to sustain an active microbial population (Allden, 1981). According to Allden (1981), sub-optimal

levels of energy and protein in pastures are seldom accompanied by any syndrome other than an insidious reduction in the production of milk, meat or fibre.

Basic concepts for ensuring a balanced nutrition for ruminants on forage-based diets:

According to Leng (1990), the priority for improving the utilisation of low-digestible forage by ruminants, is to optimise the availability of nutrients from fermentative digestion. This can be achieved by:

1. Ensuring that there are no deficiencies of microbial nutrients in the rumen and, therefore, the microbes in the rumen grow efficiently and, through fermentative activity, extract the maximum possible amounts of carbohydrate from the forage (*i.e.* the production rates and ratio of microbial cells to volatile fatty acids (VFA) produced is high).

2. Ensuring that the microbial cells (which provide most of the protein to the animal) synthesised in the rumen are not lysed and fermented in the rumen but are available for digestion and absorption as amino acids from the intestines.

In order to augment and balance the nutrients absorbed the efficiency of utilisation of nutrients (that arise from fermentative and intestinal digestion), needs to be optimised. This is achieved by supplementing with critical nutrients that escape or bypass rumen fermentation.

According to Coombe, 1981 it is generally believed that nitrogen (N) deficiency is the primary limiting factor in the utilisation of low-quality residues by grazing animals, especially where there is no scope for selection of green herbage. This deficiency of the forage restricts the capacity of the rumen microflora to proliferate, thus causing a decline in the rate of cellulose conversion per unit of time (Romero *et al.,* 1990). According to Leng (1990), the first priority in optimising fermentative digestion of forage, is ensuring adequate $NH_3$-N in the rumen to supply the majority of N for microbial growth. In diets based on agricultural byproducts and low-quality roughage, the rumen ammonia concentration is the major limitation to the growth of

rumen organisms. According to Preston & Leng (1987), this must be above a certain critical level for a considerable part of the day. There is still some controversy about the optimal rumen ammonia concentration. Satter & Slyter (1974) suggested that 50 - 80 mg/l $NH_3$-N rumen fluid was the optimum for maximising microbial growth yield. This suggestion has been widely accepted. Results from more recent studies, however showed that the optimum $NH_3$-N level in the rumen fluid varied and is dependent on the suggested parameter *i.e.* maximum voluntary intake of low-quality forage and the optimum digestibility of the forage Perdok *et al.* 1988).

According to Wallace (1979) the rumen ammonia concentration which is required for optimal rate of degradation of substrate in the rumen appears to be different for different substrates. Orskov (1992) suggests that the minimum requirement for degradable N must be the potential yield of microbial N. This assumption however, would have to be modified when sources of nitrogen like urea are used, and thus where degradation to ammonia occurs very rapidly. According to Satter & Roffler (1975) ammonia levels in the rumen greater than 5 mg $NH_3$-N/100 ml are ineffective in generating greater microbial protein synthesis. They stated that the amount of urea that could be utilised for various levels of natural protein was dependent on the total digestible nutrients (TDN) in the diets. Studies by Boniface *et al.* (1986), and Perdok *et al.* (1988), showed that to maximise feed intake, ammonia levels have to be much higher than the level accepted for optimisation of digestibility (Figure 2). The intake of low-quality roughage was optimised at about 20 mg $NH_3$-N/100 ml, although the digestibility remained constant from 8 mg $NH_3$/100 ml. The enzyme pool in the rumen, responsible for degrading soluble carbohydrates is optimised at 6 – 10 mg $NH_3$-N/100 ml (Leng *et al.*, 1993).

Various methods, such as supplementation with non-protein nitrogen, rumen undegradable protein and readily fermentable energy and fats, have been applied to improve the utilisation of low-quality forages and pastures. Because of the cost of protein and the competition for it by other feed industries as well as by man himself, the possibilities of using non-protein nitrogen (NPN), supplements has aroused much interest (Coombe, 1981).

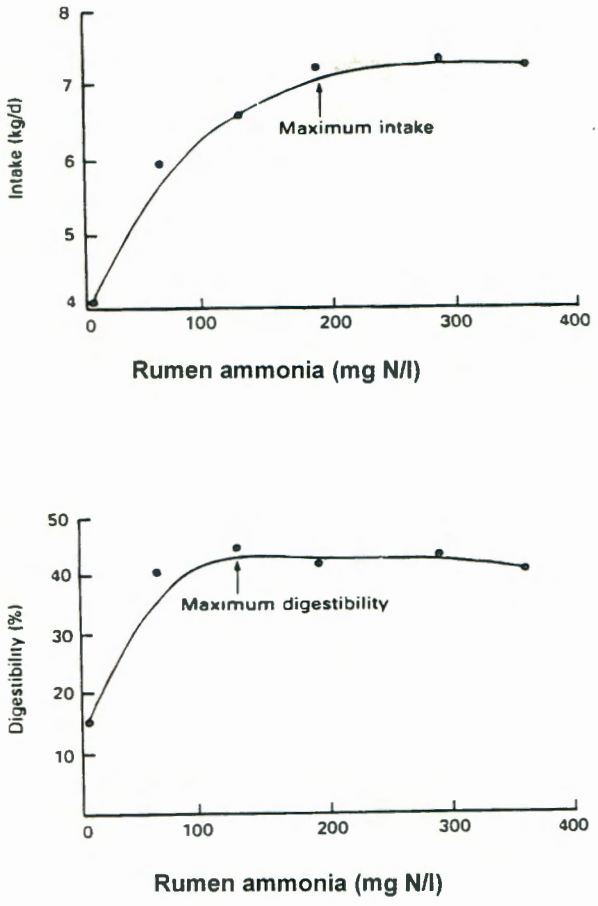



**Figure 2 The effect of the concentration of ammonia in the rumen on the intake and digestibility (measured in nylon bags in the rumen) of straw by cattle (Perdok *et al.*, 1988).**

*1.3.2 Why is there a need for slow/sustained release NPN products?*

NPN will be of little benefit to ruminants unless it is converted into ammonia and subsequently utilised for microbial protein synthesis in the rumen. One of the most intriguing problems in rumen ecology is the extent to which ammonia serves as the nitrogenous material for synthesis of microbial cells. Ammonia, as mentioned in prior paragraphs, appears rapidly in the rumen fluid when the diet contains much soluble nitrogen. Most rumen bacteria assimilate it in preference to amino acids. Considerable quantities of feed ammonia (usually given as urea) can be assimilated by the animal, via preliminary assimilation by the rumen microbes. According to Hungate (1966) however, there are limits to the amount of nitrogenous substrate

which an organism can assimilate. Amino acids in excess of this limit is available for supplying energy in the form of ammonia . The ammonia appears to the extent that the available amino acids exceed their assimilation into microbial cells. The excess of ammonia is absorbed into the blood stream through the rumen epithelium and depending on the amount of urea consumed, this may cause ammonia toxicity.

There is not consistency about the rumen ammonia and blood ammonia nitrogen (BUN) levels that causes toxicity. According to Lewis *et al.* (1957), $NH_3$-N levels from 80 mg/100 ml can cause toxicity and can be used as diagnostic measurement. Ensminger & Olentine (1978), suggested that BUN levels of 1 mg/100 ml leads to toxicity in cattle and lambs. Ammonia toxicity is however dependent on the pH. Ammonia is absorbed from the rumen rapidly as the pH rises toward 7 or higher. At acid pH's of 6 of lower, absorption is slow or nil (Lewis, 1960).

Therefore, in spite of the fact that urea is to date extensively used as a protein substitute in the rations of ruminants, the amount that may be safely included in the diet is still limited by this same factor identified in 1911, namely that of its rapid hydrolysis in the rumen. According to Bloomfield *et al.* (1960), the hydrolysis of urea in the rumen releases ammonia at a rate 4 times faster than its assimilation into amino acids and rumen microbes. However, even at subtoxic doses this absorption from the rumen represents a loss of nitrogen, because most of the nitrogen is excreted in the urine and therefore not available to the micro-organisms (Olivier & Cronje, 1964). According to Satter & Roffler (1974) maintenance of ruminal ammonia concentrations in excess of the bacterial requirement would result in wastage of nitrogen, adding cost but no benefit.

Therefore, although NPN is the cheapest form of supplementary protein, it is however, only effective under a limited range of conditions (several authors, compiled by Minson, 1990). Due to the economic advantage of NPN compared to natural protein nitrogen, coupled with an expanding need of protein for human nutrition, a feeding system that could utilise larger amounts of NPN than presently recommended, is desirable. According to Johnson (1976), there can be no greater contribution to ruminant nutrition than for scientists to define the conditions under which NPN utilisation can be maximised.

The utilisation of NPN by ruminants is often less efficient than the utilisation of natural protein supplements. According to Orskov (1992), there is substantial evidence in the literature that the utilisation of urea is lower than degradable dietary protein, but that utilisation improved if urea was released slowly. Part of this inefficiency has been attributed to excess ammonia production in the rumen that is absorbed, converted to urea and excreted in the urine (Rihani *et al.,* 1993). The ability of micro-organisms to utilise NPN sources to synthesise protein is potentially of enormous benefit, especially in foregut fermenters, grazing low-quality forages. It is however necessary to provide other nutrients in combination with the nitrogen to ensure efficient utilisation.

The eating pattern of grazing domesticated herbivores generally involves periods of forage ingestion early in the day, during the late afternoon and early evening, which lead to relative continuity in fermentative activity throughout each 24 h (Doyle, 1987). Exceptions do occur, depending on the physiological status of the animal, for example during lactation when ruminants spend more time eating. Fibre digestion by rumen micro-organisms reaches a peak 5 to 6 hours after ingestion. Feeding of a NPN source once a day will therefore be utilised ineffectively by ruminants. Campbell *et al.* (1963), showed that through frequent feeding, urea nitrogen compares very favourably with protein N in the feeding of dairy heifers. By increased frequency of feeding, levels of urea higher than presently recommended can be utilised. A modification in feeding practice that might improve forage utilisation would be the administration of protein concentrates in small doses during the day, even if the forage are consumed in larger amounts. This could avoid the initial excess of protein or nitrogen, which, may result in a loss of nitrogen as ammonia. It also would supply nitrogen at later stages when fibre is digested and nitrogen is needed. Additionally, the administration of protein in small doses would spare some of the previously synthesised microbial cells the decomposition of which release ammonia at periods some time after food is ingested. Consequently, it is desirable to provide NPN supplements either frequently or in a form that is hydrolysed slowly.

According to Doyle (1987), frequent administration of urea, (achieved by spraying it onto low-quality forage or by continuous infusion into the rumen) tends to increase intake as well as increase nitrogen retention. Although frequent administration of

urea is desirable, it is not always possible to achieve in practice. In many other situations however, little or no advantage to provision of rumen ammonia on a continuous basis was found (Streeter *et al.*, 1973; Forero *et al.*, 1980). The study of Owens & Zinn (1988) who concluded that the value of slow-release NPN supplements in ruminant nutrition remains to be demonstrated, supported this. According to Forero *et al.* (1980) the reason for the lack of efficient production after ingestion of slow-release NPN products could be due to a shortage of branched–chain organic acids or amino acids in the rumen for efficient NPN utilisation. Furthermore, the supplementation of NPN is of no use if there is still green herbage available. Rumen ammonia nitrogen levels after no urea supplementation, one dose of urea and two doses of urea are presented in Figure 3 (Falvey, 1982).

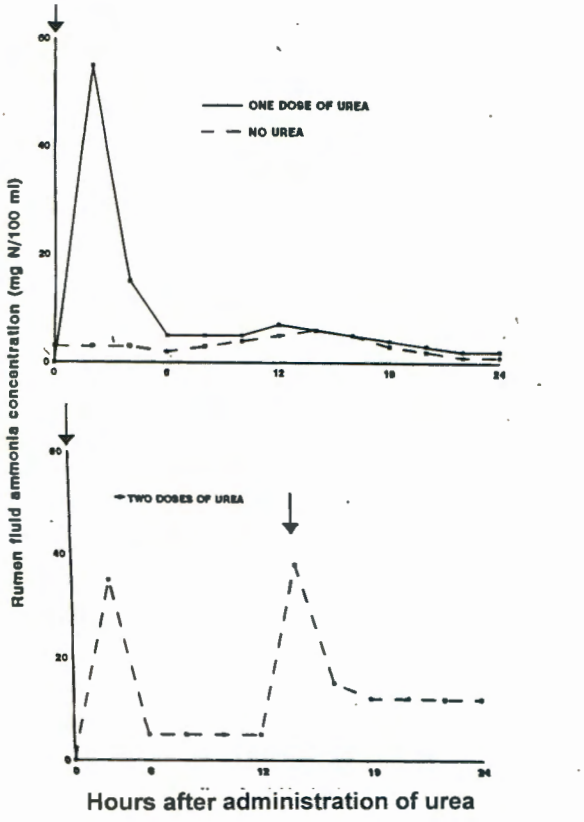



**Figure 3 Rumen ammonia nitrogen levels after no urea supplementation, one dose of urea and two doses of urea are presented (Falvey, 1982).**

### *1.3.3 Slow-release products evaluated in the past*

Although it is clear that rumen micro-organisms can utilise ammonia for protein synthesis, many reports in the literature documented lower efficiency of utilisation of urea compared to true protein sources (Potter *et al.,* 1969; Williams *et al.,* 1969, Orskov, 1992). It is therefore clear that the use of NPN as a protein substitute in the rations of ruminants is limited in the diet because of its rapid hydrolysis in the rumen. Consequently, it will be desirable to give NPN supplements either frequently or in a form in which it is hydrolysed slowly (Olivier & Cronje, 1964; Romero *et al.,* 1976; Forero *et al.*, 1980; Doyle, 1987). In 1971 Huston (Huston *et al.,* 1974) concluded that slow-release urea could be as effective as protein as a source of ammonia when supplied to mature ewes consuming roughage with a low nitrogen content.

According to Males *et al.* (1979), the hourly feeding of urea may increase synthesis of microbial protein and help cows to maintain their condition during the winter grazing period. Hourly feeding of a supplement is however an impractical management procedure and efforts have been intensified to find an ideal sustained release urea product. According to Johnson (1976), it has been concluded by several researchers that the fermentation of starch or starch feedstuffs favours the utilisation of NPN over both the fermentation of fibrous carbohydrates and simple sugars. Johnson (1976), suggested that the successful use of degradable protein together with maximum levels of NPN to the upper limits of microbial protein synthesis, necessitates the development of a sustained release product.

The ideal source of nitrogen to compliment ruminant diets containing carbohydrates with different fermentation rates, would therefore be one that would release nitrogen through the ammonia pool on a steady basis and coinciding with the fermentation rate of the carbohydrate. By feeding combinations of nitrogen sources with varying solubility, this requirement might be satisfied. From an economic perspective the developing of a sustained release form of urea to increase NPN utilisation becomes obvious.

The rate of ammonia release can be controlled either by decreasing the activity of rumen urease by the use of urease inhibitors or by modification of urea into products that release ammonia slowly. The ideal sustained release urea supplement must include more than the prevention of ammonia toxicity via lower ammonia release in the rumen. It should also provide essential branched-chain fatty acids (Mathison *et al.,* 1994). According to Males *et al,* (1979), there must be a sustained release of $NH_3$, over a 12 to 24 h period while energy is simultaneously available from fermentation.

Several products, formulated to increase the utilisation of urea as a source of nitrogen, have been tested and appeared on the market in recent years (Johnson, 1976). These attempts to minimise the rapid release of ammonia have varied in method as well as in degree of success (Forero *et al.,* 1980). Urea derivatives such as biuret, iso-butylidene diurea (United Nations - Economic Commission of Europe, 1977, as cited by Forero *et al.,* 1980), iso-butyraldehyde monourea (Mathison *et al.,* 1994), were evaluated for slow-release qualities. An arbitrary formaldehyde treatment of urea has been observed to lower both its solubility and hydrolysis in the intact rumen. Consequently the efficiency of N-utilisation from selected slow-release urea-formaldehyde complexes was studied by various workers.( Pal & Negi, 1977; Lall *et al.*, 1982; Kaushal & Swan, 1983; Sharma & Gupta, 1985, Makkar *et al.*, 1988). Complexes of urea with formaldehyde resulted in slow ammonia production in the rumen and exhibited higher microbial protein synthesis, although none of the products meets the criteria of sustained release over a period of 12 to 24 hours. Products either released ammonia too rapidly or the nitrogen was so tightly complexed (by the presence of an inert moiety formed as a result of polymerisation and condensation), in which case too little ammonia were released. This lead to poor performance where urea-formaldehyde complexes were tested *in vivo* (Lall *et al.,* 1982; Kaushal & Swan, 1983; Makkar *et al.*, 1988).

