HANDLING AND DISTRIBUTING UREA

For Presentation at

Soil Fertility Shortcourse

Sponsored by

South Carolina Plant Food Educational Society
and
Clemson University, College of Agricultural Sciences
November 29, 30 and December 1, 1983

by

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Introduction

The term organic chemistry was used before 1828 when organic compounds were believed to be produced only in living organisms and contained a vital force. In 1828 the chemist, Frederick Waller, was able to form from purely inorganic salts a substance, urea, which had long been known as a product of human metabolism and a normal component of urine. Waller was trying to make ammonium cyanate from lead cyanate and ammonia (1). But, as is the case in so many great discoveries, he found something else. He performed the first organic synthesis by producing urea. Waller's discovery not only gave us one of our leading nitrogen fertilizers but started the whole science of synthetic organic chemistry.

Urea has come a long way since Waller's discovery. Its advantages over other nitrogen fertilizer compounds have caused its use to increase dramatically. In 1933, 800 tons of urea was produced, all by DuPont. In 1981 production of solid urea in the United States exceeded 4.3 million tons, almost eight times greater than production in 1965 (2). Urea has emerged as the leading solid nitrogen material in the U.S., and far exceeds other nitrogen materials in world trade. As new large-scale nitrogen production units are built throughout the world, urea will continue to increase its market share.

Reasons for Growth of Urea

Several important advantages of urea over other nitrogen sources account for urea's present and expected future growth. It can be made with less pollution and fewer problems than can ammonium nitrate, the principal competing nitrogen material. There are problems in producing high-strength (+65%) nitric acid, a necessary intermediate for production of solid ammonium nitrate, and in preventing excessive emission of polluting fumes (nitric oxides). Also an aerosol is produced during prilling of ammonium nitrate which is difficult to remove from the prilling tower effluent.

Urea is synthesized according to the following chemical reaction:

$$\overset{\text{Ammonia}}{2NH_3} + \overset{\text{Carbon Dioxide}}{CO_2} \xrightarrow[\text{Heat}]{\text{Pressure}} \overset{\text{Urea}}{CO(NH_2)_2} + \overset{\text{Water}}{H_2O}$$

The carbon dioxide is a byproduct of ammonia production, thus making urea a natural supplement to ammonia production and leading to economies that make urea one of the lowest cost nitrogen sources.

Urea has other advantages. Urea is neither explosive nor a fire hazard. Thus, it can be shipped by inland waterway whereas this cannot be done routinely with ammonium nitrate.

Urea is also less corrosive than most other fertilizer compounds. TVA tests show that the corrosion rate for uninhibited ammonium nitrate solution is much greater than that of urea solution. While the corrosion rates of solution probably do not exactly match those of solids, the ratios of the rates should be about the same. In storage the wettest granules are usually those on the top and sides of the pile next to the building walls and bulkheads. This advantage of urea is important because many blenders (especially small blenders) insist on storing bulk fertilizer in galvanized steel buildings regardless of instructions to the contrary. Corrosion rates are also lower on carbon steel elevators, conveyors, applicators, and other metal equipment.

Urea contains the highest percentage of plant food of any solid nitrogen source. More nitrogen can be stored or shipped in a given volume as urea than any dry nitrogen material except very high density ammonium nitrate prills (about equal). The bulk densities and plant food contents of several dry materials, including urea, are shown in table 1.

Another advantage of urea is its relatively high critical humidity. Figure 1 gives the critical relative humidities of several fertilizer compounds and mixtures of these compounds. The critical relative humidity of urea is 75.2 percent. The critical relative humidity of ammonium nitrate is 59.4 percent. However, even 75.2 percent is low for high humidity areas and special precautions need to be observed when urea is stored in bulk in these areas.

Size Problems

Nonsegregating bulk blends can only be made from raw materials with well matched particle size distributions (3). Diammonium phosphate (DAP) and granular potash are the most used materials in bulk blends and the size of urea pellets for blending should closely match the size of these two materials. Figure 2 compares the particle size of ureas with DAP. The diammonium phosphate curve represents the average particle size of DAP in the United States as determined in a 1973 survey by The Fertilizer Institute.

The particle size of urea has been a problem. Development of granular urea was a partial answer to the particle size problem, but there appears

Material	Canadian Size Guide Number
Diammonium phosphate	215[a]
Granular potash	240[b]
Urea A (prilled)	150[a]
Urea B (granulated)	260[a]
Urea C (TVA pan granulated)	210[a]
Urea D (TVA falling curtain)	215[c]
Urea G (commercial prilled)	220[d]

a. TVA Publication Z-146
b. TVA Bulletin Y-147
c. TVA Falling Curtain Urea Description
d. Commercial data

The closer the size guide number of the raw materials the lower the probability of segregation. Urea "A" and granular potash would not make a good blend.

