BIBLIOGRAPHIC DATA SHEET

PN-AAJ-320

AF25-0000-0000

1. TITLE AND SUBTITLE (200)

TVA fertilizer patents

4. PERSONAL AUTHORS (100)

Mackey, J. J.; Aldridge, J. W.

5. CORPORATE AUTHORS (101)

National Fertilizer Development Center, TVA

6. DOCUMENT DATE (110)	7. NUMBER OF PAGES (120)	8. ARC NUMBER (170)
1980	36p.	631.88.M157

9. REFERENCE ORGANIZATION (130)

TVA

10. SUPPLEMENTARY NOTES (500)

11. ABSTRACT (950)

12. DESCRIPTORS (920)

Technological change
Technology
Research
Patents
Improvements
Fertilizers
Abstracts

13. PROJECT NUMBER (150)

931083200

14. CONTRACT NO.(140)

PS/TVA-1-74

15. CONTRACT TYPE (140)

16. TYPE OF DOCUMENT (160)

AID 590-7 (10-70)

631.88
M151

PN-AAJ-32

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FOREWARD

Fertilizer research has been an important function of the Tennessee Valley Authority from the time it was established in 1933 to the present. During this period there have been extensive changes in the fertilizer industry. New and improved products have been developed and more efficient manufacturing methods have emerged. Products and processes developed by TVA are in widespread use today in the fertilizer industry.

This bulletin is a collection of abstracts of patents granted to TVA on fertilizer technology and related topics over about 45 years. It contains 200 abstracts of patents. The abstracts have been divided into 13 major sections. Each section reflects the improved technology through this period of time. Abstracts of some of the patents ued to TVA since 1968 have already appeared in *Fertilizer Abstracts*, a journal published monthly since 1968. Inventor and subject indexes are provided in this bulletin.

Copies of complete patents can be obtained from the U.S. Patent and Trademark Office, Washington, DC 20231. There is a nominal charge for such copies.

TABLE OF CONTENTS

Page

PHOSPHATE ORE TREATMENT 1

PHOSPHORUS PRODUCTION 2
- Rock Reduction and Furnace Design 2
- Phosphorus Recovery 3
- Red Phosphorus 4
- Byproduct Recovery and Utilization 4

CALCIUM METAPHOSPHATE 6

PHOSPHORUS OXIDATION 7

ELECTRIC FURNACE PHOSPHORIC ACID 8

WET PROCESS PHOSPHORIC ACID 10

CALCIUM PHOSPHATES 11
- Mono-, Di-, Triple, and Concentrated Calcium Phosphates 11
- Superphosphates and Ammoniated Superphosphates 13

NITROGEN PHOSPHATES 14
- Nitric Phosphates 14
- Ammonium Phosphates 15
- Polyphosphates 17
- Vapor Phase and Other Nitrogen Phosphates 21

POTASSIUM, SECONDARY NUTRIENT, AND MICRONUTRIENT CONTAINING 21

FLUID FERTILIZER 23
- Solution 23
- Suspension 25

CONTROLLED RELEASE 26

SULFURIC ACID AND SULFATES 27

MISCELLANEOUS 28
- Crystallization, Granulation, and Coating 28
- Stack Gas Treatment 29
- Other 30

1 Selective Flocculation of Colloidal Phosphate Ore in the Presence of Clay. J. F. Haseman. *U.S.* 2,660,303, Nov. 24, 1953, Appl. Sept. 10, 1951; 4 pp. Phosphate ore is recovered from collodial slimes by selective flocculation. Starch is dispersed in H_2O using heat and agitation. The dispersion is diluted to a concentration of ~ 1% starch and added in amounts of ~ 5-10 lb of starch/ton of colloidal particles of phosphate rock, clay, and other matrix solids in aqueous suspension. The resulting phosphate flocs are separated from the suspension.

2 Settling Finely Divided Solids from Gelled Suspensions. J. E. Davenport. *U.S.* 2,922,761, Jan. 26, 1960, Appl. Aug. 20, 1954; 7 pp. Finely divided solids are settled from a gelled suspension of phosphate tailings containing ~ 10-15% solids. The entire body of gelled suspension is subjected to intermittent shear in rectilinear direction at a rate of ~ 100 ft/hr. A frequency of shear of ⩾ once in 12 hr is maintained through the suspension. The time required for settling to produce a suspension containing ~ 30% solids is reduced by ~ 5 yr.

3 Treating Phosphate Rock to Eliminate Fluorine. H. A. Curtis. *U.S.* 2,044,774, June 23, 1936, Appl. Nov. 15, 1934; 3 pp. Phosphate rock is treated in a continuous process to remove most of the fluoride which is present. Ground phosphate rock, preferably sized +80 -4 mesh, is passed countercurrently to a stream of gas consisting essentially of steam produced by the direct combustion of H_2 and O_2. The temperature of the combustion product is controlled by admitting steam to maintain the phosphate rock just below its sintering point. The furnace is designed so that the gases passing upward from the high temperature zone of 1300-1400° are cooled to 100-150° by the descending rock. The heated rock from the high temperature zone is cooled to 100-150° by ascending steam which has been admitted near the bottom of the furnace. This steam is produced by treating a portion of the gases evolved for the removal of F and CO_2 leaving substantially purified steam.

4 Treating Phosphate Rock to Eliminate Fluorine. R. L. Copson. *U.S.* 2,143,865, Jan. 17, 1939, Appl. Nov. 30, 1936; 4 pp. Phosphate rock, particularly fluorapatite, is treated to eliminate F and render it available as a plant food or to prepare it for further chemical treatment. The interior of a rotatable, horizontal, cylindrical, refractory-lined furnace, equipped with a plurality of inlets for the admission of superheated steam, is heated. Phosphate rock is fused in a fusion furnace and transferred to the cylindrical furnace which is rotated so that the inlets are above the level of liquid charged into it. Superheated steam is admitted through the inlets and the furnace is rotated until the inlets are located at the bottom of the furnace. Steam in an amount of ~ 0.2-0.5 lb/lb of phosphate is admitted through the inlets and passed through the bed of molten phosphate for ~ 10-20 minutes until substantially all the F has been removed.

5 Defluorinating Rock Phosphate. K. L. Elmore. *U.S.* 2,368,649, Feb. 6, 1945, Appl. Oct. 23, 1941; 2 pp. A fusion charge of phosphate rock is prepared by adding acidic oxide material in proportions such that for each mole of CaO in excess of $Ca_3(PO_4)_2$ equivalent in the rock there is present 2 moles of SiO_2 and 1 mole of FeO or Al_2O_3. The charge has a fusion temperature substantially below the fusion temperature of phosphate rock alone. The melt has a relatively low viscosity at temperatures immediately above its fusion temperature. The charge is fused and the fused charge is contacted with a H_2O-containing atmosphere for long enough to remove most of the F. The product is suitable for use as a plant food without further chemical treatment.

6 Method for Defluorinating Phosphate Rock. K. L. Elmore. *U.S.* 2,474,831, July 5, 1949, Appl. Nov. 28, 1947; 7 pp. In a process for defluorinating phosphate rock a charge of phosphate rock and naturally occurring siliceous material in which the proportion of SiO_2 is ~ 18-27% is introduced into a vertical shaft furnace in discrete masses. The amount of SiO_2 used is in excess of that required to satisfy the equation: $Ca_{10}F_2(PO_4)_6 + H_2O + SiO_2 \rightarrow 3[Ca_3(PO_4)_2] + CaSiO_3 + 2HF$. A stream of hot combustion gases containing ⩾ 4% of H_2O vapor, preferably 10-20%, is directed vertically upward against the bottom of the charge continuously. The flow rate of combustion gases through the central part of the charge is substantially greater than the flow rate through the charge adjacent to the walls of the reaction zone. Therefore, the upper portion of the charge forms a sintered ring surrounding a central melting zone. Molten material from which the greater proportion of F has been volatilized is withdrawn from a lower part of the reaction zone. At intervals fresh portions of charge are added to the upper part of the body of charge in the reaction zone.

7 Method for Defluorinating Phosphate Rock. T. N. Hubbuch and T. P. Hignett. *U.S.* 2,499,385, Mar. 7, 1950, Appl. Nov. 29, 1947; 7 pp. An improved furnace and method of operation for defluorinating phosphate rock is described. A charge of phosphate rock and SiO_2 is introduced into a vertical shaft furnace in discrete masses. The amount of SiO_2 is in excess of that required to satisfy the equation: $Ca_{10}F_2(PO_4)_6 + H_2O + SiO_2 \rightarrow 3[Ca_3(PO_4)_2] + CaSiO_3 + 2HF$. A stream of hot combustion gases containing ⩾ 4% H_2O vapor is passed upward against the bottom of the charge continuously. The flow rate through the center of the charge is greater than through the outside portions so a sintered ring surrounding a central melting zone is formed. Defluorinated molten material is withdrawn from a lower part of the furnace and fresh portions of charge are added to an upper part at intervals. The improvement consists of introducing a plurality of streams of hydrocarbon fuel in admixture with air into a lower part of the furnace. The streams are introduced at a velocity of ~ 30-120 ft/sec and at an angle of 10-30° downward from the horizontal to a central part of the bottom of the furnace. A lower part of the charge is melted to form an arch delimiting the bottom of the body of the charge. The resulting hot combustion gases are deflected upward against the arch and through the body of charge.

