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60. Controlled release technology. Controlled release technology (Agricultural), volume 7:251-274.

CONTROLLED RELEASE TECHNOLOGY

AGRICULTURAL

Controlled release technology in agriculture encompasses the controlled delivery of plant nutrients, ie, fertilizers, as well as control chemicals, eg, herbicides (qv), insecticides, fungicides (qv), etc, to a target in a manner which maximizes its use efficiency, minimizes potential negative effects associated with overdosage, and/or extends the time in which sufficient dosages are delivered. Controlled release fertilizer (CRF) technologies are emphasized here.

A goal of controlled release fertilizer research since the 1940s has been the development of a product that delivers its nutrients at a rate matching the demand rate of the plant to which it is applied. Such a fertilizer would represent the ultimate in use efficiency; agronomic performance, ie, crop yield, quality, and appearance; agronomic safety; and labor savings, ie, reduced application frequency. It also would minimize potential losses to the environment.

The benefits of controlled release fertilizers come at a cost premium, eg, the cost of controlled release nitrogen (CRN) can be anywhere from 2.5 to 10 times the cost of nitrogen from a conventional fertilizer such as urea. Because of the large price differential with conventional fertilizers, usage of CRFs has been limited. In 1990, controlled release nitrogen sources accounted for only 1% of total U.S. nitrogen fertilizer consumption. Usage of CRFs has been limited primarily to specialty markets where their advantages justify the increased cost, ie, high to medium value agricultural crops, consumer lawn and garden, lawn and landscape care companies, golf courses, nurseries and greenhouses, and professional turf applications.

The wholesale value of CRFs serving the U.S. specialty markets was estimated at $175 million in 1990. Of this total, agriculture comprised $14 million (6.8 thousand t of CRN); nonagricultural markets accounted for $161 million (93.9 thousand t of CRN).

U.S. agricultural use of controlled release fertilizers is concentrated primarily in the Southeast and California on high value crops such as strawberries, tomatoes, bell peppers, melons, and citrus. Figure 1 shows the breakdown of agricultural use of CRFs both by crop type and product. Strawberry production accounts for over half of the 1990 agricultural consumption of CRFs in dollars. However sulfur-coated urea (SCU) accounts for the largest tonnage (61%) of agriculture usage.

Nonagricultural markets represented significant outlets for CRFs in the United States in 1990. In total, these markets accounted for 93% of the demand for CRN. As shown in Figure 2, about ¾ of the nonagricultural market ($161 million total) is divided approximately evenly between golf course, consumer lawn and garden, and nurseries and greenhouses. Urea–formaldehyde (UF) products

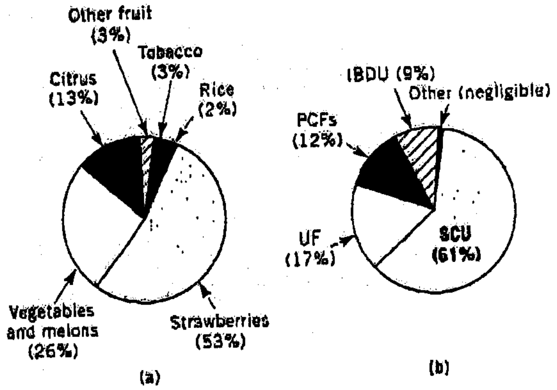


Fig. 1. United States agricultural crop markets for manufactured controlled release fertilizers, 1990. (**a**) Total percentage ($14 million) of market value by crop; and (**b**) total percentage (6,800 t) of consumption by product type. IBDU is isobutylidene diurea; PCF, polymer-coated fertilizer; UF, urea–formaldehyde; SCU, sulfur-coated urea. Courtesy of SRI International.

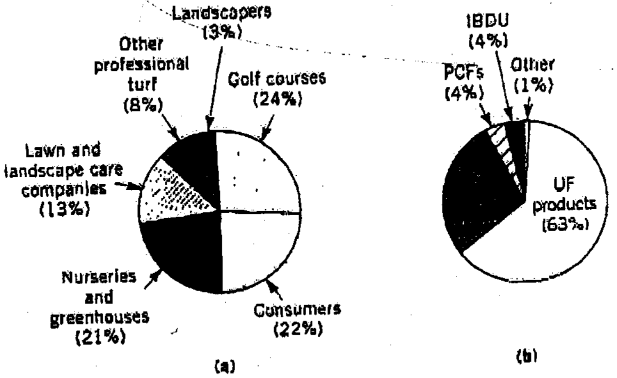


Fig. 2. United States nonagricultural markets for manufactured controlled release fertilizers, 1990. (**a**) Total percentage ($161 million) of nonagricultural market value; and (**b**) total percentage (93,900 t) of controlled release nitrogen consumption by product type. IBDU is isobutylidene diurea; PCF, polymer-coated fertilizer; UF, urea–formaldehyde; SCU, sulfur-coated urea. Courtesy of SRI International.

were the largest source of CRN for these markets (63% of total), followed by SCU (28% of total).

Numerous technologies have been developed with varying degrees of success to maximize the various benefits of controlled release. Heightened attention to environmental concerns has prompted increased activities worldwide in the development and commercialization of controlled release fertilizers.

Synthetically produced CRFs are categorized either as nitrogen reaction products or coated fertilizers. Nitrogen reaction products are produced by the chemical reaction of water-soluble nitrogen compounds, such as urea or ammonia, to create nitrogen fertilizers possessing more complex molecular structures. These complex molecules have limited water solubility and are slowly broken down in the soil environment to nitrogen forms which the plant can assimilate. The limited solubility and the rate of decomposition controls the nitrogen availability to the plant.

Coated fertilizers achieve controlled release by coating a soluble fertilizer core (substrate) with a water-insoluble barrier which limits the access of water to the fertilizer and thus limits its dissolution rate.

Nitrogen Reaction Products

Urea–Formaldehyde Reaction Products. Urea–formaldehyde (UF) reaction products represent one of the older controlled release nitrogen technologies. An early disclosure of the reaction products of urea [*57-13-6*] and formaldehyde [*50-00-0*] was made in 1936 (1) (see AMINO RESINS AND PLASTICS). In 1948, the USDA reported that urea (qv) and formaldehyde (qv) could react to produce a controlled release fertilizer at urea to formaldehyde mole ratios (UF ratio) greater than one (2).

Urea–formaldehyde reaction products represented the first synthetically produced form of controlled release nitrogen and were commercialized in 1955 under the trade names Uramite (DuPont) and Nitroform (Nitroform Corp.).

The urea–formaldehyde reaction results in a distribution of methylene urea (MU) polymers of varying molecular weights or polymer chain lengths and of varying water solubility.

Granular Compositions. Granular compositions of UF reaction products are divided into three classes, each based on their degree of water solubility as affected by their polymer distributions, ie, ureaform, the least water-soluble class; methylene ureas; and methylene diurea/dimethylene triurea (MDU/DMTU) compositions, the shortest-chain MU oligomers and the most water-soluble.

Each class of UF products contains certain amounts of unreacted urea. MDU/DMTU compositions, the lowest molecular-weight distribution, contain the highest amount of unreacted urea nitrogen, and ureaform contain the least amount.

Ureaform is the oldest class of UF reaction products. Ureaform, as defined by the American Association of Plant Food Control Official (AAPFCO-1964), is sparingly soluble. It contains at least 35% total nitrogen with at least 60% of the total nitrogen as cold water-insoluble nitrogen (CWIN), determined by AOAC Method 945.01 (1990). Further, it must have an Activity Index (AI), ie, the percent of CWIN that is soluble in hot (100°C) water, of not less than 40%. Ureaform is composed largely of longer-chained UF polymers, primarily tetramethylene pentaurea (TMPU) and longer. Unreacted urea nitrogen content is usually less than 15% of the total nitrogen.

Methylene ureas are a class of sparingly soluble products which evolved during the 1960s and 1970s. These products contain predominantly intermediate chain-length polymers, primarily trimethylene tetraurea (TMTU) and tetramethylene pentaurea (TMPU). The total nitrogen content of these polymers is 39 to

40% with between 25 and 60% of the nitrogen present as CWIN. The unreacted urea content generally is in the range of 15 to 30% of the total nitrogen. This class of granular UF products is not specifically defined under AAPFCO Official Terms and Definitions.