No fertilizer organization in the United States has adopted the size guide number; however, similar systems are being discussed. Use of the SGN system in Canada is voluntary.

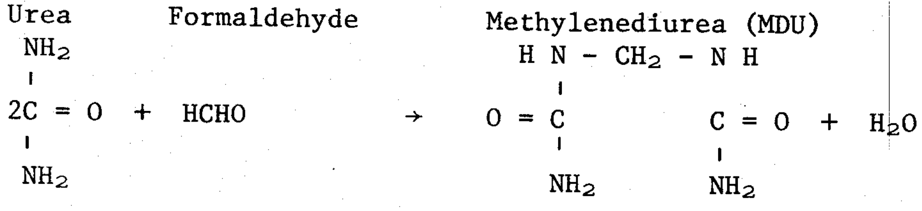
Most raw material suppliers will provide an average screen analysis of their product. However, there is usually variation between shipments of material. A dealer having trouble with analysis should check the materials by running his own screen analysis. A description of a good method for running screen analysis is given in the "Proceedings of TVA Fertilizer Bulk Blending Conference, August 12, 1973." Copies of this publication are available from the TVA Technical Library, Muscle Shoals, Alabama 35660.

Mechanical Strength

Most urea prills still have some mechanical weakness and can be degradated during handling and can be broken by high speed applicator fans (5). If urea pellets in a blend are broken during application, streaks of lush growth will while unbroken granules are spread more evenly. Granule hardness gives some indication of tendency to break during application. Another test is the impact test where the pellets are thrown against a hardened steel plate. Little information is available on the impact strength and hardness of urea granules; however, the producer of urea G, mentioned above, indicates its impact resistance is 90 percent.

Small amounts of formaldehyde are added to most urea as a hardener and a conditioning agent. Manufacturers should be encouraged to make their products as hard and as impact resistant as possible.

As a result of questions about health hazards related to use of formaldehyde (6), The Fertilizer Institute (TFI) studied the problem and determined that formaldehyde reacts immediately and irreversibly with molten urea to form principally methylenediurea (MDU), which is the true conditioning agent in the finished product. TFI recommended that industry change its traditional reference of percent formaldehyde conditioning agent to percent MDU by multiplying the percent formaldehyde value by the factor 4.4 (6). The chemical reaction which occurs between urea and formaldehyde to form MDU is shown below.



$$\underset{\text{Urea}}{2\,\mathrm{NH_2-C(=O)-NH_2}} + \underset{\text{Formaldehyde}}{\mathrm{HCHO}} \rightarrow \underset{\text{Methylenediurea (MDU)}}{\mathrm{NH_2-C(=O)-NH-CH_2-NH-C(=O)-NH_2}} + \mathrm{H_2O}$$

Chemical Compatibility

One of the major nonagronomic problems with urea is its incompatibility with ammonium nitrate and other nitrates. Mixtures of ammonium nitrate and urea form an adduct that makes the mixture more soluble than either compound alone. This is helpful in production of urea-ammonium nitrate solution but causes difficulty in a blend of the two as solids. As shown in figure 1, the combination in solid form has a critical relative humidity of 18 percent at 86°F. This means that the mixture will absorb moisture under almost any conditions and that the two compounds must be kept apart.

The usual advice for companies planning to use both urea and ammonium nitrate is to keep them as widely separated as possible and to be absolutely certain that the compounds do not become mixed. Cases can be cited where urea and ammonium nitrate have been stored successfully in the same building, but it can be assumed that sooner or later they will become mixed. Mixing has occurred by movement of dust through the air, dribbling from conveyor belts onto piles below, and inadvertent return of surplus material by a front-end loader driver to the wrong pile. The only reliable solution is to limit the nitrogen source to either urea or ammonium nitrate.

Urea also has only limited compatibility with normal and triple superphosphate. Widely varying results have been reported from the blending of urea with granular superphosphate. Occasionally a reaction occurs which releases water of hydration from the superphosphates, wetting the mixture and causing it to become soggy and unusable. The reaction which occurs is shown below.

$$CaH_2(PO_4)_2.H_2O + 4CO(NH_2)_2 \rightarrow CaH_2(PO_4)_2.4CO(NH_2)_2 + H_2O$$

This is usually no problem if material is taken directly to the field and applied; however, serious results can occur if such a mixture is bagged. Sometimes this reaction does not occur and until recently it was not known why some mixtures became wet and others did not. Work at TVA shows that some granular superphosphates have less water of hydration than others and that they mix better with urea than do those with high water of hydration.

Good drying will produce superphosphate with low water of hydration. If a problem occurs, discussion with the supplier of the superphosphate or change of superphosphate source may solve the problem. Even well dried superphosphate can pick up water of hydration from the atmosphere and some protection from the atmosphere is in order during long storage. Ceilings and roll-up fronts for storage bins prevent air circulation and are effective ways of preventing moisture absorption. If this is not practical, covering the pile with a sheet of plastic is helpful.

