Note: This is a reference cited in *AP 42, Compilation of Air Pollutant Emission Factors, Volume I Stationary Point and Area Sources.* AP42 is located on the EPA web site at www.epa.gov/ttn/chief/ap42/

The file name refers to the reference number, the AP42 chapter and section. The file name "ref02_c01s02.pdf" would mean the reference is from AP42 chapter 1 section 2. The reference may be from a previous version of the section and no longer cited. The primary source should always be checked.

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FORMALDEHYDE USE IN UREA–BASED FERTILIZERS

Report
of
The Fertilizer Institute
Formaldehyde Task Group

February 4, 1984

The Fertilizer Institute
Washington, D.C.

REPORT OF TFI'S TASK GROUP ON FORMALDEHYDE USE IN UREA–BASED FERTILIZERS

SUMMARY

Through its Task Group on Formaldehyde, The Fertilizer Institute (TFI) examined the use of formaldehyde for in-process production of conditioning agents for solid urea and in the manufacture of slow-release ureaform fertilizers. TFI initiated this effort because of health concerns raised by reports on formaldehyde's potential to induce nasal tumors in laboratory animals.

TFI's Task Group on Formaldehyde sought data on the exact chemical form of the added "formaldehyde," as it has been traditionally reported by the fertilizer industry, in both solid urea and ureaform fertilizers. Additionally, the Task Group examined the potential of formaldehyde exposure during the production, handling, and use of urea-based fertilizers.

All evidence reviewed uncovered no significant employee or public exposure to formaldehyde during the storage, handling, or use of formaldehyde-based additives in production of urea-based fertilizers. The Task Group 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 (46–0–0). For ureaform on the other hand, the Task Group determined that the final product consists of a polymer of methyleneureas, similar to the MDU in solid urea. Studies on use of methyleneureas as fertilizers demonstrated that no detectable formaldehyde is released in the soil.

The Task Group recommended that the industry change its traditional reference of "% formaldehyde" as a conditioning agent to "% methylenediurea," assuming complete conversion of formaldehyde to methylenediurea (MDU), by multiplying the % formaldehyde value by the factor (4.4). The Task Group emphasized that the chemical test employed to measure the "% formaldehyde" does not distinguish between "free," unreacted formaldehyde and the subsequently formed stable compounds, such as MDU.*/

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INTRODUCTION

Recent toxicology studies have linked exposure of laboratory animals to gaseous formaldehyde with nasal cancer and have raised concerns about its potential carcinogenic effects in humans. As a result, federal and state regulatory programs have focused on possible restrictions on use of and exposure to formaldehyde.

Since approximately 95% of the domestic solid urea producers condition urea with a formaldehyde-based additive, historically reported as "formaldehyde," and all slow-release, ureaform fertilizers are produced from the reaction of urea and formaldehyde, TFI initiated an investigation into the use of formaldehyde (1) in the production of conditioning agents for solid urea and (2) in the production of ureaform fertilizers.1/ TFI's efforts were guided by a Task Group of industry experts, and this report compiles the Task Group's findings and recommendations on formaldehyde use in urea-based fertilizers.

This report covers the following subjects: (1) formaldehyde-based additive use in manufacturing urea fertilizers; (2) current urea and ureaform manufacturing practices; (3) formaldehyde chemistry relevant to production of urea and ureaform fertilizers; (4) formaldehyde exposure potentials during production, handling, and use of urea fertilizers; and (5) the Task Group's findings and recommendations on continued use of formaldehyde in urea-based fertilizers.