MDU/DMTU compositions are the newest class of UF fertilizers and were developed during the 1980s. These granular compositions are predominantly shorter-chain polymers with at least 60% of their polymeric nitrogen in the form of the cold water-soluble polymers methylene diurea (MDU) and dimethylene triurea (DMTU). The total nitrogen content of these polymers is above 40%; generally less than 25% of their total nitrogen is present as CWIN. Because of the shift in polymer distribution to lower-weight polymers, these compositions contain higher percentages of unreacted urea than ureaforms and methylene ureas. AAPFCO defines MDU and DMTU individually as sources of slowly available nitrogen.

Liquid Compositions. Urea–formaldehyde reaction products also are available commercially as liquids that can be categorized into two classes, ie, water suspensions and water solutions.

UF suspensions comprise a family of liquid products in which the UF reaction products are present as a microcrystalline dispersion of longer-chain UF polymers (CWIN) in a water solution of urea and water-soluble UF compounds. Typically, these products contain about 25% of the total nitrogen as CWIN.

UF solutions are clear water solutions. They contain only very low molecular-weight, water-soluble UF reaction products plus unreacted urea. Various combinations of UF solutions are found. They contain a maximum of 55% unreacted urea with the remainder as one or more of methylolureas, methylolurea ethers, MDU, DMTU, or triazone, a cyclical oligomer. AAPFCO has defined this class of compounds as urea–formaldehyde products (water-soluble).

Physical and Chemical Properties. The reaction of urea and formaldehyde forms a white solid. The solubility varies with the methylene urea polymer chain length; longer-chain, higher molecular-weight UF polymers are less water-soluble than short-chain polymers. Physical properties of the methylene urea polymers which have been isolated are compared to urea in Table 1.

Prior to the development of analytical techniques to quantify specific methylene urea oligomers, methylene urea polymer distributions were characterized by physical (solubility) methods. Products were separated into three fractions (3).

Fraction I is cold water-soluble nitrogen (CWSN), ie, that portion of the total nitrogen that is soluble in cold water (22°C) when 1 gram or 1.4 grams of product is placed in 250 mL of water. Fraction I can consist of unreacted or residual urea,

Table 1. Physical Properties of Methylene Urea Polymers

Product	Melting point, °C	Water solubility, g/100 g	Temperature, °C
urea	132.7	100	17
MDU	205–207	2.5	25
		7.0	50
		0.1	25
DMTU	231–232	4.4	100

methylol ureas, MDU, DMTU, and other soluble UF reaction products. Fraction II is the cold (22°C) water-insoluble nitrogen (CWIN) which is hot (100°C) water-soluble (HWS). Compositionally, this fraction comprises the medium molecular-weight polymers, TMTU and TMPU. Fraction III is hot (100°C) water-insoluble nitrogen (HWIN). Compositionally, these are the higher molecular-weight methylene urea polymers, TMPU and higher.

The nitrogen content of granular urea–formaldehyde reaction products typically ranges from 35 to 42% depending on the methylene urea polymer distribution.

An improved method (4) of characterizing the lower molecular-weight, ie, water-soluble methylene ureas, was developed in the 1980s using high pressure liquid chromatography (hplc). This method permits the identification of urea and individual water-soluble methylene urea oligomers, and the characterization of their distribution. By this method, urea, MDU, and DMTU can be quantified; development of a similar method for quantifying TMTU and TMPU is underway. Higher molecular-weight polymers continue to be characterized by solubilities in cold and hot water, ie, CWIN and HWIN.

Table 2 gives the typical total nitrogen analysis and the unreacted urea and UF polymer distribution of various UF reaction products.

Table 2. Total Nitrogen Analysis of UF Reaction Products

		Total nitrogen as specific fraction[a], %		
UF reaction product	Total nitrogen, %	Fraction I, % composition[b]	Fraction II, % composition[c]	Fraction III, % composition[d]
		Granular products		
ureaform	35–38	30 urea, MDU, DMTU	40 TMTU, TMPU	30
methylene ureas	39–40	65 urea, MDU, DMTU	20 TMTU, TMPU	15
MDU/DMTU	40–42	90 urea, MDU, DMTU	7 TMTU	3
		Liquid products		
UF suspension compositions	18	75 urea, methylol ureas, MDU, DMTU	15 TMTU, TMPU	10
methylol urea solutions	26–30	100 urea, methylol ureas		
MDU solutions	26	100 urea, methylol ureas, MDU		
urea–triazone solutions	28	100 urea, triazone		

[a] Fraction I: cold water-soluble nitrogen (CWSN); Fraction II: cold water-insoluble nitrogen (CWIN), which is hot water-soluble; Fraction III: hot water-insoluble nitrogen (HWIN).

[b] MDU: methylene diurea [*13547-17-6*]; DMTU: dimethylene triurea [*15499-91-9*].

[c] TMTU: trimethylene tetraurea [*35710-95-3*]; TMPU: Tetramethylene pentaurea [*50837-30-4*].

[d] Composition is mix of pentamethylene hexaurea (PMHU) [*35710-96-4*] and higher molecular-weight urea.

Agronomic Properties and Nutrient Release Mechanism. The conversion of UF reaction products to plant available nitrogen is a multistep process, involving dissolution and decomposition. Materials are slow to enter the soil solution by virtue of their low solubility. Longer polymer chain products are less soluble than shorter chains and take longer to become available to the plants.

Once in the soil solution, urea–formaldehyde reaction products are converted to plant available nitrogen through either microbial decomposition or hydrolysis. Microbial decomposition is the primary mechanism. The carbon in the methylene urea polymers is the site of microbial activity. Environmental factors that affect soil microbial activity also affect the nitrogen availability of UF products. These factors include soil temperature, moisture, pH, and aeration or oxygen availability.

The rate of nitrogen released (mineralization) from UF reaction products is directly affected by polymer chain length. The longer the methylene urea polymer length, the longer it takes for the nitrogen to become fully available. For ureaform and methylene urea products, the rate of mineralization is reflected by the cold water insoluble nitrogen (CWIN) content and its Activity Index. Figure 3 shows the results of a greenhouse study in which Kentucky bluegrass was treated with 2 lb N/1000 sq ft (2 lb N/M) (9.76 g/m^2) of a number of UF products varying in CWIN content. As shown, the rate of nitrogen availability, as reflected by the leaf fresh weight, was directly correlated to the CWIN content. It should be noted that the efficiency of nitrogen utilization also decreases with increasing polymer length, as reflected by a decrease in the Activity Index. It is questionable if the very long methylene urea polymers (HWIN) are effectively used by the crop.

Nitrogen release from MDU/DMTU compositions cannot be predicted from WIN values, since these polymers are largely water-soluble. Instead, hplc procedures must be used to characterize these products. MDU/DMTU compositions were developed to maximize the nitrogen efficiency of UF reaction products. They have greater agronomic efficiency than products containing high levels of water-insoluble polymers and yet retain agronomic and environmental safety over conventional soluble fertilizers such as urea by nature of their greatly reduced solubility.

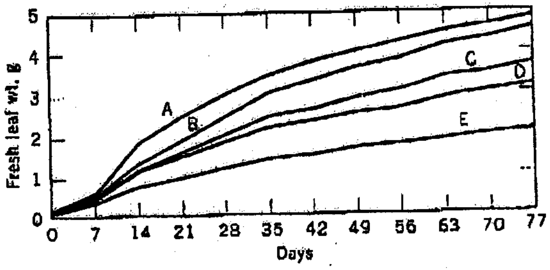
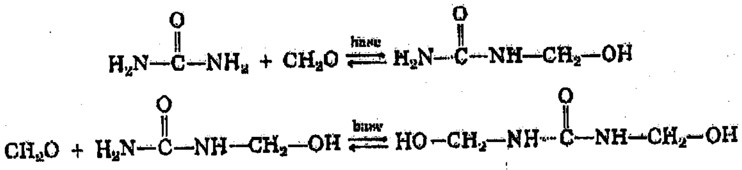


Fig. 3. Response of Kentucky bluegrass to urea, A, and methylene urea (MU) products varying in cold water-insoluble nitrogen (CWIN). B is 27% CWIN; C, 50% CWIN; D, 65% CWIN; and E, 80% CWIN. Application of 2 lb N/1000 sq ft (9.76 g/m^2). Courtesy of The O.M. Scott & Sons, Co.