Bin closures and plastic sheets are also effective in keeping urea dry. Except under the most extreme conditions, only the top 6 to 8 inches of urea will become wet. But even this can be a nuisance and result in the loss of considerable urea during long-term storage. Completely dehumidified bulk blend plants have been built. This is not as expensive as it sounds because only enough dehumidification is required to keep the relative humidity inside the building below the critical relative humidity of the most sensitive material. The building must be tight and pressured slightly so that air will flow from the building through openings rather than moist air flowing into the building. Of course the tighter the building the less dehumidification is required. Dust control and other pollutants can be a problem in a closed building. If personnel is required to work in the building, dust and gases (such as carbon monoxide) should be monitored closely.

TVA built a dehumidified bulk storage building for about 20,000 tons of granular fertilizer, including urea, in 1966. In the original design humidity was controlled and the building pressurized with dehumidified air from ten 5-ton refrigeration units. Operation of this building in Muscle Shoals, Alabama, where the average relative humidity is fairly high, reveals that under the worst conditions only five of these units were required and during periods of low relative humidity all machines are frequently off. In 1981 this building was expanded and now stores 30,000 tons. It is being dehumidified with four of the original air conditioners.

It is estimated that the cost for such an installation would be about $1 per ton of fertilizer stored. The average bulk blend plant could probably install a satisfactory unit for less.

Another disadvantage of urea is that it contains biuret. The effect of biuret on crops is an agronomic problem and will not be covered in detail here. However, choice of urea with a low biuret content should be considered. Although most urea produced in the United States does not contain enough biuret to be harmful to the soil, foliar spray made from urea with a high biuret content can be harmful to some crops. Table 2 lists the biuret content of samples of urea from several different sources.

Other Urea Fertilizers

TVA is producing 28-28-0 and 35-17-0 grades of urea-ammonium phosphate by combining urea melt with freshly made ammonium phosphate slurry and granulating the mixture. This has the advantage of providing a high nitrogen fertilizer combined with phosphate in a nonsegregating mixture. A 19-19-19 grade, which is mostly a nonsegregating blend, can be made by combining 28-28-0 with potash. The 35-17-0 is especially productive on rice in the west, and commercial companies have started to produce similar products using the TVA pipe-cross reactor. A company in California produces a 32-16-0 grade and a company in Arizona is interested in producing a 30-15-0 grade containing sulfur.

The tendency of urea and ammonium nitrate to form a highly soluble adduct is highly advantageous when making a nitrogen solution. The nitrogen content of a solution made entirely with urea is 18.7 percent with a saturation temperature of 32°F. The maximum from ammonium nitrate alone is 19 percent nitrogen. However, if the two are combined in proper proportions, a 32 percent nitrogen solution can be made with about the same saturation temperature.

As the supply of urea is increased it is likely that its use as a supplemental nitrogen source in liquid fertilizers will increase. Urea-ammonium nitrate solution is the major source of supplementary nitrogen in liquid fertilizer but the ammonium nitrate in this solution lowers the plant food content of many formulations containing potash. Ammonium nitrate reacts with the potash in liquid fertilizers to produce potassium nitrate and ammonium chloride. Potassium nitrate is relatively insoluble at ordinary temperatures and its presence in liquid fertilizers raises the salt-out temperatures and lowers the nutrient contents of grades produced. Urea does not react with potash, and potash containing grades made with urea as a supplementary nitrogen source usually contain more nutrients than grades made with urea-ammonium nitrate solution. This is clearly shown in figure 5 where the salt-out temperature of the 14-7-7 grade is lowered from 80°F to 10°F by substituting urea for urea-ammonium nitrate solution. As indicated, a small amount of ammonium nitrate can be added before it begins to react with the potash and affects these salt-out temperatures. If ammonium nitrate is added to lower the salt-out temperature further, care must be taken not to add too much.

Using urea as supplementary nitrogen in fluid fertilizers requires handling another solid. But since the trend is to use all solids in fluid fertilizer plants to lower freight costs and to obtain lower cost raw materials, handling one more solid should present no problems.

Another product still being studied is urea phosphate. This dry white crystalline material contains 17.7 percent nitrogen and 44.9 percent P_2O_5. Relatively pure urea phosphate crystallizes from mixtures of urea and wet-process acid. About 10 percent of the impurities stay with the urea phosphate and 90 percent remain in the byproduct liquor. The byproduct liquor can be used to produce suspensions or solid fertilizer. Controlled pyrolysis of urea phosphate yields mixtures of urea and short chain ammonium polyphosphates. The pyrolyzates are highly soluble and are suitable for a conversion to ammonium polyphosphate liquid fertilizers. These properties of urea phosphates suggest a low energy consuming process for converting wet-process phosphoric acid into clear polyphosphate containing liquid fertilizer from which most of the impurities have been removed.