HISTORY – FORMALDEHYDE IN UREA

In crop year 1981, about 5 million tons of solid urea were domestically produced, with over 80% used as fertilizer.2/ Approximately 95% of the domestic urea fertilizer producers condition their urea with a formaldehyde-based additive and virtually all solid urea producers employ some type of conditioning agent to improve product handling. Conditioning agents are used to harden the product, reduce dust generation during handling, and/or provide anticaking properties for storage.*/

The European chemical industry introduced a variety of new fertilizers including urea in the early decades of this century. Urea was first marketed in 1915 by Badische Anilin- und Soda-Fabrik (BASF), Germany. Working in Muscle Shoals, Alabama, the U.S. Department of Agriculture tested urea as a fertilizer from 1921 – 1924. By the early 1930's, U.S. industry was producing urea liquor and crystal. During these years, high value was placed on water insoluble (slow-release) nitrogen fertilizers, and formaldehyde was originally added to a urea-ammonia liquor to convert a portion of the urea to water insoluble nitrogen. Resulting technology developments led to the commercial production of slow-release nitrogen fertilizers, called ureaform or urea-formaldehyde.

Although crystal urea was marketed in this country from 1933, urea in solid form was not produced in significant quantities in the U.S. before World War II. However, from the 1940's through the 1960's, U.S., European, and Japanese scientists continued work on ways to condition urea with a variety of compounds. Several patents were issued for the use of formaldehyde as a urea conditioning agent. Patented methods for adding formaldehyde or formaldehyde mixtures included spraying, coating, dusting, or passing urea particles through a gaseous formaldehyde atmosphere to cause a reaction on the surface of the particle.

A few patents for the addition of various conditioning agents to molten urea prior to prilling or crystallization appeared in the mid 1960's and early 1970's. Work done in-house by many urea producers made the addition of formaldehyde-based additives to urea melt a common practice throughout the industry by the mid 1970's.

Industry experts attribute the popularity of formaldehyde-based additives to the improved product handling characteristics mentioned above. Additionally, the introduction of granulation technology required the use of such conditioning agents.

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*/ Bibliography No. 1104 (1957 – 1978), an appendix to reference 6 of this report, compiled by the library of the Tennessee Valley Authority's National Fertilizer Development Center, lists 17 scientific papers and 70 patents on the conditioning of solid urea.

USE OF FORMALDEHYDE–BASED ADDITIVES (FBAs) IN UREA AND UREAFORM FERTILIZER PRODUCTION

Formaldehyde–Based Additives (FBAs)

The FBAs used to condition prilled or granular urea are available in several commercial forms. The two most commonly used in the fertilizer industry are Formalin and urea-formaldehyde (UF) concentrates. FBA is usually injected into the urea production process to produce, *in situ*, the urea conditioning agent.

Formalin is a water solution of formaldehyde (30–52 w%) stabilized with methanol to minimize polymer precipitation. Formalin is generally stored at 15° C (60° F) or above to minimize polymer precipitation. Since the flash point with 15 w% methanol is 50°C (122° F), an optimum storage temperature range is 23–26 °C (75–80° F). Formalin is transported in stainless steel, aluminum, or lined tank trucks or rail cars and stored on-site in atmospheric pressure tanks. Since the vapors from Formalin solution may be flammable, suitable venting precautions must be taken.

UF–concentrates consist of formaldehyde and urea in a water solution. The formaldehyde, urea, and water react reversibly yielding a stable solution with a low vapor pressure at ambient temperatures. As discussed more fully below, at ambient temperatures, the predominate chemical species are methylolureas. A UF–concentrate of 60% formaldehyde, 25% urea, and 15% water has no flash point up to its boiling point and is normally stored at 15° C (60 °F); its freezing point is about –20°C (–4° F). At temperatures above 35°C (95°F), the viscosity gradually increases because of polymerization. UF–concentrates are transported in stainless steel, aluminum, or lined tank trucks or rail cars and are stored on-site in atmospheric pressure tanks.

Urea Process Description

Urea is produced by reacting ammonia and carbon dioxide in a urea production process using either a "once through," "partial recycle," or "total recycle" system. The basic difference in the three processes is the method of handling the unreacted ammonia and carbon dioxide. The once through process makes no attempt to recycle ammonia and carbon dioxide. Instead, the off-gases are typically used in the production of other fertilizer products. On the other hand, partial recycle processes recycle ammonia back to the urea process and vent any excess carbon dioxide. Both ammonia and carbon dioxide in the off-gas are recycled in the total recycle process.