8 Furnace for Defluorinating Phosphate Rock. L. H. Almond. *U.S.* 2,770,451, Nov. 13, 1956, Appl. July 6, 1954; 4 pp. Molten defluorinated phosphate rock is produced in an improved furnace with minimized corrosion in the hearth section. The furnace has a hearth section surmounted by a shaft section. Means are provided for charging phosphate rock at the top of the shaft section. At least one fluid fuel burner is located in the hearth section and a taphole is in the bottom of the hearth section. The improved structure is a substantially round vertical-walled hearth section constructed of a single layer of graphite blocks. A vertical-walled shaft section surmounts the hearth section and is supported independently of the hearth section. The internal diameter is the same as

that of the hearth section. Uniform pressure is exerted on each graphite block of the hearth section towards the vertical axis of the furnace by a plurality of tensioned bands. A film of cooling H_2O flows over the external surface of the hearth section in direct contact with the graphite blocks.

9 Agglomerating Fine Phosphate Rock. H. A. Curtis. *U.S.* 2,040,081, May 12, 1936, Appl. Sept. 21, 1934; 2 pp. A process is described for agglomeration of fine phosphate rock for use as a constituent of a P reduction furnace charging stock. Phosphate rock, sized ≤ 10 mesh and containing a substantial amount of -100 mesh rock, is mixed with a small amount of H_3PO_4 or H_2SO_4 diluted with enough H_2O to wet the rock surfaces. Mixing is continued as in a pugmill until a stiff paste forms. The paste is discharged into a rotary dryer to form and dry spheroidal masses. For 100 wt parts of phosphate rock 8-14 wt parts of 30-50 wt % H_2SO_4 or 6-8 wt parts of 25-40 wt % H_3PO_4 are used.

10 Preparing Phosphate Charging Stock. H. A. Curtis and A. J. Abrams. *U.S.* 2,029,309, Feb. 4, 1936, Appl. Aug. 22, 1934; 3 pp. Phosphorus reduction furnace charging stock is prepared by mixing fine phosphate rock and fine silica and heating to 850-1000° while mixing continuously. Fine coking coal, which may be preheated to 125-170°, is added to the hot phosphate rock-silica mixture wt ratio of 1:2-10, preferably 1:4. The resultant mixture is agitated until it contains semi-coke. It then is passed between rolls to increase its apparent density and to complete carbonization of the densified mixture.

11 Agglomerated Carbonaceous Phosphate Furnace Charge of High Electrical Resistance. W. J. Darby. *U.S.* 3,335,094, Aug. 8, 1967, Appl. July 18, 1963; 7 pp. An agglomerated, briquetted charge for an electric P furnace is prepared by mixing phosphate rock, coal, and silica in proportions such that the SiO_2:CaO wt ratio > ~ 0.85:1 and the fixed C content is ~ 4% in excess of stoichiometric. The charge mixture is formed into briquets which are introduced into a calcining unit together with a stream of air. The air is of sufficient quantity to oxidize the surface of the briquets. The temperature of the briquets is increased to about 1600°F during a period of ~ 30 minutes and then cooled. The product briquets have an outer layer from which the C has been removed leaving an electrical insulating skin of calcined phosphate-silicate ~ one-sixteenth to one-tenth of an in. thick. The specific resistance is >~ 160 million ohms/cm^3.

12 Method of Briquetting. J. C. Barber, G. H. Megar, and T. S. Sloan. *U.S.* 3,202,744, Aug. 24, 1965, Appl. June 19, 1961; 7 pp. Division of *U.S.* 3,084,029. Centrifugal force is applied to sludge from a phosphate rock smelting operating. A H_2O slurry containing solids and carbonaceous material is removed as overflow. The H_2O slurry which contains < 7 wt % P is allowed to settle and supernatant H_2O is removed. The wet residue is mixed as a binder with phosphate rock, C, and silica. The mixture is briquetted for use as phosphate furnace feed.

PHOSPHORUS PRODUCTION

ROCK REDUCTION AND FURNACE DESIGN

13 Producing Phosphorus and Phosphate Fertilizer. H. A. Curtis. *U.S.* 2,069,225, Feb. 2, 1937, Appl. June 5, 1935; 3 pp. Elemental P and a phosphate fertilizer are made from phosphate rock, silica, and C by first reducing a charge of rock, silica, and C in an electric furnace. A gaseous mixture of CO and P is produced. A substantial proportion of the elemental P is separated from the gaseous mixture by condensation and electrical precipitation. A separate portion of phosphate rock is fused by contacting with the products of combustion of the gaseous mixture remaining after separation of most of the P. The fused phosphate rock is atomized and cooled rapidly to form a phosphate fertilizer of proper size for direct application to the soil.

14 Producing Phosphorus. H. A. Curtis. *U.S.* 2,072,981, Mar. 9, 1937, Appl. Mar. 18, 1936; 4 pp. Run-of-the-mine phosphate rock is crushed and screened to separate the coarse portion from the fine portion. A charge of the coarse phosphate rock, silica, and C is reduced in an electric furnace heated to reaction temperature by the passage of an electrical current through the charge. The fine, solid portion of the charge entrained in the gas is separated in a dust separator maintained at a temperature above the dew point of elemental P. The phosphate reduction furnace gas is cooled indirectly and condensed P is separated. The fine portion of the phosphate rock is sintered in a sintering furnace. The furnace is heated with the products of combustion of the reduction furnace gas after P separation and a limited quantity of preheated air. The quantity of air is limited to the amount of O_2 content required to oxidize elemental P remaining and a part of the CO in the gas. Only enough CO is oxidized to supply heat required to sinter the fine phosphate rock. The sintered rock is mixed with the run-of-the-mine phosphate rock in the first step. Air for the sintering furnace is preheated by heat exchange with the hot gaseous mixture of fuel gas withdrawn from the sintering furnace. A fuel gas containing > 17.5% CO with a calorific value > 60 Btu/ft^3 is recovered.

15 Producing Phosphorus. H. A. Curtis and R. L. Copson. *U.S.* 2,143,001, Jan. 10, 1939, Appl. Dec. 7, 1935; 4 pp. Elemental P is produced in a resistance type electric furnace. The process eliminates the difficulty of disposing of residual CO containing small amounts of P. The heat valve of the CO is utilized in the gaseous reduction products and the required electric power is reduced. A molten mixture of phosphate rock and silica is charged below and adjacent to the zone of maximum temperature in an electric furnace. This zone is between the electrodes. The liquid level is maintained below the maximum temperature zone. Coke is fed into the furnace above the maximum temperature zone. A column of coke is maintained at a height above the level of molten mixture to cause the coke to penetrate the entire depth of the mixture. The charge of phosphate rock and silica is reduced with the coke which is heated by the electric current applied to the coke above and adjacent to the surface of the molten mixture. A gas containing elemental P and a Ca silicate slag are formed. The slag is withdrawn from the furnace hearth. The elemental P is condensed in an indirectly cooled condenser and separated from the uncondensed portion of the gas. Products of combustion of the uncondensed gas are used in direct contact to fuse the phosphate rock and silica charge.

16 Phosphorus Combustion Furnace. C. J. McFarlin. *U.S.* 2,532,322, Dec. 5, 1950, Appl. June 1, 1946; 5 pp. An improved P combustion furnace is described for the production of P_2O_5 and recovery of H_3PO_4. The combustion products are cooled rapidly by indirect means and thus without dilution. The furnace has a graphite wall. The outside of the furnace wall is cooled so the inside surface is kept below its oxidizing temperature. A circular hearth floor formed of a single thickness of graphite blocks is disposed in a flat metal pan which sits in a pool of H_2O. Alternately, a refractory hearth may be used. The hearth wall is formed of a single thickness of graphite blocks. The top is dome shaped to enclose a vertical combustion chamber with a height:diameter ratio of 2-3:1. A phosphorus burner is centrally located adjacent to the top of the combustion chamber. An outlet for hot combustion gases is adjacent to the hearth floor. A film of H_2O flows downward over the outside of the wall continuously.

17 Apparatus for Producing Phosphorus. H. A. Curtis and R. L. Copson. *U.S.* 2,117,301, May 17, 1938, Appl. Dec. 7, 1935; 5 pp. Elemental P is produced in an enclosed resistance type electric furnace. The furnace has an inlet on one side of the hearth at a level below the electrodes for admission of molten phosphate rock and silica. An outlet for the removal of $CaSiO_4$ slag is substantially opposite the inlet. Ferrophosphorus is withdrawn through a second outlet below and adjacent to the slag outlet. A plurality of electrodes are located in the furnace wall above and adjacent to the level of molten liquid in the hearth. The furnace shell has an inlet in the top for admission of carbonaceous material and silica and an outlet for phosphate reduction furnace gas. The height of the furnace wall is such that the ratio of maximum melt depth:distance from top of melt to top of furnace is inversely proportional to ratio of density of melt:density of the solid carbonaceous material charged.

18 Electric Furnace for Phosphate Reduction. S. A. Hardin. *U.S.* 2,509,228, May 30, 1950, Appl. Feb. 26, 1949; 6 pp. An electric furnace for smelting ores has a C hearth section with semicircular end portions. It also has a monolithic walls-and-roof section of refractory concrete superimposed on the hearth section and supported only in a region adjacent to the hearth section. The monolithic walls and roof have inner surfaces of a curvature substantially that of an inverted catenary with a width:height ratio of ~ 1.4-1.6:1 from the hearth to the apex of the catenary. One or more electrodes project vertically through suitable openings in the roof to a location adjacent to the hearth section. They are disposed in the longitudinal center line of the furnace. A plurality of feed chutes project into the furnace through suitable openings near the electrode and are adapted to pile up charge around the electrodes. Conventional means for withdrawing gases from the upper part of the furnace, for energizing the electrodes, and for withdrawing molten material from the hearth section are provided.