In an attempt to match ammonia release and energy availability other approaches have been investigated. These vary from liquid supplements to various combinations of urea and processed starch. In 1968 a starch controlled urea product was manufactured by passing mixtures of finely ground starch and urea through a cooker-extruder under controlled conditions, causing the starch to

gelatinise. This starch-urea product was marketed commercially under the trade name of Starea. Studies have shown that although Starea is not comparable to natural protein sources, such as fish meal and oilcake meals, it resulted in lower ruminal $NH_3$-N compared per se when urea is fed (Kargaard, 1976). Other workers followed the same approach to improve the utilisation of urea (Deyoe *et al.*, 1968; Muhrer *et al.,* 1968; Huston *et al.,* 1974). The preparation methods for these products, however, involve extensive processing and often heat treatment of grains and urea, which may add substantially to the cost of the product. Increasing fuelcosts however make it necessary to develop feedstuffs that require minimum processing (Koeln *et al.*, 1985a).

In 1985, Koeln *et al.* (1985a) developed a method of impregnating whole grain with a urea solution. It was thought that impregnation would potentially decrease processing costs, allow for feeding urea with whole grains in a form acceptable to the animals and eliminate the need for further supplementation (Koeln *et al.,* 1985a). Although the *in vitro* ammonia release rate of this product , peaked at 5 to 12 hours (Koeln, *et al.,*1985a), ruminal ammonia N after feeding the impregnated corn, peaked under 6 hours (Koeln, *et al.,* 1985b). An alternative approach in an attempt to match ammonia release and energy availability is molasses-based liquid supplements containing NPN. These supplements have in many cases been used successfully, although intake problems occured (Huber, 1972). According to Preston & Leng (1987), this is mainly due to large differences among animals in the amount they consume. Animals often consume the mixture sporadically which may lead to large fluctuations in rumen ammonia levels, from excessive to less than optimum levels for efficient rumen fermentation. Although no other development has received more marketing success than the liquid supplement *i.e.* combinations of molasses and urea there is much difference in opinion about its real success (Johnson, 1976; Males *et al.,* 1979; Doyle, 1987; Preston & Leng, 1987). According to Johnson, 1976, the fact that the liquid supplement industry flourishes without sufficient proof and definitive scientific research on the abilities of these materials to foster rumen microbial protein synthesis, is within our scientific discipline, inexcusable.

An attempt was also made to combine urea, salseed-meal, molasses and gum acacia to produce slow-release urea pellets. Although rumen ammonia nitrogen at 2 h post feeding were lower than with untreated urea, blood urea nitrogen, digestibilities of different nutrients and nitrogen retention were not significantly different among treatments (Reddy & Prasad, 1987). In 1980, a slow-release urea compound, made by coating prilled urea with a tung oil, linseed oil talc -catalyst mixture, was evaluated for ammonia-nitrogen release rate. The compound gave a ruminal ammonia -nitrogen peak 1hr post feeding and there seemed to be little difference between dry matter digestibility and nitrogen retention values for prilled urea and the slow-release supplement (Owens, *et al.*, 1980).

Böhme (1997), evaluated a slow-release liquid urea-molasses product, Bonded Urea Plus® (manufactured and distributed by F. S. L. Bells Wiltshire, UK). Bonded Urea Plus® containes ureides, larger, more stable urea/molasses molecules that are more resistant to enzyme attack than urea and therefore converted to ammonia at a slower rate. An additional advantage of product is the simultaneous release of sugar to provide the rumen bacteria with energy along with the released nitrogen. Böhme (1997), however, found no advantage in supplementing Bonded Urea Plus® instead of urea-molasses in licks for sheep fed low-quality hay. No differences in the rate of ammonia in the rumen of sheep were observed between the two products.

None of the currently available products meets the criteria established for successful a sustained release urea product. It seems from the numerous products tested that the major process of sustaining the release of urea is that of simply shielding the urea from solution in the aqueous media in the rumen. Once the material was dissolved or penetrated, the urea would almost immediately be hydrolysed (Johnson, 1976). Several attempts have been made to slow ammonia release from urea by coating it with water insoluble materials, such as fat and waxy type materials (Helmer & Bartley, 1971). Hansen (US Patent 3,295, 984), encapsulated urea with a copolymer of dicyclopentadiene and ester of unsaturated acid. The patent claims slower ammonia release, reduced toxicity, more efficient utilisation of nitrogen and improved palatability.

Although coated products, slows down the conversion of urea to ammonia it has not gained commercial acceptance in the ruminant feed industry yet. This approach is however a common procedure in the process for manufacturing of slow-release coated fertilisers, which reduce the dissolution rate of urea in the soil. A wide variety of materials have been used as coatings, but the most important of these are waxes, polymers and sulfur. Sulfur-coated urea (SCU) has been produced commercially since 1972 and has gained wide expectance as turf fertiliser. The release of N from an individual SCU pellet is termed "catastrophic" in that each individual fertiliser pellet releases N all at once. Variations in individual pellet coating thickness and uniformity within an SCU product provides N release over an extended period (Peacock & DiPaola, 1992).

A similar approach was followed in this study. It is believed that the coating of urea prills will assist in solving problems *re* the level of inclusion of urea in rations. The first is commonly referred to as "bin hang-up" and is due to the hygroscopic nature of urea which causes the concentrate (often used in dairy rations) which urea is presented in, to absorb moisture, swell and ob the obstruct the flow of the concentrate from the bin in which it is stored. The pellets in the centre of the bin expand in size, disintegrate and stick together. Other prills are held together by microscopic urea crystals formed on the pellet surfaces (recrystallisation due to moisture migration). This may result in an uneven distribution of urea and a subsequent risk of toxication (Kertz & Everett, 1975). The second problem associated with the use of urea is the unpalatability when included at higher dietary levels. The hygroscopic nature of urea exacerbates the unpalatability and handling characteristics of urea as due to the moisture conditions to which the ration is exposed. By encapsulating urea prills it may decrease solubility and reduce the hygroscopic nature thereof, which may improve palatability and storage characteristics.

Due to this motivation it was decided to test the effect of different layers of polymer coating on the release rate of urea. Objectives of the research were thus:

1. To select and manufacture a water-insoluble, non-toxic, low-cost, polymer to coat feedgrade urea prills with variable thickness.

2. To evaluate and compare the products *in vitro* in distilled water.

3. To select the product with the best slow-release potential, and compare the ammonia release rate *in vivo* with that of untreated urea.

## 1.4 Controlled release technology

The concept of controlled release is a novel approach to the safe and effective use of any toxic active ingredient, whether pesticide, drug, fertiliser of food additive. Controlled release may be defined as a technique or method in which active chemicals are made available to a specified target at a rate and duration designed to accomplish an intended effect. During the last decade, controlled release technology has received increasing attention in the face of a growing awareness that substances ranging from drugs to agricultural chemicals are frequently excessively toxic and sometimes ineffective when administered or applied by conventional techniques/methods. The principal advantage of controlled-release technology is that much less of the active ingredient is required for the same period of activity than is recommended in conventional methods of application (Das, 1983). One of the problems in controlled-release technology is to combine the active agent with a degradable carrier in an economic manner and achieve a release profile that suits requirement.

Many techniques are available for the design and preparation of controlled delivery systems. They include dissolving or physically trapping the active agent in an appropriate natural or synthetic polymeric matrix or chemically binding it to a suitable polymer. Pesticides have also been micro-encapsulated in natural and synthetic polymers (Kydonieus, 1980a). Natural film-forming materials or micro-capsules prepared from gelatin, cellulose derivatives, and synthetic polymeric films have been widely used for micro-encapsulation. According to Kydonieus, 1980b), the advantages of controlled release are impressive, the merits of each application have to be examined individually. The positive and negative effects must however be

carefully comported before large expenditures for developmental work are committed. According to Das (1983) some of the disadvantages are:

1. Cost of controlled release preparation and processing, which may be higher than that of standard formulations.
2. Effect of the endproduct of the polymer matrix.
3. Fate of polymer additives, such as plasticisers, stabilisers, antioxidants, fillers, etc.
4. Environmental impact of the polymer degradation products following heat, hydrolysis, oxidation, solar radiation and biological degradation.
5. Cost and time in securing government registration of the product.

### *1.4.1 Polymer systems for controlled release*

Once an application has been thoroughly investigated and found suitable, one must select (1) the controlled release technology that best fits the application and (2) the basic physical form of device and the rate-controlling polymer matrix and active agent to be used. Table 1 categorises the various controlled release technologies, including physical as well as chemical systems (Kydonieus, 1980b).

## Table 1 Categorisation of Polymer Systems for Controlled Release

I **Physical Systems**

- A. Reservoir systems with rate-controlling membrane
  1. Micro-encapsulation
  2. Macro-encapsulation
  3. Membrane systems
- B. Reservoir systems without rate-controlling membrane
  1. Hollow fibers
  2. Poroplastic® and Sustrelle®Ultramicroporous Cellulose Triacetate
  3. Porous polymeric substrates and foams
- C. Monlithic systems
  1. Physically dissolved in nonporous, polymeric, or elastomeric matrix
     a. nonerodible
     b. erodible
     c. environmental agent ingression
     d. degradable
  2. Physically dispersed in nonporous, polymeric, or elastomeric matrix.
     a. nonerodible
     b. erodible
     c. environmental agent ingression
     d. degradable
- D. Laminated Structures
  1. Reservoir layer chemically similar to outer control layers
  2. Reservoir layer chemically dissimilar to outer control layers
- E. Other physical methods
  1. Osmotic pumps
  2. Adsorption onto ion-exchange resins

II. **Chemical systems**

- A. Chemical erosion of polymer matrix
  1. Heterogeneous
  2. Homogeneous
- B. Biological erosion of polymer matrix
  1. Heterogeneous
  2. Homogeneous

Only the slow-release system relevant to this study will be discussed briefly *i.e.* reservoir systems with rate-controlling membrane.

### *1.4.2 Reservoir systems with rate-controlling membrane*

These include micro-capsules and macro-capsules. Micro-encapsulation is a procedure that applies several uniformly thin polymeric coating around small solid particles, droplets of liquid, or dispersions of solids in liquids. Resulting capsules can range from a few tenths of a micrometer to several thousand micrometers. Capsules greater than 2000 – 3000 µm are called macro-capsules. There are no real differences between micro- and macro-capsules with respect to the release characteristics or type of active agent that can be encapsulated.

### *1.4.3 Wurster process*

The method used in this study for encapsulating urea prills and thus for the manufacturing of the slow-release urea compound (SRUC) is known as the Wurster process. This process was invented in 1959 and is a technique specially designed for applying coatings around particles (Kydonieus, 1980b). In the Wurster process, the particles to be coated are fluidised on an upward-moving airstream. The high-velocity-airstream is introduced into the fluidised bed causing a spout, and resulting into a cyclic flow of the particles. When the particles enter the high velocity spout, they are accelerated and physically separated from each other. A spray nozzle mounted at the base of the spout applies the coating material (Figure 4) (Das, 1983).

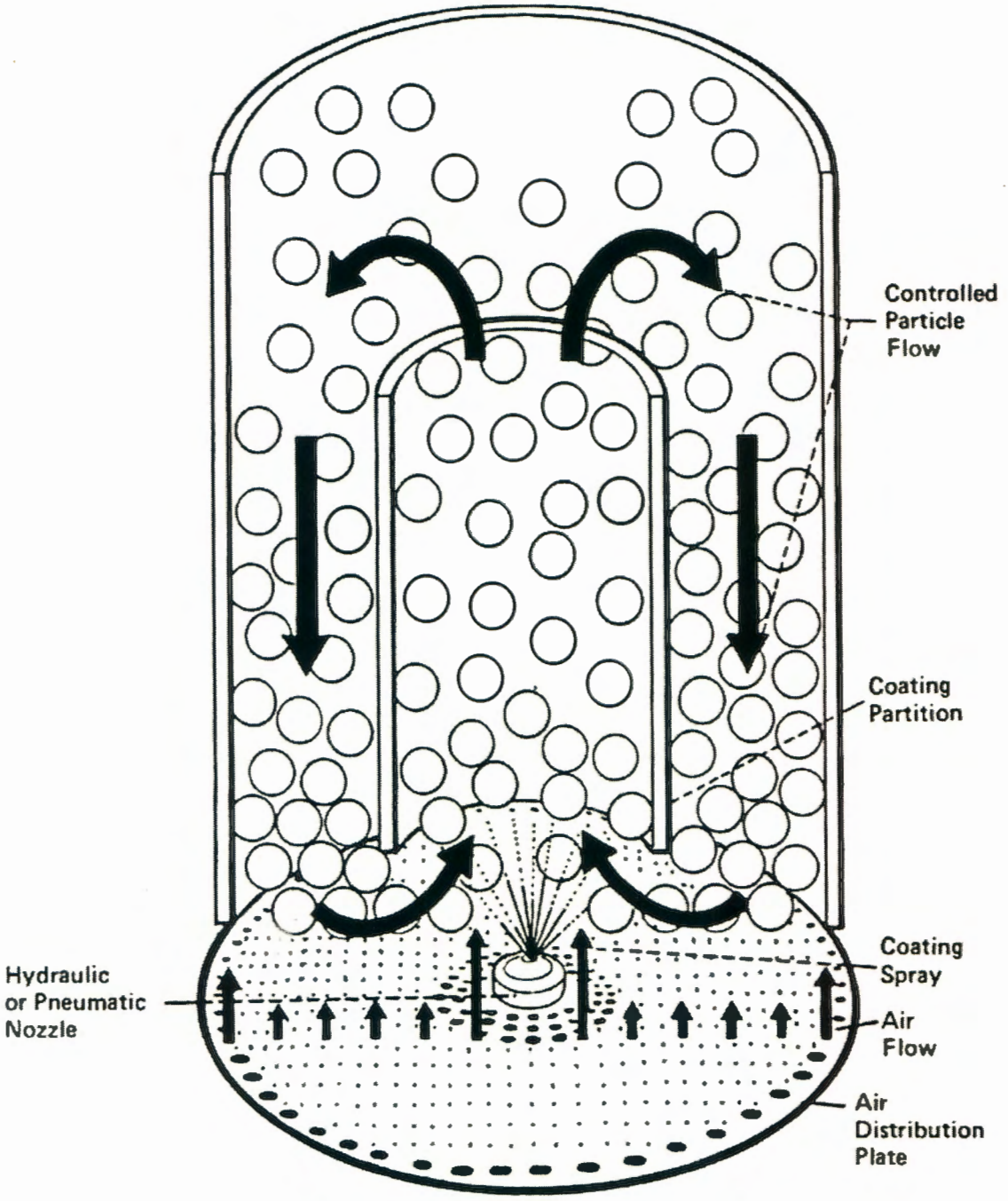



**Figure 4 Diagram of Wurster coating chamber of a fluid bed dryer.**

Fluidised-bed spray drying as used in the Wurster technique, is a method of micro-encapsulation and is a controlled release technology that categorises under reservoir systems with a rate-controlling membrane and thus implies that products release their contents by permeation through the membrane

According to Kydonieus (1980a) the process air which moves the particles also serves to dry the coating. Excellent drying conditions are therefore achieved in this process, due to the relatively large amounts of air used. When the particles clear the top of the partition, they are already dry to touch. When the airstream and particles clear the top of the partition, the air in the spout spreads out to fill the expansion chamber. As the air spreads out and slows down, the particles settle out to the top of the bed and then descend to the bottom. The particles re-enter the partition, again to be accelerated by the high-velocity air stream (fluidised) and are coated again. Particles cycling in this manner pass the nozzle every 6 to 10 sec. and receive an additional coating with each pass. The process is continued until the desired amount of coating has been applied. The Wurster process is essentially an encapsulating method, for one is covering the surface of particles with a coating. Since smaller particles have more surface area per unit weight, small particles require more coating to achieve the same level of protection. In practice the Wurster process is normally used when the particle size of the coated product is larger than 106 μm. Meisen & Mathur (1978), who tested this technique developed a process for manufacturing slow-release polymer coated urea (SCU) in a spouted bed. The Wurster technique has gained its success for the coating of pharmaceutical tablets.