All urea processes in use in the United States react ammonia and carbon dioxide at elevated pressures and temperatures to form ammonium carbamate (I) which is dehydrated to form urea (II). The reactions are:

$$CO_2 + 2NH_3 \longrightarrow \underset{\text{I}}{NH_4OCONH_2} \longrightarrow \underset{\text{II}}{NH_2CONH_2} + H_2O \qquad (1)$$

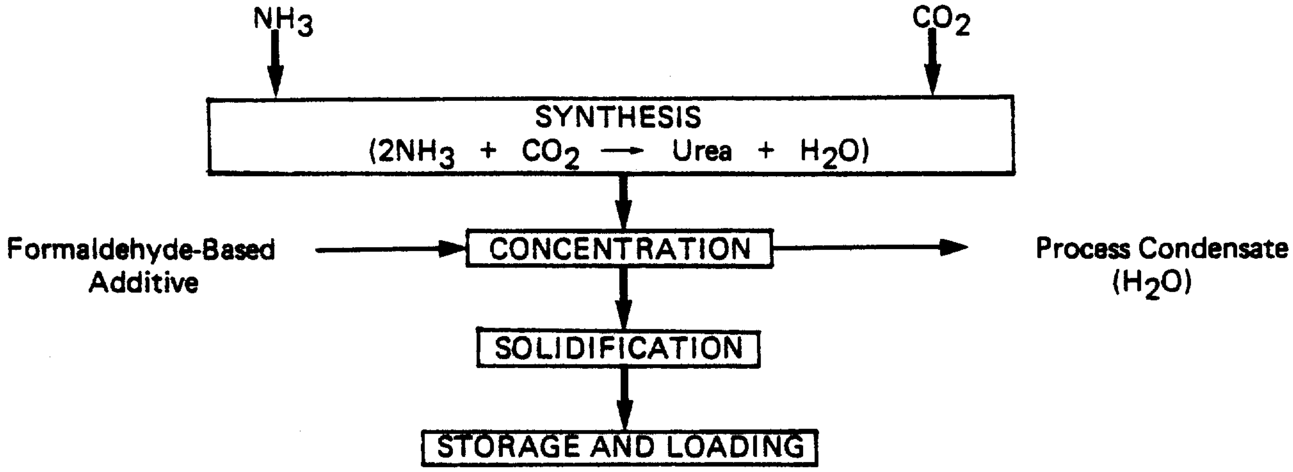
The reactions take place in reactor vessels at pressures ranging from 170 to 400 atmospheres and at temperatures from 121° C to 182°C (250 – 360°F).

The first reaction, forming ammonium carbamate, is highly exothermic while the carbamate dehydration reaction, to form urea, is slightly endothermic. Reactors are typically operated to allow the dehydration reaction to proceed to 40 to 60 percent completion resulting in an overall net exothermic heat effect. Purification of the ammonia, carbon dioxide, and ammonium carbamate in the liquid stream from the reactor results in about a 70% urea solution.

To produce a solid product, the urea solution is concentrated prior to actual prilling, granulation, or crystallization. The concentration step takes place in flash evaporators designed with minimum residence time to prevent the formation of biuret ($NH_2CONHCONH_2$) which is undesirable because of its deleterious effect on some crops.

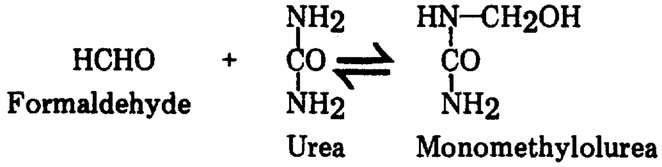
The overwhelming majority of domestic solid urea producers use formaldehyde-based additives to produce a conditioning agent in prilled or granulated urea. Additives are typically introduced in the concentration step of the process. Figure 1 provides a flow diagram outlining the urea production process.