19 Rotating Electric Phosphorus Furnace. M. M. Striplin, Jr., S. A. Hardin, and W. H. Bundy. *U.S.* 2,744,944, May 8, 1956, Appl. Dec. 17, 1954; 8 pp. Phosphate rock is smelted in a vertical, round, rotatably mounted crucible which has a C hearth. The crucible rotates at a controlled speed of 0.66-5.45 in./hr depending on the size composition of the burden. A stationary cover is superimposed on the crucible and there is a gas-tight seal between the crucible and the cover. Three vertical graphite electrodes extend substantially through the cover and are positioned at the apices of an equilateral triangle. The diameter of each electrode in in. = k $(P^{0.50}/3)$ where P is total furnace power input in W and k is 0.036-0.043. The center-to-center electrode distance in ft = k $P^{0.50}$ where k is 0.002-0.0026. The distance, in ft, of each electrode from the interior wall of the crucible = k $P^{0.50}$ where k is 0.0015-0.0019. A transformer tap and electrical connections are used to energize the electrodes with 3-phase alternating current with one electrode on each phase. The total furnace input is ~ 30-50 kW/ft^2 of hearth area. A method is provided to raise and lower the electrodes vertically through a distance necessary to maintain the peripheral ohm factor, r, at 0.75-1.25. This factor is calculated: r = (E/I) ¶D where E is the electrode voltage in V, I is the electrical current in amps, and D is the electrode diameter in in. A selected uniform burden depth is maintained in the furnace by use of a large central feed chute and a plurality of smaller feed chutes placed around the crucible. The bottom of the furnace is H_2O-cooled.

20 Glazed Ceramic Ware and Method of Making. G. R. Pole. *U.S.* 2,063,953, Dec. 15, 1936, Appl. Feb. 27, 1936; 2 pp. A ceramic ware with an improved glaze finish is prepared by contacting either unglazed or previously salt glazed ceramic ware with a gaseous mixture containing P_2O_5. The ware is maintained at glazing temperature, ~ 1230° during treatment. The process is useful for wares difficult or practically impossible to glaze by the usual NaCl method, such as wares with high lime or high alumina content.

PHOSPHORUS RECOVERY

21 Separating Phosphorus. H. A. Curtis. *U.S.* 2,039,297, May 5, 1936, Appl. May 14, 1935; 2 pp. Elemental P is separated from hot gaseous mixtures produced in P reduction furnaces by continuously contacting the mixtures with a solution of $Ca(OH)_2$:H_2O in a wt ratio of 0.1-0.2-100 (lime:H_2O). The gaseous mixture which separates is principally CO saturated with H_2O vapor. Any elemental P remaining can be removed by an adsorbent. The lime H_2O containing condensed P, dust particles, and precipitated P oxidation products are withdrawn from the bottom of the condenser and permitted to stratify. The layers of lime H_2O, condensed P, and sludge are separated. The sludge is dried and incorporated with a P reduction furnace charging stock. The lime H_2O is recycled to the condenser with $Ca(OH)_2$ added as needed.

22 Separating Elemental Phosphorus from Impurities. L. H. Almond. *U.S.* 2,135,486, Nov. 8, 1938, Appl. Aug. 17, 1937; 4 pp. Elemental P is separated from a mass containing elemental P and solid impurities, such as obtained by separating dust from phosphate reduction furnace gas or by indirect condensation of P from phosphate reduction furnace gas. Enough H_2O is mixed with the mass to form a semifluid mixture. This mixture is fed continuously to a flash distillation zone maintained at ~ 750-800°F. The P and H_2O in the mixture are flash distilled and separated from the solid impurities continuously. The solid impurities are withdrawn from the flash distillation zone continuously.

23 Recovery of Phosphorus from Sludge. J. C. Barber, G. H. Megar, and T. S. Sloan. *U.S.* 3,084,029, Apr. 2, 1963, Appl.

June 19, 1961; 7 pp. Phosphorus sludge, formed during the production of P by smelting phosphate rock, is fed to a vessel where centrifugal force is supplied. The centrifugal force causes P globules in the sludge emulsion to coalesce to liquid P which has a greater density than the impurities in the sludge. A H_2O slurry containing $< \sim 7$ wt % P is removed as overflow, and a liquid underflow containing $> \sim 93$ wt % P is recovered. Treatment of the sludge with a small amount of a dispersant, such as NaOH, decreases viscosity and stickiness and thus permits the sludge to be pumped and handled more readily.

24 Recovery of Phosphorus from Sludge. J. C. Barber, G. H. Megar, and T. S. Sloan. *U.S.* 3,113,839, Dec. 10, 1963, Appl. June 19, 1961; 7 pp. Division of *U.S.* 3,084,029. Phosphorus sludge formed during the production of P by smelting phosphate rock is treated by adding $< \sim 2$ wt parts of NaOH/1000 wt parts of sludge. This quantity is sufficient to raise the pH of the sludge from ~ 3.0 to ~ 6.0. The resulting mixture is agitated for ~ 2-6 days and then is burned to recover P_2O_5 vapor. Alternately, the treated sludge is subjected to centrifugal force to recover P liquid in the centrifuge underflow.

25 Recovery of Phosphorus from Sludge. J. C. Barber, G. H. Megar, and T. S. Sloan. *U.S.* 3,136,604, June 9, 1964, Appl. June 19, 1961; 7 pp. Division of *U.S.* 3,084,029. Phosphorus sludge formed during the production of P by smelting phosphate rock is treated by adding < 1 wt part of ammonium lignosulfonate/1000 wt parts of sludge to reduce the viscosity. Material sufficiently caustic to raise the sludge pH from ~ 3.0 to ~ 6.0 is added. The resulting mixture is agitated for ~ 2-6 days and burned to recover P_2O_5 vapor. Alternately, the treated sludge is subjected to centrifugal force and P recovered in liquid form.

26 Method of Decreasing Sludge Formation in Phosphorus Furnace Sump. G. H. Megar and Arnett Hendrix. *U.S.* 3,428,430, Feb. 18, 1969, Appl. Apr. 21, 1966; 7 pp. In the production of elemental P by reducing a phosphate rock blend in an electric furnace, offgases are scrubbed with sprays of H_2O to condense the P vapor. Ammonium hydroxide is usually added to the condenser H_2O to maintain the pH to 5.5-6.0. The mixture is run to a condenser sump where a layer of relatively pure molten P collects at the bottom. Above this is a layer of sludge comprised of P droplets, solid impurities, and H_2O. Above the sludge layer at a poorly-defined boundary is a H_2O layer containing P droplets and solids in suspension. The furnace gases contain SiF_4 which reacts with the condenser H_2O to precipitate hydrated SiO_2. The precipitated SiO_2 occludes P and thereby promotes sludge formation. Addition of aqueous NH_4F to the condenser spray H_2O to maintain a F:Si atomic ratio of ~ 6-10:1, preferably ~ 6.5:1, causes formation of soluble $(NH_4)_2SiF_6$ from all the SiF_4, preventing formation of SiO_2. Less sludge is formed, and the P is easier to recover in pure form.

RED PHOSPHORUS

27 Making Red Phosphorus. T. W. DeWitt. *U.S.* 2,397,951, Apr. 9, 1946, Appl. Oct. 25, 1943; 2 pp. Finely divided red P is prepared by heating yellow P at a temperature effective to convert the yellow P to red P. Heating is discontinued when ~ 50% of the yellow P has been converted and the mixture is still in a fluent condition at the conversion pressure and temperature. The fluent mixture is removed from the heating zone and the unconverted yellow P is separated from the red P without any appreciable further conversion, thus preventing any appreciable agglomeration of red P particles. Separation may be effected by flash, vacuum, or steam distillation. Times required for 50% conversion are ~ 2 hr or 30 minutes at ~ 300 or 320° and 1.46 or 2.08 atm., respectively.

28 Purification of Red Phosphorus. J. R. Tusson. *U.S.* 2,476,335, July 19, 1949, Appl. Nov. 23, 1946; 4 pp. Red P contained in a mixture of red and yellow P is separated and purified to such a degree with respect to yellow P that it will not ignite in air spontaneously. Yellow P is heated for a time and to a temperature sufficient to convert a substantial portion to red P. A mud consisting of solid red P in admixture with liquid yellow P is separated continuously from a hot slurry of such a mixture. The separated mud is passed upward through an inclined vaporization zone which is divided into two sections. The average temperatures of the first and second section are ~ 344 and 200-280°, respectively. The P mixture is agitated continuously during its ascent through both sections of the vaporization zone. All aggregates in the second section are crushed with pressure sufficient to break up aggregates but not enough to break up individual particles of red P. A stream of inert gas is introduced continuously into the upper section. It passes downward through both sections of the zone in intimate contact with the P. A stream of inert gas containing yellow P is withdrawn from the first section and coarse particles of purified, nonautoinflammable red P is withdrawn from the second section of the vaporization zone.

