Slowly Available Nitrogen Fertilizers

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It is important to develop fertilizers which can supply proper quantities of nitrogen needed by the crops in every stage of growth in connection with its supply from the soil, as such fertilizers can prevent top dressing in the early stage of growth, save labor for additional fertilizers in the middle stage and improve the ripening of crops in the later stage.

on the other hand, as fertilizer is one of the most important mateterials for agricultural production, the development of new ones is required to be made on the principle of low price and mass-production. They, of course, must be good in properties as fertilizers. Many kinds of slowly available fertilizers have recently been developed to meet these demands, and most of them are con densates of urea and aldehydes.

The reason is that urea is a good material for fertilizers being the highest in nitrogen content in addition to its low price, and contrary to the high hygroscopicity of urea at high temperatures and high humidity, the condensates with aldehydes are extremely low in hygroscopicity and in solubility in water. Further-more,aldehydes which are by-products of petrochemical and other chemical industries are decreasing in price every year in inverse proportion to increase in production.

The following is an outline of the properties and effects of slowly available nitrogen fertilizers which are now on the market or in the development stage. Their materials, chemical composition and nitrogen content etc. are shown in Table 1.

Table 1. Slowly available nitrogen fertilizers.

Name	Materials	Chemical formula or composition	Nitrogen content (%)	solubility in water
Ureaform*	Urea, formaldehyde	Mixtures of methylene ureas	ca. 40	
	Urea	NH_2CONH_2	46. 65	100
	Methylene diurea	U-CH_2-U	42. 41	2. 18
	2 methylene 3 urea	U-CH_2-U'-CH_2-U	41. 16	0. 14
	3 methylene 4 urea	U-CH_2-U'-CH_2-U'-CH_2-U	40. 56	0. 01
	4 methylene 5 urea	U-CH_2-U'-CH_2-U'-CH_2-U'-CH_2-U	40. 21	trace
Urea-Z	Urea, acetaldehyde	Mixtures of ethylene ureas	31-35	ca. 4
	Ethylene	U-C_2H_4-U	38. 34	

	diurea 2 ethylene 3 urea	$U-C_2H_4-U'-C_2H_4-U$	36.19	
CDU* (Cyclo-diurea)	Urea, acet-aldehyde	2 oxo- 4 methyl- 6 ureido hexahydropyrimidine	32.54	0.12
IB*	Urea, iso-cutylaldehyde	Isobutylidene diurea $\begin{matrix}CH_3\\CH_3\end{matrix}>CH-CH<\begin{matrix}U\\U\end{matrix}$	32.16	0.1-0.01
FU*	Urea, furfural	2 furfurilidene 3 urea	24.99	hardly soluble
Guanylurea Sulfate	Lime nitrogen	$H_2N-\overset{\overset{NH}{\|}}{C}-U\cdot 1/2\ H_2SO_4\cdot 1/2\ H_2O$	34.99	easily soluble
Phosphate		$H_2N-\overset{\overset{NH}{\|}}{C}-U\cdot H_3PO_4$	28.00 (35% as P_2O_5)	easily soluble
Glycoluril	Urea, glyoxal	$C_2H_2\ (CON_2H_2)_2$	39.42	hardly soluble
Oxamide		$(NH_2CO)_2$	31.81	0.02

* commercially available

U: NH_2CONH- (ureido group),

U': $-NHCONH-$ (ureidene group)

Ureaform

This was developed in the United States in 1946, and the oldest one among the slowly available nitrogen fertilizers now in use. It was put on the market in this country in 1956. In the U.S. Ureaform is applied to long-year crops as lawn, and its principal component is 3-methylene-4 urea, while in Japan lower condensates as methylene-2 urea or 2-methylene-3 urea are used for short-term crops.

All these fertilizers are mixtures of methylene type compounds including urea itself. Experimental data now in hand show that the methylene ureas can be hydrolyzed by

acids, but they are mainly decomposed by bacteria in the soil. And the bacteria taking part in the decomposition are considered to be aerobic ones.

Methylene ureas, therefore, cannot be decomposed to be available a long time in the paddy field which is apt to be in reductive condition after the flooding of water. They are low in solubility (2-0.1 g/100 ml water), but leaching occurs because of their non-adsorption to the soil.

In consequence, they cannot be expected too much for the application to the paddy field. They, however, slowly decompose to be available under upland condition according to tempereture and water content and are very useful to reduce the damage by high concentration of salts. They are the lowest in hygroscopicity among the slowly available fertilizers.

IBDU (isobuthylidene diurea)

This was developed in Japan and marketed in 1962. The component is a condensate of 1 mol of isobuthyldehyde and 2 mols of urea.

