

Prereactor for Liquid Raw Materials in Mixed Fertilizer Manufacture

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A continuous prereactor, consisting of a compact concentric pipe arrangement, has been developed in which all the liquid raw materials required for granulated mixed fertilizers are premixed and prereacted before introduction into the solid raw materials. The prereactor has been successfully operated in full scale production plants. Its advantages are substantial elimination of ammonium chloride fume and loss of free ammonia, simplicity of construction, flexibility of operation, and absence of toxic gas evolution.

MOST CONVENTIONAL PROCESSES for the manufacture of granulated mixed fertilizer used in the United States consist of introduction of solid raw materials and recycle into an ammoniator into which the liquid raw materials are introduced separately underneath the bed of solids, which is kept in agitation by a tumbling or milling action (3, 4). The usual solid raw materials are one or more of the following: normal superphosphate, triple superphosphate, ammonium sulfate, potassium chloride, and potassium sulfate. The usual liquid raw materials are one or more of the following: water, sulfuric acid, phosphoric acid, anhydrous ammonia, aqueous ammonia, and nitrogen solution (an aqueous solution of ammonia, ammonium nitrate, and/or urea).

In the ammoniator liquids and solids are uniformly blended and certain desirable chemical reactions take place, primarily neutralization of sulfuric and phosphoric acids to form ammonium sulfate and ammonium phosphates, and reaction of ammonia with superphosphates to form ammonium phosphates and dicalcium phosphate.

Certain undesirable reactions may also take place. Some of the acids usually react with potassium chloride to form hydrochloric acid, which in turn reacts with ammonia to form ammonium chloride in the form of a dense white fume constituting an atmospheric pollutant. Removal of this fume from the mixer exhaust stack is difficult and requires highly efficient fume removal equipment. Other undesirable chemical reactions are decomposition of nitrogen compounds to nitrogen oxides and elemental nitrogen. This may result in significant loss of nitrogen and constitute a personnel hazard due to the toxic nature of some of the gases (2). Furthermore, under unusual circumstances concentrations of the decomposition gases may become great enough to cause flash fires in the ammoniator.

A further problem in conventional processes is incomplete absorption of ammonia by the superphosphates, which also results in loss of nitrogen and may

cause unpleasant and unsafe working conditions around the ammoniator.

These problems can be overcome, or minimized, if the sulfuric and phosphoric acids are neutralized before introduction into the ammoniator. If this is done, there can be no reaction between potassium chloride and acid, and thus no ammonium chloride fume formation. Furthermore, under the conditions of uniform and intense mixing in a prereactor, there should be little or no decomposition of the nitrogen compounds, as this is believed due to the localized action of strong acids in excessive proportions on ammonium nitrate and urea in conventional ammoniators. Also, absorption of ammonia by the superphosphates should be improved, because there is no competition for the ammonia by acid. For some ratios—for example, 1-4-4—acids should be preneutralized in a way to preserve the heat of the neutralization reactions, as in such grades one of the principal functions of acid is to generate heat as an aid to granulation.

In recent years a number of preneutralization processes have been developed (7, 5). Most of these operate on the principle of neutralizing the acids in an open tank with substantially the stoichiometric proportion of ammonia or nitrogen solution and separate introduction of the additional ammonia or nitrogen solution required for ammoniation of the superphosphates. These processes are particularly advantageous for very high nitrogen ratios such as 2-1-1, where external removal of water and heat is helpful, and they have to a large extent overcome the above problems. However, they have certain disadvantages. Additional metering and control equipment is required, because the nitrogen solution or ammonia is introduced into the process in two streams rather than one. A fair-sized neutralization tank and exhaust equipment are required, which constitutes a space problem in many plants. When nitrogen solutions containing both ammonium nitrate and urea are used, a toxic gas may be formed which is dangerous to operators (5).

The present work was undertaken to develop a prereactor in which all of the liquid raw materials required for mixed fertilizer manufacture could be combined, reacted, and introduced into the ammoniator in a single stream. The advantages of such a prereactor were expected to be simplicity and compactness of construction, elimination of ammonium chloride fume, improvement of ammonia absorption by superphosphates, elimination of undesirable decomposition reactions by carrying out the preneutralization in the presence of a substantial excess of ammonia, and wide flexibility in grades that can be produced, including both low and high nitrogen ratios.

This paper is a progress report of the present state of development of a prereactor which has been shown in plant operation to have the above advantages. Further experience will undoubtedly result in improvements and may also reveal limitations not now recognized.