Figure 1

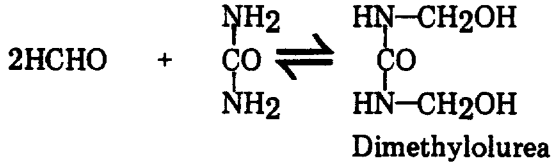


Urea-Formaldehyde Chemistry

At room temperature and neutral pH, addition of formaldehyde to urea in a water solution forms a group of compounds called methylolureas via a readily reversible reaction. This reaction occurs in the commercially available UF—concentrations.3/ Equations (2) and (3) illustrate the basic equilibrium reactions:



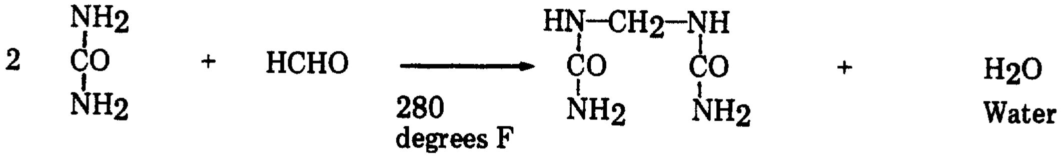
$$\underset{\text{Formaldehyde}}{HCHO} + \underset{\text{Urea}}{\begin{matrix} NH_2 \\ | \\ CO \\ | \\ NH_2 \end{matrix}} \rightleftharpoons \underset{\text{Monomethylolurea}}{\begin{matrix} HN\text{—}CH_2OH \\ | \\ CO \\ | \\ NH_2 \end{matrix}} \qquad (2)$$



$$2HCHO + \begin{matrix} NH_2 \\ | \\ CO \\ | \\ NH_2 \end{matrix} \rightleftharpoons \underset{\text{Dimethylolurea}}{\begin{matrix} HN\text{—}CH_2OH \\ | \\ CO \\ | \\ HN\text{—}CH_2OH \end{matrix}} \qquad (3)$$

At elevated temperatures, methylolureas are reactive and somewhat unstable compounds subject to polymerization or the release of formaldehyde vapor. Furthermore, all the contained formaldehyde in methylolureas is measured in the iodine titration analytical method as free formaldehyde. The formaldehyde in UF—concentrates is bound as methylolurea, probably in the dimethylol form, because of the large excess of formaldehyde present.

In the urea production process, FBA is injected into molten urea or a hot urea solution. At the temperature of urea process, ≈187 °C (280° F), formaldehyde reacts to form methylenediurea and water.[4] The reaction is only reversible in the presence of strong acids. Regardless of the source of the formaldehyde, the chemistry of each process is similar, as illustrated in equation (4):



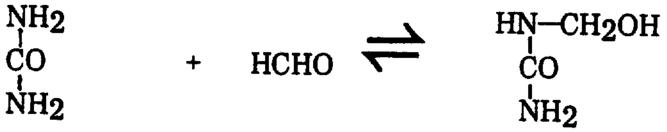
$$2\;H_2N{-}CO{-}NH_2 + HCHO \xrightarrow[\text{280 degrees F}]{} H_2N{-}CO{-}NH{-}CH_2{-}NH{-}CO{-}NH_2 + \underset{\text{Water}}{H_2O} \qquad (4)$$

Methylenediurea (MDU)

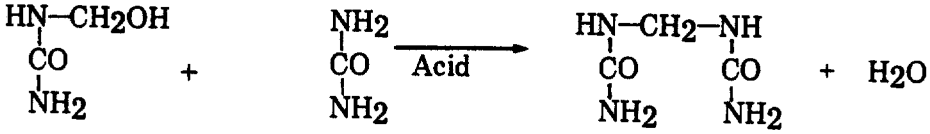
Assuming 100% yield of MDU, the weight ratio of MDU formed to formaldehyde reacted is 4.4:1.