If the water is not removed from the impure urea phosphate adduct, it can be used as a fluid fertilizer. (A patent has been issued, however, on using the adduct this way.) The mixture has a low pH but can be successfully applied with corrosion resistant equipment. Because of the low pH, impurities and micronutrients not normally soluble in fluid fertilizers are soluble in this fluid. Potash and sulfuric acid can be added to the mixture. Sulfuric acid is added as a sulfur source.

Urea also forms an adduct with sulfuric acid. Urea-sulfuric acid mixtures, such as that shown by the formula below, have been made. Mixtures made by this process have also been patented.

Grade: 30-0-0-31.7S

Raw Material	Lb/Ton Product
Urea (46-0-0)	1217
Sulfuric acid (96.9%)	783

This fluid can be handled in corrosion resistant equipment. Both of these mixtures, however, should be handled with caution because they can cause skin and eye damage.

Pilot-plant studies also indicate that urea phosphate may have other unique and useful applications for which a high degree of purity is not necessary. For example, urea phosphate has been shown to have agronomic advantages as a solid fertilizer either alone or in a mixture with urea. It is believed that the acidic nature of the material reduces nitrogen loss from coapplied urea (7)(8). In this process urea and phosphoric acid are reacted as before. The crystals, however, are not separated from the mother liquor, but are granulated together using a process where air is blown into a reactor. Acid is added along with urea which is added as either a solid, a melt, or solution. Air is also blown into a drum granulator where the granules are formed and into a dryer where the product is dried. No cooling is required. The final product is a 16-41-0 grade granular urea phosphate or, if extra urea is added, the grades can have higher nitrogen and lower phosphate ratios.

Urea is also a major ingredient in many controlled release fertilizers, such as TVA sulfur-coated urea. With proper production techniques the thickness of the coating on the granules can be controlled so that as the sulfur decomposes a desired nitrogen release rate is obtained.

Urea also forms a polymer with formaldehyde. Until the advent of vinyls and other hydrocarbon based plastics, urea formaldehyde was familiar as the plastic used in light colored objects such as telephones and combs and is still used in many plastic items. In plastic items the urea nitrogen is not available but the amount of polymerization can be varied so that the nitrogen is available at controlled rates.

TVA has also combined urea melt with solid ammonium sulfate to make a compound containing 40 percent nitrogen and 4 percent sulfur. While only limited quantities of this product have been produced in the pilot plant, it appears to be a satisfactory fertilizer.

Conclusion

Urea properly used is an excellent fertilizer which has a wide range of physical and chemical properties useful in fertilizer production. Agronomic problems exist but they can be overcome by using well known techniques. There are some who because of agronomic limitations will not accept urea. There is little question that economics, safety and storability favor urea. Usually the farmer who buys a blend is only interested in top agronomic performance at lowest cost and only specifies a given ratio without regard to ingredients. This allows blenders to choose the most economical nitrogen source and an increasing number are choosing urea.

Most problems with urea have practical solutions. A major objective now is to convince the user that the problems can be overcome and to teach him how to overcome them.

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BULK DENSITIES OF COMMERCIAL FERTILIZERS

PRODUCT	USUAL GRADE	AVERAGE BULK DENSITY (LB/FT^3)
UREA		
PRILLED	46-0-0	45
GRANULAR	46-0-0	46
AMMONIUM NITRATE		
PRILLED		
HIGH DENSITY	33.5-0-0	58
LOW DENSITY	33.5-0-0	45
GRANULAR	33.5-0-0	46
UREA AMMONIUM PHOSPHATE	28-28-0	48
	34-17-0	48-50
UREA AMMONIUM SULFATE	40-0-0	45
AMMONIUM SULFATE	21-0-0	60
SULFUR-COATED UREA	36-0-0	45-47
DIAMMONIUM PHOSPHATE	18-46-0	55
MONOAMMONIUM PHOSPHATE	11-52-0	56
NORMAL SUPERPHOSPHATE	0-19-0	68
TRIPLE SUPERPHOSPHATE	0-45-0	66
POTASSIUM CHLORIDE		
GRANULAR	0-0-60	67
COARSE	0-0-60	68

TABLE I

Company	% Biuret	
	Granulated	Prilled & Crystalized
A	1.2	
B	1.2	
C	1.5	
D	1.5	
E		0.75
F		0.80
G		0.5
H		1.20