29 Purification of Red Phosphorus. Philiip Miller. *U.S.* 2,537,078, Jan. 9, 1951, Appl. Apr. 1, 1948; 4 pp. Red P contaminated with yellow P and Fe is finely divided so that ≥ 90% is -100 mesh. The finely divided material is suspended in H_2O and air in fine bubbles. These bubbles are passed through the resulting slurry for ~ 4-7 hr until evolved white fumes are no longer visible. The P is kept in suspension by agitating the slurry and the temperature is maintained at 60-80°. The partially purified P is separated from the resulting acidified H_2O and is washed with H_2O. Nonautoinflammable red P containing < 15 ppm of Fe is separated from the wash H_2O.

30 Stabilizing Red Phosphorus. Sol Skolnik and G. L. Bridger. *U.S.* 2,559,684, July 10, 1951, Appl. Apr. 27, 1949; 3 pp. Finely divided red P, normally susceptible to ignition under the influence of impact or friction, is stabilized by mixing with concentrated H_3PO_4 or H_2PO_4. The resulting mixture is dried at a low temperature until substantially all uncombined moisture is removed. A free-flowing product consisting of fine particles of red P coated with highly concentrated acid is produced. The preferred amount of acid is 5-7%, as P_2O_5. The product must be protected from moisture because the acid coating is highly hygroscopic.

BYPRODUCT RECOVERY AND UTILIZATION

31 Making Calcium Fluoride. Nathan Gilbert and I. A. Hobbs. *U.S.* 2,573,704, Nov. 6, 1951, Appl. Feb. 27, 1950; 4 pp. Waste gases from the defluorination of phosphate rock by fusing in the presence of silica and H_2O vapor are passed upward through a bed of oolitic and pisolitic limestone. The limestone is in coarse particles sized 1/4-2 in. The temperature

of bed and gases is maintained above the dew point of the gases and below the decomposition point of limestone (825°). The lower portion of the bed is screened to separate it into a fraction of fine particles composed essentially of CaF_2 and a fraction of coarser particles composed of unreacted limestone. The coarser fraction is recycled to an upper part of the limestone bed.

32 Alkaline Process for the Manufacture of Cryolite. Grady Tarbutton, T. D. Farr, T. M. Jones, and H. T. Lewis, Jr. *U.S.* 2,963,344, Dec. 6, 1960, Appl. Oct, 13, 1958; 5 pp. A process is described for the manufacture of specification grade cryolite from F evolved in the processing of phosphate rock. Specification grade cryolite has a F content of ⩾ 85% of that represented by the formula Na_3AlF_6. The maximum limit of impurities is P_2O_5 0.1, SiO_2 0.6, Fe_2O_3 0.25, and SO_3 5%. An impure NH_4F solution is prepared which contains F, P, Si, and Fe compounds. The solution is heated to boiling. Enough NaOH and a soluble Al salt are added to the solution to bring the Na and Al content to ~ 90-100% of the theoretical amount to form Na_3AlF_6 with all the F present in the solution. The percentage of Na and Al required is dependent on the $F:P_2O_5$ wt ratio. At a $F:P_2O_5$ wt ratio of 25:1, ~ 90% of theoretical is used and is increased as the wt ratio increases. At $F:P_2O_5$ wt ratios of > 125:1 the Na and Al content is ~ 100% of theoretical. The solution is neutralized to the phenolphthalein end point by the addition of CO_2 and cooled. Product Na_3AlF_6 precipitates and is separated and washed.

33 Manufacture of Ammonium Cryolite. Grady Tarbutton, T. D. Farr, T. M. Jones, and H. T. Lewis, Jr. *U.S.* 2,981,597, Apr. 25, 1961, Appl. Oct. 13, 1958; 7 pp. Specification grade ammonium cryolite, $(NH_4)_3AlF_6$, is produced from the F evolved from processing of phosphate rock. An impure aqueous solution of NH_4F is prepared which contains a $F:P_2O_5$ wt ratio of 1-400:1, at least enough NH_4^+ to form $(NH_4)_3AlF_6$ with all F present, and $F:SiO_2$ and $F:Fe_2O_3$ wt ratios of ⩽ 15:1 and ⩽ 100:1, respectively. The pH is adjusted in relationship to the $F:P_2O_5$ wt ratio. The minimum pH is ~ 4.0 at a $F:P_2O_5$ ratio of ~ 1:1 and the maximum pH is ~ 7.0 at a ratio of ~ 400:1. A soluble Al salt is added in amounts of ~ 90-100% of the theoretical amount required to form $(NH_4)_3AlF_6$ with all F present. The quantity of Al salt is in relationship to the $F:P_2O_5$ wt ratio also, varying from 90 to 100% of theoretical as the $F:P_2O_5$ ratio increases from 1:1 to 400:1. The product ammonium cryolite precipitates and is separated and washed.

34 Manufacture of Cryolite from Waste Gases. Grady Tarbutton, T. D. Farr, T. M. Jones, and H. T. Lewis. *U.S.* 2,981,598, Apr. 25, 1961, Appl. Oct. 13, 1958; 6 pp. Specification grade cryolite is produced from scrub liquors resulting from scrubbing waste gases evolved during the processing of phosphate rock. An impure aqueous solution of NH_4F is prepared which contains F, P, Si, and Fe compounds in the following wt ratios: $F:P_2O_5$ 5-400:1, $F:SiO_2$ ⩾ 15:1, and $F:Fe_2O_3$ ⩾ 100:1. The solution pH is adjusted to be 4.0-6.0 after a later addition of Na and Al salts. Enough soluble Na and Al salts are added to furnish 95-100% of the theoretical amount to form Na_3AlF_6 with all F present. The pH and quantity of Na and Al salts are adjusted in relationship to the $F:P_2O_5$ wt ratio. The pH is ~ 4.0 and 6.0 at a $F:P_2O_5$ wt ratio of ~ ⩽ 15:1 and ⩾ 40:1, respectively. The quantity of Na and Al salts added is ~ 95% of theoretical at $F:P_2O_5$ wt ratio of ⩽ 15:1 and 100% at ⩾ 40:1. The resulting precipitated cryolite is washed, dried, and recovered as product.

35 Anodic Oxidation of Ferrophosphorus. L.H.D. Fraser. *U.S.* 2,133,289, Oct. 18, 1938, Appl. Oct. 15, 1936; 3 pp. Acid Fe phosphate is prepared from ferrophosphorus, a byproduct from the production of elemental P in a blast furnace or an electric reduction furnace. The ferrophosphorus is made an anode in an electrolyte consisting of an aqueous solution of H_3PO_4, H_2SO_4, or HCl. The cathode is an electrical conductor which is chemically inert to the electrolyte under the conditions of operation, such as Pb and C. A direct current, at an anode current density of 5-50 amps/ft^2, is passed between the anode and the cathode to produce a solution of the acid Fe phosphate.

36 Anodic Oxidation of Ferrophosphorus. L.H.D. Fraser. *U.S.* 2,133,290, Oct. 18, 1938, Appl. Oct. 15, 1936; 3 pp. This is a companion to *U.S.* 2,133,289. Ferrophosphorus is made the anode in an electrolyte consisting of an aqueous solution of an alkali metal hydroxide such as NaOH or KOH. The cathode is a chemically inert conductor, such as Pb or C. A direct current, at an anode current density of 5-50 amps/ft^2, is passed between the anode and the cathode to produce a solution of the alkali metal phosphate and insoluble Fe_2O_3. The Fe_2O_3 is of colloidal size and may be used as paint pigment.

37 Anodic Oxidation of Ferrophosphorus. L.H.D. Fraser. *U.S.* 2,173,103, Sept. 19, 1939, Appl. Oct. 15, 1936; 4 pp. This is a companion to *U.S.* 2,133,289 and *U.S.* 2,133,290. The P contained in ferrophosphorus is converted into Fe phosphate by anodic oxidation. The ferrophosphorus is the anode in an aqueous solution of an electrolyte. The electrolyte contains an inorganic compound such as an alkali metal hydroxide, an alkali metal salt of an inorganic acid, an inorganic acid, or a mixture of an alkali metal salt with an inorganic acid or an alkali metal hydroxide. A chemically inert conductor under operating conditions, such as Pb or C, is the cathode. A direct current at an anode density of 5-50 amps/ft^2 is passed between the anode and cathode. An insoluble Fe phosphate is formed and separated from the electrolyte.

38 Treating Ferrophosphorus. G. L. Bridger. *U.S.* 2,320,342, June 1, 1943, Appl. Mar. 17, 1942; 3 pp. Fine ferrophosphorus and fine limestone are mixed in amounts to give a $CaO:P_2O_5$ ratio of ⩾ 4:1. The mixture is charged into a rotary kiln which is maintained at ~ 1000-1200°. The lower limit is that at which the limestone is converted to CaO at a reasonably rapid rate and the upper limit is such that none of the constituents or products are fused or melted. The mixture is held in the kiln in intimate contact with a free O_2-containing atmosphere for a time sufficient to obtain the desired degree of oxidation. For production of Ca phosphate fertilizer, all of the P and Si is oxidized and a part of the Fe may be oxidized. For production of Fe, the constituents are oxidized in ~ 15% excess of that required for the oxidation of P to P_2O_5, Si to SiO_2, and Mn to MnO. When the ferrophosphorus is treated solely to remove Si, only a slight excess of O_2 over that required to oxidize Si alone is used. Thus, 100 wt parts of ferrophosphorus containing Fe 67.0, P 19.7, and Si 8.4% was ground to -40 mesh with 60% -100 mesh. Limestone (180 wt parts) containing 48.6% CaO was ground to -20 mesh with 50% -100 mesh. The two were mixed and fed continuously to a rotary kiln which was heated to 1000-1200°. The kiln was heated by combustion of byproduct CO from phosphate

reduction furnaces. Air was used in substantial excess of that required for combustion of the gas. Time required was ~ 40 minutes. The product was a granular, nodulized material containing total P_2O_5 19.7, citrate soluble P_2O_5 12.4, CaO 32.2, SiO_2 8.2, and Fe_2O_3 40.0%. The degree of oxidation of the ferrophosphorus was 89.0%.