### *1.4.4 Solvents*

The proper selected solvent is a important component of any coating system (Das, 1983). Since for any solvent-based coating, a rate-limiting factor for any coating method is the drying of the coating, which is the evaporation of the solvent. The use of relatively large amounts of air results in the rapid removal of solvent from the applied film. To take best advantage of the good drying conditions on the Wurster process, Kydonieus (1980a) therefore suggests that one seek fast-drying solvents. Together with its drying qualities, the solvent must of course also dissolve the film-forming material. Since the selection of solvents and solvent blends are difficult, the use of solubility parameters and evaporation rates are suggested. In 1966, Crowley *et al.*, (as cited by Kydonieus, 1980a), developed solubility maps for various resins, by combining the use of solubility parameters and hydrogen binding and dipole movement. According to these authors, hydrogen bonding and dipole moments also

affect the drying properties. According to Das (1983) solvents should always be evaluated with the film former in question, since the interaction of the film former will change the relative evaporation rate of solvents. However, the most rapid drying solvent would not always be the best choice. Advantages such as cost, compatibility with other ingredients, safety in handling, safety of residues in product and solvent power for the resin, have to be considered in combination with drying qualities (Kydonieus, 1980a).

### *1.4.5 Equipment*

Wuster equipment is available in a variety of sizes and configurations. The largest unit available has a column of 21 $ft^3$ and can accommodate 450 kg of most materials. For the purpose of this study a laboratory unit was used. The laboratory units are usually designed to be very versatile, and are supplied with positive displacement gear pumps. Air atomising nozzles are used instead of conventional hydraulic nozzles because the spray rates used in all units of this size are too low.

### *1.4.6 Urea-formaldehyde polymers*

The reaction of urea and formaldehyde was first studied in 1896 during which various amounts of urea and formaldehyde in acid solutions of various strengths were used (Goldschimidt, 1896). Although no use for the white granular deposits (with the empirical formula $C_5H_{10}N_4O_3$), that were obtained, were found, many investigations and research led to the first commercially available urea-formaldehyde varnish solutions in 1925. Urea-formaldehyde resins were sold to the organic coatings industry in 1936 and its commercial importance has never ceased.

Urea-formaldehyde resins are heat-convertible and are used in baking coatings and air-drying coatings. When they are baked at temperatures of 200 °F to 350 °F, they produce very hard and colourless films. These films are however, quite brittle, are sensitive to changes in humidity and crack easily. A method was developed to modify the polymers, so as to render them soluble in hydrocarbon solvents, and

compatible with common coating vehicles, *i.e.* oleoresinous varnishes, alkyds and nitrocellulose (Stevens, 1990). The usual method of modification is to make the initial condensation products of urea and formaldehyde react with high boiling primary alcohols such as n-butanol in such a way that by formation of ether groups by a partial reaction between the hydroxymethyl groups of the urea formaldehyde polymer and a low molecular mass aliphatic alcohol in slightly acidic medium. This modification led to the development of alkylated urea formaldehyde polymers This introduction of butyl or other alkyl radical into the molecule, improves the solubility characteristics. The new alkylated resins are more soluble in aromatic and aliphatic hydrocarbons solvents, such as xylol and white spirit, less soluble in alcohol and insoluble in water. They are also more compatible with oleo resinous varnishes and particularly oil-modified alkyds.

In spite of their lightfastness, hardness after cure and clarity, alkylated urea formaldehyde polymers, are however still not suitable for use as the sole component in commercial varnishes because they are too brittle and do not provide the elasticity required of a useful varnish. Fortunately alkylated urea-formaldehyde resins are compatible with a wide range of alkyd resins as the combination produces films having excellent properties. The breakthrough in the use of the alkylated urea formaldehyde polymers therefore, came through their use, in combination with alkyd polymers. Valuable coatings with high gloss durability and other properties superior to unmodified alkyd polymers can now be produced. According to Lourens (1995), the most frequently used mixtures usually contains about 60 percent alkyd and 40 percent amino polymer (alkylated urea-formaldehyde).

### *1.4.7 Alkyds*

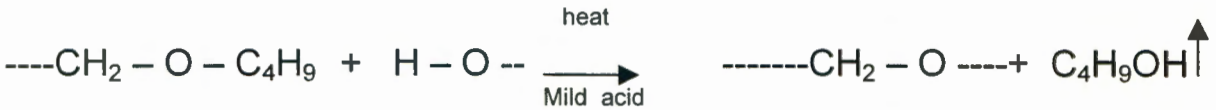
The word alkyd implies oil or fatty acid modified polyesters. The production of alkyds involves the use of acids and alcohols similar to those used for polyesters, plus, either vegetable oils, or the fatty acids obtained from the oils. The first stage in the production of an alkyd is known as the fatty acid process and involves the use of phtalic acid, glycerol and fatty acid. This is followed by reacting the oil and glycerol

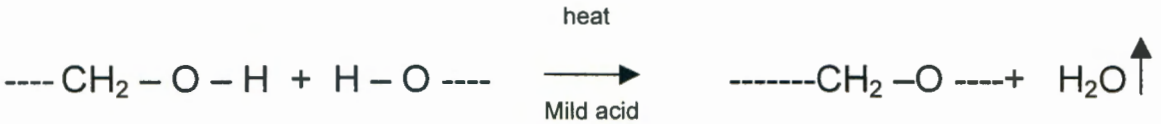
to form a monoglyceride, a process known as alcoholysis which is followed by adding phtalic acid to complete the reaction. When the product has reached a certain viscosity and acid value, the process of alkyd production is complete. Alkyds are characterised on the basis of the oil used in their manufacture e.g. a linseed oil alkyd or a coconut oil alkyd, and on the basis of their oil content, (69 % linseed oil alkyd, or a coconut oil alkyd containing 36 % of fatty acid).

Short oil alkyds have oil contents of less than 45 %. These are the hardest of the alkyds and non-drying oils used in this category include coconut and castor oil, and are often blended with amino resins. Medum oil length alkyds have oil contents between 45 % and 60 % and are the most versatile of the three catagories while the softest types are the long oil alkyds with oil contents between 60 % and 80 %.

### *1.4.8 General Chemistry: The mechanism of acid catalysis in amino polymer/alkyd systems*

Urea-formaldehyde polymers have two functional sites attached to the amino nitrogens. Reaction takes place mainly between the hydroxyl groups of the alkyd and the free hydroxymethyl groups of the urea polymer. Under the acid condition the butoxy groups split off easily as butanol and crosslinking with the alkyd can occur.




All the crosslinking reactions between the amino polymer and the alkyd are acid catalysed and therefore the selection of an acid catalyst is an important step in formulating coatings containing amino polymers. The alkyd possesses hydroxyl groups to provide a site for cross-linking with the reactive groups in the amino resins. This reaction needs heat for it to take place, and mildly acidic conditions. The curing

of acid catalysed urea formaldehyde/alkyd polymer systems at room temperature is made possible by removal of the butoxy groups from the amino polymer and the resulting reaction of these with the hydroxyl groups of the alkyd. For a given acid catalyst concentration, temperature and urea formaldehyde polymer to alkyd polymer ration the curing speed is a function of the evaporation rate of the solvent and the size of the urea polymer molecule (Lourens, 1995).

Conventional butylated urea formaldehyde polymers contain free hydroxymethyl groups and amino hydrogens in addition to the butoxy groups, these polymers can also selfcondense (Koral, & Petropoulos, 1966). The amino polymer therefore needs to react with the alkyd polymer to produce the desired crosslinks, but will simultaneously lose some of its functionality through selfcondensation reactions. The rates of these two competing reactions are of the same order of magnitude and the formation of polymerised blocks of amino polymer in cured coating has a profound effect on its mechanical properties. These polymerised blocks form rigid clusters that, after curing give rise to decreased flexibility. The use of excess amino polymer as the crosslinking agent results in a significant amount of selfcondensation. This results in films with greater hardness and chemical resistance, but of much poorer flexibility (Koral *et al.*, 1966).

According to Koral *et al.* (1966), hardness in the urea polymer/alkyd system is caused by the hard amino polymer domains inside the softer alkyd system. Reaction takes place mainly between the hydroxyl groups of the alkyd and the free hydroxymethyl groups of the urea polymer. Reactions also occur between the hydroxyl groups of the alkyd and the hydroxymethyl groups, formed by the splitting of the methylol ether groups. Under acid conditions the butoxy groups split off easily as butanol and crosslinking with the alkyd can occur. Alkyd resins contain sufficient, unreacted acid groups to produce and acidic environment together with adequate hydroxyl groups for cross-linking. Urea-formaldehyde resins are manufactured and sold for many different applications and as far as possible the properties of the resins are tailored to suit the requirements for each specific use.

Properties important to the resin user:

A) Amount of formaldehyde evolved
1. during mixing with catalyst,
2. on curing with acid catalysts,
3. on curing by heating and
4. on time ageing after cure.

B) The water resistance of the crosslinked resin. Structures made with urea-formaldehyde resins, which have to tolerate damp conditions, or conditions of high humidity must be relatively stable to hydrolysis.

C) Tack. In some applications urea-formaldehyde resins are required to lend tack to a product e.g. chipboard manufacture.

D) Storage life.

E) Stability of the resin suspension in water.

F) Biodegradability.

Properties E and F are important for materials used in the agriculture market, especially nitrogen fertilisers.

In general, amino/alkyd or polyester blends are among the cheapest of the modern synthetic coating systems and could be used in most situations except where special properties such as chemical resistance, long term durability or absolute non-yellowing are required.

# Chapter two

## 2 THE DEVELOPMENT AND EVALUATION OF POLYMER COATED UREA AS A POTENTIAL SLOW-RELEASE SUPPLEMENT FOR RUMINANTS

E. Upton, R. Sanderson[1], C.W. Cruywagen, J. Coetzee[2] and W.A. Smith[2]
Department of Animal Sciences and [1]Institute for Polymer Science, University of Stellenbosch, Stellenbosch, 7600 South Africa

### 2.1 Abstract

The effect of polymer encapsulation of urea prills on the release rate of urea in distilled water was studied in order to evaluate this approach's potential as a slow-release urea product for ruminants. The Wurster method was used to encapsulate urea prills with a copolymer of urea formaldehyde and a castor-coconut alkyd. A 2 x 2 x 2 x 2 factorial design was used for the making of 16 individual products. The slopes of the urea release curves represented the release rate of the encapsulated products. These were compared to identify the process variables that had an effect on the release rate. Two of the coating variables, coating weight and alkyd: resin ratio, had the main effects on the release rate of urea ($P = 0.0001$ and $P = 0.0135$, respectively). A coating weight of 125 g coating per 100 g urea, resulted in a significantly lower dissolution rate than 75 g per 100 g of urea did, while an alkyd:resin ratio of 70:30 resulted in a slower dissolution rate than a ratio of 60:40. Coating weights of 125 g and 75 g/100 g urea represented mean coating percentages of 56 % and 44 % respectively. The crushing strength of the encapsulated products was significantly higher ($P = 0.0001$) than that of untreated urea. Results from this study validate the evaluation of the encapsulated products in the rumen of sheep to study the potential of this approach as a slow-release source of non-protein nitrogen in the ruminant feed industry.

*Keywords: Nutrition, NPN, slow-release urea, encapsulation, polymer.*

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[2] Current address: Voermol Feeds, PO Box 13, Maidstone 4380

## 2.2 Introduction

The supplementation of nitrogen (N) to livestock that consume low-quality forages is a common practice to improve the utilisation of forage. Due to the high cost of natural proteins and the unique ability of ruminants to convert non–protein nitrogen (NPN) compounds to good-quality microbial protein, the feeding of urea is an effective way of removing the N-limitation to microbial growth, and of increasing voluntary intake of ruminants (Lee *et al.,* 1987). However, despite the fact that urea is the most widely used non-protein nitrogen (NPN) source, its inclusion is limited due to rapid hydrolysis in the rumen and a release rate of ammonia at a much faster rate (4 times) than its assimilation into amino acids by rumen microbes (Bloomfield *et al.,* 1960).

Many authors have tried to overcome this disadvantage and, during the past decade, the search for a slow-release urea product for the ruminant feed industry has varied in both method and success. These attempts varied from the use of liquid supplements (Doyle, 1987), impregnation of grain with urea (Koeln *et al.*, 1985a), various combinations of starch and urea (Deyoe *et al.*, 1968; Houston *et al.*, 1974) and modified forms of urea (Kaushal & Swan, 1983; Makkar *et al.*, 1988). Böhme (1997), evaluated a slow-release liquid urea-molasses product, Bonded Urea Plus® (manufactured and distributed by F.S.L. Bells Wiltshire, UK). Bonded Urea Plus® contains ureides, which are larger, more stable urea/molasses molecules that are more resistant to enzyme attack than urea and therefore converted to ammonia at a slower release rate. An additional advantage of the product is the simultaneous release of sugar to provide the rumen bacteria with energy along with the released nitrogen. Böhme (1997), however, found no advantage in supplementing Bonded Urea Plus® instead of urea/molasses in licks of intensive fed sheep on low-quality hay. No differences between the two products in the rate of ammonia production in the rumen of sheep.

None of the products currently available nor potential products meet the criteria established for a sustained - release urea product. They either release ammonia too rapidly or the nitrogen is so tightly complexed that little ammonia is released.

Furthermore, potential products require heat treatment and extensive processing, which does not merit the development of a marketable product.

An ideal slow-release urea supplement should have a sustained release of ammonia over a period of 12 to 24 hours, as energy is made available from fermentation. It should also prevent ammonia toxicity (Males *et al.,* 1979) and, according to Mathison (1994), it should also provide essential branched–chain fatty acids. It should be non-toxic and the subsequent production benefits should warrant the additional costs. Many horticulture investigators have studied the efficiency of fertilisers, particularly nitrogenous fertilisers, by controlling the rate of release of nutrients to match plant requirements. Since the use of urea as a fertiliser is also limited by its rapid dissolution in water and rapid hydrolysis, we investigated the approaches followed by the fertiliser industry to reduce N loss in soil. The need to control nitrogen losses initiated a wide range of research approaches that fall under four development categories: (1) slightly soluble materials such as urea formaldehyde (2) nitrification and urease inhibitors (3) and fertilisers coated with semi-permeable or impermeable membranes. Although coated products, undoubtedly, retards the conversion of urea to ammonia it has, not yet gained commercial acceptance in the ruminant feed industry. This approach is however a common procedure used in the process for manufacturing coated fertilisers with a reduced urea dissolution rate in the soil. A wide variety of materials have been used as coatings. The most important are waxes, polymers and sulfur. Sulfur-coated urea (SCU) has been produced commercially since 1972 and has gained wide acceptance as turf fertiliser. The release of N from an individual SCU pellet is termed "catastrophic" in that all individual fertiliser pellets release simultaneously. Variations in the coating thickness and uniformity of individual pellets within an SCU product provides N release over an extended period (Peacock & DiPaola, 1992). A similar approach of controlled release was followed in this study in an attempt to develop to reduce the hydrolysis of urea in the rumen of the animal.

## 2.3 Materials and Methods

### *2.3.1 Encapsulation of urea prills*

Commercial feedgrade urea (Kynoch, South Africa) with a nitrogen content of 46.6 % and a particle size range of 0.5 to 2 mm was used. The coating materials consisted of a commercial urea formaldehyde resin (Plascon, South Africa) with a non-volatile content of 63 %, and a commercial castor-coconut alkyd (Plascon, South Africa) with a non-volatile content of 55 % and 5.2 % OH. Butanone (99 %) was used as solvent and with a mixture of toluene sulfonic acid monohydrate (10 % solution, Saarchem), Iso-butanol (99 %, Saarchem) and n-Butanol (99 %, Saarchem) was used as catalyst. The catalyst was prepared by dissolving 10 g toluene sulfonic acid monohydrate in 90 g of a 50 % mass/mass solution of iso-butanol and n-butanol, to make up a 10 % acid solution.

### *2.3.2 Experimental design used*

A 2 x 2 x 2 x 2 randomised factorial block design (Statgraphics) comprising of four coating variables was used to create 16 individual products and determine which product variable had a significant effect on the release rate of urea from the encapsulated product. These variables with their individual experimental range of contents were as follows: alkyd:resin ratio (60:40 & 70:30), percentage catalyst (3 % & 6 % of Resin solids), percentage solvent (70 % & 90 % of polymer mass) and coating/polymer mass (75 g & 125 g/100 g urea). A 17$^{th}$ intermediate product was produced to subjectively evaluate the practicability of the Wurster process. Ranges were the following: alkyd:resin (65:35), percentage catalyst (4.5 %) and coating mass (100 g/100 g urea). This product did not form part of the statistical analyses. The compositions of the products are shown in Table 1.