This substance makes urea free as a result of hydrolysis. So its solubility is not constant, though it is estimated to be 0.1-0.01 g/100 ml water by the ordinary method. The quickness of their availability differs with the size and hardness of grains because their decomposition and availability are influenced by their contact with water.

When they are merely mixed with ordinary high analysis compound fertilizers (2-4 mm in the diameter of grains), they are suitably applied to the upland crops, but too quick to become available in case they are used for basal dressing to the paddy rice. They show good results in the paddy field when the grain is larger in size (5-8 mm) and higher in hardness. The experimental results throughout the country are summarized in Table 2.

Table 2. Yield Index and the number of case of IB compound fertilizer effect on puddy Rice

1961~1964 IB 100% Comp. Fert.			1965~1966 IB 80% Comp. Fert.		
Numb. of Case		Yield Index	Numb. of Case		Yield Index
	Control	IB all basal dress		Control	IB basal dress
16	100	107.8	11	100	105.4
	Control	IB basal+top dress		Control	IB basal+top dress
19	100	105.2	11	100	109.3

CDU (crotonylidene diurea)

This fertilizer was developed by BASF in Germany in 1957 and is now on the market under the name of Floranid. It is a single compound made by the condensation of 2 mols of acetaldehyde and 2 mols of urea. The formal chemical name is 2-oxo 4-methyl 6-ureido hexahydropyrimidine. It was put on the market as a slowly available fertilizer in this country since 1963.

It is as useful as Ureaform to prevent damage by high concentraton and slowly available to the upland crops. However it has yet been proved to be sufficiently effective to the rice plant in paddy fields probably owing to the fact that they are decomposed by soil bacteria, especially aerobic ones.

Recently it has been made clear that the urea molecule on the side chain is made free by hydrolysis with acids and the pyrimidine ring is broken by the attack of various kinds of bacteria. So it may be expected that CDU become sufficiently effective to the rice plant in paddy fields when a suitable fertilizer is combined with it.

Among aldehydes acetaldehyde, the material of CDU, is a by-product of petrochemical industries and expected to be in the greatest quantities in future. So its price will be lowered with the increase in production.

Guanylurea

Guanylurea is a weakly basic substance produced by hydrolysis of dicyandiamide with acids and combined with the acids used for hydrolysis in the salts as shown in Table 1. There are also nitrate and carbonate of it.

In Japan the use of this substance as fertilizer has been examined since 1930 or so. A tendency that urea takes the place of guanylurea as a material for melamine resin is conspicuous recently, making the production of this substance as a fertilizer possible.

Guanylurea contains much components as fertilizer (T-N 33% in sulfate, T-N 28% and T-P_2O_5 35% in phosphate, etc.), and is low in hygroscopicity. In addition to these properties, it has been known recently that it has the effect of nitrification inhibitor, and its nitrogen is more adsorptive to the soil than that of ammonium phosphate.

It has been put on the market as a fertilizer for paddy field since 1967, but time needed for decomposition to be available differs with the kind of soil, being 2 weeks at the earliest and 8 weeks at the latest according to the kind of clay minerals and the development of reductive condition after flooding.

The above-mentioned 4 kinds of slowly available nitrogen fertilizers were put on the market in the latest several and their productions are shown in Table 3.

Tabel 3. Production of slowly avail. nitrogene fertilizers

	(t)
1965	19,300
1966	26,300
1967	36,000

Those that follow are not yet on the market, but investigations are now in progress to put them to practical use.

Urea-Z

The study of this substance started in Germany in 1956. It is a condensate of urea and acetaldehyde as CDU. But CDU is not produced by the condensation because the reaction is carried out around the neutral point, at pH 6-8. It is considered to be a mxture of ureid which has ethylene bond. It is hardly soluble in water and decomposed by hydrolysis to be available.

Difurfurylidene triureid

This is a condensate of 2 mols of furfural and 3 mols of urea and least in solubility in water, showing markedly slow availability even in the paddy field. It, howeyer, has a gloomy prospect of practical use for the present owing to the high price of the material, furfural.

Oxamide

It was shown for the first time by the studies in this country in 1955 that oxamide is a superior substance as a slowly available nitrogen fertilizer. Its use as a fertilizer, however, has not progressed ever since because there was no development in its mass-production.

The mass-production of this substance has a definite outlook recently. The mechanism of its decomposition to be available in the soil is also coming to light gradually.

Glycoluril (acetylene urea)

Glycoluril is a condensate of 1 mol of glyoxal and 2 mols of urea. It is known that this substance is hardly soluble in water,and slowly decomposed by bacteria.

Nitrification inhibitors and coating fertilizers are also included in the slowly available fertilizer in a broad sense. They, however, are too much different from the group mentioned above in the prime object of application and in the composition to be dealt with in this paper.