TABLE 2

	CALCIUM NITRATE	AMMONIUM NITRATE	SODIUM NITRATE	UREA	AMMONIUM CHLORIDE	AMMONIUM SULFATE	DIAMMONIUM PHOSPHATE	POTASSIUM CHLORIDE	POTASSIUM NITRATE	MONOAMMONIUM PHOSPHATE	MONOCALCIUM PHOSPHATE	POTASSIUM SULFATE
CALCIUM NITRATE	46.7											
AMMONIUM NITRATE	23.5	59.4										
SODIUM NITRATE	37.7	46.3	72.4									
UREA	—	18.1	45.6	75.2								
AMMONIUM CHLORIDE	—	51.4	51.9	57.9	77.2							
AMMONIUM SULFATE	—	62.3	—	56.4	71.3	79.2						
DIAMMONIUM PHOSPHATE	—	59°	—	62°	—	72°	82.8					
POTASSIUM CHLORIDE	22.0	67.9	66.9	60.3	73.5	71.3	70°	84.0				
POTASSIUM NITRATE	31.4	59.9	64.5	65.2	67.9	69.2	—	78.6	90.5			
MONOAMMONIUM PHOSPHATE	52.8	58.0	63.8	65.2	—	75.8	78°	72.8	59.8	91.6		
MONOCALCIUM PHOSPHATE	46.2	52.8	68.1	65.1	73.9	87.7	78°	—	87.6	86.8	93.7	
POTASSIUM SULFATE	76.1	69.2	73.3	71.5	71.3	81.4	77°	—	87.8	79.0	—	96.3

NOTE: VALUES FROM LITERATURE FOR PURE SALTS EXCEPT AS NOTED BELOW:
°APPROXIMATE VALUES OBTAINED BY TVA

CRITICAL HUMIDITIES OF FERTILIZER SALTS AND MIXTURES AT 86° F (VALUES ARE PER CENT RELATIVE HUMIDITY)

FIGURE I

CALCIUM NITRATE	AMMONIUM NITRATE	SODIUM NITRATE	UREA	AMMONIUM CHLORIDE	AMMONIUM SULFATE	DIAMMONIUM PHOSPHATE	POTASSIUM CHLORIDE	POTASSIUM NITRATE	MONOAMMONIUM PHOSPHATE	MONOCALCIUM PHOSPHATE	POTASSIUM SULFATE
46.7											
23.5	59.4										
37.7	46.3	72.4									
—	18.1	45.6	75.2								
—	51.4	51.9	57.9	77.2							
—	62.3	—	56.4	71.3	79.2						
—	59°	—	62°	—	72°	82.8					
22.0	67.9	66.9	60.3	73.5	71.3	70°	84.0				
31.4	59.9	64.5	65.2	67.9	69.2	—	78.6	90.5			
52.8	58.0	63.8	65.2	—	75.8	78°	72.8	59.8	91.6		
46.2	52.8	68.1	65.1	73.9	87.7	78°	—	87.6	86.8	93.7	
76.1	69.2	73.3	71.5	71.3	81.4	77°	—	87.8	79.0	—	96.3

NOTE: VALUES FROM LITERATURE FOR PURE SALTS EXCEPT AS NOTED BELOW:
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CRITICAL HUMIDITIES OF FERTILIZER SALTS AND MIXTURES AT 86° F (VALUES ARE PER CENT RELATIVE HUMIDITY)