**Table 1 The compositions of the products according to a random 2 x 2 x 2 x 2 factorial block design (Statgraphics)**

| PRODUCT | ALKYD: RESIN | CATALYST (% OF RESIN SOLIDS) | SOLVENT % | COATING WEIGHT (g) |
|---|---|---|---|---|
| A | 60:40 | 3 | 70 | 75 |
| B | 70:30 | 3 | 90 | 75 |
| C | 60:40 | 6 | 70 | 75 |
| D | 70:30 | 3 | 90 | 125 |
| E | 70:30 | 6 | 90 | 125 |
| F | 60:40 | 3 | 70 | 125 |
| G | 60:40 | 6 | 90 | 125 |
| H | 60:40 | 6 | 70 | 125 |
| I | 65:35 | 4.5 | 80 | 100 |
| J | 70:30 | 6 | 90 | 75 |
| K | 70:30 | 6 | 70 | 75 |
| L | 60:40 | 6 | 90 | 75 |
| M | 70:30 | 3 | 70 | 125 |
| N | 70:30 | 3 | 70 | 75 |
| O | 60:40 | 3 | 90 | 75 |
| P | 60:40 | 3 | 90 | 125 |
| Q | 70:30 | 6 | 70 | 125 |

**Table 2 The coating mass as variable according to the remaining coating variables, catalyst %, solvent % and alkyd:resin ratio**

| Mass polymer/100 g urea | Mass material used (g) for each individual variable | | | | | |
|---|---|---|---|---|---|---|
| | Alkyd:resin | | % Catalyst | | % Solvent | |
| | 60:40 | 70:30 | 3 | 6 | 70 | 90 |
| 75 g | 60 g:34.92 g | 60 g:22.45 g | 6.6 g | 13.2 g | 175 g | 675 g |
| 125 g | 100 g:58.18 g | 100 g:37.40 g | 11 g | 22 g | 291.67 g | 1125 g |

creating the concept of different layers of coating. The final step in the coating process was drying.

**Figure 1 Modified fluidised-bed apparatus.**

### *2.3.4 Laboratory Evaluation of Products*

The coated product was tested for dissolution rate, total coating percentage and crushing strength.

#### 2.3.4.1 Determination of dissolution rate:

The relative effectiveness of the coating in controlling the rate of urea dissolution was determined by an adapted version of a conventional method developed by Blouin *et al.* (1971). The method is a static test in which ca. 2 g of each of the product was dried at 60 °C for 24 hours and weighed. Each of the dried product

samples was placed in a separate Schott bottle containing 100 ml distilled water at 38°C. The temperature was controlled by using a shaking water. At time intervals of 2, 6, 10, 15, 24, 36 and 48 hours after the prills were inserted, 5 ml of each solution was taken and stored in a 10 ml politop at –10 °C. Samples were thawed at room temperature one hour before they were analysed. This procedure was repeated for four periods for each product. The mass (g) of urea dissolved in the water was determined according to an industrial method from Somchem (AECI Product Specification No. 353, (Falter *et al.,* 1975). A volume of 2 ml of each sample, 2 ml Ethanol, and 10 ml 2 % N,N-dimethylaminobenzaldehyde (DMB) solution were pipetted into a 100 ml volumetric flask and made up to 100 ml with distilled water. All the samples were read within 2 hours of preparing. A Varian Scan ultraviolet spectrophotometer was used for the determination of the amount of urea dissolved in the distilled water. A wavelength of 420 nm was used with a slit width of 1nm. Quartz cuvets of 1 cm were used throughout. The DMB forms a covalent derivative with the free amino group of the peptide in the urea structure. This derivative absorbs in the near-ultraviolet or visible region (420 nm) (Figure 2).

Preparation of 2 % N,N - dimethylaminobenzaldehyde (DMB)

A solution of 2 % N,N - dimethylaminobenzaldehyde was prepared by adding 10 g of N,N - dimethylaminobenzaldehyde (DMB) (99 %, Saarchem) to ca. 50 ml of distilled water and then adding 37.5 ml concentrated $H_2SO_4$ (99 % Saarchem) dropwise. Care was taken to prevent the solution from getting to hot. The solution was quantitatively transferred to a 500 ml volumetric flask and made up to 500 ml with distilled water. This solution was freshly prepared daily and stored at –10 °C between readings.

Preparing of Blank solutions

A blank solution was prepared by pipetting 10 ml of the 2 % DMB solution and 2 ml Ethanol (99 %, Saarchem) into a 100 ml volumetric flask. The solution was made up to 100 ml with distilled water. This solution was used to calibrate the UV -

spectrophotometer. Urea standard solutions ranging from 0 (Blank) to 1000 PPM were prepared for the standard curves. A standard curve was fitted for every set of readings. This curve was used to calculate the concentration of the urea released from the encapsulated products.

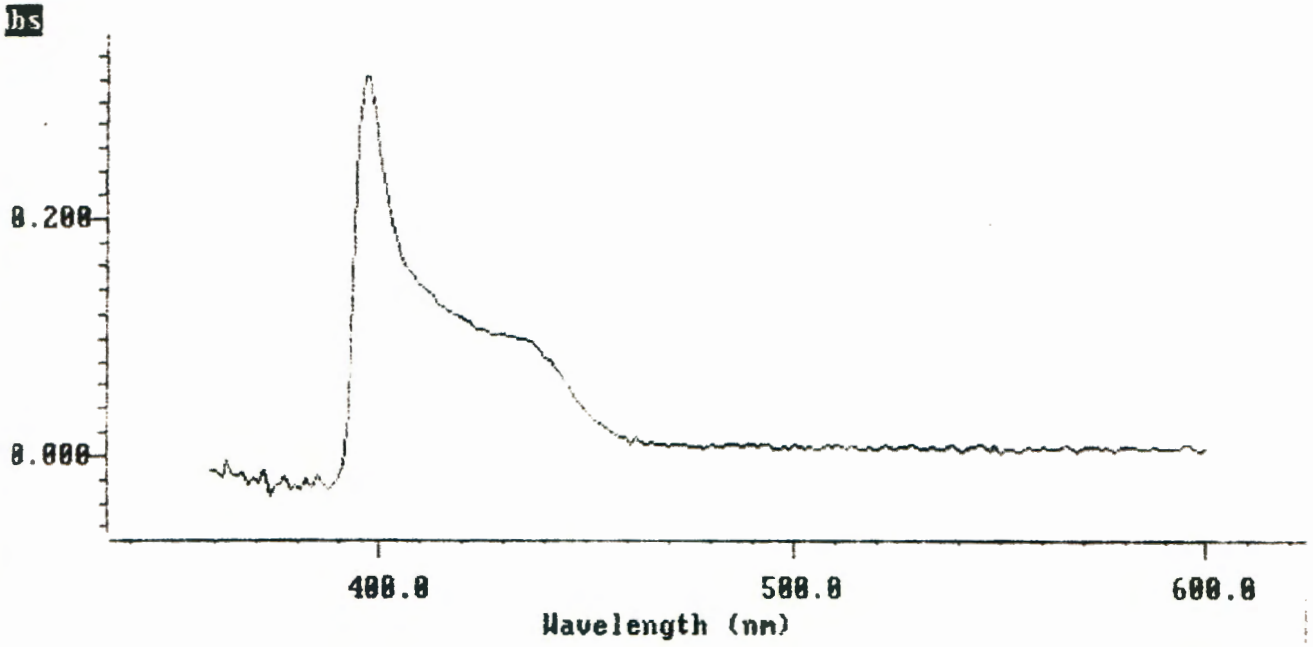



**Figure 2 The UV absorption curve of the complex formed between N,N - dimethylaminobenzaldehyde (DMB) and the free amino group of urea.**

The absorption values were read on the ultraviolet spectrophotometer and converted to the equivalent concentration values according to the standard urea curves (a correlation between refractive index and concentration) and its coefficients. The potential of the products to serve as slow-release compounds was evaluated on the basis of the dissolution rate of urea from the encapsulation and not the actual individual concentrations at given times. The slope of each release graph was therefore calculated as concentration (PPM/time(hours)) to represent the dissolution rate. Data were subjected to analysis of variance (ANOVA), (Snedecor & Cochran, 1991). The ANOVA was prepared with the aid of "Statistical Analysis System" (SAS, 1989). The slope of each product's release curve was calculated and represented the dissolution rate of urea from the encapsulated product during the four periods.

The dissolution rate of urea was calculated separately for each product and a mean value was presented using least square means (LSMEANS).

#### 2.3.4.2 Determination of total coating percentage

For the coated urea, the coating was accepted to be the water-insoluble portion of the sample. The actual coating percentage was determined as follows. The 2 g sample of the encapsulated product used in the determination of the dissolution rate was left for a further 24 hours at room temperature in the water to ensure that all the urea was dissolved. The insolubles were filtered, washed and dried at 80 °C to constant weight. The coating percentage was calculated from the following equation:

% Coating = wt of residue (g)/(wt of sample) X 100

Salman (1988) compared this value with the expected percentage of coating, which is equal to the weight of the polymer in the coating solution divided by the final weight of the product. However, because a significant amount of coating was lost during the coating process (clogging of pipes and nozzle etc.) a second method was also used. The value for the coating percentage was compared with the expected percentage of coating as calculated by measuring the mean weight of 30 uncoated urea prills divided by the weight of 30 coated prills.

#### 2.3.4.3 Determination of crushing strength

The crushing strength test was carried out according to standard methods (Salman, 1988). The crushing strength, *i.e.*, force per unit area of sample required to induce fracturing, or cracking of the sample, was determined for 20 prills of equal size, one at a time. The instrument used was a fruit pressure tester or penetrometer (NR. 43692; Effegi, Italy) and the units were kg/area. The test was carried out to compare the strength of uncoated urea with that of the encapsulated products as well as the strength between the individual encapsulated products. It was expected that

crushing strength would be indirectly proportional to fracture ease and nitrogen release.

### *2.3.5 Surface studies*

An atomic force microscope (Topometrix Explorer 2000) was used to examine and compare the uniformity of the coating surface. A force constant of 30 - 80 Newton/m was used. The average roughness of the surface was calculated automatically by the following equation:

$$R_a = 1/N \sum^{n}_{i=0} |Z_I - Z|$$

Where:
N = Total number of points in image matrix,
$Z = 1/N \sum^{n}_{i=0} Z_I$ and
$Z_I$ = the height of the *i*th point over a reference value

More representative of the entire line profile are the mean values of Rp and Rt:

Rp = maximum height of the profile above the mean line, $(Z_{max} - Z)$,
Rt = maximum peak to valley height in the profile $(Z_{max} - Z_{min})$,
$Rpm = 1/Y \sum^{y}_{i=0} (Rp)_I$ and
$Rtm = 1/Y \sum^{y}_{i=0} (Rt)_I$.

## 2.4 Results and discussion

The quality of the coating and the feasibility of using the Wurster method for micro-encapsulation depends on a number of process variables. Preliminary experiments were conducted and variables were subjectively examined to set optimum coating conditions before statistical procedures for the manufacturing of the encapsulated products and the physical evaluation of the coating/product variables commenced. Process variables that were considered included (1) atomising air pressure (2)

fluidising air flow rate (air volume), (3) process temperature, (4) viscosity of coating solution and (5) flow-rate of coating solution.

Atomising air pressure ranges of 9 to 11 lb. and 100 to 120 $Nm^3/h$ for fluidising airflow rate were found to be optimum. Values higher than the upper limit caused particle attrition and gave rise to a high powder content and prevented the uniform coating of prills. Values below the lower limit prevented fluidisation and proper atomisation of the coating solution and also prevented uniform coating. These values coincide with the conditions used by Salman (1988) when encapsulating urea with various polymers. The slight differences in our operating values compared to those found in the literature, could be attributed to the fact that the mass of urea (1 kg) coated by Salman (1988) was greater than used in our study (100 g). The amount of urea to be coated by us was limited by the capacity of the ventilator. It was only the effect that these variables had on the practicability of the process and the physical product were observed, and not its effect on the dissolution rate of the urea from the product. Salman (1988) found in similar studies however, that when operating within the pressure and flow rate ranges of 10 to 25 lb. and 100-200$m^3/h$, no major change in the dissolution of urea from the encapsulation was observed.

The process temperature is dependant on type of coating material and especially the solvent used. According to Salman (1988), the polymer solution temperature at the spray nozzle should be within the boiling point range of the solvent, in order to achieve instant drying of the coated particles. However, although the boiling point of butanone is 80 °C a temperature of higher than 26 °C did not seem necessary, since the combination of both a acid catalyst and slight heat was effective for crosslinking between the alkyd and resin polymers, evaporation of the solvent, and thus for rapid drying. At temperatures lower than 20 °C, however, the coating did not dry immediately, and resulted in agglomeration of particles.

It was also observed that the viscosity of the coating solution *i.e.* the amount of solvent used to dissolve the polymer had an effect on the uniformity of the coating and fluency with which the process proceeded. When the solvent content was below 70 % of the total coating mass, there was a high occurrence of blocked tubes and nozzle assembly, and a subsequent wastage of time and material. A solvent content

above 90 % would result in high costs. A flow rate of 0.3 to 0.5 U/min. was found to be positively affected by the solvent- and catalyst percentage of the coating. High solvent or catalyst concentrations allowed for fast flow rates, due to the rapid evaporation of the solvent and consequent fast drying times. A moderate flow rate of 0.3-0.5 U/min. however, resulted in a more uniform coating. According to Salman (1988), lower flow rates have the disadvantage of increasing operating times and consequently energy costs. In the commercial process therefore, a compromise is required between good quality coating and energy savings. According to the manufacturer of the Aeromatic, the test data obtained from this unit cannot always be accurately transferred to large production units and it is recommended that a small production machine be used (size 4). Should results, however, after evaluation in this study and in the rumen of animals show further potential as a slow-release supplement for ruminant feed, fluid - bed dryers with an hourly capacity of 10 000 kg are commercially available. It should be noted that the process variables were co-ordinated in such a way that continuous spraying could be carried out. Process variables were only subjectively examined and did therefore not form part of the factorial design.

*Product description*

The polymer coated urea prills comprise:

a inner core of a solid urea pellet and

a polymer coating consisting of a copolymer of urea formaldehyde and an alkyd.

A cross-sectional photomicrograph of polymer coated urea prills is shown in Figure 3.

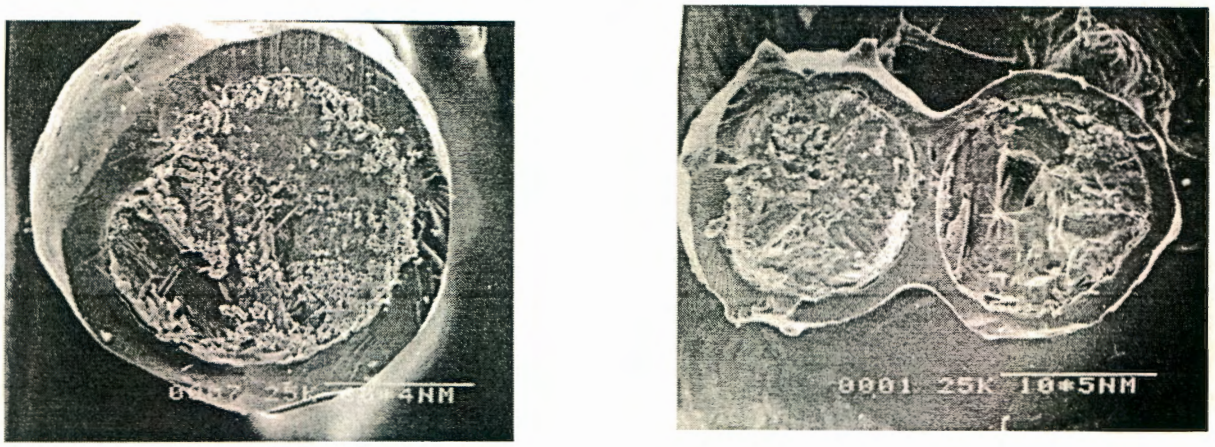



**Figure 3 A cross-sectional photomicrographs of polymer coated urea prills.**

*2.4.1 Effects of principal coating variables on the dissolution rate*

The most important variables considered and examined in this study were the coating variables and their effects of the dissolution rate of urea. The 2 x 2 x 2 x 2 factorial block design included the following variables: alkyd:resin ratio, catalyst content (%), solvent content (%) and the coating weight (thickness). The factorial design gave rise to the production of 16 products.