39 Iron-Phosphorus-Silicon Alloy. H. S. Jerabek. *U.S.* 2,289,365, July 14, 1942, Appl. Aug. 29, 1941; 2 pp. Ferrophosphorus, obtained as a byproduct during the reduction of phosphate charging stock to produce elemental P, is used in conjunction with other metals or alloys to produce alloys which have good casting and corrosion resistant properties. The alloys contain 2-13% P and 6-22% Si with the total of P and Si being ≤ 26%. The balance is substantially all Fe. Part of the Fe may be replaced by ≤ 35% of a metal selected from Al, Cr, Cu, Mu, Mo, Ni, Ti, and V.

40 Production of Lightweight Aggregate from Molten Slag. E. L. Stout, W. C. Scott, Jr., and J. M. Stinson. *U.S.* 2,590,901, Apr. 1, 1952, Appl. Apr. 20, 1951; 4 pp. A strong lightweight aggregate is produced from phosphate-reduction furnace slag. A stream of slag at ≥ 1350°, preferably 1450-1550°, is introduced into an expansion zone which has a layer of inert granular material saturated with H_2O in the bottom. The slag flow rate is 90-245 lb/minute/ft^3 of effective expansion space. At least one stream of H_2O is introduced into the stream of slag at a point beneath the stream of slag and adjacent to its entrance into the expansion zone. The quantity of H_2O is controlled at 7-20 wt % of slag. The resulting mixture is agitated in the expansion zone by jets of inert gas introduced beneath the mixture. The resulting molten mixture is overflowed into a cooling zone.

41 Production of Lightweight Aggregates from Molten Slag. E. L. Stout, W. C. Scott, Jr., and J. M. Stinson. *U.S.* 2,590,902, Apr. 1, 1952, Appl. Apr. 20, 1951; 3 pp. Slag produced in smelting phosphate rock is expanded by introducing molten slag continuously into the top of a short, substantially vertical cylindrical zone having an open bottom. The slag flow rate is controlled so the cylinder is kept filled and the slag passes downward through the cylinder in ~1 sec. At least one stream of H_2O is introduced into the zone tangentially at a velocity high enough to impart a swirling motion to the resulting emulsion-like mixture of H_2O and molten slag. The H_2O flow rate is controlled to give a slag:H_2O ratio of 2.5-13:1. The mixture is dropped continuously from the open bottom of the cylindrical zone into a cooling zone.

42 Production of Lightweight Aggregates from Molten Slag. L. A. Edwards. *U.S.* 2,643,485, June 30, 1953, Appl. Apr. 26, 1951; 3 pp. An apparatus is described for uniformly expanding molten slag such as that produced in electric-furnace smelting of phosphate rock. Heat from the molten slag is used to convert H_2O into steam which is introduced into the molten slag uniformly. The apparatus is one or a chain of H_2O-tight receptacles. Each receptacle has a false bottom with a plurality of openings. Each opening has a loose-fitting plug with a head large enough to cover the opening and a shank slightly longer than the thickness of the false bottom. The shanks are bent a short distance below the false bottom. Means are provided to introduce H_2O below the false bottom and molten slag above the false bottom.

CALCIUM METAPHOSPHATE

43 Making Calcium Metaphosphate. H. A. Curtis. *U.S.* 2,113,574, Apr. 12, 1938, Appl. Aug. 17, 1935; 4 pp. Calcium metaphosphate, substantially free from other phosphates, is produced from limestone or phosphate rock and elemental P in a continuous process. The limestone or phosphate rock is charged into the top of a shaft furnace. Phosphorus reduction furnace gas is oxidized with a limited amount of air. Enough air is used to oxidize all the elemental P to P_2O_5. The products of combustion are mixed with a separate current of inert gas to lower the flame temperature to below the melting point of Ca pyrophosphate but substantially above the melting point of Ca metaphosphate. The mixture of P reduction furnace gas combustion products and inert gas is contacted with the shaft furnace charge of limestone or phosphate rock. Gaseous products are removed from near the top of the shaft furnace. A portion of these gaseous products form the source of the inert gas used to lower the temperature of the P reduction furnace gas combustion products. Fused Ca metaphosphate is withdrawn from the bottom of the shaft furnace.

44 Production of Calcium Metaphosphate. Phillip Miller. *U.S.* 2,589,272, Mar. 18, 1952, Appl. Mar. 16, 1949; 6 pp. A stream of fluid P is introduced continuously into a combustion zone in intimate contact with a continuous stream of air. A continuous stream of finely divided phosphate rock is introduced into the combustion zone concomitantly. The phosphate rock in suspension in the combustion zone is intimately contacted with gaseous products of combustion from burning the P. A gaseous effluent is withdraw from the combustion zone and passed through a bed of phosphate rock in a secondary reaction zone. The rock is in lumps of substantial size. The rate of molten P going into the reaction zone is controlled to maintain temperatures in the combustion and secondary reaction zones above the melting point of Ca metaphosphate. The resulting Ca metaphosphate is passed from the secondary reaction zone to the combustion zone. The rate of introduction of finely divided phosphate rock is maintained at 70-90% of that required to form Ca metaphosphate by reacting with all the P_2O_5 formed when the molten P was burned. The P_2O_5:CaO ratio is controlled at 0.95-1:1 in the resulting Ca metaphosphate in the combustion zone. Molten Ca metaphosphate product is withdrawn from the combustion zone.

45 Apparatus for Making Calcium Metaphosphate. H. A. Curtis and R. C. Heaton. *U.S.* 2,173,825, Sept. 26, 1939, Appl. July 23, 1936; 4 pp. An apparatus is described for the production of Ca metaphosphate from phosphate rock or other Ca containing material and a hot gaseous mixture containing P_2O_5. The P_2O_5 is produced by oxidizing P or phosphate reduction furnace gas containing P. Means of volatilizing and oxidizing elemental P and reacting the resulting P_2O_5 are combined in one apparatus. A horizontal refractory lined combustion chamber is equipped with means for admitting elemental P or phosphate reduction furnace gas and enough air to oxidize all the P. It has a hearth in the bottom of the chamber in the end adjacent to the points of admission of the P and air. Fused Ca metaphosphate is withdrawn through a tap hole in the wall of the chamber at the hearth level. A second hearth at a higher level is at the opposite end of the chamber. A vertical refractory lined shaft is on top of the combustion chamber. It opens into the chamber

above the elevated hearth. The shaft is equipped with an internally H_2O cooled, horizontal grate of parallel metal tubes, each of which is covered with a refractory sleeve in the zone between the refractory lined walls of the shaft. There is an inlet in the top of the shaft for charging phosphate rock and an outlet for residual gaseous combustion products. The grate supports a column of phosphate rock and, at the same time, permits withdrawal of fused Ca metaphosphate. The reaction is carried out at ~ 1000-1300° to allow separation of Ca metaphosphate which fuses at ~ 975° from phosphate rock which fuses at ~ 1500°.

46 Making Calcium Metaphosphate Fertilizer. H. A. Curtis. *U.S.* 2,173,826, Sept. 26, 1939, Appl. Feb. 15, 1938; 3 pp. A fine Ca containing material, such as phosphate rock or limestone, is mixed with dilute H_3PO_4 (30-45 wt %) in stoichiometrical proportion for the formation of monocalcium phosphate. The mixture is fed through a plurality of heated zones, which maintain the heated mixture at an increasing temperature gradient ≤ 1000-2000°. The zones are adapted to successively remove free H_2O and produce monocalcium phosphate, to convert the monocalcium phosphate into a Ca metaphosphate which is only partially available as a plant food, and to fuse the Ca metaphosphate. The fused Ca metaphosphate is entirely available as a plant food. It is maintained readily available by cooling to solidify.

47 Making Calcium Metaphosphate. R. L. Copson. *U.S.* 2,233,401, Mar. 4, 1941, Appl. Nov. 9, 1939; 3 pp. A hot gaseous mixture containing metaphosphoric acid is formed in a heating zone in which the lowest temperature is above the melting point of Ca metaphosphate. Hot metaphosphoric acid is separated from the gaseous mixture outside the heating zone and mixed with a Ca containing material. The mixture so formed is returned to the heating zone to react and form fused Ca metaphosphate. The preferred Ca containing material is phosphate rock, but limestone, lime, or other readily available Ca containing material may be suitable although not as economical.

48 Making Calcium Metaphosphate. H. A. Curtis. *U.S.* 2,184,287, Dec. 26, 1939, Appl. Feb. 26, 1938; 6 pp. Elemental P is burned in a heating zone to form a hot gaseous mixture containing P_2O_5. Water is admitted to the hot mixture to hydrate the P_2O_5 and to partially cool the mixture to the temperature required for separation of metaphosphoric acid. The metaphosphoric acid is separated from the gaseous mixture outside the heating zone and then returned to the coolest section of the heating zone. Fine phosphate rock (-325 mesh) is admitted and reacts with a substantial portion of the metaphosphoric acid to form fused Ca metaphosphate. The fused Ca metaphosphate moves through the heating zone countercurrent to the flow of the hot gaseous mixture and is withdrawn from the heating zone. Unreacted metaphosphoric acid is recycled.