FIGURE I

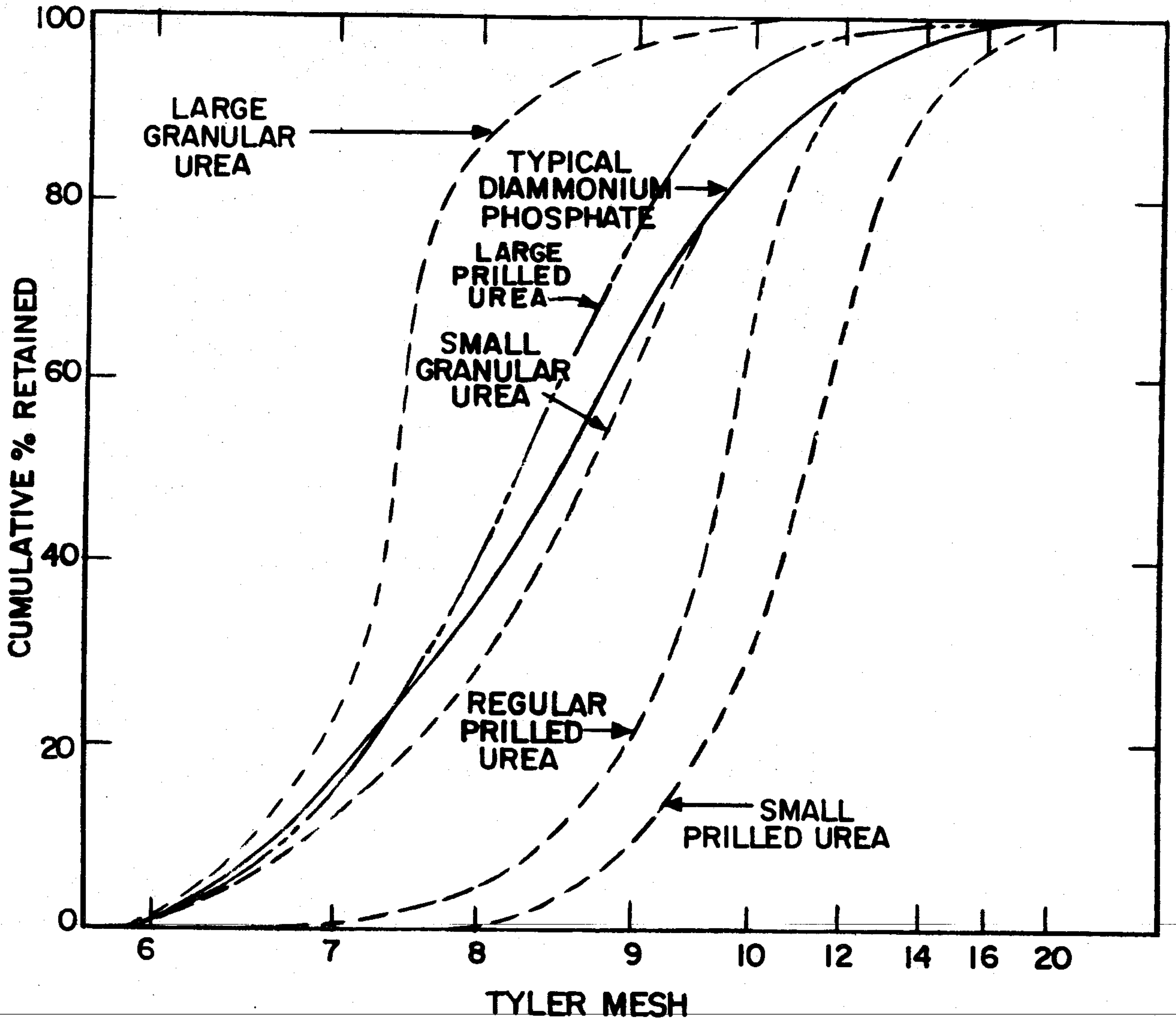


FIGURE 2

PARTICLE-SIZE DISTRIBUTION OF UREAS COMPARED WITH THAT