Micro-encapsulation is one of the major controlled-release reservoir systems with rate-controlling membranes, and although the method of release was not examined in this study, it is suggested that it is via permeation through the walls. According to Kydonieus (1980), all the physical polymeric systems for controlled release are in controlled by the diffusion of the active agent through a polymer barrier or by an inward diffusion of an environmental fluid. If however, the polymer phase is not homogeneous, cracks and pores observed under magnification could also be the major paths of release (Das, 1983). Typical release graphs of individual products can be seen in Figures 4a and 4b, where the average release values over 4 periods are shown. The release of urea from the encapsulated products (Table 1) was only 100 % complete in one of the products after 48 hours (product C). The highest release values were observed for Products A, C, O, L.

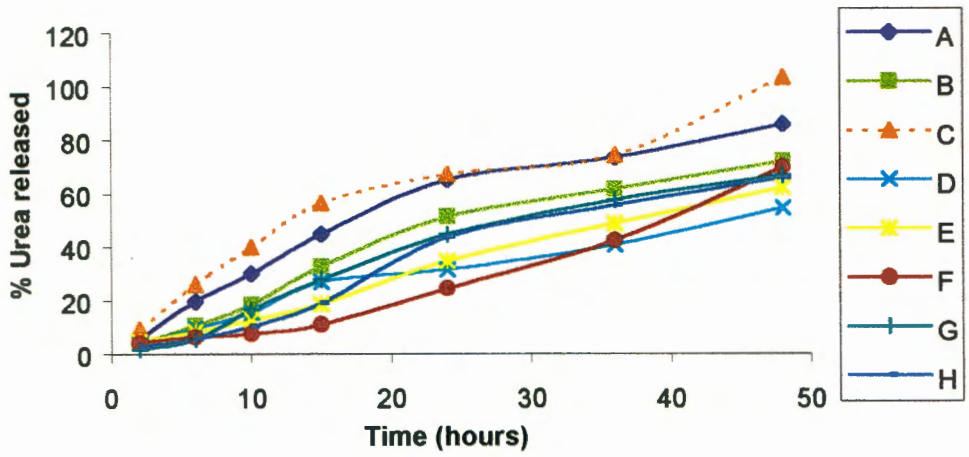
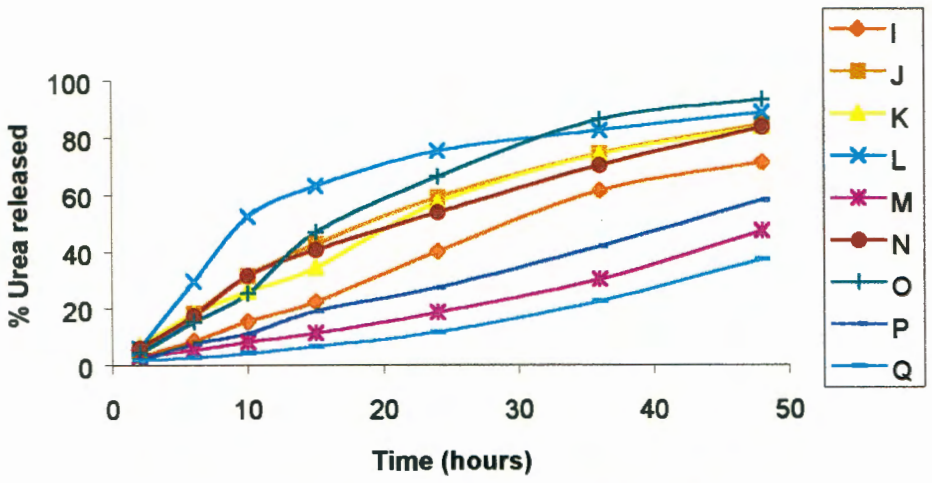


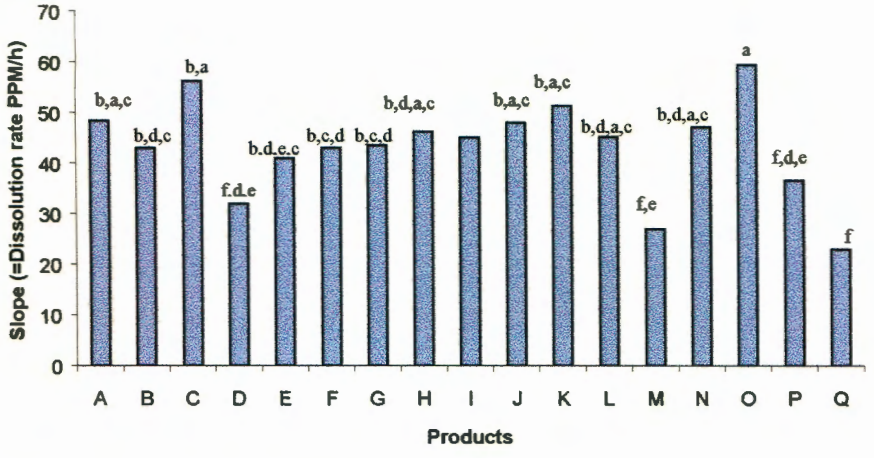

**Figure 4a The percentage urea released from the encapsulated products A-H**




**when evaluated in distilled water at 38 °C.**

**Figure 4b The percentage urea released from the encapsulated products I-Q when evaluated in distilled water at 38 °C.**

The potential of these products to serve as slow-release compounds was evaluated on account of the dissolution rate of urea from the encapsulation. The slope of each graph represents the dissolution rate (Figure 5) and was calculated as concentration (PPM)/time (hours).




± SEM (Standard error of mean) 5.4624888

* a,b,c,d,e,f Values with different superscripts differ significantly (P < 0.05)

**Figure 5 The dissolution rate (PPM/h) of urea from the 16 encapsulated products and the least square means of each product.**

In Figure 5 it is shown that the slopes of the release graphs in Figure4a and 4b from products D, E, M, Q and P are clearly lower than that of the other products (31.9, 40.9, 27.0, 22.9 and 36.5, respectively, vs. slopes of over 40 for the remaining products).

Analysis of variance showed that the dissolution rates of the products were only significantly ($P < 0.0001$) affected by two of the four coating variables viz. alkyd:resin ration ($P = 0.05$) and coating weight ($P = 0.0001$), *i.e.* the composition of the copolymer. No interactions were observed between these two main effects (alkyd:resin ratio and coating weight) ($P = 0.2241$).

### 2.4.1.1 Alkyd:Resin Ratio

The effect of the alkyd:resin ratio on the dissolution of urea is indicated in Figure 6.

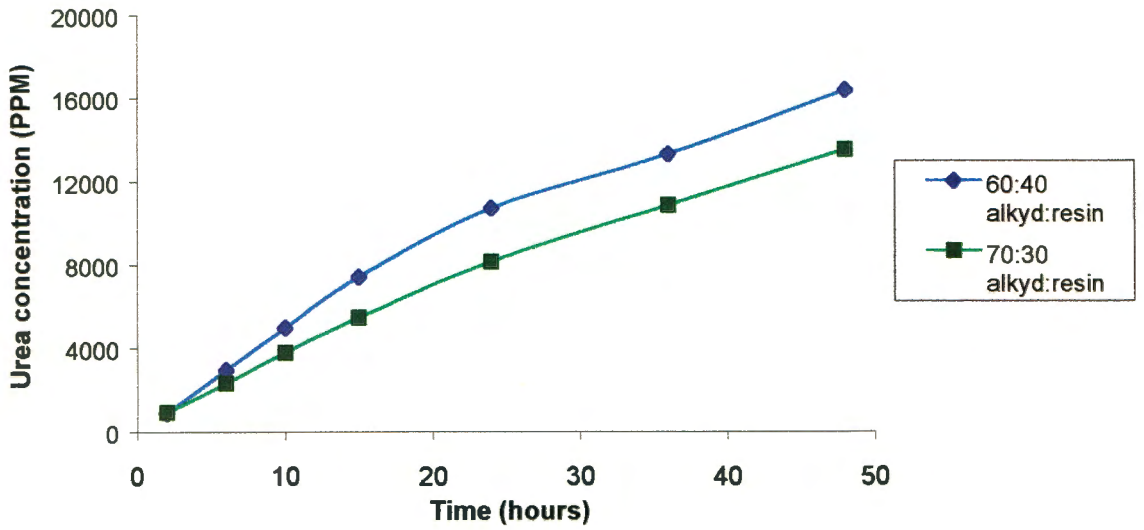



**Figure 6 Effect of alkyd:resin ratio on the dissolution of urea in distilled water at 38 °C from encapsulated products over a period of 48 hours.**

There was a significant difference (P = 0.0043) between the release rate of urea from the encapsulated product with 60 % alkyd vs. the 70 % alkyd product (Slope = 47.3 vs. 39.0 respectively).

It is shown that as the alkyd percentage increases, the dissolution rate decreases. This can be explained by the fact that the alkyd component in the copolymer increases the hardness and the chemical resistance of the polymer. Conventional butylated urea formaldehyde polymers contain free hydroxymethyl groups and amino hydrogens in addition to the butoxy groups. These polymers can also self-condense (Koral & Petropoulos, 1966). The amino polymer therefore needs to react with the alkyd polymer to produce the desired crosslinks, but will simultaneously lose some of its functionality through selfcondensation reactions. The rates of these two competing reactions are of the same order of magnitude and the formation of

polymerised blocks of amino polymer in cured coating has a profound effect on its mechanical properties. These polymerised blocks form rigid clusters that, after curing give rise to decreased flexibility. The use of excess amino polymer as the crosslinking agent results in a significant amount of self-condensation. This results in films with greater hardness and chemical resistance, but of much poorer flexibility (Koral *et al.,* 1966). According to Lourens (1995) the mixtures of alkyd and amino polymers such as urea formaldehyde resins are composed of 50 to 90 % alkyd and 50 to 10 % amino polymer. This makes the ratio used in this study within the theoretical range. Futhermore, because the hydroxyl groups in the alkyd provide the sites for cross – linking, it makes sense that more alkyd implies more crosslinkings and more resistance to water.

#### 2.4.1.2 Coating weight

The effect of coating weight on the dissolution rate of urea from the encapsulated products is shown in Figure 7. It was found that a higher coating weight (125 g/100 g urea) had a significantly lower dissolution rate (P = 0.0001) than did a coating weight of 75 g per 100 g of urea. According to Blouin *et al.* (1971) the rate of diffusion of the substrate through the coating is a function of the thickness of the coating. Blouin *et al.* (1971) have also found that thicker coatings give lower diffusion rates, assuming that coating qualities are the same, *i.e.* the same coating conditions are used in each case.

The fact that coating weight and alkyd percentages have a significant effect on the dissolution rate, is confirmed when referring to the release graphs of Figures 4a & 4b. Products A, C, O, L which have the highest percentage of released after 20 hours all have the constitution of 60 % alkyd and 75 g coating.

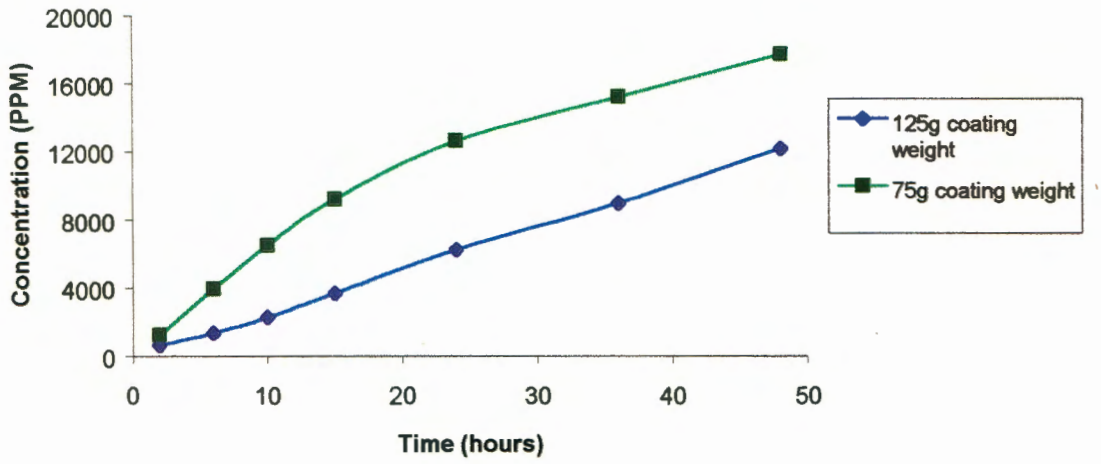



**Figure 7 The effect of coating weight on the dissolution rate of urea from encapsulated products at 38 °C.**

The fact that only two of the original four variables had a significant effect on the dissolution rate of urea from the encapsulated products resulted in the composition of four products from the original 16 products, as indicated in Table 3. For the remainder of this study, any of the 16 original products that contained the same coating weight and the same alkyd:resin ratio were considered equal.

**Table 3 The composition of four resulting products**

| RESULTING PRODUCTS | COATING WEIGHT (g/100g urea) | ALKYD:RESIN | ORIGINAL PRODUCTS FROM 2 x 2 x 2 x 2 FACTORIAL DESIGN |
|---|---|---|---|
| I | 75 | 60:40 | A, C, L, O |
| II | 75 | 70:30 | B, J, K, N |
| III | 125 | 70:30 | D, E, M, Q |
| IV | 125 | 60:40 | F, G, H, P |

### *2.4.2 Total coating %*

The coating percentages for the encapsulated products were 56 % (125 g coating weight) and 44 % (75 g coating weight), respectively,. The difference in expected coating weight (as calculated by Salman, 1988) and the actual coating percentage was due to coating losses in the process, as coating stick to the sides of the container, the nozzle assembly and the pipes. The weight loss due to solvent evaporation is unknown. The calculated coating percentage, however, obtained by weighing of 30 coated and uncoated prills correlated highly with that of the values measured by using the equation in 2.3.5 ($r = 0.988$; $P = 0.0001$).

### *2.4.3 Crushing strength and moisture*

The crushing strengths (measured as described in *2.3.6)* of the encapsulated products was found to be significantly higher ($n = 20$, $P = 0.0001$), than those of untreated urea prills (Table 4). Products I and IV (alkyd:resin ratio, 60:40) had the highest crushing strength of the four products. According to Koral & Petropoulos (1966) the hardness in the urea polymer/alkyd system is caused by the harder amino polymer domains inside the softer alkyd system, thus explaining the higher crushing strength of coatings with a higher percentage of amino polymer (urea formaldehyde resin).

The effect of encapsulation on reducing water absorption was not determined. However, it was noticed that the strong encapsulating film reduced caking in humid conditions, thereby suggesting that the coated product could resist moisture absorption. According to Salman (1988), an increase in crushing strength and a decrease in moisture absorption for coated urea improves its storage and handling characteristics. In similar studies with polymer coated urea, he found that particle attrition is reduced due to the strong encapsulating film, which resulted in a reduced powder content of the product. Secondly, due to the fact that coated product resists caking, the provision of anticaking agents such as kaolinite is unnecessary. Finally, Salman (1988) suggests that coated urea or similar products can be shipped in bulk, therefore eliminating the need for polyethylene-lined bags resulting in lower costs.

It is believed that the coating of urea prills will assist in solving two additional problems belonging to the level of inclusion of urea in rations. The first is due to the hygroscopic nature of urea which causes the concentrate urea is presented in, to absorb moisture, swell and occlude the flow of the concentrate from the bin in which it is stored in ("bin hang-up"). As a result, the pellets in the centre of the bin expand in size, disintegrate and stick together. Other prills are held together by microscopic urea crystals formed on the pellet surfaces by recrystallisation, due to moisture migration. This results in an uneven distribution of urea and a subsequent risk of toxicity (Kertz & Everett, 1975). A second problem associated with the use of urea at higher dietary levels is the unpalatability. The hygroscopic nature of urea exacerbates its unpalatability and handling characteristics as a consequence of the moisture conditions to which a ration is exposed.