Laboratory Work

Laboratory tests were conducted with a continuous-flow concentric-pipe prereactor made from stainless steel tubing. Several different combinations of the liquids water, anhydrous ammonia, nitrogen solution (37% N, 66.8% NH_4NO_3 , 16.6% free NH_3 , and 16.6% H_2O), sulfuric acid (60° Bé.), and phosphoric acid (75% H_3PO_4) were preblended and prereacted, and then discharged into a stainless steel beaker.

In one series of tests sufficient sulfuric acid (60° Bé.) was prereacted with nitrogen solution to neutralize the free ammonia. No additional water was used and the products were discharged from the reactor pipe in the form of a thin boiling paste at temperatures as high as 250° F. Approximately 3 feet of reaction tube was needed to complete the neutralization and no clogging occurred.

To determine the most advantageous arrangement for blending water, anhydrous ammonia, and nitrogen solution, water and nitrogen solution were mixed satisfactorily in a simple tee. However,

the flow of both developed pulsations when anhydrous ammonia was added through a second tee. The pulsations were eliminated by replacing the second tee with a concentric pipe arrangement. The plant scale blending pipe was patterned after the laboratory device.

Phosphoric acid (75% H_3PO_4 , wet process) and anhydrous ammonia were prereacted at a calculated $NH_3-H_3PO_4$ mole ratio of 1.5 in laboratory tests of limited scope. The purpose was to find a method for eliminating internal clogging of the reactor discharge tube section while producing concentrated ammonium phosphates. Clogging was avoided by blending approximately 2 pounds of water into each pound of ammonia previous to its introduction into the reactor section and feeding the acid through the inner pipe. To prevent clogging while starting the liquid flows, compressed air was fed through each liquid supply tube for a few minutes before and during each start-up.

Description of Prereactor

The general arrangement required to blend and react the liquids in simple concentric pipes was adequately established using laboratory apparatus. However, problems as to materials of construction, method of discharging the products into the ammoniator-granulator, and sizing of the components for efficient performance were necessarily solved in plant scale development work.

The Davison Trenton process plant at Curtis Bay, Md., was used in the initial plant tests. An inexpensive mild steel prototype with very thick reactor and discharge pipe walls ($3/4$ -inch wall thickness) was installed and used in normal granulation operations. The sections of the expendable test unit were joined with standard pipe flanges and thus could be removed and altered or replaced with a minimum of time and

expense. If malfunction or poor performance of any one component was observed, an improved replacement for the component was fabricated, installed, and observed in operation. In this manner, the final prereactor design evolved.

Figure 1 shows the details of the prereactor now being used in Trenton process granulation operations. Each liquid raw material is metered and sup-