OF TYPICAL DIAMMONIUM PHOSPHATE

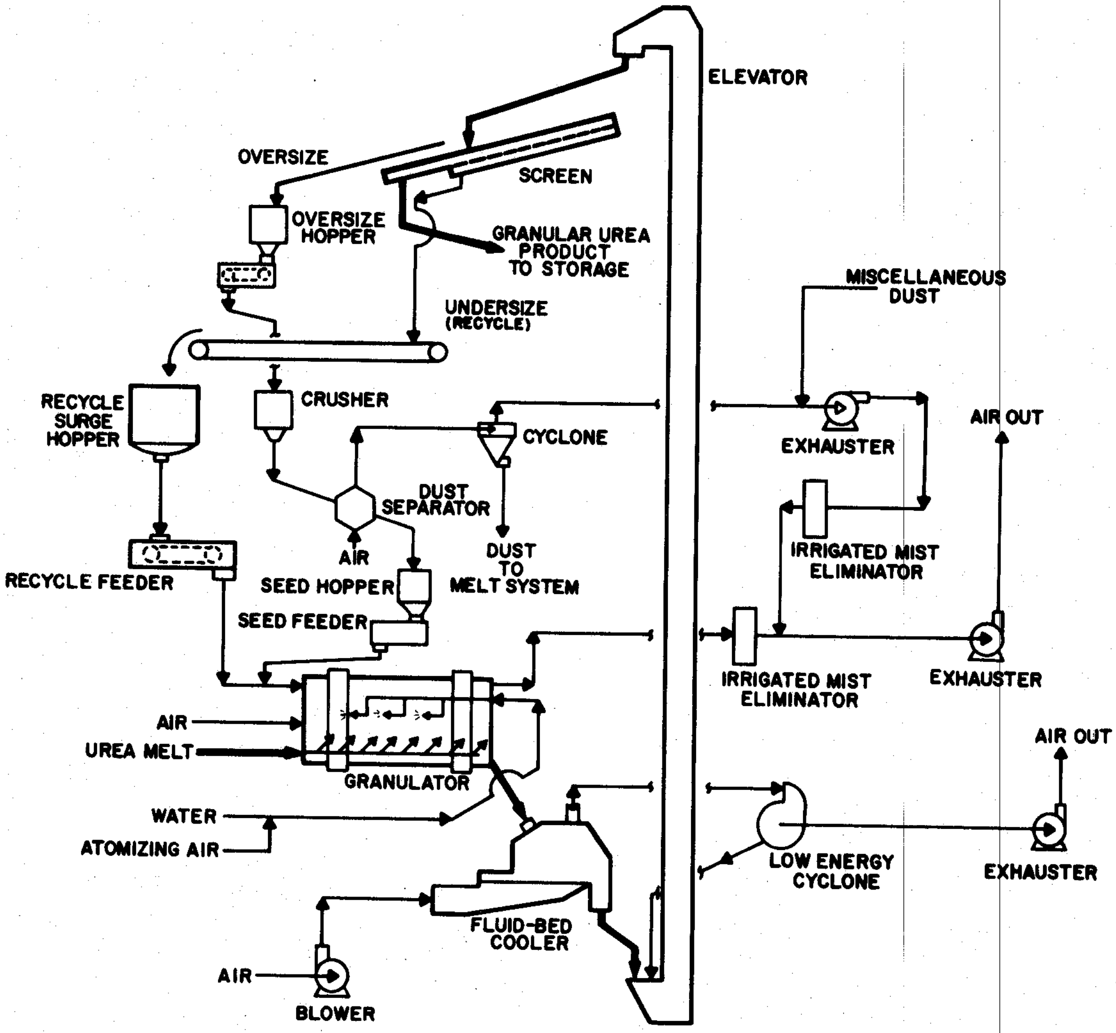
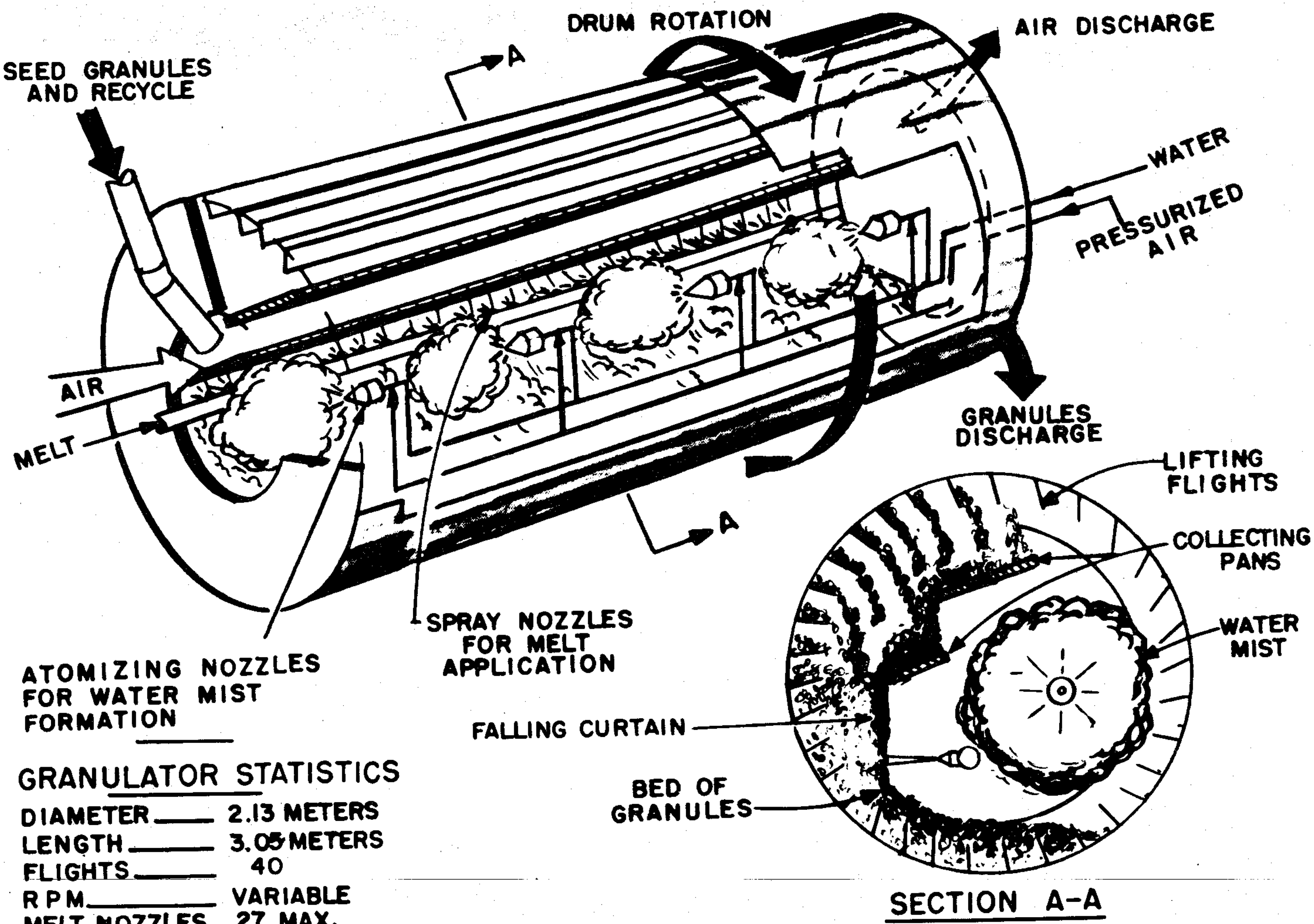