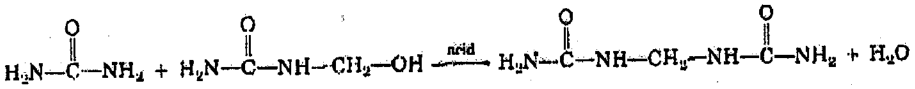
Manufacturing and Processing. Urea–formaldehyde fertilizers are prepared from the reaction of formaldehyde with excess urea (U/F mole ratio 1). The reaction proceeds in two steps. In Step 1, urea and formaldehyde are combined to form monomethylol [*1000-82-4*] and dimethylolurea [*140-95-4*] intermediates.



$$H_2N-\overset{\overset{O}{\|}}{C}-NH_2 + CH_2O \overset{base}{\rightleftharpoons} H_2N-\overset{\overset{O}{\|}}{C}-NH-CH_2-OH$$

$$CH_2O + H_2N-\overset{\overset{O}{\|}}{C}-NH-CH_2-OH \overset{base}{\rightleftharpoons} HO-CH_2-NH-\overset{\overset{O}{\|}}{C}-NH-CH_2-OH$$

These compounds are stable only under basic conditions and must be held at high pH if stored for considerable periods of time. In Step 2, these methylolureas further react under acidic conditions with urea to form the various methylene urea oligomers. Water generated from the condensation reaction is removed by evaporation when producing granular UF products.



$$H_2N-\overset{\overset{O}{\|}}{C}-NH_2 + H_2N-\overset{\overset{O}{\|}}{C}-NH-CH_2-OH \xrightarrow{acid} H_2N-\overset{\overset{O}{\|}}{C}-NH-CH_2-NH-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O$$

Methylene diurea (MDU) is the shortest chain of the urea–formaldehyde oligomers. MDU can further react with additional monomethylol urea to form dimethylene triurea (DMTU), the next higher oligomer. DMTU can also be formed from the condensation reaction of urea with dimethylol urea. In similar fashion, higher chain-length polymers are obtained by continued reaction with additional methylolureas.

In actual practice, the reaction of urea with formaldehyde produces a distribution of polymers of varying chain length. The distribution is affected by the U/F mole ratio as well as reaction conditions such as pH, temperature, and reaction time. In general, higher U/F ratios produce polymer distributions with lower average chain length; lower U/F ratios produce higher molecular-weight polymer distributions. By careful control of U/F mole ratios and reaction conditions, it is possible to engineer products with optimal methylene urea polymer chain lengths.

Various processes can be employed to manufacture urea–formaldehyde products. They are generally categorized into two types, ie, dilute solution processes and concentrated solution processes. Table 3 lists select U.S. manufacturers of UF reaction products and their products.

The dilute solution process (5,6) carries out the reaction completely in a water medium. Step 1 involves reacting urea and formaldehyde in a water solution. The solution is held at elevated temperature under basic conditions to produce methylol ureas. Methylol urea solutions are marketed as end products by a number of companies and are also used as precursors in the production of methylene urea products. Step 2 entails acidifying the urea–methylol urea solution to a pH normally less than 3. The acid catalyzes the exothermic reaction which produces the methylene urea polymers. The solution is held at low pH for a prerequisite time and temperature and then neutralized with a base. Varying

Table 3. U.S. Manufacturers of UF Reaction Products

UF reaction product	Manufacturer	Trade name
	Granular products	
ureaform	NOR-AM Chemical Co.	Nitroform
	Omnicology, Inc.	Organiform
	O.M. Scott & Sons	Granuform
methylene ureas	O.M. Scott & Sons	ProTurf HiTech Scotts ProGrow
	NOR-AM Chemical Co.	Nutralene
	Lebanon Chemical Corp.	Country Club Greens Keeper
MDU/DMTU compositions	O.M. Scott & Sons	Scotts Triaform
	Liquid products	
methylol urea solutions	CoRoN Corp.	CoRoN
	Georgia Pacific Corp.	GP 4340 GP 4341
	Arcadian Corp.	Formalene
	C.P. Chemical Co., Inc.	Nitro 26-CRN
MDU solutions	Arcadian Corp.	N-Sure
urea–triazone solutions		Trisert
UF suspensions	W.A. Cleary Chemical	FLUF
	Georgia Pacific Corp.	RESI-GROW
	Arcadian Corp.	Slo-Release

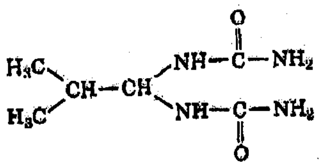
methylene urea chain lengths can be produced depending on U/F mole ratio, reaction temperature, and reaction pH. Methylene diurea (MDU) is quite soluble in water and is sold as a component in liquid UF products. Longer-chain polymers are relatively insoluble and precipitate out of solution. These are sold as UF suspensions by a number of manufacturers; or can be filtered, dried, and granulated, then sold as granular products.

The concentrated solution processes (CSP) use little or no water. In one process (7), the methylol urea reaction is carried out at pH 8 and at elevated temperature, 70°C. Only enough water is used to aid in the dissolution of the urea. The second stage of this CSP reaction involves acidifying the concentrated solution to pH 2–3. This immediately precipitates out the various methylene urea polymers in the form of a semisolid. This semisolid is dried and granulated to a final product. In another process (8), which utilizes no water, commercially available UF concentrate, ie, formaldehyde plus dimethylolurea solution, is incorporated directly into molten urea. The high (130°C) temperature catalyzes the formation of short-chain methylene urea polymers which are soluble in the urea melt. Granulation is achieved through solidification of the melt.

Uses. Urea–formaldehyde fertilizer products serve varied markets including consumer and professional turf, ie, golf course and other sports turf, ornamental nurseries, and greenhouses and specialty, ie, medium and high cash value agricultural crops. The liquid products are typically directed to the consumer home lawn market serviced by lawn care service companies. The granular UF reaction products are blended or reacted *in situ* with other nitrogen–phosphorous–potassium (N–P–K) nutrients. Ureaform, notably, is used as a high WIN source in blended fertilizers.

Urea–Other Aldehyde Reaction Products. Urea can also react with other aldehydes to form slow release nitrogen fertilizers. However, cost constraints associated with higher aldehydes have either precluded or limited broad commercial development of these products. Two exceptions are isobutylidene diurea (IBDU), registered trademark of Vigoro Industries, and crotonylidene diurea (CDU), registered trademark of Chisso-Asahi Fertilizer Co.

Isobutylidene Diurea. This is the condensation product of urea and isobutyraldehyde. Unlike the condensation of urea with formaldehyde, which forms a distribution of different UF polymer chain lengths, the reaction of urea with isobutyraldehyde forms a single oligomer. Although similar in chemical structure to methylene diurea (MDU), its physical properties are quite different (Table 4).



Isobutylidene diurea [*6104-30-9*] is a nonhygroscopic white crystalline solid available in fine (0.5–1.0 mm), coarse (0.7–2.5 mm), and chunk (2.0–3.0 mm) particle sizes. The AAPFCO official definition requires a minimum nitrogen content of 30% with 90% of the nitrogen in water-insoluble form prior to grinding (3).

Nitrogen from isobutylidene diurea becomes available to plants through hydrolysis. In the presence of water, the compound will hydrolyze to urea and isobutyraldehyde. The rate of hydrolysis is accelerated by low pH and high temperatures. Unlike UF polymers that rely on soil microbial populations to make the nitrogen available, isobutylidene diurea is primarily dependent on water as the critical element to nitrogen availability. Its low water solubility controls the transport of the product into the soil solution. Once in the soil solution, the rate of hydrolysis is affected by both soil pH and temperature. Because of its limited solubility, the rate of dissolution is affected by the particle size of the product and the amount of water available. The powder form is mineralized much more rapidly than large particle granules under the same field conditions. Because the release is not microbe dependent, it can become available at low temperatures. This and the dependency on moisture are the distinguishing characteristics of isobutylidene diurea.

The agronomic response of IBDU is compared to other nitrogen reaction products in Figure 4. In this study, various products were applied to Kentucky bluegrass at 3 lb N/M (14.6 g/m^2). Plant growth as measured by leaf fresh weight was monitored weekly.