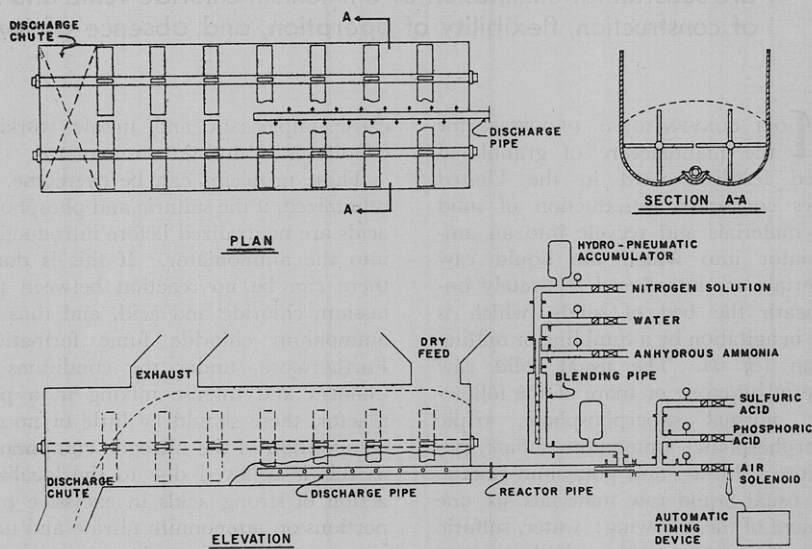


Figure 1. Arrangement of prereactor in granulation pug mixer

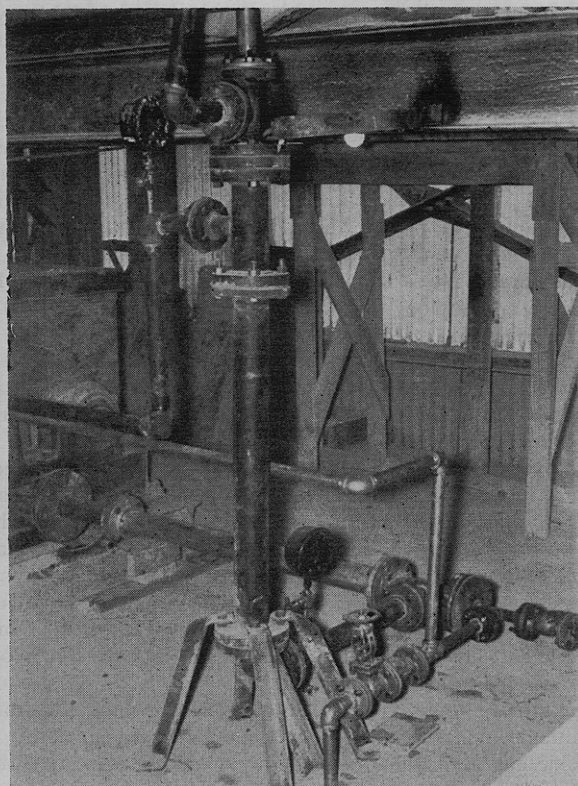


Figure 2. Prereactor in early stage of development

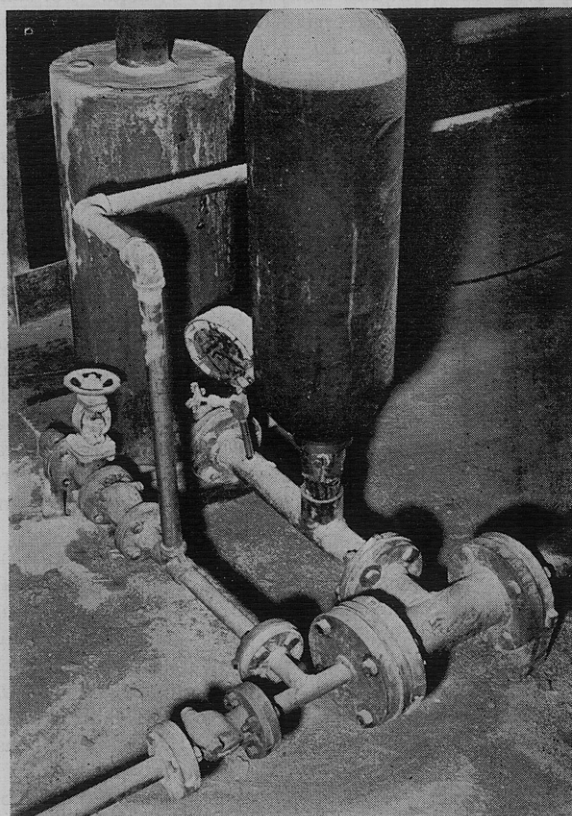


Figure 3. Reactor tee and other components of prereactor

plied to the prereactor through conventional instruments and piping (not shown). Also not shown is a surge tank arrangement in the water supply system, which may be necessary when water is used from city supply systems. Each supply line is provided as shown with a gate valve, a check valve, and a pressure gage immediately upstream from the prereactor.

The water and nitrogen solution, supplied through 1½-inch pipes, blend in a 1½-inch pipe tee and subsequently discharge from a perforated 1½-inch pipe into a 6-inch pipe section 42 inches long. Anhydrous ammonia is supplied through a 1½-inch pipe, then flows through a 3-inch pipe tee, and enters the 6-inch pipe section, where it blends with the nitrogen solution and water. The preblended liquids then flow through a 3-inch pipe section into a 3-inch pipe tee (the reactor tee). Sulfuric and phosphoric acids, supplied through 1-inch lines, preblend in a 1-inch pipe tee and subsequently flow through a 1-inch acid discharge pipe which passes concentrically through the reactor tee and terminates in a simple shower head arrangement 3 inches inside the reactor pipe section. The shower head is 1¾ inches in outside diameter and has 25 drilled discharge holes, each 3/16 inch in diameter. Its purpose is to break up the acid flow into many small streams, thus assuring that neutralization by ammonia is largely completed in the reactor pipe section, 3 inches in diameter and 4 feet long.

The discharge pipe is 3 inches in diameter and 10 feet long and has 18 discharge holes ½ inch in diameter, which are located along each side at 6-inch intervals. The preblended and prereacted liquids discharge laterally into the lower region of the pug mixer approximately 2 feet beneath the surface of the bed of dry materials. The discharge pipe was designed and located with due regard for two important aspects of mixed fertilizer granulation—efficient ammoniation of the superphos-

phates and uniform wetting of the dry materials.