**Table 4 Effect of encapsulation on the crushing strength of urea**

| PRODUCTS (Refer to table 3) | CRUSHING STRENGTH (kg/area) (LSMEANS) | SEm |
|---|---|---|
| I | $2.346^{b}$ | 0.15155 |
| II | $1.85^{c}$ | 0.15774 |
| III | $2.255^{b,c}$ | 0.1728 |
| IV | $3.805^{a}$ | 0.1728 |
| V (untreated urea) | $0.17^{d}$ | 0.1728 |

* LSD = 0.4649 *

$SE_M$ = Standard error of mean

[a,b,c,] Means with different superscripts differ (P<0.05)

[d,] Means with different superscripts differ highly significantly (P < 0.01)

### *2.4.4 Surface studies:*

The exterior surfaces of the original products (A - Q) as presented in Table 1 were compared, and the uniformity of the coating examined. The exterior surfaces of products proved to be quite uniform and typical of that of an amino/alkyd copolymer (Figure 8). Surface cracks were however, identified and it is suggested that these could be the main path by which urea is released (Figure 9). According to Salman (1988) the uniform distribution of the resin component in a less viscous solution to cover the whole surface is hindered. Therefore, a low-viscosity solution produces a coating film that is much less uniform and less dispersed and results in higher dissolution. Although cracks are observed in products with a lower viscosity, dissolution measured in this study proved not to be significantly effected by the solvent percentage *i.e.* viscosity.

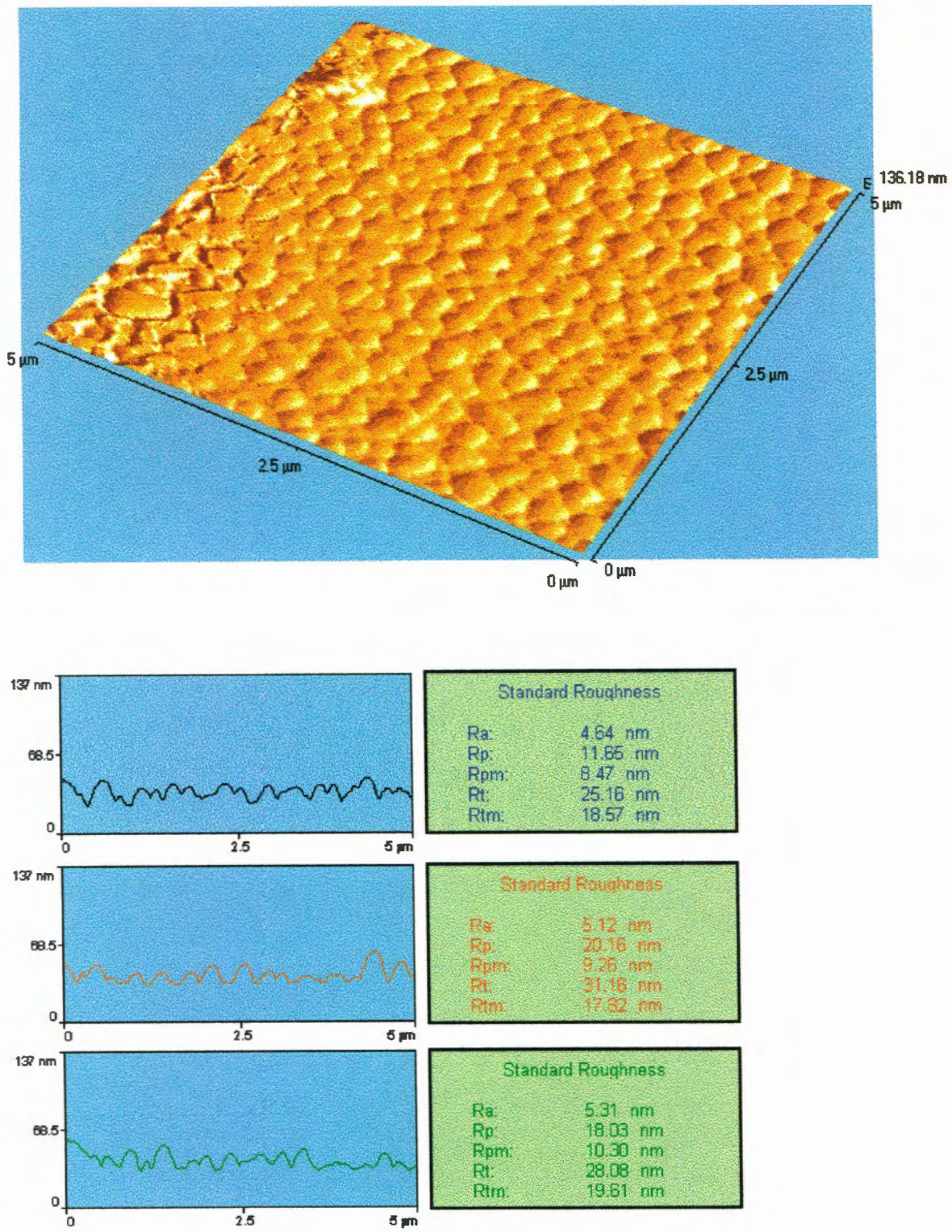
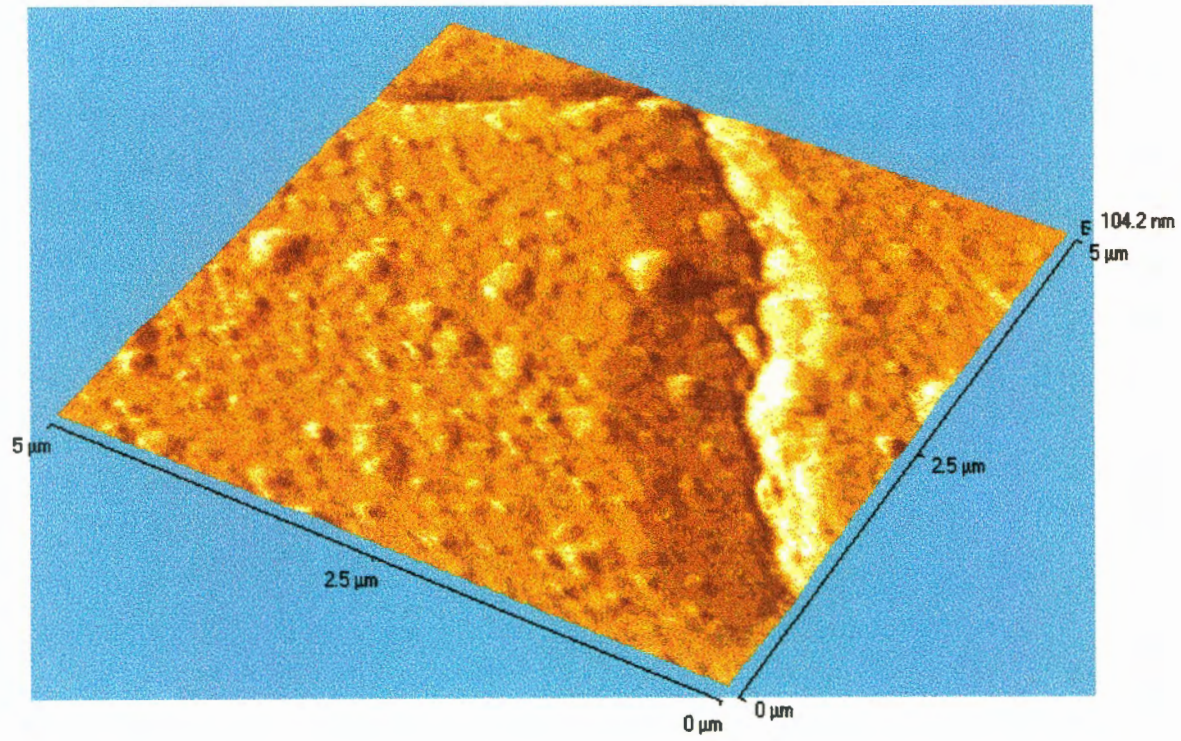



**Figure 8 ATM image (5µm x 5µm scan) of the top surface of Product G.**



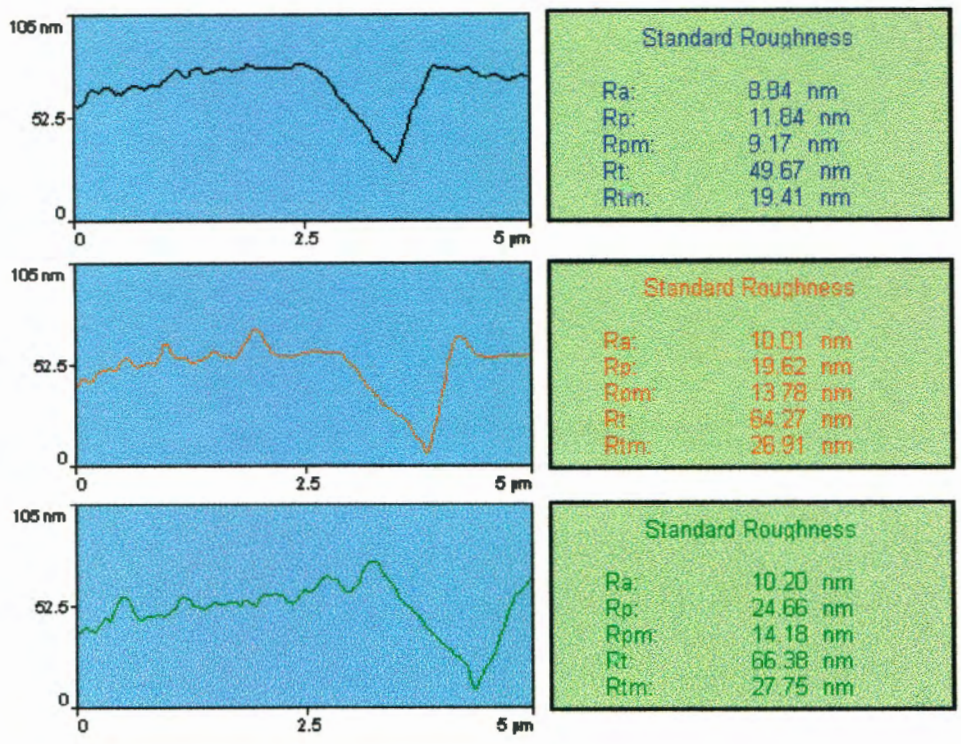




**Figure 9 ATM image (5µm x 5µm scan) of the top surface of Product H.**

## 2.5 Conclusions

The coating of feedgrade urea with a copolymer consisting of an amino resin such as urea - formaldehyde and a short oil alkyd - like coconut oil, has merit. It effectively reduced the dissolution rate of urea from an encapsulated product in distilled water at 38 °C. Increases in individual pellet coating - thickness and uniformity within a slow-release compound will probably provide N release over an extended period. These conclusions are in agreement with theoretical considerations discussed in Section 2.1. The products with the slowest dissolution rate were obtained with an alkyd percentage of 70 % and a coating weight of 125 g/100 g urea. The percentage catalyst and percentage solvent did not significantly affect the dissolution rate, although these variables do have an influence on the coating process itself. Coatings that contained the highest percentage of solvent, *i.e.* 90 %, and the highest catalyst percentage were easier to work with and created less practical problems in terms of clogging of the nozzle and the peristaltic pump tubing. These products also dried easier and percentage solvent is therefore a definite rate-limiting factor to keep in mind. This is explained by the fact that for a given acid catalyst concentration, temperature, and urea formaldehyde polymer to alkyd polymer ratio, the curing speed is a function of the evaporation rate of the solvent and the size of the urea polymer molecule. Two properties of the encapsulated product that have a practical effect on its acceptability are its storage potential and its resistance to normal handling, due to the higher crushing strength. Polymer coated urea products can be shipped in bulk, therefore eliminating the need for costly polyethylene-lined bags. Results of this study supports the feasibility of producing a slow-release urea compound that has a variation of coating thickness and has uniformity within the compound and ultimately leads to nitrogen release over an extended period.

It is suggested that the release of urea from coated prills should be predictable, to enable efficient utilisation of the product's slow-release characteristics. It must be the objective of future studies to develop and experimentally evaluate a mathematical model to make this possible.

Considering the above, the evaluation of the product's potential in the rumen of sheep or cattle is merited. Most new products normally go through a low-volume, high-cost developmental stages. It could be assumed, however, that should this product show similar potential when tested in the rumen, a large market for commercial farm use of bulk polymer-coated urea could be established in the agricultural industry.

# Chapter three

## 3 EVALUATION OF POLYMER COATED UREA AS A SLOW-RELEASE SUPPLEMENT IN THE RUMEN OF FISTULATED DOHNE MERINO WETHERS

**E. Upton, C.W. Cruywagen, R. Sanderson[1] and J. Coetzee[2]**

Department of Animal Sciences and [1]Institute for Polymer Science, University of Stellenbosch, Stellenbosch, 7600 South Africa

### 3.1 Abstract

The rate of urea release by a slow-release urea compound (SRU), was evaluated in the rumens of fistulated sheep. The SRU's consisted of urea prills encapsulated with a copolymer of a urea formaldehyde resin and a short-oil alkyd. Four products with different coating weights and coating constitutions were evaluated in terms of the rumen ammonia and blood urea nitrogen (BUN) concentrations of sheep and compared to the rumen ammonia where untreated urea was used as baseline. In a complete randomized design, fifteen 5 year old fistulated Dohne Merino wethers were allotted into five groups. An equivalent of 15 g urea was administrated directly into the rumen of each animal and samples of rumen liquid and blood were taken 0, 1, 2, 4, 6, 8, 12, 16, 20, 24, 36, 48 h after administration. The SRU's resulted in significantly lower rumen ammonia peaks (P = 0.0001) than untreated urea, while the peaks also emerged at a significantly later time. Untreated urea resulted in the maximum ammonia concentration at two hours after administration of the urea (P = 0.0685) while the SRU's reached a maximum at six hours after administration in the rumen. No significant differences between the four SRU's were found. Responses for blood urea-N were similar to those observed for rumen ammonia nitrogen. The encapsulation was effective in decreasing the rate of ammonia release from the urea for up to six hours after administration.

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[2] Current address: Voermol Feeds, PO Box 13, Maidstone, 4380

## 3.2 Introduction

Providing supplemental protein and non-protein nitrogen (NPN) to ruminants consuming low-quality forages is a common approach to enhance forage utilisation and improve livestock performance. This is especially important in South Africa, since most of the country is only suitable for extensive animal production systems. According to Köster (1997), this kind of supplemental protein and NPN has been common practice in South Africa for the last five decades, although it has often not been optimised in terms of economic returns. Due to the high cost of natural protein sources and the unique ability of ruminants to convert NPN to protein, there is a need for optimising the utilisation of NPN. The amount of urea that can be safely included in the diet of ruminants is limited because of its rapid hydrolysis in the rumen, releasing ammonia at a rate much faster than its assimilation into amino acids and rumen microbes (Bloomfield *et al.*, 1960).

Ammonia can be absorbed into the portal circulation of the animal. It therefore follows that there is competition between the absorption and microbial utilisation of rumen ammonia. The rate of ammonia absorption is dependent on the concentration available in the rumen and particularly the rumen pH (Doyle, 1987).

According to Briggs (1983), the practical use of urea in animal feeding depends on urea cost effectively supplying ammonia for protein synthesis by rumen micro-organisms and to avoid high rumen ammonia, which can be toxic. Urea toxicity occurs when the rumen ammonia concentration exceeds 100 mmol/l. This correlates to a blood ammonia level of 1 to 1.5 mmol/l. However, even at subtoxic levels, the absorption of ammonia from the rumen represents a loss of nitrogen, because most of this nitrogen is excreted in the urine (Olivier & Cronjè, 1964).

Several attempts (Dee *et al.,* 1968; Huston *et al.*, 1974; Koeln *et al.*, 1985; Preston & Leng, 1987) have been made to maximise the utilisation of urea in order to compare favourably with the feeding of true protein sources to animals, and to fill the need for a feeding system that could include larger amounts of urea. Alternative approaches include coating urea with water insoluble materials to reduce its exposure to urease.

Coatings used included sugar cane wax, castor wax, a copolymer of dicyclopentadiene and esters of unsaturated acid and clay-like materials (Helmer & Bartley, 1971). None of these products however, gained commercial acceptance yet.