In the production of ureaform fertilizers, the reaction pathway proceeds through the formation of MDU. The reaction does not stop at MDU, however, but continues to form a polymer of methyleneureas. Because of the higher initial concentration of formaldehyde in the ureaform process than in solid urea production, MDU is formed from methylolurea.[5]

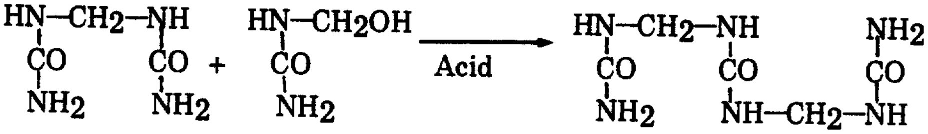
Equations (5), (6), and (7) provide the basic reaction sequence:



$$H_2N{-}CO{-}NH_2 + HCHO \rightleftharpoons HOCH_2{-}NH{-}CO{-}NH_2 \qquad (5)$$



$$HOCH_2{-}NH{-}CO{-}NH_2 + H_2N{-}CO{-}NH_2 \xrightarrow{\text{Acid}} H_2N{-}CO{-}NH{-}CH_2{-}NH{-}CO{-}NH_2 + H_2O \qquad (6)$$



$$H_2N{-}CO{-}NH{-}CH_2{-}NH{-}CO{-}NH_2 + HOCH_2{-}NH{-}CO{-}NH_2 \xrightarrow{\text{Acid}} H_2N{-}CO{-}NH{-}CH_2{-}NH{-}CO{-}NH{-}CH_2{-}NH{-}CO{-}NH_2 \qquad (7)$$

Reaction (7) is simply repeated to yield longer chain lengths of the polymer.

Formaldehyde–Based Additives (FBA) In Urea Production

FBA, when added to the hot urea process at low concentration, immediately and essentially irreversibly reacts to form methyleneureas, at which point the formaldehyde loses its chemical identity. The principal reaction product in the resulting urea product is methylenediurea (MDU).[4] MDU is the actual conditioning agent for solid urea produced with FBA. FBA is usually added to urea at a level of 1.3 to 2.2 w% measured as MDU -- equivalent to 0.3 – 0.5 w% formaldehyde as determined by the chromatropic acid test.

MDU conditions urea forming a harder crystal that is less prone to caking or dusting. MDU also has dessicant properties which minimize recrystallization that occurs on the surface of urea particles during cyclic exposure to moisture.

Urea Fertilizer Storage, Transportation & Application

Solid urea is often stored in bulk warehouses holding up to 100,000 tons. The material is then transferred from storage to either bagging or bulk loading facilities using fixed or mobile reclaiming equipment. FBA is used to reduce product caking and dusting during storage and handling of solid urea fertilizer.

Prilled granulated urea is transported by ship, truck, or rail cars in bags or in bulk to the point of end use. In addition to its primary uses as the highest nitrogen content solid fertilizer and as an animal feed supplement, urea is a raw material for the production of adhesives, textile finishes, paper coatings, and molding compounds. As a fertilizer, urea is added to mixed fertilizers to increase their nitrogen content or is directly applied to fields.

Ureaform Fertilizers

Ureaform fertilizers are produced from a mixture of urea, UF—concentrate (25 w% urea, 60 w% formaldehyde, and 15 w% water), sodium hydroxide, and water. The reaction to produce ureaform is initiated by addition of acid, forming a wide distribution of methyleneurea polymers. The degree of polymerization is controlled by the ratio of urea to formaldehyde, temperature, time, and amount of acid (pH). The final product contains unreacted urea, methylenediurea, methylenetriurea, and longer chain polymers; nevertheless, the resulting ureaform must have at least 60% cold-water insoluble nitrogen by definition. But, the basic subunit of the polymer is analogous to the methyleneureas and nitrogen release characteristics vary considerably (2 months to 3 years) depending on the reaction conditions used.