Table 4. Physical Properties of Less Common Nitrogen Reaction Products

	Isobutylene diurea	Crotonylidene diurea	Oxamide	Melamine
CAS Registry Number	*[6104-30-9]*	*[1129-42-6]*	*[471-46-5]*	*[108-78-1]*
molecular formula	$C_6H_{14}N_4O_2$	$C_6H_{12}N_4O_2$	$C_2H_4N_2O_2$	$C_3H_6N_6$
nitrogen content, %	31.0[a]	32.0[b]	31.8	66.0[c]
water solubility, g/100 mL	0.1 at 15°C 0.3 at 40°C	0.06 at 20°C 0.22 at 50°C 0.50 at 70°C	0.04 at 7.5°C	
melting point, °C	205	259[d]		345[d]
specific heat, J/(g·K)[e]	1.6–1.7			
heat of formation, J/mol[e]				
water solution	84			
solid urea/liquid aldehyde	54			
specific gravity				
true	1.3		1.7	1.6
apparent	0.7–0.9			
sublimation temperature, °C			265	
decomposition temperature, °C		259	290	345

[a] Commercial-grade product. Theoretical content is 32.18%.

[b] Fertilizer-grade product.

[c] High nitrogen content distinguishes it from other controlled release nitrogen sources.

[d] With decomposition.

[e] To convert J to cal, divide by 4.184.

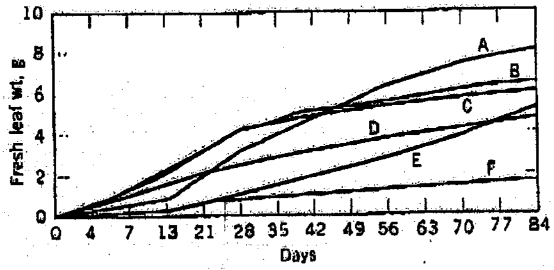
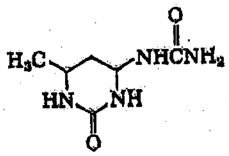


Fig. 4. Response of Kentucky bluegrass to select nitrogen reaction controlled release products. Application of 3 lbs N/1000 ft^2 (14.6 g/m^2). A is IBDU; B, urea; C, oxamide (powder); D, nitroform; E, oxamide (granular); and F, melamine. Courtesy of The O.M. Scott & Sons Co.

Manufacturing, Processing, and Uses. Isobutylidene diurea is manufactured by the condensation reaction of urea and isobutyraldehyde. The reaction can be carried out both in aqueous solution and between solid urea and the liquid aldehyde. The presence of acid catalyzes the reaction. Commercially, isobutylidene diurea is made by spraying the liquid aldehyde into a paddle mixer containing acid treated solid urea. Patents on the technology are held by Mitsubishi Chemical Industries (Japan) and Farbwerk Hoechst Aktiengesellschaft (Germany). Mitsubishi produces IBDU from isobutyraldehyde recovered as a byproduct of 2-ethylhexyl alcohol production. Prior to 1986, all isobutylidene diurea consumed in the United States was imported from Japan. In 1986, IB Chemicals brought domestic production on stream with a 20,000 t/yr facility in Bucks, Alabama. IB Chemicals is a joint venture company held by Virginia Chemicals, Inc. (Hoechst Celanese Corp.), Mitsubishi Chemical Industries of America, and Mitsubishi International Corp. Briquetted forms, ie, Woodace Briquettes, Mitsubishi Chemical Industries, continue to be imported from Japan.

IBDU is used on turfgrasses, in commercial nurseries, and in landscaping, forestry, and specialty (medium to high value) agriculture. Although some fine-size IBDU 31-0-0 is used for direct application to golf course greens, most of the turfgrass use is in the form of blended fertilizers, often in combination with other types of controlled release fertilizers (CRF). Vigoro Industries has exclusive marketing rights in North America and sells to turfgrass markets under the trade name ParEx, to nurseries as Woodace, and to specialty agriculture under the name Certified Harvest King.

Crotonylidene Diurea (CDU). Crotonylidene diurea [*1129-42-6*] is produced by the acid catalyzed reaction of urea with either crotonaldehyde or acetaldehyde. The condensation reaction produces a ring-structured compound. Table 4 lists select properties.



CDU in pure form is a white powder. It is made slowly available to the soil solution by nature of its limited solubility in water. Once in the soil solution, nitrogen from CDU is made available to the plant through a combination of hydrolysis and microbial decomposition. As with any CRF which is dependent on microbial action, the mineralization of CDU is temperature dependent. Product particle size has a significant effect on CDU nitrogen release rate. Smaller particles mineralize more rapidly because of the larger surface contact with the soil solution and the microbial environment. The rate of nitrogen release is also affected by pH because CDU degrades more rapidly in acidic soils.

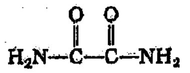
Manufacturing, Processing, and Uses. In commercial production, aqueous urea solution is mixed with acetaldehyde in 1:1 molar ratios. An acid catalyst is introduced into the reaction mixture which is staged at various process temperatures. After neutralization with a base, the CDU is separated from the mother liquor by filtration or spray drying.

CDU is manufactured by Chisso Corp. (Japan) and marketed as CDU by Chisso Asahi Fertilizer Co., Ltd. It is also produced by BASF (Germany) under Japanese license. It is sold under the trade name Crotodur in Europe.

CDU has very limited use in the United States. It is used primarily in Japan and Europe where it is produced. It serves the turf and specialty agriculture markets and is typically formulated into granulated N–P–K fertilizers.

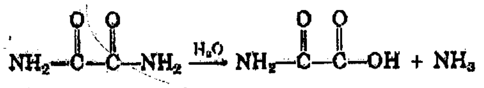
Other Reaction Products. Nitrogen reaction fertilizers are commercially available that do not involve reactions between urea and aldehydes. These are oxamide and melamine.

Oxamide. Oxamide [*471-46-5*] is a nonhygroscopic single compound. It has a molecular weight of 88.08, a nitrogen content of 31.8%, and is a white crystalline solid with very limited solubility in water. Table 4 lists select physical properties.



$$H_2N-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-NH_2$$

Following slow dissolution into the soil solution, oxamide undergoes stepwise hydrolysis to liberate ammonia. Oxamic acid is formed in the first step.



$$NH_2-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{H_2O} NH_2-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH + NH_3$$

Oxalic acid, HOOC–COOH, the product of the second hydrolysis step, can be toxic to plants if present in sufficient quantity before being further converted by soil microbes to carbon dioxide. As with other insoluble products that release nitrogen through hydrolysis, eg, IBDU, the rate of hydrolysis is greatly affected by the particle size of the product which affects dissolution rate into the soil solution. Unlike isobutylidene diurea, however, the release rate is not affected by pH. Oxamide (granular) is a very slow release nitrogen source. The agronomic activity of oxamide (granular and powder) on Kentucky bluegrass is compared to other nitrogen reaction products sources in Figure 4.

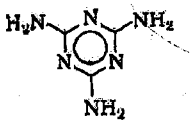
Manufacturing, Processing, and Uses. Oxamide can be prepared by several methods. One method involves the oxidation of hydrogen cyanide followed by hydrolysis to oxamide by a two-step reaction. Hydrogen cyanide (HCN) is oxidized with either copper oxide or nitrogen dioxide to produce cyanogen (C_2N_2). Cyanogen is then converted to oxamide by acid-catalyzed hydrolysis using concentrated hydrochloric acid or a mixture of hydrochloric and acetic acids.

Another method, utilized by Ube Industries, Ltd. (Japan), involves the oxidation of methanol and carbon monoxide to form an oxalic diester. This then reacts with ammonia in a second step to form oxamide.

Oxamide is produced commercially by Ube Industries, Ltd. (Japan) and a pilot process is being operated by Enichem (Italy). It is not produced domestically as a commercial fertilizer, although it was the subject of much research and development activity by the Tennessee Valley Authority's (TVA) National Fertilizer Research and Development Center. It is made in small quantities for industrial use by Allied Chemical, Hummel Chemical Co., and United Guardian, Inc. Oxamide has application as a controlled release nitrogen source for the turf and specialty agricultural markets.

Melamine. Melamine, 2,4,6,-triamino-1,3,5-triazine [*108-78-1*] is a white crystalline powder, sparingly soluble in cold and hot water, with a molecular weight of 126 (Table 4). It has a very slow mineralization rate. After an initial delay of one to two months, it releases very slowly by microbial decomposition over the period of one to two years. Because of this slow availability, melamine has been cogranulated with urea to increase the upfront nitrogen response. The agronomic response of melamine on Kentucky bluegrass (greenhouse) is compared to other noncoated controlled release nitrogens in Figure 4.

Melamine is produced by heating urea under pressure in the presence of a catalyst. The result is a ring structure as shown below. The reaction by-products, ammonia and carbon dioxide, can be recycled for urea production.