In the fertiliser industry, urea prills have been successfully coated with various polymer matrixes to reduce their rate of hydrolysis in the soil. The same approach was followed in an earlier study (Upton *et al.*, 1999a) where urea prills were encapsulated with a copolymer consisting of an urea formaldehyde resin and a short-oil alkyd. Products were evaluated in distilled water at 38 °C. The main effects on the dissolution of urea from the encapsulation were the composition and the weight of the coating. These results motivated the evaluation of these products in the rumen of fistulated sheep (Upton *et al.*, 1999a). The aim was to determine the dissolution rate of urea from the encapsulated polymer coated urea products in the rumen of sheep in terms of rumen ammonia and blood urea-N concentrations and compare it to that of untreated urea in order to evaluate its value as a slow-release NPN compound in the rations of ruminant diets.

## 3.3 Materials and Methods

Fifteen 5 year old fistulated Dohne-Merino wethers, weighing between 55 and 60 kg were allotted into five groups in a trial to determine and compare rumen ammonia and blood urea-N levels of four slow-release compounds (SRU) with feedgrade urea as control. Four slow-release products were manufactured according to results obtained in a preceding study (Table 1). The products consisted of an inner urea core encapsulated with a co-polymer coating of urea formaldehyde and an alkyd. The wethers were kept indoors in individual wooden slatted pens. The animals were fed once a day (07:30), and during a 10-day adaptation period they received a basal diet of wheat straw (< 3 % crude protein) *ad libitum*, 20 g 50 % mixture of Voerfos 12 (Voermol, Tongaat) and salt, as well as 150 g molasses. Animals were adjusted to urea at a rate of 3 g of feed urea per day up to the level of 15 g. The diets for all the animals were iso-energetic and iso-nitrogenous during the adaptation period. Drinking water was freely available. The wethers were randomly assigned to the

different treatments. At the onset of the trial the feedgrade urea was replaced with coated urea (according to the respective treatments). In the Treatments I & II, 27 g of the products were administrated intraruminally, while the amount was 34 g for Treatments III & IV (also equivalent to ca. 15 g urea). For Treatment V (control), 15 g of uncoated feedgrade urea was administered into the rumen of each animal. For the analysis of rumen ammonia and BUN, samples of rumen liquid and blood were taken at 0 h (just before administration of treatment), 1, 2, 4, 6, 8, 12, 16, 20, 24, 36, and 48 hours after administration of the various treatments.

**Table 1 Coating weight and the composition of the different slow-releasing urea products**

| PRODUCTS | Variables | |
|---|---|---|
| | **Coating weight (g)** | **Composition (% alkyd)** |
| **I** | 75 | 70 |
| **II** | 75 | 60 |
| **III** | 125 | 60 |
| **IV** | 125 | 70 |
| **V (urea)** | 0 | No coating |

Rumen fluid samples were collected with a 100 ml syringe attached to a perforated tube with a 50 m mesh nylon bag placed over the end to strain out larger particles (Mathison *et al.*, 1994). An amount of approximately 40 ml of rumen fluid was obtained at each collection. The pH was determined immediately after each sampling, where-after 9 ml of the rumen fluid was acidified with 1 ml of a $H_2SO_4$ solution (50 %, v/v). The samples were centrifuged at 2000 r/min. for 5 min. and the supernatant was removed and frozen at –20 °C until analysed for rumen ammonia nitrogen (Rigani *et al.*, 1993).

Blood samples were taken from the *vena jugularis externa* at the same time intervals as rumen sampling. The blood was centrifuged at 2000 r/min. for 10 min. Plasma was removed and stored at –20 °C until analysed. BUN was determined on all

plasma samples with the aid of an urea kit (Boehringer Mannheim, cat: 777510). The kit applies a method for the determination of urea in plasma and urine of Fawcett & Scott (1960) and is an enzymatic colorimetric test with salicylate.

A completely randomised design was used for the experiment, consisting of 5 treatments and 15 animals. The data of the experiments were analysed separately, using the PROC GLM and PROC COR procedure of SAS. A Tukey test was used to test for differences among means.

## 3.4 Results and Discussion

The effect of urea encapsulation on various rumen parameters is shown in Table 2. Ruminal ammonia-nitrogen levels and BUN levels of wethers administered different treatments directly into the rumen, are shown in Figure 1 and Figure 2 respectively.

### *3.4.1 Rumen $NH_3$ – N concentration*

Figure 1 displays the mean release of ruminal $NH_3$-N versus time after feeding the 5 different types of SRU's to the animals. Plotted values are the mean values of 3 animals. The pattern of accumulation of rumen ammonia nitrogen in sheep administrated urea were consistent with results obtained from other experiments (Johnson, 1976; Martin *et al*, 1982; Mathison *et al.*, 1994).

Curves indicate that the SRU products resulted in significantly ($P = 0.0001$) lower peaks than untreated urea, with maximum ammonia-N concentrations ranging from 16.1 mg to 23.5 mg N/100 ml vs. 53.3 mg/100 ml for untreated urea. The maximum NH3-N concentrations resulting from the SRU's were less than 50 % of that resulting from urea (Figure 1). According to Perdok *et al.* (1988), the intake of low-quality forage was optimised at about 20 mg $NH_3$-N/100 ml, while digestibility was unaffected at concentrations above 8 mg $NH_3$ – N/100 ml. Research by Leng *et al.* (1993) suggested that the enzyme pool in the rumen that degrade carbohydrates (fibre and strarch) is optimised at 6 - 10 mg $NH_3$-N per 100 ml. Results in Figure 1

suggests that the rumen ammonia concentrations resulting from the SRU products can be maintained at a relatively high level for more than 8 hours. According to Preston and Leng (1987) this should be advantageous to the micro-organisms since maximal fiber digestion occurs more than 5 h after fiber enters the rumen. The products exhibit an average ammonia concentration of 7.8, 12.5, 8.3 and 8.6 mg/100 ml (Products I - IV respectively) vs. the average of 20.4 mg/100 ml from untreated urea. Although differences between products were not major, product II tended to result in higher ruminal ammonia levels than did products I, III and IV.

No significant differences were found between the individual SRU's for the time taken to reach maximum $NH_3$ but the peaks from the SRU's were significantly later than that resulting from untreated urea. Untreated prilled urea resulted in the maximum concentration at two hours after administration of the urea ($P = 0.0685$), while products I, II, III and IV reached the maximum at six hours after administration in the rumen ($P < 0.01$).

The means for several parameters for the different treatments are shown in Table 2. The total area beneath each product's curve serves as an indication of the consistency of $NH_3$-N release in the rumen for the urea and the encapsulated products. Although no significant treatment differences were found ($P > 0.05$), the $NH_3$-N release for urea tended to be higher for untreated urea, suggesting a potential for the method of encapsulation. The products seemed to release urea over the first 6 hours, reaching a maximum then followed by a rapid release of urea which decreased with time. These results suggest that the four products do not release $NH_3$–N at a slower rate than that of untreated urea. It tended to release less $NH_3$ and reached a lower $NH_3$-N concentration peak at a later time ($P < 0.01$) post-feeding. A mixture of SRU and urea would spread the optimum rumen ammonia levels over a broader time frame.

**Table 2 The LS means for different parameters for sheep fed different supplements containing untreated urea or urea encapsulated with variable coating thickness and composition**

| | | TREATMENTS | | | | |
|---|---|---|---|---|---|---|
| **PARAMETER** | **SEm** | **I** | **II** | **III** | **IV** | **V (control)** |
| Max Rumen $NH_3$-N (mg/100 ml) | 7.02 | 21.4 [a] | 23.5 [a] | 16.1 [a] | 20.2 [a] | 53.3 [b] |
| Time of max. rumen $NH_3$ N (hours) | 0.82 | 6.0 [a] | 6.7 a | 4.3[a] | 6.0 [a] | 1.7 [b] |
| Max. blood urea (mg/100 ml) | 9.03 | 35.6 [a] | 35.7 [a] | 29.7[a] | 29.4[a] | 50.5 [a] |
| Time of max. blood urea (hours) | 3.17 | 22.7 [a] | 6.7 [b] | 17.3 [a] | 18.7 [a] | 7.3[b] |
| Rumen –$NH_3$- area | 62.22 | 194.5 [a] | 292.9 [a] | 199.1 [a] | 211.6 [a] | 347.2 [a] |
| Blood urea (area) | 208.26 | 845.4 [a] | 865.0 [a] | 868.6 [a] | 867.6 [a] | 1259.9 [a] |
| ph min | 0.134 | 6.1 [a] | 6.2 [a] | 6.2 [a] | 6.4 [a] | 6.0 [a] |
| ph max | 0.134 | 6.8 [a] | 6.85 [a] | 7.0 [a] | 6.91 [a] | 6.91 [a] |
| phmaxT | 9.16 | 16.0 [a] | 8. 7 [a] | 4.0 [a] | 20. 7 [a] | 1. 7 [a] |

[a] Means within the same row with equal superscripts did not differ significantly (less than 5 %)

$SE_m$ Standard error of the mean

### *3.4.2 Blood urea concentration (BUN)*

Figure 2 indicates the mean BUN profile of the animals. Plotted values are the mean of 3 animals. The response for blood urea-N was similar to that observed for rumen $NH_3$-N. This is in agreement with the observations of various researchers (Lewis, 1957; Preston *et al.,* 1965 & Thomas *et al.,* 1984) who reported high correlations between blood urea concentration and ruminal ammonia-N concentration.

In our study, rumen ammonia-N concentrations at 2 h post feeding were highly correlated with BUN values at 4 h and 6 h post-feeding ($r = 0.93$, $P = 0.0001$ and $r = 0.91$, $P = 0.0001$, respectively), while rumen ammonia-N concentrations 4 h post feeding were highly correlated with BUN values at 6 h and 8 h post-feeding ($r=0.891$, $P = 0.0001$ and $r = 0.832$, $P = 0.0001$, respectively).

In all the treatments rumen ammonia-N concentrations increased rapidly after administration, and peaked ca. 2 h after administration (untreated urea) or 6 h after administration (Product I - IV), and declined relatively slowly over the next 8 h. The blood urea nitrogen concentration showed a distinct lag period of about 2 h, before

increasing. This is in agreement with observations by others that changes in blood urea-N concentration follow increases and decreases in the rumen-ammonia-N level ranging from 2 h (Lewis *et al.,* 1957) to 4 - 6 h (Lewis, 1957). BUN values resulting from product I - IV differed significantly ($P < 0.05$) from that of urea, and reached peak values that ranged between 12.3 – 16.3 mg/100 ml for uncoated urea.

This would suggest that rumen $NH_3$-N originating from uncoated urea hydrolysis was abundant and absorbed rapidly into the blood, while the slower release of urea from the coated products resulted in $NH_3$ levels that were apparently used more efficiently by rumen microbes.

No significant differences occurred between the SRU products. There was a significant difference in the time at which peak BUN concentrations were reached. Product II and untreated urea differed significantly ($P < 0.05$) from the rest of the treatments, reaching a peak at 6.6 h and 7.3 h respectively vs. 22.7 h, 17.3 h and 16.7 h respectively for products I, III and IV (Table 2). The latter three treatments did not differ significantly from each other ($P > 0.01$).

Based on results with sheep, Preston *et al.* (1965), suggested that BUN concentrations in excess of 10 mg/100 ml indicated protein wastage. With finishing steers, maximum performance was associated with BUN concentrations of 7 to 8 mg/100 ml. For growing steers, BUN levels between 11 and 15 mg/100 ml were associated with maximum rates of gain, leading Byers and Moxon (1980) to suggest that BUN levels associated with maximum performance may be higher for growing cattle than for finishing cattle. Figure 2 indicates that in terms of protein adequacy all the treatments are indicative of a certain level of protein wastage, although it is far less excessive for the SRU's than untreated urea.

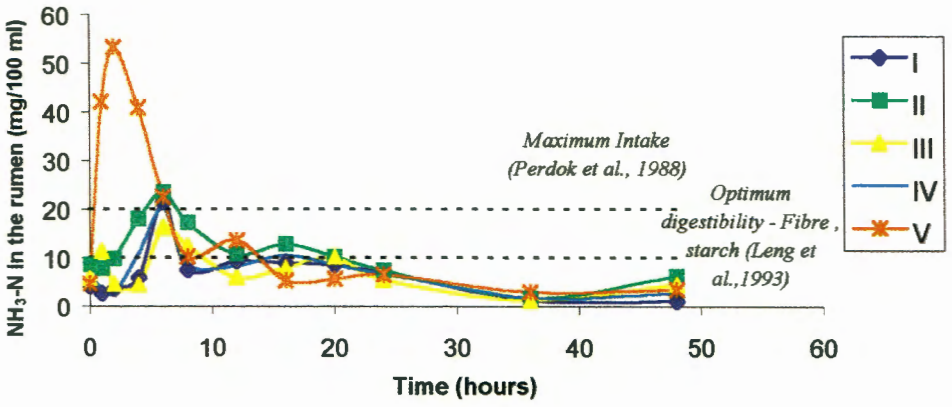


**Figure 1 Ruminal ammonia nitrogen levels of fistulated wethers administrated SRU or urea directly in the rumen.**

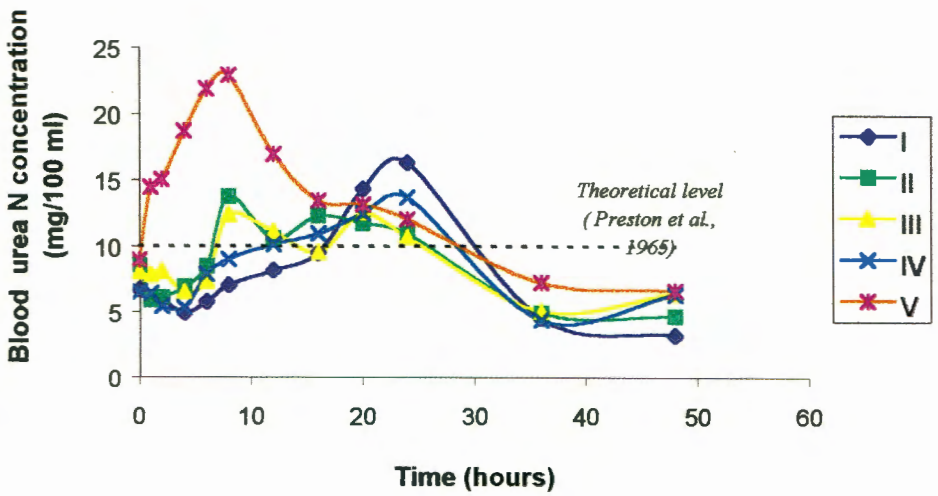


**Figure 2 Blood urea nitrogen levels of fistulated wethers administrated urea or SRU directly in the rumen.**

### *3.4.3 Ruminal pH*

Changes in ruminal pH over time were similar for all treatments (Figure 3) and no significant differences were found. Koeln *et al.* (1985b) found that under conditions of controlled feeding, ruminal pH values may be higher during the first 2 h post feeding for animals fed urea diets. This corresponds with data found in our study.

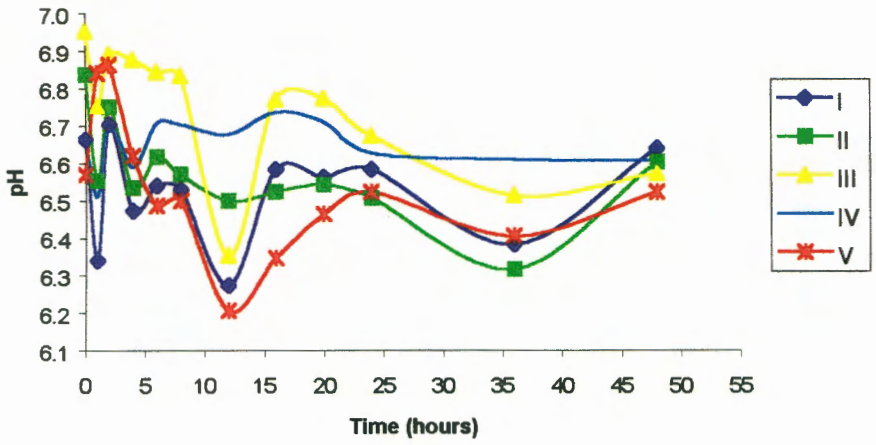


**Figure 3 Changes in ruminal pH of wethers during 48 hours postfeeding.**

According to Lewis (1960) there is a direct relationship between rumen pH and rumen ammonia- and BUN concentration. An increase in pH enhances the conversion of $NH_4^+$ to $NH_3^+$ ($NH_4^+ \longrightarrow NH_3 + H^+$), which is quickly absorbed into the blood stream. Ammonia toxicity was noticed when rumen ammonia concentration reached a value of 176 mg/ 100 ml or BUN reached 0.4 mg/100 ml. At rumen pH values of 8.0 and higher, the BUN rises considerably (Lewis, 1960). Coombe *et al.* (1960), however postulated that at pH values 7.3 and lower, a high rumen ammonia concentration is not necessarily toxic. pH values in our study were well below 7.3.