A 1-inch compressed air supply line enters the blended acid line in a simple pipe tee. The air line is equipped with a solenoid valve which is arranged with an automatic timing device, so that on a preset timing cycle (usually 5 minutes) a 2- or 3-second blast of compressed air passes through the reactor and discharge pipe sections and assures that the discharge orifices remain open.

Hydropneumatic accumulators (Greer Hydraulics, Inc., Brooklyn, N. Y.) are located in the nitrogen solution supply line and in the preblended nitrogen line for the purpose of dampening out pressure pulsations caused by the blending and reaction actions. Each is a 5-gallon steel vessel equipped with a spring-loaded feed valve and containing a rubber bladder which is inflated to 5 p.s.i.g. (about one half of the normal line pressure).

Several corrosion-resistant materials of construction are used for the prereactor components. The preblending section is constructed of Type 304 stainless steel. The reactor tee is Type 316 stainless steel and the acid discharge pipe is Hastelloy C. The reactor pipe section is Teflon-lined mild steel and the discharge pipe is Teflon-lined Type 316 stainless steel. The Teflon lining has shown excellent resistance to the severe neutralization reaction environment. After 10 months of plant service, the original reactor section shows negligible deterioration.

Figure 2 shows a prereactor at an early stage of development, installed for use in a typical Trenton process pug mixer. The vertical section in the foreground is the nitrogen solution-water-ammonia blending pipe. The reactor tee in the lower background receives liquids from the blender pipe and contains the concentrically located acid discharge nozzle. The horizontal Teflon-lined reactor pipe extends to the left of the reactor tee, flanging to the discharge pipe seen entering the bottom

of the pug mixer in the midline a few inches below the paddle shafts. The air supply check valve is on the right.

Figure 3 shows a portion of the reactor pipe section, the reactor tee, liquid feed lines, and the hydropneumatic accumulator located in the blended nitrogen line. Figure 4 shows a portion of the reactor pipe flanged to the discharge pipe which enters the pug mixer through a flanged access fitting. Figure 5 shows the discharge pipe located in the mixer immediately below the arc formed when the paddles rotate. The bar seen at the termination of the pipe is an anchor post.

Operating Results

Previous to the development of the prereactor and the design of the location of the discharge section beneath the arc of mixer paddle rotation, introduction of liquid raw materials into pug mixers presented difficulties (4). Various approaches were used, all of which involved multiple pipes and spargers for distributing the liquids. The mineral acids discharged from one set of pipes or spargers, ammonia and water through a second set, and nitrogen solution through a third set. Anhydrous ammonia and nitrogen solution were not preblended because of resultant flow pulsations. The spargers were usually arranged so that the mineral acids entered the mixer in close proximity to the other liquids. Although the better designs helped to assure rapid neutralization of the mineral acids by ammonia, the reactions occurred in the mass being granulated and undesirable side reactions were unavoidable. Separate liquid flows into the mass were also undesirable because they complicated the problem of uniformly distributing the liquids into the dry materials.