The production process was developed by Melamine Chemicals, Inc. in the early 1970s. Marketing rights for melamine as a CRF were acquired by Pursell Industries in 1988. Melamine CRF products are currently available as Nitrazine 66N, a melamine powder (66% nitrogen). This powder also can be an agglomeration granulated with molten urea to form a homogeneous granular product containing from 50 to 67% melamine and from 50 to 33% urea. This granular product, Nitrazine-U, which contains 55 to 60% nitrogen, is not currently available commercially.

The slow mineralization rate suggests the use of melamine for very long-term crops. Powdered melamine (Nitrazine 66N) is used in fertilizer spikes and stakes for houseplants and ornamentals.

Coated Fertilizers

Coated fertilizers is a term characterizing those products in which a soluble fertilizer core (substrate) granule is covered with a water-insoluble coating. The coating limits or controls the rate of water penetration to the soluble fertilizer core, and in some products controls the release rate of solubilized fertilizer from within the granule to the external environment. The three categories of coated fertilizers are those using sulfur as the coating material, those that employ a polymeric material, and those hybrid products that utilize a multilayer coating of sulfur and polymer.

Coated fertilizers represent the fastest growing segment in controlled release fertilizer technology. During the 1980s, coated fertilizer products grew at a rate of about 10% per year, UF product usage grew at about 2% per year, and all manufactured controlled release fertilizers, coated and nitrogen reaction products, grew at a rate of about 4% per year. The growth of coated fertilizers is the result of more favorable economics, increased flexibility in nutrient release patterns as compared to nitrogen reaction products, and the flexibility in controlling the release of other nutrients in addition to nitrogen.

Sulfur-Coated Fertilizers. Sulfur-coated urea technology (SCU) was developed in the 1960s and 1970s by the Tennessee Valley Authority, now called the National Fertilizer and Environmental Research Center. A commercial-scale demonstration plant (9.1 t/h) was put in operation by TVA in late 1978. Sulfur was chosen as the principle coating material because of its low cost and its value as a secondary nutrient.

Physical and Chemical Properties. Sulfur-coated ureas (SCUs) typically have bulk densities of 720–800 kg/m^3 (45–50 lb/ft^3). The color ranges from brown to tan to bright yellow depending on the source of urea, whether or not a sealant is used, and the type sealant employed. Soft wax sealants are typically used as a secondary coating over the sulfur coating to fill in imperfections in the sulfur coating and to provide handling integrity to the brittle sulfur coat.

Product particle sizes vary from standard size of 6/14 mesh–U.S. Std. Sieves to mini-size granules of 10/16 mesh–U.S. Std. Sieves for small particle blends, to micro-size granules of 14/35-U.S. Std. Sieves for use on golf course tees and greens. Approximate mm corresponding to mesh sizes are 6 mesh/3.36 mm; 10 mesh/2 mm; 35 mesh/0.5 mm.

The total nitrogen content of SCUs vary with the amount of coating applied; SCUs available in the early 1990s range from 30 to 40% nitrogen. The release characteristics of SCU are determined by the Katz Method, a two-hour dissolution (WIN) test at room temperature, and adaptations of the 7-day dissolution rate (DR) developed by TVA (9). The Katz Method procedure is similar to the method used to analyze UF reaction products, however, the grinding step is by-passed as this would destroy the sulfur coating. The 7-day DR test involves total immersion of the product in water for 7 days and measurement of the percent of the total nitrogen leached into the water. By pulling aliquots at various time intervals and measuring the amount of nitrogen dissolved, a leach profile can be generated which gives improved insight into the release characteristics of the product. Laboratory WIN (Katz) and 7-day DR tests are reasonably good quality control tools for a given process, but have been found to be inadequate predictors of agronomic response when comparing different technologies. For instance, SCUs with and without wax sealants have been found to have dramatically different agronomic release at similar DRs or Katz WIN values.

Agronomic Properties and Nutrient Release Mechanisms. The mechanism of nutrient release from SCU is by water penetration through micropores and imperfections, ie, cracks or incomplete sulfur coverage, in the coating. This is followed by a rapid release of the dissolved urea from the core of the particle. When wax sealants are used, a dual release mechanism is created. Microbes in the soil environment must attack the sealant to reveal the imperfections in the sulfur coating. Because microbial populations vary with temperature, the release properties of wax-sealed SCUs are also temperature dependent.

The release rate of an SCU particle is directly affected by the coating thickness and the coating quality. Particles with higher sulfur loads, ie, thick sulfur coatings, typically show fewer imperfections than particles with lighter coatings. There is the risk, however, that particles with too thick sulfur coating will exhibit lock-off, ie, they may never effectively release their nutrient. Because of the continuous horizontal rotary coating drum method of coating application, SCU product is in reality a statistical blend of granules with many different coating weights, thicknesses, and qualities. This blend of granules minimizes the effects of individual particles receiving light or heavy coatings.

In turf applications, SCU, with or without wax sealant, provides improved safety and longevity over urea. This is shown in Figure 5 which rates the quality of Kentucky bluegrass with time after being treated with 2 lb N/1000 sq ft (9.76 g/m^2) of urea and two types of SCU. In this particular test, a quality rating of 3 or less is acceptable. Urea provided acceptable turf quality for 11 weeks, whereas the two SCU products (37% nitrogen) gave quality turf for 16 weeks.

Depending on the coating weight, nitrogen application rate, and environmental conditions, SCUs can have residual characteristics which provide agronomic response from 6 to 16 weeks in turfgrass applications.

Manufacturing and Processing. The process for sulfur-coated urea, as developed by TVA (10), involves the precision application of three coating materials to a soluble fertilizer core, usually granular urea. The coatings include molten sulfur, a hydrocarbon/oil (soft wax) sealant, and a flow conditioner. The process involves preheating urea prior to coating with molten sulfur. Preheating the urea allows better adhesion of the sulfur and more time for the molten sulfur to wrap the urea prior to solidifying. The quality of the urea substrate as well as the sulfur are key to producing a quality product.

Sulfur has two crystalline forms and undergoes a transformation in crystalline structure with time (aging). At the time of application, most of the sulfur in the coating is present as monoclinic sulfur with a small portion of amorphous sulfur. With time, however, the monoclinic sulfur is converted to orthorhombic sulfur which has a slightly higher density. This density change causes shrinkage in the sulfur coating. Because solid sulfur is inelastic and brittle, the shrinkage often causes stress fractures and micropores in the coating. The degree of imperfections can be influenced by the conditions under which the sulfur is applied and the conditions under which the product is cooled. The TVA process employs a soft, waxlike, hydrocarbon/oil sealant to effectively seal up any imperfections in the sulfur coating. The sealant most commonly used by industry consists of a 70/30 blend of heavy paraffinic oil, eg, Shell-Flex 790, with a polyethylene wax, eg, Allied AC-6. This sealant is semiflowable at ambient temperature which allows it to fill in cracks as they occur. The soft nature of the wax necessitates application

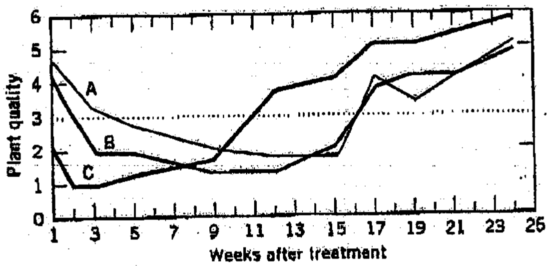


Fig. 5. Response of Kentucky bluegrass to sulfur-coated urea. Application of 2 lbs N/1000 ft^2 (9.76 g/m^2). Quality ratings of 1–3 are good, 4–6 fair. Quality rating of 3 is the minimum quality acceptable. A is SCU (wax); B, SCU (no wax); and C, urea. Courtesy The O.M. Scott & Sons Co.

of a flow conditioner, such as diatomaceous earth, to keep the granules from sticking together. Typical SCU compositions of the TVA type consist of 14% sulfur, 2.1% sealant, and 2.5% conditioner.

Some SCU products are produced without sealant. These are produced under carefully controlled process conditions that have been optimized to minimize the formation of stress fractures in the sulfur coating (11). However, such products are more prone to attrition damage when handled than SCU products with a sealant coating.

Sulfur-coated urea is produced in North America by a number of suppliers including ICI Canada (Courtright, Ontario), Lesco, Inc. (Martins Ferry, Ohio), Pursell Industries (Sylacauga, Alabama), and The O.M. Scott & Sons Co. (Marysville, Ohio). All produce a number of fertilizer grades and particle sizes. Sulfur-coated ureas and compound (N–P–K) fertilizers also are produced by Mitsui Toatsu (Japan).