## 3.5 Conclusions

This study indicated that the encapsulation of urea prills with a copolymer of urea formaldehyde resin and a short oil alkyd was effective in decreasing the rate ammonia release from urea, for up to six hours after administration of the products in the rumen. No significant differences between the different encapsulated products were observed. The effect of feeding polymer coated urea on certain rumen and blood parameters in sheep is discussed in a following paper. It is also suggested that further research on the subject is focussed on the encapsulation of urea prills with the same copolymer. Only ammonia production was measured in this study and no measurements of ammonia utilisation were undertaken. It is suggested that in a next approach a nitrogen balance with the respective products should also be tested. The use of mixtures of products including untreated urea is also warranted.

# Chapter Four

## 4 EFFECT OF FEEDING POLYMER COATED UREA ON CERTAIN RUMEN AND BLOOD PARAMETERS IN SHEEP

**E. Upton, C.W. Cruywagen, R. Sanderson[1] and J. Coetzee[2].**

Department of Animal Sciences and [1]Institute for Polymer Science, University of Stellenbosch, Stellenbosch, 7600 South Africa

Several attempts of encapsulating urea prills with various forms of coatings to sustain the release of ammonia, have been attempted in the past. This is true for both the ruminant nutrition industry and the fertiliser industry (Johnson, 1976; Christianson, 1988; Salman, 1988; Peacock *et al.*, 1992). Research has always been motivated by the assumption that the major process of sustaining urea release was that to shield the urea from solution in an aqueous media. Once the coating was dissolved or penetrated by the media into which it was submerged, the urea was immediately hydrolysed (Johnson, 1976). The main coating variable that affected the release rate of ammonia from coated products was found to be the coating weight of the encapsulation. It was found that, as the total coating weight increased, the dissolution decreased. This led to the idea of developing a slow-release urea supplement, consisting of a mixture of polymer-coated urea prills comprising of different coating weights, in order to support a constant $NH_3$-N throughout the day (Upton *et al.*, 1999a).

In a previous experiment, the authors (Upton *et al.,* 1999b) managed to sustain the ammonia release from polymer encapsulated urea prills for up to 6 hours in the rumen of fistulated sheep and keeping it above a certain critical level for a considerable part of the day. Although there was no significant difference between a coating weight of 44 % or 56 % a trend towards slightly better results for the 56 % coating was observed. These results, obtained after administrating coated and untreated urea directly into the rumen, motivated the present study in order to determine if development to a marketable product was merited.

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[2] Current address: Voermol Feeds, Maidstone, PO Box 13, 4380

The aim of this study was to examine the response of rumen ammonia nitrogen and blood urea nitrogen (BUN) levels of wethers, after feeding polymer encapsulated urea prills and untreated urea.

Four Dohne Merino wethers (5 years of age) were used in the trial. The experiment was a 2 x 2 Latin square design. Sheep received the experimental diets for 10 days prior to the next experimental period to avoid possible carry over effects. Animals were kept on a basal diet of wheat straw (< 3 % crude protein) *ad lib.* maize meal (200 g) and molasses syrup (6 g/day). During each trial, the animals were adapted to urea at a level of 3 g/urea per day for 10 days up to 15 g urea per day. During the trial, animals orally received a slow release urea (SRU) product (coating weight 56 %) equivalent to urea 0.4 g urea per kg body weight (20 g, 20.6 g, 20 g and 22.8 g urea for animals A, B, C and D respectively). Rumen liquor and blood samples were taken at 0, 1, 2, 4, 6, 8, 12, 16, 20, 24, 36 and 48 hours after oral intake of the different diets. The experimental design is indicated in Table 1.

**Table 1 The experimental design for used to determine the effect of feeding polymer coated urea on certain rumen- and blood parameters in sheep**

| PERIOD | A | B | C | D |
|---|---|---|---|---|
| I | SRU | SRU | Urea | Urea |
| II | Urea | Urea | SRU | SRU |
| III | *K | K | K | K |

* Control – No urea added

During a preceding trial, difficulty was experienced with the ingestion and palatability of the SRU products, probably due to the strong formaldehyde and butanone odor still present from the urea formaldehyde resin used to encapsulate the urea prills. This was overcome by baking the product at 80 °C for 24 h. In order to stimulate intake, no wheat straw was fed from 14:00 on the day preceding the first period of the trial. This led to acute toxicity in one of the animals receiving untreated urea. Animals receiving only the supplement containing maize meal, treated urea and

molasses syrup experienced no toxicity symptoms. The patterns of mean rumen ammonia nitrogen and blood urea concentrations, over time are presented (Figures 1 and 2) and the mean values (± s) in Tables 2 and 3. The mean rumen ammonia-N values differed between treatments, reaching a peak of 66.9 mg N/100 ml for urea vs. 17.5 mg N/100 ml for the SRU-product (Table 2). Time when maximum concentration was reached also differed. Urea peaked at 2 hours after feeding while the SRU-product peaked 6 hours after feeding the SRU treatment. BUN followed a similar curve with peak values of 16.7 mg N/100 ml for urea vs. 13.3 mg N/100 ml for the SRU-product (Table 3). Time to reach maximum BUN also differed between treatments (6 h vs. 24 h). Both the rumen- and blood ammonia nitrogen curves of the control treatment were lower than that of the other treatments for the trial. The relative order of magnitude of ruminal ammonia N concentration was in close agreement to concentrations found when administrating the treatments directly into the rumen (Upton *et al.,* 1999b). The maximum mean ammonia values were, however, lower when compared to values obtained during the previous trial, in spite of higher levels of urea fed. This is probably due to the more gradual intake of the products when provided via the feed.

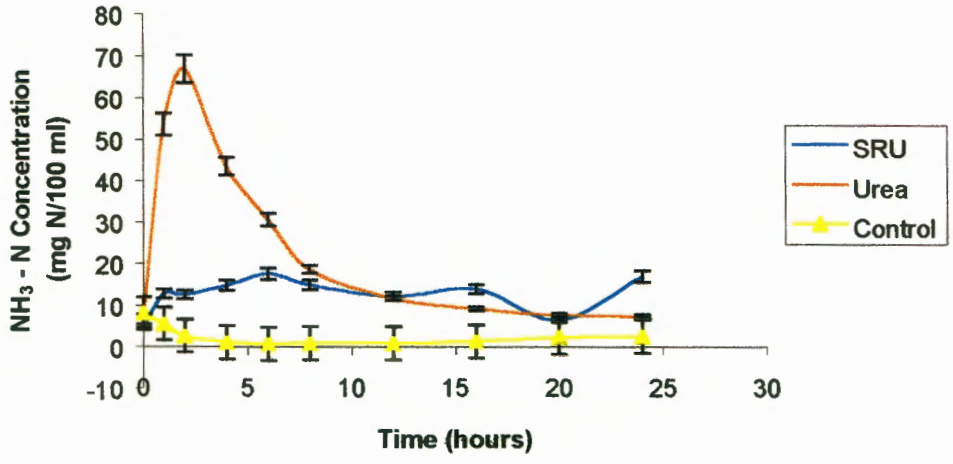


**Figure 1 The mean rumen $NH_3$-N concentration for weathers fed polymer coated urea, untreated urea and a N-free supplement (Control).**

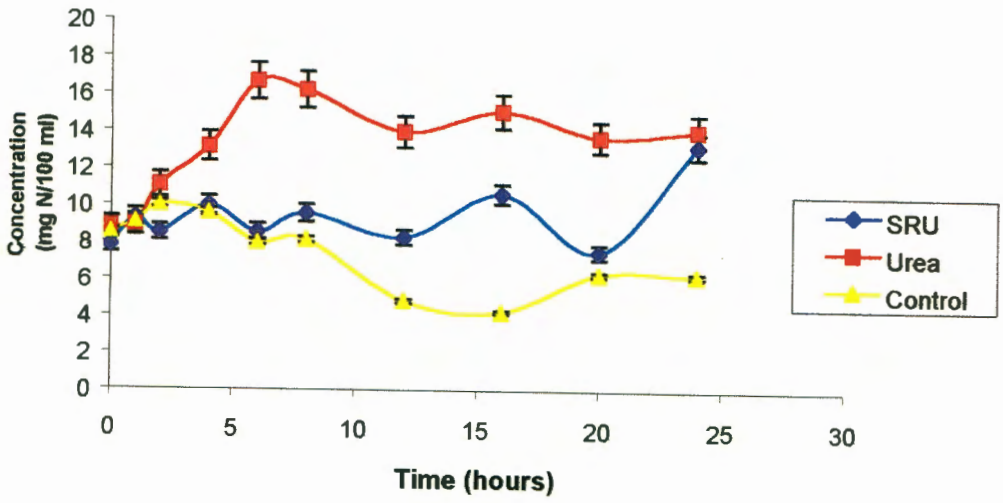


**Figure 2** **Blood urea nitrogen (BUN) for wethers fed polymer-coated urea (SRU), untreated urea (Urea)and a N-free supplement (Control).**

**Table 2 The mean rumen ammonia levels for sheep fed polymer coated and untreated urea**

| Treatment | Time (hours) | n | Mean (mg N/100 ml) | SE |
|---|---|---|---|---|
| Polymer-coated | 0 | 4 | 5.0 | 0.79 |
| urea | 1 | 3 | 12.7 | 2.25 |
| | 2 | 3 | 12.5 | 1.46 |
| | 4 | 3 | 14.7 | 4.30 |
| | 6 | 4 | 17.5 | 4.01 |
| | 8 | 4 | 14.8 | 2.29 |
| | 12 | 4 | 12.0 | 2.92 |
| | 16 | 4 | 13.8 | 2.34 |
| | 20 | 3 | 8.5 | 2.44 |
| | 24 | 4 | 16.9 | 5.54 |
| Untreated urea | 0 | 4 | 7.4 | 1.75 |
| | 1 | 3 | 53.5 | 8.3 |
| | 2 | 3 | 66.9 | 7.86 |
| | 4 | 3 | 43.4 | 1.14 |
| | 6 | 3 | 30.5 | 5.35 |
| | 8 | 3 | 18.5 | 5.05 |
| | 12 | 3 | 11.6 | 3.49 |
| | 16 | 3 | 9.0 | 2.44 |
| | 20 | 3 | 7.6 | 1.5 |
| | 24 | 3 | 7.2 | 1.68 |
| Control | 0 | 4 | 7.9 | 1.77 |
| | 1 | 4 | 5.4 | 0.95 |
| | 2 | 4 | 2.5 | 1.01 |
| | 4 | 4 | 1.0 | 0.50 |
| | 6 | 4 | 0.6 | 0.31 |
| | 8 | 4 | 0.7 | 0.12 |
| | 12 | 4 | 0.7 | 0.10 |
| | 16 | 4 | 1.2 | 0.56 |
| | 20 | 4 | 2.1 | 1.01 |
| | 24 | 4 | 2.4 | 0.74 |

**Table 3 The mean blood urea nitrogen (BUN) of the two treatments**

| Treatment | Time (hours) | n | Mean (mg N/100 ml) | SE |
|---|---|---|---|---|
| Polymer-coated Urea | 0 | 4 | 7.8 | 1.70 |
| | 1 | 3 | 9.3 | 2.66 |
| | 2 | 3 | 8.5 | 2.13 |
| | 4 | 3 | 9.9 | 3.11 |
| | 6 | 4 | 8.5 | 1.37 |
| | 8 | 4 | 9.6 | 1.53 |
| | 12 | 4 | 8.3 | 1.10 |
| | 16 | 4 | 10.6 | 2.39 |
| | 20 | 3 | 10.0 | 2.16 |
| | 24 | 4 | 13.3 | 1.87 |
| Untreated urea | 0 | 4 | 8.8 | 0.98 |
| | 1 | 3 | 8.9 | 0.82 |
| | 2 | 3 | 11.1 | 0.95 |
| | 4 | 3 | 13.1 | 1.15 |
| | 6 | 3 | 16.7 | 2.02 |
| | 8 | 3 | 16.2 | 3.14 |
| | 12 | 3 | 14.0 | 1.02 |
| | 16 | 3 | 15.1 | 2.13 |
| | 20 | 3 | 13.7 | 1.35 |
| | 24 | 3 | 14.1 | 2.06 |
| Control | 0 | 4 | 8.4 | 2.32 |
| | 1 | 4 | 9.0 | 1.93 |
| | 2 | 4 | 10.0 | 2.38 |
| | 4 | 4 | 9.6 | 2.75 |
| | 6 | 4 | 7.9 | 2.74 |
| | 8 | 4 | 8.1 | 2.70 |
| | 12 | 4 | 4.8 | 1.57 |
| | 16 | 4 | 4. | 0.84 |
| | 20 | 4 | 6.2 | 4.83 |
| | 24 | 4 | 6.2 | 3.68 |

Although the oral administration of the coated product shows potential as a slow-release supplement for ruminants, more information is required. It does, however, appear as if mastication did not have an effect on the results, when compared with data obtained from the study where administration was directly into the rumen. Results from this study did not address potential differences in palatability or

performance when different levels of the SRU-product were supplemented. Subsequent information regarding effects of inclusion of SRU–products with different coating weights vs. that of untreated urea is needed for complete evaluation of the potential use of the SRU. It is concluded that benefits of polymer coated urea include, lower peak rumen ammonia and blood urea nitrogen levels, with the potential to decrease toxicity, increase N-utilisation and being a longer lasting product, thus requiring less frequent supplementation. The latter is of the utmost importance since high labour costs, large flocks and farms, and extensive farming impede the supplementation of licks at short time intervals (every 2 to 3 days). Longer intervals (every 7 to 14 days) therefore become more popular and practical.

# Chapter Five

## 5 General Conclusions

In conclusion, this research demonstrated that the polymeric encapsulation of urea to reduce its dissolution rate in the rumen has potential to be a useful slow-release NPN supplement and merits further research and development. Amino/alkyd or polyester blends are among the cheapest of the modern synthetic systems and are considered because it is non-toxic, low-cost, biodegradable and easy to manufacture. Results showed that variations in individual pellet coating thickness and uniformity within a slow-release compound will provide N release over an extended period. Ammonia nitrogen release was found to be dependent on coating thickness, and coating constitution - the most effective coating consisting of an alkyd percentage of 70 % and a coating weight of 125 g/100 g urea.

The encapsulated products effectively decreased the rate of ammonia release from urea for up to six hours after administration of the products directly into the rumen. This sustained release of urea will probably reduce the risk of toxification. The encapsulation also has the advantages that it reduces the hygroscopic nature of urea and increases its crushing strength, thereby improving handling and storing characteristics. Furthermore it also has the potential to improve the palatability of urea. Additionally it is suggested that future research should examine the optimisation of the coating by finding ways to release fatty acids from the alkyd component and further nitrogen release from the amino resin component of the copolymer used in our study.

It is suggested that the release of urea from coated prills should be predictable, to enable efficient utilisation of the product's slow-release characteristics. It must be the objective of future studies to develop and experimentally evaluate a mathematical model to make this possible. Intake, digestibility, N-balance- and palatability studies and production performance should be performed to evaluate slow-release compounds properly.

The fact that no controlled release urea products economically suitable for livestock use are yet commercially available attests to the difficulty of the task of combining technical, agronomic and economic feasibility into a single product. According to Russell & Hespell (1981), individual scientists must take on an increasingly more holistic outlook in their research. This stems directly from the tremendous increase of scientific knowledge over the last few decades that has brought into focus how little we really know and how complex biological processes are. However, a holistic approach will require individual scientists to develop a greater interaction, understanding, and expertise in one or more additional disciplines. For the rumen there must be high degrees of interactions between nutritionists, microbiologists and polymer scientists all of which must have some relative competence in each other's field.

As long as ruminants possess their unique ability to utilise NPN as a protein substitute, as well as cellulosic materials for an energy source and man and animal are in competition for energy and protein needs, NPN use and maximisation will merit economic consideration.

# Chapter Six

## 6 REFERENCES

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