Chromotropic Acid Test For Formaldehyde

Industry, as a matter of convenience, has traditionally measured the amount of formaldehyde-derived conditioning agent by the chromotropic acid test and expressed the results as "% formaldehyde" added. *In actuality, the chromotropic acid test responds to methylene groups as well as to formaldehyde. Therefore, this test is only useful in determining the total amount of formaldehyde originally added to the urea or ureaform production process. The test does not discriminate between stable urea-formaldehyde reaction products and free formaldehyde (including methylolureas). The chromotropic acid test is not a suitable test for measuring free formaldehyde where urea-formaldehyde derivatives may be present.*

There are a number of analytical methods for checking urea for free formaldehyde. The iodine titration technique is a satisfactory quantitative test, while Tollen's reagent can be used for a qualitative check. Measurement of urea: formaldehyde reaction products is most accurately accomplished using high performance liquid chromatography, however.

FORMALDEHYDE EXPOSURE POTENTIAL DURING PRODUCTION OF UREA–BASED FERTILIZERS

The potential for occupational exposure to significant concentrations of gaseous or "free" formaldehyde in the urea manufacturing process occurs only during handling of FBAs. This exposure situation may occur during transfer of FBAs from the transport vessel or during maintenance operations on equipment containing or contaminated with FBA. After the additive is injected into the urea process, FBA and any free formaldehyde associated with it react to form methyleneureas. Since this reaction is essentially irreversible and goes to practically 100% completion, the potential for exposure to formaldehyde associated with FBA is reduced to less than quantifiable levels when the FBA is injected into the process.6/ There is no possibility, or detected occurrence, of significant occupational exposure to gaseous formaldehyde resulting from prilling, granulating, handling, or use of urea fertilizer conditioned with FBA.

FBA is received and handled in water solutions, which are transferred to storage tanks by either pumping FBA or pressurizing the transport tank. As noted previously, FBA solution is typically maintained at 15°C (60°F) while stored in atmospheric pressure tanks. FBA is pumped from its storage tank through stainless steel piping and metered into the urea process at an appropriate location in the concentration step. The injection location is determined by the water content of the FBA used and the allowable water content of the concentrated urea solution. The transfer system is completely closed and exposure to gaseous formaldehyde does not occur as a result of the normal operation of FBA transfer.

Available data on formaldehyde levels in and around the urea production process frequently are below or near the limits of detection. Average formaldehyde levels varied from not detectable (< 0.005 parts per million (ppm)) to one ppm.*/ The highest exposure levels for formaldehyde were measured around pumps used to transfer FBA to the urea process. The formaldehyde concentrations around urea concentrators and solidification processes (prilling or granulating) typically were 0.05 ppm.6/

Thus, the potential for occupational exposure during the urea fertilizer manufacturing occurs chiefly during maintenance and repair operations. Standard operating procedure requires maintenance personnel to follow standard health and safety precautions, such as proper ventilation or personal protective equipment, to keep unavoidable exposures to formaldehyde as low as possible.

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*/ Current Occupational Safety and Health Administration Standards limit formaldehyde exposure to 3 ppm as a time weighted average for an eight-hour day. In April 1981, NIOSH published Current Intelligence Bulletin Number 34, which recommended limiting formaldehyde exposure to lowest feasible levels. The formaldehyde content of air samples was determined by the chromotropic acid test.

LACK OF FORMALDEHYDE EXPOSURE POTENTIAL DURING HANDLING, STORAGE, AND USE OF UREA FERTILIZERS

Solid urea fertilizer (46–0–0) typically contains the conditioning agent, methylenediurea (MDU), in the range of 1.3 to 2.2 w%, which corresponds to 0.3 to 0.5 w% "total formaldehyde" as determined by the chromotropic acid test. Air sampling in bulk storage facilities have yielded contradictory data, because analytical methods for sampling and analysis of low-level (< 0.05) ambient formaldehyde concentrations lack reproducibility and comparability.