SCU has found use in the following markets. Products serving these markets are generally blends of SCU with other fertilizer components.

Granular particle size	Market
standard	turf (golf courses) lawn-care companies (homeowners) nurseries specialty agriculture
mini	turf (golf tees and greens) lawn-care companies
micro	turf (golf greens)

Polymer-Coated Fertilizers. Polymer-coated fertilizers (PFC) represent the most technically advanced state of the art in terms of controlling product longevity and providing nutrient efficiency. Because most polymer-coated products release by diffusion through a semipermeable membrane, the rate of release can be altered by composition of the coating and the coating thickness. Polymer coatings can be categorized as either thermoset resins or thermoplastic resins (see COMPOSITE MATERIALS, POLYMER-MATRIX). Because of the relative high coatings cost of most polymer-coated products compared to SCU, their use has been primarily restricted to high value applications. Polymer-coated fertilizer technologies vary greatly between suppliers.

Grace Sierra Horticultural Products Co. This company uses technology originally patented by Archer Daniels Midland Corp. for the production of polymer-coated products. The alkyd resin coating technology, developed in the early 1960s, involves coating a soluble fertilizer core with a thermoset copolymer of dicyclopentadiene and a glycerol ester (linseed oil) dissolved in an aliphatic hydrocarbon solvent.

Nutrient release patterns vary with the amount of coating applied and the substrate used. Coating weights vary from 10 to 20%. Typically, commercial products are blends of different coating weights. Coated substrates include, but are not limited to, urea, potassium sulfate, and ammonium nitrate-based N–P–K fertilizers.

The Osmocote product line is based on coating prilled N–P–K fertilizers. Product longevities range from 5 to 16 months, depending on the temperature. The Osmocote line also includes a coated N–P–K miniprill which lasts 2–3 months.

The Sierra product line contains secondary and minor elements. Sierrablen products, ie, blends of Osmocote with uncoated nutrients for quicker initial response, contain iron. Blends of Osmocote with uncoated granules are sold to the specialty agriculture high value crops markets under the trade name Agriform.

High-N products are blends of Osmocote with coated granular urea. These blends are made with heavier coating weights and provide the longest longevities in Grace-Sierra's product line. The cost of the heavier coatings is offset through the use of coated urea which has a lower cost per unit of nitrogen than coated N–P–K complex fertilizers.

Grace-Sierra products, like most polymer-coated products, release by diffusion kinetics through a semipermeable membrane. Water vapor penetrates the resin coating and dissolves the water-soluble fertilizer core. The dissolved nutrients then diffuse back out through the coating to the environment. The release pattern is much more linear than SCU technology, which releases by matrix kinetics through coating imperfections. The difference in release mechanism is easily seen by looking at the growth response of Kentucky bluegrass. Bluegrass treated (2 lb N/1000 sq ft) (9.76 g/m^2) in the greenhouse with a number of polymer-coated fertilizers is compared to urea. Fresh weights were recorded weekly and plotted in Figure 6 as cumulative yield as a function of time. The linear release patterns of the polymer-coated fertilizers are quite apparent.

The coating material is a copolymer of dicyclopentadiene and a glycerol ester of linseed oil. This material is dissolved in mineral spirits and applied in multiple layers to the fertilizer in a batch coating drum operating at 65–70°C. About 3% resin is applied in each coating cycle which takes about 20 minutes. About half the cycle is devoted to applying the coating; the remainder is used for evaporation of the solvent. The solvent is recovered and recycled back into the system. The process goes through repeated coating cycles until the desired coating weight is achieved. Grace-Sierra operates production facilities in Milpitas, California; Charleston, South Carolina; and Herleen, The Netherlands.

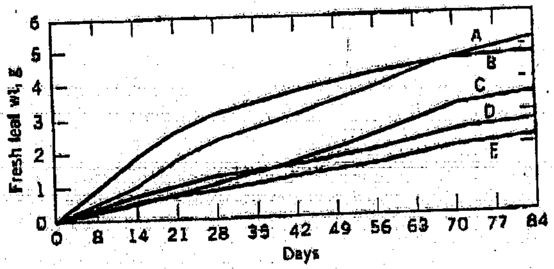


Fig. 6. Response of Kentucky bluegrass to polymer-coated fertilizors of select manufacturers. Application of 2 lbs N/1000 ft^2 (9.76 g/m^2). A is Mulitcote 4 (29-0-0) (Haifa); B, urea; C, Pursell; D, Nutricote (Chisso-Asahi); and E, Grace-Sierra. Courtesy of The O.M. Scott & Sons.

High product costs limit distribution to high value crop markets. This includes commercial ornamental production such as nurseries and greenhouses, citrus production, and strawberry production. Limited amounts are sold to the consumer lawn and garden market.

Chisso-Asahi Fertilizer Company, Ltd. This company utilizes thermoplastic resins, such as polyolefins, poly(vinylidene chloride), and copolymers, as their coating materials. The coatings are dissolved in fast-drying chlorinated hydrocarbon solvents and are applied to a variety of substrates including urea, diammonium phosphate [*7783-28-0*], potassium sulfate [*7778-80-5*], potassium chloride [*7447-40-7*], and ammonium nitrate/potassium sulfate-based N–P–K fertilizers.

Chisso-Asahi produces a number of different fertilizer grades. Because the thermoplastic polymers used are highly impermeable to water, release controlling agents such as ethylene–vinyl acetate and surfactants are added to the coating to obtain the desired diffusion characteristics. Coating thicknesses are essentially the same for all products with the release pattern being controlled by the level of release controlling agent. Release rates can also be altered by blending talc resin into the coating. Release patterns are characterized by a water leach test conducted at 25°C. A designation T-180 means the product releases 80% of its nutrient over 180 days when placed in water at room temperature. Products ranging from T-90 to T-360 are marketed.

As with other polymer-coated fertilizers, nutrients are released by diffusion through the coating. The various releasing agents incorporated into the coating change the permeability characteristics. The amount of release agent contained in the coating determines how fast the nutrients will diffuse. Typical of most polymer-coated fertilizers, the release is largely affected by temperature. However, the manufacturer attempts to minimize this effect by dispersing mineral fillers into the coating. Figure 6 shows the turfgrass growth response to a typical Asahi coated fertilizer marketed as Nutricote in the United States.

Chisso-Asahi uses a spouted bed process for the production of their coated materials (12). A 12,000 t/yr facility is located in Japan. The semicontinuous process consists of two batch fluid-bed coaters. A dilute polymer solution is prepared by dissolving 5% polymer and release controlling agent into a chlorinated hydrocarbon solvent such as trichloroethylene. The solution is metered into the spouted bed where it is applied to the fertilizer core. Hot air, used to fluidize the granules, evaporates the solvent which is recovered and reintroduced into the process. Mineral talc, when used, is either slurried into the polymer solution or introduced into the fluidizing air.

Asahi Chemical Industries uses this process to coat N–P–K fertilizers, marketed as Long, High Control, and Nutricote.

Urea and ammonium sulfate [*7783-20-2*] are coated by Chisso Co. under the trade names LP Cote and Meister. All U.S. consumption of these products is sourced from Japan. Chisso-Asahi products are marketed through very specific distribution channels (Table 5). Coated N–P–K products are marketed primarily to commercial nurseries and greenhouses. Coated urea products are marketed in blends to commercial nurseries, as well as to professional turf and strawberry growers.

Exxon Chemical Canada. Exxon Research and Engineering Co. has developed a coating technology based on neutralized ionic elastomers, ie, the neutral-

Table 5. Distributors of Chisso-Asahi PCF

Distributor	Product type	Trade name
Plantco, Inc.	coated N–P–K	Nutricote
O.M. Scott & Sons	coated N/K	ProKote[a]
Vigoro Industries	coated urea	Escote Woodace[b]
Helena Chemical	coated urea	Meister

[a] Blended with uncoated nutrients.