FIGURE 3

FALLING-CURTAIN GRANULATION PLANT USING EVAPORATIVE COOLING, FLOW DIAGRAM

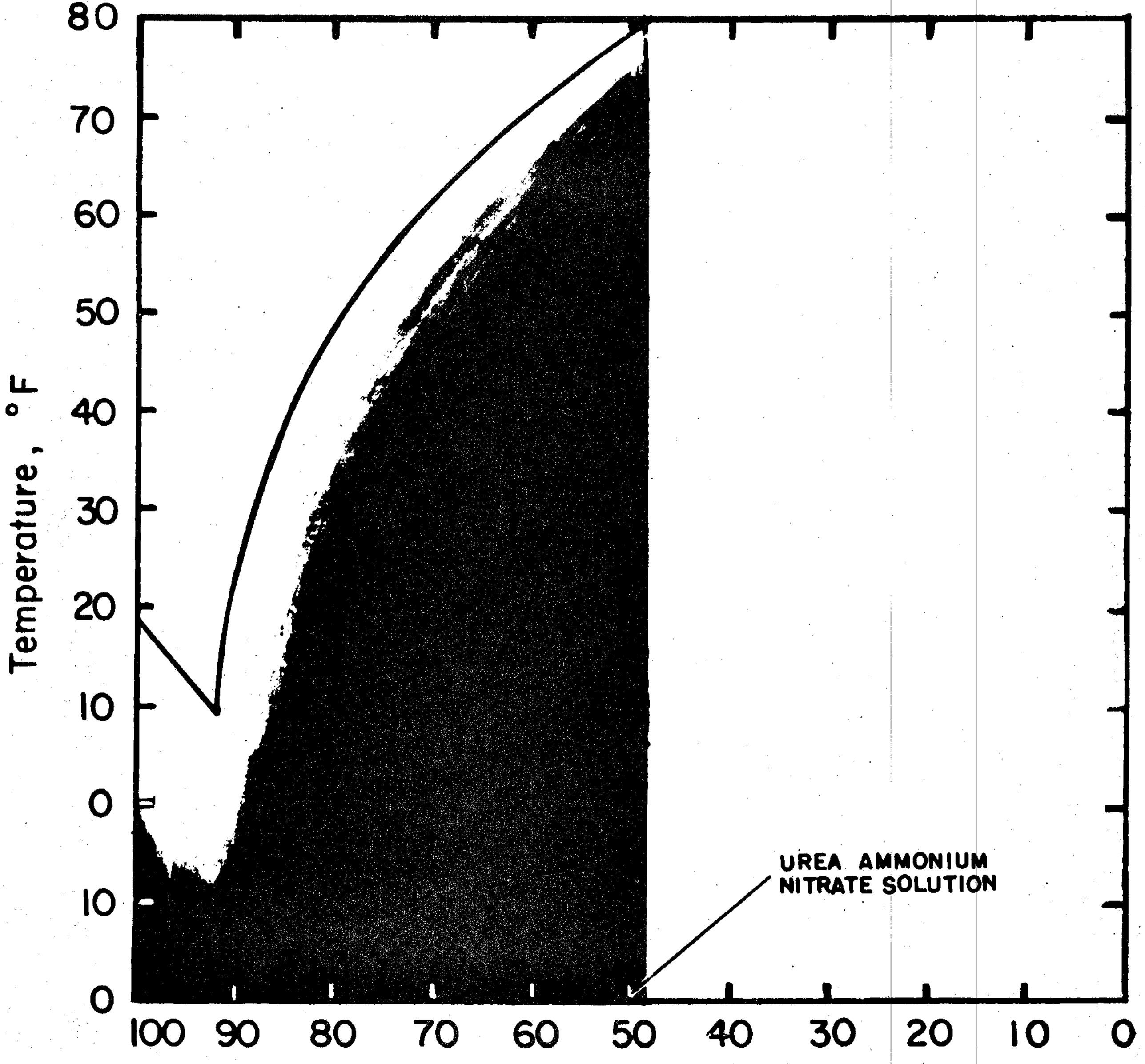


GRANULATOR STATISTICS

DIAMETER	2.13 METERS
LENGTH	3.05 METERS
FLIGHTS	40
RPM	VARIABLE
MELT NOZZLES	27 MAX.
WATER NOZZLES	5 MAX.

FIGURE 4

SCHEMATIC DIAGRAM OF GRANULATION DRUM



Percent of Supplementary Nitrogen from Urea

FIGURE 5

EFFECT OF AMMONIUM NITRATE ON SALT-OUT TEMPERATURE OF 14-7-7 SOLUTION

COURTESY
VISTRON CORP.,
CLEVELAND, OHIO