Analyses of urea fertilizers for free, unreacted formaldehyde have yielded values for free formaldehyde of ≤ 100 ppm in the solid sample.*/ Moreover, in laboratory experiments duplicating boxcar conditions, 55°C (130° F), no detectable gaseous formaldehyde was released from urea fertilizer.6/

Furthermore, detailed studies on the nutrient values and chemical/biological pathways of methyleneureas have shown that such compounds can be used as a source of soil nitrogen without releasing any detectable formaldehyde in the soil.7–10/ Researchers at the U.S. Department of Agriculture concluded that methyleneureas at applications of up to one percent do not inhibit soil microflora and that no measurable chemical hydrolysis of methyleneureas to formaldehyde and urea occurs in normal soils.8/

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*/ Analysis was performed by iodine titration method with a detection limit of 100 ppm (0.01%).

CONCLUSIONS & RECOMMENDATIONS OF TFI'S FORMALDEHYDE TASK GROUP

In summary, TFI's Formaldehyde Task Group collected data showing that addition of a formaldehyde-derived conditioning agent, historically referred to as "formaldehyde," to hot urea fertilizer process results in the *in situ* formation of methylenediurea (MDU). A similar family of compounds, methyleneurea polymers, is formed in the ureaform production process. And, in light of additional data on occupational exposure to formaldehyde in the fertilizer industry and on the chemical pathway of methyleneureas in soils, the Task Group concluded:

1. While the formaldehyde-based additives (FBAs) to urea can release formaldehyde gas, such additives may be safely used in urea fertilizer production.
2. Formaldehyde, in any of its forms, reacts immediately and essentially irreversibly with urea in the hot production process to form methyleneureas, at which point the formaldehyde loses its chemical identity.
3. The principal reaction product formed upon injection of FBA to urea process is MDU. MDU is the actual conditioning agent for urea and not "formaldehyde," as has been historically reported by the fertilizer industry.
4. In the production of ureaform (slow-release) fertilizers, formaldehyde reacts irreversibly with urea to yield polymers of methyleneurea, which are chemically similar to MDU.
5. Evolution of gaseous formaldehyde, if any, from solid urea-based fertilizers approaches limits of detection during any phase of their storage, handling, or use.
6. The traditionally-used chromotropic acid test for determining the "% formaldehyde" in solid urea actually only measures the equivalent amount of formaldehyde originally added to the process and not the amount of "free" or gaseous formaldehyde in the product. Assuming complete conversion of FBA to MDU, the percentage of MDU present in urea may be calculated by simply multiplying "% formaldehyde" by the factor (4.4).

In light of the above conclusions, the Task Group recommended:

1. Fertilizer industry should refer to the actual urea conditioning agent, methylenediurea (MDU). The percentage of MDU in urea can be measured by the currently used analytical procedure for measuring "total formaldehyde," i.e. the chromotropic acid test, as is discussed in Conclusion 6.
2. Through TFI, seek change of the Agency for International Development (AID) standards for urea (46—0—0) to reflect Recommendation 1.*/

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*/ In response to TFI's efforts, the U.S. Agency for International Development (AID) specifications dated September 7, 1982, require a minimum 0.2% formaldehyde equivalent of MDU in urea (46—0—0).

FOOTNOTES

1. TFI Survey of Urea Producing Member Companies, July 1980.
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3. Walker, J.F., *Formaldehyde*. American Chemical Society Monograph No. 159. Robert E. Krieger Publishing Co., Huntington, NY (1975), pp. 219–221, 377–392.
4. Murray, T.P., Austin, E.R., Howard, R.G., and Horn, R.C. *Anal. Chem.,* 54, 1504 (1982).
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6. Letter to Edwin M. Wheeler from Billy J. Bond dated July 1, 1981, transmitting an unpublished report of Tennessee Valley Authority's National Fertilizer Development Center, Muscle Shoals, AL.
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