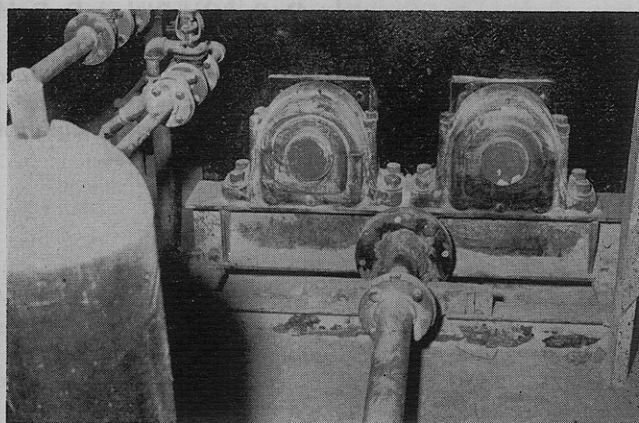


Figure 4. Prereactor distribution pipe entering pug mixer

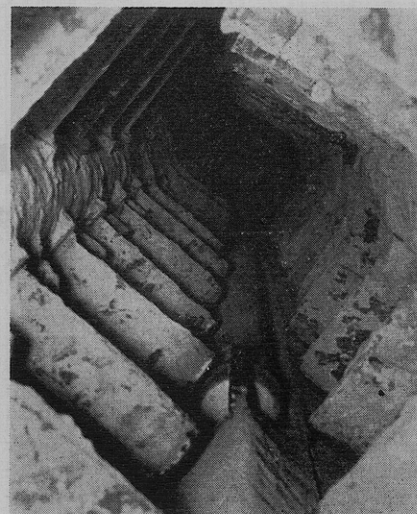


Figure 5. Prereactor distribution pipe inside pug mixer

Table I. Typical Proportions of Liquids Prereacted

Grade	Lb./Ton of Fertilizer Product				
	Anhydrous ammonia	Nitrogen solution ^a	Sulfuric acid (66° Bé. H ₂ SO ₄)	Phosphoric acid (75% H ₃ PO ₄)	Additional water
3-12-12	77 (3) ^b		105		210
5-20-20 (Formula A)	125 (5) ^b		125		350
5-20-20 (Formula B)	98 (4) ^b	50 (1) ^b	105		300
5-20-20 (Formula C)	77 (3) ^b	96 (2) ^b	55	130 (3-1/2) ^c	275
10-20-20	48 (2) ^b	410 (8-1/2) ^b	80	150 (4) ^c	None
12-12-12		510 (10-1/2) ^b	115		None
15-15-15		750 (15-1/2) ^b	225	150 (4) ^c	None

^a 41.4% N, 6% urea, 19% free NH₃, 65.6% NH₄NO₃, 9.4% H₂O.
^b Units of N shown in parentheses.
^c Units of P₂O₅.

Table II. Granulation Plant Operating Data with Prereactor

	3-12-12	5-20-20 (Formula A)	12-12-12	15-15-15
Production rate, tons/hour	36	36	20	15
Recycle rate, tons/hour	25	25	25	40
Water usage, lb./ton produced	210	350	None	None
Material temperatures, ° F.				
Recycle entering mixer	125	115	120	120
Material leaving mixer	205	200	170	175

Performance of the prereactor in plant granulation operations has been satisfactory, and its use has resulted in important improvements. The heavy ammonium chloride fume from the mixer is eliminated by neutralizing the mineral acids inside the pipe. After start-up operations have provided a bed of material above the discharge pipe, a section of the mixer top cover is often removed by the control operator to permit unimpaired observation of the granulating mass. In previous systems, the dense fumes rising from the mass interfered with this practice.

Other advantages to the granulation operation which have resulted from the prereactor include unobstructed mixer paddle action, more uniformly regulated wetting of the materials being granulated, and automatic means for clearing par-

tially clogged discharge orifices (which could also be used on other feed systems).

Table I shows the range of liquids that have been used through the prereactor in plant operations. Maximum and minimum limits on usage of the various liquid raw materials have not been established and performance thus far indicates considerable flexibility. Schedules have not yet permitted granulation of the high nitrogen 2-1-1 and X-O-X ratio grades; but it is believed that both types of grades can be successfully produced.

Table II presents typical prereactor granulation data. The water usages were determined by requirement for granule size control in the mixer. With well controlled operations, less water has been required than with previous sparger systems. It was not previously

feasible to use five units of anhydrous ammonia in the formulations. Decreased water usage and improved ammonia neutralization have resulted in increased material temperatures in the mixer. Those shown for 3-12-12 and 5-20-20 grades were 5° to 10° F. above the usual previous figures for the grades. Only a few 12-12-12 and 15-15-15 grade production operations with the prereactor have been made. Consequently it is not known whether the temperatures and recycle rates shown for the grades are optimum. Limited experience has indicated that sufficient moisture can be evaporated from the mass in the mixer to accomplish reduced recycle requirements with high liquid nitrogen usages. However, further plant tests will be needed for verification.

There is no evidence of significant decomposition of nitrogen compounds in the prereactor, nor of the formation of toxic gases, as reported with other types of prereactors. A slight ammonia odor over the pug mill is usually detectable only during start-up operations, before a normal bed of material has accumulated over the discharge pipe and when formulations require high rates of ammoniation for the superphosphates.

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GRANULAR FERTILIZERS

Interaction between Dicalcium and Monoammonium Phosphates Granulated Together

COMMERCIAL AMMONIATED SUPERPHOSPHATES normally contain monocalcium phosphate, monoammonium phosphate (MAP), and diammonium phosphate singly or in various proportions; dicalcium phosphate dihydrate (DCPD) and anhydrous dicalcium phosphate (DCPA)—prin-

cipally the latter—and perhaps more basic calcium phosphates such as hydroxyapatite and colophane (3). The qualitative and quantitative distribution of these compounds changes with methods and degree of ammoniation of superphosphate. The composition of superphosphates ammoniated to vary-

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ing degrees is reflected partially by the Association of Official Agricultural Chemists (AOAC) procedures for determining water- and citrate-soluble phosphorus (3). Hence, for many practical purposes, AOAC water solubility may be used as a means of characterizing the chemical properties of