[b] Also contains IBDU.

ization of various ionomers with metal cations such as zinc. PCT application (PCT/US87/00979) describes zinc neutralized sulfonated EPDM elastomers (see ELASTOMERS, SYNTHETIC-ETHYLENE PROPYLENE RUBBER) which have moisture barrier properties three orders of magnitude better than polyurethane. The barrier properties can be further improved by blending with other elastomers, such as styrene–4-vinylpyridine (13), or they can be made biodegradable by neutralizing with an amine-terminated caprolactone, instead of zinc (14,15). A second group of zinc neutralized ionic elastomers, ie, zinc-ethylene–methacrylic acid, has been described (16). Exxon Chemical Canada has developed a line of controlled release fertilizers, currently in the development stage, which use the Exxon technology.

Exxon Chemical Canada's products are distinguished from many of the other polymer-coated fertilizer technologies by very thin coatings. Using ultrathin coatings of 2 to 4%, Exxon can control the release of fertilizers over 2- to 12-month time periods. The coating technology is adaptable to a number of fertilizer materials, with urea being the primary substrate used. Product release patterns are altered by the thickness of the coating as well as the composition of the polymer.

Exxon products appear to release via a unique mechanism. Like other polymer-coated technologies, the penetration of water into the granule is purely by diffusion. However, as water enters the particle, an osmotic pressure is created as the fertilizer is solubilized. This pressure causes an expansion of the elastomeric coating and the particle swells to many times its original diameter. As the particle swells, the coating becomes increasingly thinner to the point where it cannot contain the internal pressure and the nutrient is released.

Agronomically, Exxon products have been successful on a number of crop applications under varied climatic conditions from the plains of Canada to the heat and humidity of Florida.

Exxon currently operates a small developmental unit located in Redwater, Alberta, Canada. It utilizes a sophisticated polymer coating of neutralized ionic elastomers. The polymeric materials are dissolved in a fast-drying organic solvent, such as toluene, prior to application to the fertilizer. On the small-scale developmental unit, the polymer solution is applied to the fertilizer substrate in a batch fluid bed. The fluidizing air strips off the organic solvent leaving a thin but tough elastomeric film around each particle. The organic solvent is reclaimed and recycled back to the process for subsequent use.

Exxon Chemical Canada is currently test marketing this developmental technology on a number of applications including high value vegetable crop, turf, and ornamental nurseries.

O.M. Scott & Sons. The O.M. Scott & Sons Co. (Scotts) has developed a series of coated products which utilize copolymer blends of vinylidene chloride copolymerized with methyl methacrylates, acrylonitriles, methyl acrylates, and/or vinylidene–vinyl chloride monomers.

These coated products contain from 5 to 15% coatings, are free-flowing, lack tackiness, and are resilient to handling. The nutrient release mechanism is a combination of diffusion and flow induced crystallization. Water vapor first must diffuse through the polymer coating to solubilize the fertilizer core. The osmotic pressure created by the solubilized core is thought to cause a change in the morphology of the polymer coating, from amorphous to crystalline. The crystallinity creates microchannels through which the fertilizer solution can be transported.

Scotts technology (17) uses fluid-bed (Wurster column) technology to apply polymeric coatings to a number of fertilizer substrates including urea, potassium nitrate, potassium sulfate, and monoammonium phosphate (MAP). The coating material is applied as a water-borne latex onto the fluidized substrate. As the substrate is fluidized with warm air (40–50°C), water is driven off and the latex coalesces into a continuous film around the fertilizer particle. The particular latex compositions used have selected glass-transition and blocking temperatures, which enable quick removal of the water before the soluble fertilizer core dissolves. This obviates the need to use precoats prior to the latex application.

Scott latex-coated products are designed for high temperature environments and long cycle crops such as commercial ornamental production and specialty agriculture.

Pursell Industries. In 1988, Pursell Industries acquired the production and marketing rights to a new developmental coating technology from Melamine Chemicals, Inc. This technology, known as the reactive layer coating (RLC) process, polymerizes two reactive monomers as they are applied to the fertilizer substrate in a continuous coating drum. These *in situ* reactive layer polymerizations form an ultrathin membrane coating which controls nutrient release by osmotic diffusion.

A number of products are being marketed under the trade name POLYON. These include coated basic fertilizer materials, ie, urea, potassium nitrate, potassium sulfate, potassium chloride, ammonium sulfate, ammonium phosphate, and iron sulfate, in various particle sizes. Coatings weights on urea vary from 1.5 to 15%, depending on the release duration desired. Table 6 lists typical products.

Nutrients are released from POLYON-coated fertilizers by osmotic diffusion. The RLC process permits application of ultrathin, hence lower cost, membrane coatings which distinguishes this technology from many other polymer-coated fertilizers. The coating thickness determines the diffusion rate and the duration of release. POLYON-coated urea at a 4% coating (44% N) will release at twice the rate and will have half the duration as an 8% coating (42% N).

During the manufacturing process for POLYON (18,19), the fertilizer substrate is coated with an excess of liquid diphenylmethane diisocyanate. This excess allows the diisocyanate to react with both the substrate surface and a layer of any one of several liquid polyester, or other polyols, which are subsequently applied over it. The two solvent-free liquids react, polymerizing *in situ*, to form a polyurethane coating which also is chemically bonded to the fertilizer core. The advantage of RLC technique is that the liquid coating materials can be applied and polymerized to the desired coating thickness in a continuous coating process drum without the need for solvents and associated recovery equipment. As a result, production costs are lower than many other commercial polymer-coated fertilizer technologies.

POLYON-coated products are marketed for turf and commercial nursery applications and specialty, medium to high cost, agricultural crop applications.

Haifa Chemical. Haifa Chemicals, Ltd. (Haifa, Israel) has developed a line of resin-coated products. Fertilizer granules are heated in a rotating pan and treated with a fatty acid and metal hydroxide, such as stearic acid [*57-11-4*] and calcium hydroxide [*1305-62-0*]. The two react to form a coating of the metal salt of a fatty acid, such as calcium stearate [*1592-23-0*]. Multiple layers of the fatty acid salt are reacted *in situ* followed by the application of a paraffin topcoat. Coating weights are relatively large compared to other technologies, but this is offset by the comparatively low cost of the coating materials. Substrates coated include potassium nitrate, urea, and triple superphosphate (TSP). The various coated components are blended together into different grades which are being marketed in the United States, under the name Multicote, for a variety of applications including specialty agriculture, turf, and commercial ornamental production (Table 7). The agronomic response to Haifa-coated urea (multicote 4 (29-0-0)) on turf is compared to other polymer-coated fertilizers in Figure 6.

Table 6. Polyon Products

POLYON-coated basic material	Coating, wt %	Analysis grade[a]
urea	4	44-0-0
urea	8	42-0-0
microurea	11	41-0-0
potassium nitrate	5	12-0-42
potassium chloride	3	0-0-60
ammonium sulfate	5	20-0-0

[a] Analysis grade refers to the primary nutrient content of a fertilizer. Nitrogen content is expressed as % elemental N. Phosphorus content is expressed as % P_2O_5, and potassium as % K_2O, given in the order N–P–K.

Table 7. Haifa Products Marketed as Multicote

Product	N, %	P_2O_5, %	K_2O, %
Multicote 4(1-1-1)	12	12	12
Multicote 4(3-1-1)	20	6	6
Multicote 4(2-1-1)	14	7	14
Multicote 4(1-0-1)	18	0	18
Multicote 4(3-1-2)	17	6	12
Multicote 4(KNO_3)	9	0	32
Multicote 4(urea)	29	0	0

Other Polymer-Coated Technologies. A number of other polymer-coated fertilizer technologies have been developed and are being marketed in Japan (Table 8). These products are used primarily in Japan on paddy rice and upland field agriculture.

Polymer/Sulfur-Coated Fertilizers. Polymer/sulfur coated fertilizers (PSCF) are hybrid products that utilize a primary coating of sulfur and a secondary polymer coat. These fertilizers were developed to deliver control release performance approaching polymer-coated fertilizers, but at a much reduced cost. Sulfur is employed as the primary coating because of its low cost. Low levels of a polymer surcoat are used to control nutrient release rate. Unlike the soft wax (hydrocarbon/oil) sealants used to cover imperfections in the sulfur coatings of SCUs, the polymers in this class of products are chosen to provide a continuous membrane through which water and nutrients must diffuse. The water permeability characteristics of the polymer controls the rate of water diffusion into the particle. The combination of the two coatings permits a positive cost/benefit value over products with singular coatings of sulfur or polymer.

Products are granular, free-flowing, and dust-free by nature, since no flow conditioner dust is used as with sulfur-coated fertilizers. They possess excellent abrasion resistance and handling integrity. Since the outer coating is a hard polymer, the products do not leave waxy residues on material handling and application equipment.