49 Granular Fertilizer from Calcium Metaphosphate. T. P. Hignett, A. B. Phillips, and R. D. Young. *U.S.* 2,945,754, July 19, 1960, Appl. Apr. 19, 1956; 5 pp. A granular, nonhygroscopic, fertilizer is produced which contains a variety of forms of phosphate. A substantial proportion of the phosphate is H_2O-soluble and therefore available as plant food immediately and an increased amount of soluble phosphate is maintained in the soil for a long period of time. The fertilizer contains an ammonium salt, Ca metaphosphate, incompletely hydrolyzed metaphosphate, and Ca orthophosphate. Calcium metaphosphate is introduced into a rotating drum and a rolling bed of solid material is maintained in the drum. A concentrated acid selected from H_2SO_4, H_3PO_4, and HNO_3 is introduced beneath the surface of the rolling bed in the initial half of the drum. Enough ammoniating fluid is introduced beneath the bed surface in the final half of the drum to neutralize the acid. The material within the drum is maintained at ~ 160-215°F. Water is introduced beneath the bed surface in an amount so that the total H_2O less that evaporated is ≤ ~ two-thirds of that required for complete hydrolysis of Ca metaphosphate. Retention time in the drum is ~ 3-8 minutes. At least partially granulated fertilizer is withdrawn from the drum. A potash salt may be introduced into the drum with the Ca metaphosphate.

50 Granulation of Calcium Metaphosphate. A. B. Phillips, R. D. Young, and E. H. Brown. *U.S.* 3,012,874, Dec. 12, 1961, Appl. June 3, 1959; 4 pp. Vitreous Ca metaphosphate is ground until it will pass a 14 mesh screen and ~ 40% will pass a 100 mesh screen. The ground material is introduced into a rotating drum at 180-225°F and moistened with ~ 200-250 lb of hot H_2O/ton of product. The H_2O is ~ 190-200°F and the drum temperature is maintained at ~ 180-225°F. A granular fertilizer product is withdrawn. It consists essentially of granules containing agglomerated vitreous Ca metaphosphate particles held together in a matrix of hydrated polymers of Ca metaphosphate. The granules contain ~ 61% total P_2O_5 of which ~ 15% is H_2O-soluble.

PHOSPHORUS OXIDATION

51 Oxidizing Elemental Phosphorus. H. A. Curtis. *U.S.* 2,110,870, Mar. 15, 1938, Appl. July 14, 1936; 2 pp. Solid or liquid P is volatilized and oxidized from crude mixtures by admitting the elemental P to the surface of molten Ca metaphosphate on the hearth of a combustion chamber. At least enough air to oxidize all of the P to P_2O_5 is admitted into the combustion furnace. A hot gaseous mixture is formed which contains substantially all of the P_2O_5. Calcium metaphosphate is added to the hearth of the furnace as required to supply a heated surface for volatilization of the elemental P. Fused Ca metaphosphate and impurities are withdrawn from the hearth of the chamber. The hot gaseous mixture containing substantially all of the P_2O_5 is withdrawn from the combustion chamber. The P_2O_5 thus formed is suitable for making H_3PO_4 and phosphates.

52 Oxidizing Elemental Phosphorus. J. N. Junkins. *U.S.* 2,125,297, Aug. 2, 1938, Appl. Aug. 4, 1936; 3 pp. Elemental P is introduced into a liquid confining zone which is uncovered and centrally located in a gas confining zone. Enough heated primary air is admitted to the gas confining zone immediately above the surface of the P to vaporize all of the P and oxidize a limited amount of it. A gaseous mixture of P and partially oxidized P is formed. Enough secondary air is admitted to convert all of the P and partially oxidized P to P_2O_5. The hot gaseous mixture containing P_2O_5 is passed in adjacent heat exchange relationship to both the primary air and the liquid confining zone.

53 Oxidation of Crude Phosphorus. L. H. Almond. *U.S.*

2,221,770, Nov. 19, 1940, Appl. Sept. 29, 1939; 4 pp. Crude P containing a substantial proportion of solid impurities is treated so that oxidized P substantially free from such impurities may be obtained. An atmosphere containing vapors of elemental and oxidized P is established in a vaporizing chamber. Crude P and air are continuously injected into the chamber. The quantity of air is controlled so that only a small part of the O_2 required for complete oxidation of the P is supplied. However, enough air is injected to maintain the temperature of the partially oxidized combustion products above the fusion point of the solid impurities (~ 900-1100°). The combustion products are held in the vaporizing chamber long enough for most of the fused solid impurities to separate and collect in the bottom of the chamber. The impurities are withdrawn and the elemental and oxidized P are discharged through a separating chamber into a combustion chamber. Oxidation is completed using air supplied separately.

54 Oxidizing Phosphorus. G. L. Frear. *U.S.* 2,374,188, Apr. 24, 1945, Appl. Dec. 30, 1940; 8 pp. All of the elemental P and only a small proportion of the CO in a phosphate reduction furnace gas is preferentially oxidized. A uniform gaseous mixture is formed of the reduction furnace gas and air containing an excess of O_2 required to combine with the elemental P to form P_2O_5 but $\leqslant$ 50% excess. The gaseous mixture is passed through an enclosed zone at a rate of $\leqslant$2.5 lb of elemental P/hr/ft^3 of enclosed space. The gaseous mixture is maintained in the zone uniformly at ~ 500° for long enough to oxidize substantially all of the P to P_2O_5.

55 Oxidation of Phosphorus with Steam. K. L. Elmore. *U.S.* 2,613,134, Oct. 7, 1952, Appl. Sept. 27, 1950; 5 pp. Superheated steam and P vapor in a ratio of 16-30:1 are mixed. The resulting mixture of vapors is passed over and in intimate contact with a catalyst in a reaction zone. The catalyst is selected from Cu, Cu phosphide, Pt, and the Pt phosphides. It is supported on a material selected from Al orthophosphate, metaphosphate, and phosphide. The temperature of catalyst and vapors is maintained at ~ 650-900° and the vapor flow rate is ~ 500-2000 vol of vapor/vol of catalyst/hr. A complex vaporous equilibrium mixture in which substantially all P is oxidized to pentavalent and trivalent states is withdrawn from the reaction zone.

56 Oxidation of Phosphorus with Steam. J. F. Shultz. *U.S.* 2,613,135, Oct. 7, 1952, Appl. Sept. 28, 1950; 6 pp. Superheated steam and P vapor in a ratio of ~ 16-35:1 are mixed. The resulting mixture of vapors is passed over and in intimate contact with a catalyst in a reaction zone. The catalyst is selected from Cu, Pt, their phosphides, and mixtures thereof. It is supported on a material selected from Ti and Zr pyrophosphates. The temperature of the catalyst and vapors is maintained at ~ 650-900°, and the vapor flow rate is maintained at ~ 500-7500 vol of vapor/vol of catalyst/hr. A vaporous mixture of reaction products is withdrawn from the reaction zone. Substantially all the P is present in pentavalent and trivalent states. The mixture is cooled and partially condensed. A resulting liquid phase composed of H_3PO_4 containing a minor proportion of H_2SO_4 is separated from a gaseous phase composed essentially of H_2 containing a minor proportion of phosphine.

57 Phosphorus Burner Assembly. R. B. Burt and J. C. Barber. *U.S.* 3,050,374, Aug. 21, 1962, Appl. Mar. 30, 1959; 4 pp. A burner assembly is described which permits efficient burning of P of variable qualities over a wide range of combustion rates under close control. Lower oxides of P are eliminated in the P_2O_5 produced. Reaction between P_2O_5 and phosphate dust or other solid reactants is improved. The P burner assembly has an air duct with an inlet and an outlet. A source of low-pressure air with sufficient capacity to maintain a flow of air through the duct at > 250 linear ft/sec is connected to the inlet. The duct is large enough to carry most of the air needed for combustion of P at the given velocity and under low pressure. Molten P is injected within the stream of air at a point within the duct and adjacent to the outlet. When the air stream is maintained above the critical velocity of ~ 250 ft/sec, the P is atomized into fine droplets which are burned immediately. Finely divided solid material such as phosphate rock, metals, or alkali salts can be suspended in the air supplied to the burner. They will react with the P_2O_5 formed more efficiently than when they are fed to the reaction chamber through separate devices.

58 Oxidation of Phosphorus with Steam. L. B. Hein, D. W. Rindt, J. F. Shultz, and Grady Tarbutton. *U.S.* 2,706,146, Apr. 12, 1955, Appl. Sept. 16, 1950; 5 pp. Phosphorus is oxidized with steam in a primary reaction zone. A vaporous mixture of reaction products in which substantially all P is present in the pentavalent and trivalent states is withdrawn from the primary reaction zone. This mixture is introduced into a secondary reaction zone which has a total surface area of $\geqslant$ ~ 9 ft^2/lb of P introduced/hr. The secondary reaction zone is maintained in the range of 500°F to the mixture dew point. A liquid composed essentially of H_3PO_4 is condensed on the surface of the secondary reaction zone. The liquid flows downward over the surface in a film exposed to the gaseous remainder of the mixture until liquid-gas equilibrium is established. Strong H_3PO_4 low in H_2PO_4 content is withdrawn. A gaseous effluent is withdrawn from the secondary reaction zone also. The effluent is partially condensed and separated into a liquid H_3PO_4 fraction and a gaseous H_2 fraction low in phosphine content.