The nutrient release mechanism is through a combination of diffusion and capillary actions. Water vapor must first diffuse through the continuous polymeric membrane layer. The rate of diffusion is controlled by the composition and thickness of the polymeric film. Once at the sulfur/polymer interface, the water subsequently penetrates the defects in the sulfur coat through capillary action and solubilizes the fertilizer core. The solubilized fertilizer then exits the particle in reverse sequence. This diffusion controlled mechanism permits greater uniformity in nutrient release as compared to the typical matrix release of sulfur-coated fertilizers. The agronomic advantages of this are reduced surge growth after application and longer residual of up to six months. The difference in nutrient release between PSCF, eg, Scott's Poly-S, and SCU is illustrated by the comparative growth response of grass in Figure 7. In addition, the combination coating renders the nutrient release much less temperature sensitive than most polymer-coated fertilizers.

PSCFs are manufactured by a two-step coating process. The first step applies the sulfur coating by techniques described in the sulfur-coated fertilizer section; the sealant coat and conditioner are not applied. The application of the polymer is accomplished by various methods depending on the nature of the polymer ap-

Table 8. Japanese Polymer-Coated Fertilizer Technologies

Company	Coating	Type	Substrate	Trade name
Showa Denko	alkyd resin	thermoset	N–P–K	Sho-Cote
Central Glass	alkyd resin	thermoset	urea, N–P–K	Cera-cote
Nissan Chemical		thermoplastic	N–P–K	
Sumitomo Chemical		thermoplastic	urea	
Kyowa Hakko		thermoplastic	N–P–K	

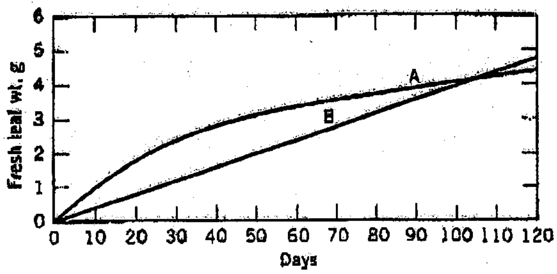


Fig. 7. Response of Kentucky bluegrass to polymer/sulfur-coated fertilizers (PSCF) and sulfur-coated urea (SCF). Application of 2 lbs N/1000 ft^2 (9.76 g/m^2). A is PSCF (Scott POLY-S); B, SCU. Courtesy of The O.M. Scott & Sons Co.

plied. Melt and reaction-coated polymers are typically applied in coating drum operations, whereas solvent borne, including latex, polymers are applied in a fluid-bed operation which utilizes heated air to strip off the solvent. The O.M. Scott & Sons Co. has commercialized a line of products under the trade name Poly-S, and Pursell Industries is marketing a PSCF under the trade name SulfurKote II.

PSCFs serve a number of markets including turf and garden, specialty agriculture, and commercial ornamental production.

BIBLIOGRAPHY

1. H. Kadawacki, *Bull. Chem. Soc. (Jpn.)* 11, 248–261 (1936).
2. K. G. Clark, J. Y. Yee, and K. S. Love. *Indust. Eng. Chem.* 40, 1178–1183 (July 1948).
3. AOAC 945.01, 15th ed., 1990.
4. AOAC 983.01, 15th ed., 1990.
5. U.S. Pat. 3,677,736 (July 18, 1972), R. Formaini (to Allied Chemical Corp.).
6. U.S. Pat. 4,089,899 (May 16, 1978), D. S. Greidinger (to Fertilizers and Chemicals, Ltd.).
7. U.S. Pat. 3,989,470 (Nov. 2, 1976), R. Czurak and R. M. Thompson (to The O. M. Scott and Sons Co.).
8. U.S. Pat. 5,102,440 (Apr. 7, 1992), W. E. Gallant, H. M. Goertz, and R. Martinez (to The O. M. Scott and Sons Co.).
9. AOAC 970.04, 15th ed., 1990.
10. *New Developments in Fertilizer Technology*, 14th Demonstration, TVA: National Fertilizer Development Center, Muscle Shoals, Ala., Oct. 5–6, 1983, pp. 30–33.
11. U.S. Pat. 3,903,333 (Sept. 2, 1975), A. R. Shirley (to Tennessee Valley Authority).
12. U.S. Pat. 4,019,890 (Apr. 27, 1977), T. Fujita and co-workers (to Chisso Asahi Fertilizer Co., Ltd.).
13. U.S. Pat. 4,701,204 (Oct. 20, 1987), L. I. Duvdevani, P. V. Manalastas, E. M. Drake, and W. A. Thaler (to Exxon Research & Engineering Co.).
14. U.S. Pat. 4,741,956 (May 3, 1988), W. A. Thaler, P. V. Manalastas, E. M. Drake, and R. D. Lundberg (to Exxon Research & Engineering Co.).
15. U.S. Pat. 4,788,081 (Nov. 29, 1988) (to Exxon Research & Engineering Co.).
16. U.S. Pat. 4,801,498 (Jan. 31, 1989) (to Exxon Research & Engineering Co.).
17. U.S. Pat. 5,089,041 (Feb. 18, 1992), H. E. Thompson and R. Kelch (to the O. M. Scott & Sons Co.).

18. U.S. Pat. 4,711,659 (Dec. 9, 1987), W. P. Moore.
19. U.S. Pat. 4,969,947 (Nov. 13, 1990) (to Melamine Chemicals, Inc.).

General References

Farm Chemicals Handbook, Meister Publishing, Willoughby, Ohio, 1990.

U.S. Pat. 4,969,947 (Nov. 13, 1990).

New Fertilizer Materials, Centre International des Engrais Chimique (CIEC), Noyes Development Corp., Park Ridge, N.J., 1968.

"Official Methods of Analysis", *J. Assoc. Off. Anal. Chem.*, (15) (1990).

Official Publication of Association of American Plant Food Control Officials (AAPFCO), Association of American Plant Food Control Officials, West Lafayette, Inc., No. 44, 1991.

Proceedings of the Symposium of Fertilizer, Present and Future, Japanese Society of Soil Science and Plant Nutrition, Sept. 25–26, 1989.

A. D. Davidson, *J. Assoc. Off. Anal. Chem.*, 769–774 (1983).

U.S. Pat. 3,223,518 (Dec. 14, 1965), L. I. Hanson (to Archer-Daniels-Midland).

J. T. Hays, "Controlled Release Nitrogen Fertilizers," *Manual Fert. Proc.* (1987).

S. P. Landels, M. M. Smart, J. Bakker, and J. Shimosato, "Controlled Release Fertilizers and Nitrification Inhibitors," *Chemical Economics Handbook*, SRI International, Menlo Park, Calif., 1989.

S. P. Landels, *Proceedings of the Controlled Release Fertilizer Workshop*, TVA: National Fertilizer and Environmental Research Center, July 30–31, 1991, pp. 87–101.

P. V. Manalastas, W. A. Thaler, E. N. Drake, and I. S. Pasternak, PCT Publication W087/06575, Exxon Research & Engineering Co., Nov. 5, 1987.

Eur. Pat. Appl. 0,276,179 (July 1, 1988), G. Pipko (to Haifa Chemicals, Ltd.).

S. Shoji, and A. Gandizer, *Controlled Release Fertilizers with Polyolefin Resin Coating*, Konno Printing, Sendai, Japan, 1992.

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PHARMACEUTICAL

Controlled-release dosage forms enhance the safety, efficacy, and reliability of drug therapy. They regulate the drug release rate to control drug action and reduce the frequency of drug administration to encourage patients to comply with dosing instructions. Conventional dosage forms often lead to wide swings in serum–drug concentrations. Most of the drug content is released soon after administration, causing drug levels in the body to rise rapidly, peak, and then decline sharply. For drugs whose actions correlate with their serum–drug concentration, these sharp fluctuations often cause unacceptable side effects at the peaks, followed by inadequate therapy at the troughs (Fig. 1). Administering smaller doses at more frequent intervals can damp concentration fluctuations, preventing over- and underdosing, but the inconvenience may cause patients to skip or delay doses, degrading efficacy. Compliance, measured as the percentage of patients taking 95% to 105% of prescribed oral medications, decreased from 67% with once-a-day regimens to 22% with four-times-a-day regimens (1). These difficulties are especially pronounced with drugs that have short half-lives and a narrow range of safe and effective concentrations. Precisely controlled release is particularly valuable for such agents (see DRUG DELIVERY SYSTEMS).