ELECTRIC FURNACE PHOSPHORIC ACID

59 Apparatus for Making Phosphoric Acid. H. A. Curtis. *U.S.* 2,026,519, Jan. 7, 1936, Appl. May 15, 1935; 5 pp. Apparatus is described for oxidation and hydration of the P in P reduction furnace vapors or P separated from such vapors during the production of H_3PO_4 by thermal methods. The oxidizer-hydrator is an enclosed U-shaped chamber with a burner at the top of one column and means for maintaining aqueous spray throughout the lower portion of the column. The bottom of the chamber has air inlets adjacent to the bottom of the first column. The second column has means for maintaining aqueous spray throughout the column and a vapor line from the top to the top of a vertical cooling chamber. Air is admitted at the top of the cooling chamber also. A vapor line at the bottom leads to an electrical precipitator for separating H_3PO_4 mist from vapors. Vapors from an electrical phosphate reduction furnace are propelled through a dust separator, the oxidizer-hydrator, the vapor cooler, and the precipitator. Approximately atmospheric pressure is maintained at the vapor outlet of the furnace. Means for withdrawing liquid are provided at the bottom of the oxidizer-hydrator, vapor cooler, and precipitator, respectively.

60 Separating Hydrated Phosphorus Pentoxide. W. H. Baskerville. *U.S.* 2,303,318, Dec. 1, 1942, Appl. Sept. 3, 1940; 7 pp. A process is described for the production of H_3PO_4 from elemental P, particularly the separation of hydrated P_2O_5 from P combustion products containing excess H_2O vapor. The combustion products are passed upwardly through a separating column packed with 1-in. Raschig rings. The top of the column is cooled sufficiently to provide a contact liquid over the packing. The velocity of the combustion products is such that the column is maintained just below its loading or flooding point, ~ 8-10 ft/sec. The temperature of the combustion products entering the column is regulated to that required for the production of a flowable H_3PO_4 of a predetermined concentration. The product H_3PO_4 is withdrawn from near the bottom of the column.

61 Making Phosphoric Acid. C. E. Hartford and M. M. Striplin, Jr. *U.S.* 2,247,373, July 1, 1941, Appl. Jan. 24, 1939; 4 pp. A process is described for the production of H_3PO_4 with a higher P_2O_5 content than orthophosphoric acid. A gaseous mixture containing P_2O_5 vapor substantially free from any hydrated P_2O_5 is produced by oxidizing elemental P with substantially dehydrate air. The P_2O_5 vapor thus formed is absorbed in H_3PO_4 containing $\geqslant$ 80% P_2O_5 while maintaining the gaseous mixture and the P_2O_5 at temperatures above the condensation point for P_2O_5 vapor in the mixture.

62 Drying Gases. M. M. Striplin, Jr. *U.S.* 2,734,596, Feb. 14, 1956, Appl. Sept. 4, 1951; 3 pp. A stream of liquid H_3PO_4 containing ~ 77 wt % P_2O_5 is passed downward through a tower at $>$ - 60 and $<$ 25.4°. A stream of moist air or other nonreactive gas is passed upward through the tower in intimated contact with the descending H_3PO_4. A stream of dry gas is withdrawn from the top of the tower and H_3PO_4 containing ~ 75% P_2O_5 is withdrawn from the bottom of the tower.

63 Manufacture of Superphosphoric Acid. M. M. Striplin, Jr., David McKnight, and E. C. Marks. *U.S.* 2,999,010, Sept. 5, 1961, Appl. Mar. 25, 1957; 4 pp. Superphosphoric acid is a mixture of 100% H_3PO_4 (72.4% P_2O_5) with meta-, pyro-, and other polyphosphoric acids in proportions that vary with the concentration. Superphosphoric acid is produced by burning P in air and passing the hot vaporous P_2O_5 mixture upward through a vertical hydration zone. A relatively cool condensate of dilute H_3PO_4 is introduced into the hydration zone as a spray of free-falling droplets. A spray of H_2O is introduced at positions above the acid introduction. The relative proportions are adjusted to maintain a concentration of ~ 72-79% P_2O_5 in collected droplets of superphosphoric acid. This acid is withdrawn from a lower part of the hydration zone. A hot, gaseous effluent is withdrawn from the upper part of the hydration zone. This effluent is condensed to provide the relatively cool, dilute H_3PO_4 introduced into the hydration zone.

64 Manufacture of Superphosphoric Acid. M. M. Striplin, Jr., David McKnight, and E. C. Marks. *U.S.* 3,015,540, Jan. 3, 1962, Appl. Nov. 23, 1960; 4 pp. Continuation-in-part of *U.S.* 2,999,010. Phosphorus is burned in air. The resulting P_2O_5 at ~ 700-1400°F is passed into a vertical hydration zone. Water, dilute H_3PO_4 (~ 40-70% P_2O_5) at ~ 150-250°F, and superphosphoric acid (~ 72-80% P_2O_5) at ~ 200-300°F are introduced into the hydration zone. The relative proportions of acids and H_2O are adjusted to maintain a concentration of ~ 72-80% P_2O_5 in the superphosphoric acid collected. A hot gaseous effluent is withdrawn at ~ 250-400°F. Dilute H_3PO_4 (~ 40-70% P_2O_5) is condensed and returned to the hydration zone. Superphosphoric acid containing ~ 72-80% H_3PO_4 is withdrawn from a lower portion of the hydration zone at ~ 300-400°F. This is cooled to ~ 150-300°F and a portion is returned to the hydration zone. The remaining cooled superphosphoric acid is withdrawn as product.

65 Process for Production of Phosphoric Acid. M. M. Striplin, Jr., and F. P. Achorn. *U.S.* 3,507,614, Apr. 21, 1970, Appl. Mar. 14, 1966; 8 pp. An improved process is described for the production of superphosphoric acid. Phosphorus is oxidized in air and the gaseous P_2O_5 is passed into a hydration zone at ~ 700-2000°F. Dilute H_3PO_4 at ~ 90-250°F and superphosphoric acid from subsequent recovery and cooling steps at ~ 90-350°F are introduced into the hydration zone. Relative proportions of hot P_2O_5, acids, and H_2O contained therein are controlled to produce and collect superphosphoric acid in the hydration zone. A hot gaseous effluent at ~ 150-400° is withdrawn. Dilute H_3PO_4 is collected from the effluent and returned to the hydration zone. Superphosphoric acid is withdrawn from the bottom of the zone at ~ 150-400°F and cooled to ~ 90-350°F. A portion of the acid is withdrawn as product and the remainder is recycled to the hydration zone. The improvement consists of preheating relatively dilute and impure wet-process H_3PO_4 to ~ 90-350°F by heat exchange with superphosphoric acid withdrawn from the hydration zone. The superphosphoric acid is cooled simultaneously. Volatiles including H_2O vapor and F are driven off and the wet-process H_3PO_4 is concentrated and condensed to poly- and higher acyclic polyphosphoric acid. The heated and treated acid is introduced into the hydration zone. The introduction of this acid substantially increases the P_2O_5 output for a given rate of burning of P.

66 Process for the Production of Highly Concentrated Phosphoric Acid. H. Y. Allgood and F. E. Lancaster, Jr. *U.S.* 3,442,611, May 6, 1969, Appl. Apr. 22, 1964; 15 pp. A process is described for the production of H_3PO_4 containing $\leqslant$ 85% P_2O_5. Elemental P is oxidized in air in a combustion zone to produce gaseous P_2O_5. The combustion gases at ~ 1000-2000°F are passed into a vertical cooling-hydration-absorption-coalescing zone. Make-up H_2O required for acid hydration is introduced into the zone. Cooled recycled H_3PO_4 containing ~ 72-85% P_2O_5 are added at ~ 150-260°F to partially cool the hot combustion gases down to ~ 300-750°F. Enough recycled H_3PO_4 is added to substantially eliminate build-up of a layer of solid polyphosphoric acids on the zone walls. Relative proportions of H_2O and recycle are adjusted to maintain a concentration of ~ 75-85% in the resulting superphosphoric acid. Additional recycled H_3PO_4 is introduced at ~ 150-260°F into sprays in the throat of a venturi meter in the cooling-hydration-absorption-coalescing zone. The flow of acid through the sprays is adjusted to maintain the temperature of gases leaving the venturi throat at ~ 150-350°F and simultaneously increasing the temperature of acid flowing through the throat to ~ 160-350°F. A gas pressure differential of ~ 38-60 in. H_2O is maintained across the venturi throat. Acid and gases leaving the venturi are passed to a cyclonic separator in a collection zone. Gases from the cyclonic separator are passed through a mist separator to remove residual droplets of acid. The gases then contain $<$ 0.1% of the P_2O_5 equivalent of the P fed to the process.

They are vented to the atmosphere. The acid, containing ~ 72-85% P_2O_5, is cooled to ~ 150-260°F. A portion is recycled and the remainder is withdrawn as product which contains ≥ 99.9% of the P_2O_5 equivalent of the P fed to the process.

WET PROCESS PHOSPHORIC ACID

67 Phosphoric Acid Manufacture. J. E. Davenport and Frank Carroll. *U.S.* 3,326,635, June 20, 1967, Appl. May 25, 1963; 8 pp. Ground phosphate rock and weak H_3PO_4 mixed and introduced into a slurry beneath a layer of foam maintained over the surface of the slurry in a digester vessel. The slurry results from the reaction of H_2SO_4, weak H_3PO_4, and phosphate rock. The foam is generated by the liberation of gases when H_2SO_4 and phosphate rock are reacted. Simultaneously with the introduction of rock and weak H_3PO_4, H_2SO_4 is added to the digester in a quantity to supply a H_2SO_4:CaO (rock) mole ratio of ~ 0.8-1.2:1. The H_2SO_4 is applied onto the upper surface of the foam layer in a manner designed to minimize penetration. The slurry and foam are agitated gently to aid in distribution of H_2SO_4 in the foam layer and to keep the solids in the slurry suspended. Agitation is not vigorous enough to cause rapid mixing of the H_2SO_4 with the slurry phase. The slurry is maintained in the digester vessel for ~ 30-120 minutes at ~ 70-115°. It then is removed and filtered. Weak H_3PO_4 from the wash is recycled to mix with phosphate rock and a product H_3PO_4 containing ≤ 50% P_2O_5 is recovered. The byproduct $CaSO_4 \cdot 0.5H_2O$ crystals are stable and resistant to hydration during filtering and washing.

68 Direct Method for the Production of High-Analysis Phosphoric Acid. T. P. Hignett, A. V. Slack, J. M. Potts, and L. B. Hand, Jr. *U.S.* 3,161,467, Dec. 15, 1964, Appl. Apr. 17, 1962; 5 pp. Concentrated H_3PO_4 with a low F content is produced by acidulating phosphate rock which has been ground to ~ 20-90% -200 mesh with fuming H_2SO_4 containing ~ 15-20% free SO_3 (~ 103-104.5% H_2SO_4 equivalent). The acid is preheated to ~ 150-200°F. The degree of fineness of the rock is inversely proportional to the % of free SO_3 in the fuming H_2SO_4. The acidulate is retained in an insulated vessel equipped to provide a tumbling action for ~ 20-60 minutes to retain a substantial amount of the autogenous heat of reaction. Fluorine and other gases are evolved and dry, firm granules are formed. These granules are withdrawn from the vessel at ~ 400-450°F and quenched in wash liquor from the end step of a countercurrent extraction system. The wash liquor contains ~ 46-58% P_2O_5. The granules are leached countercurrently with H_2O to form H_3PO_4 containing 50-60% P_2O_5. The heat for this process is supplied by heat of reaction which eliminates the necessity for supplying external heat to the system.

69 Purification of Phosphoric Acid with Urea and Nitric Acid. J. F. McCullough. *U.S.* 3,967,948, July 6, 1976, Appl. Sept. 29, 1975; 9 pp. Wet-process H_3PO_4 is partially or essentially completely purified by a process using urea and HNO_3 with the coproduction of a N solution suitable for fertilizer. Crude wet-process H_3PO_4 is mixed with ~ stoichiometric amounts of urea to prepare urea phosphate containing ≤ 50% of the impurities in the crude acid. The urea phosphate is washed with purified product acid and then is mixed with 49-72 wt % HNO_3. Nitric acid is used in an amount sufficient to give a HNO_3:urea mole ratio of 0.9-1.1:1. The resulting urea nitrate slurry is maintained at < 35° for 15-60 minutes. The H_3PO_4 is separated as product from the solid urea nitrate, which is washed with 49-72% HNO_3. The wash solution is recycled for reaction with the urea phosphate. The washed urea nitrate is treated with NH_3 and H_2O to form a N solution containing urea and NH_4NO_3.

70 Purification of Wet-Process Phosphoric Acid with Methanol and Ammonia. J. F. McCullough and L. L. Frederick. *U.S.* 3,975,178, Aug. 17, 1976, Appl. Oct. 12, 1973; 14 pp. An improved method is described for the partial purification of crude H_3PO_4 containing 50-55% P_2O_5 prepared from phosphate rock and H_2SO_4 with the coproduction of solid NP fertilizer containing most of the metallic and F impurities of the crude acid. The crude H_3PO_4 is mixed with methanol and NH_3, preferably at methanol: P_2O_5 wt ratios of 2.8-4.0:1 and NH_3:P_2O_5 mole ratios of 0.30-0.38:1 while maintaining the temperature from 55° to the boiling point of the mixture for 30-90 minutes. Subsequently the reaction mixture is separated into a clarified liquid fraction of aqueous H_3PO_4 and ammonium phosphate dissolved in methanol and a solid fraction containing 44-55% P_2O_5, 4-7% N, and the major portion of the metallic and F compounds originally present in the crude H_3PO_4. Methanol is separated from the clarified liquid fraction to obtain partially purified concentrated H_3PO_4. Phosphoric acid adhering to the solid fraction is removed by washing with methanol and then evaporating the methanol from the washed solids to recover the solid fertilizer.

71 Partial Purification of Wet-Process Phosphoric Acid with Acetone and Ammonia. H. K. Walters, Jr., Y. K. Kim, and J. D. Hatfield. *U.S.* 4,152,402, May 1, 1979, Appl. Aug. 29, 1975; 8 pp. Wet-process H_3PO_4 containing ~ 25-55 wt % P_2O_5 is partially purified using acetone and NH_3. Enough acetone and NH_3 are mixed with the crude H_3PO_4 to give an acetone:acid wt ratio of 1-5:1 and an NH_3:P_2O_5 molar ratio of 0.2-0.6:1. The mixture is maintained at ~ 25° to solution boiling point, preferably ~ 35°, for 2-10 minutes and then is allowed to settle into two separate layers. The top layer of purified acid contains ~ 60-85% of the P_2O_5 in acetone; the bottom layer contains the remaining P_2O_5 and most of the impurities. Viscosity of the bottom layer at 25° is 40-5000 cP depending on acid concentration and amount of NH_3 used. The layers are separated and the acetone is distilled from both layers for recycle to recover a final purified acid generally containing ~ 55-75 wt % P_2O_5 and an impure bottom layer which can be processed further for fertilizer manufacture.

72 Purification of Phosphoric Acid with Oxalic Acid. R. C. Sheridan. *U.S.* 4,169,882, Oct. 2, 1979, Appl. Nov. 13, 1978; 6 pp. Wet-process H_3PO_4 is purified using urea and oxalic acid with coproduction of oxamide. Impure H_3PO_4 is mixed with about stoichiometric amounts of urea to prepare urea phosphate which contains < ~ 50% of the impurities originally present in the acid. The urea phosphate is mixed with oxalic acid and with H_2O in mole ratios of 1.9-2.1:1 and 3.6:1, respectively. Mixing is at ~ 15-100°, preferably ~ 60-80°. The resulting slurry is cooled and product H_3PO_4 is separated from the urea oxalate. The urea oxalate is heated with a catalytic amount of an acidic phosphate (3-15 wt %) at ~ 15-200° to form a mixture of urea and oxamide. Alternately, the urea oxalate is contacted with NH_3 at 25-132° to form a

mixture of urea and ammonium oxalate. Thus, a solution of oxalic acid consisting of 126 g of $H_2C_2O_4 \cdot 2H_2O$ dissolved in 150 mL of H_2O was heated to 70° and treated with 316 g of urea phosphate made from wet-process H_3PO_4. The urea phosphate was added gradually over ~ a 10 min period with stirring while the temperature was maintained at 65-75°. The mixture was cooled slowly and then filtered. The filtrate (381.8 g) was concentrated by stirring and heating to 110°. The concentrate (256.8 g) contained P_2O_5 50.6, N 3.6, oxalic acid 1.3, Al 0.06, Fe 0.10, Mg 0.02, F 0.03, and SO_4 0.3%. This corresponds to 88-96% removal of the Al, Fe, Mg, F, and SO_4 impurities from the H_3PO_4 used in making the urea phosphate. The unwashed, dried urea oxalate filter cake weighed 191.7 g and contained 3.4% P_2O_5 and 23.5% N. Ten g of the urea oxalate was heated for 15 minutes at 185° to form a mixture of oxamide (2.6 g, 62% yield), urea (2.4 g), and ammonium oxalate (2.2 g). After washing to remove the soluble products, pure homogeneous crystals of oxamide were obtained. Without the presence of H_3PO_4 in the urea oxalate, the oxamide yield was only 12%.

73 Uranium Recovery from Wet-Process Phosphoric Acid. J. F. McCullough, J. F. Phillips, Jr., and L. R. Tate. *U.S.* 4,180,545, Dec. 25, 1979, Appl. Mar. 25, 1977; 9 pp. Uranium is recovered in a concentrated form from wet process H_3PO_4 using NH_3 or an ammonium salt, a reducing agent, and a H_2O-miscible solvent. The H_3PO_4 is mixed with ~ 0.05-0.20 mole of NH_3 or NH_4HCO_3/mole of H_3PO_4 and 1 g equivalent of reducing agent/g of Fe present in the acid. The mixture is held at ~ 20-100° long enough to dissolve the NH_3 or ammonium salt. A miscible solvent selected from methyl, ethyl, and isopropyl alcohol is added while maintaining the reaction mixture between 50° and reflux temperature. The solvent is added in an amount to provide a solvent:H_3PO_4 wt ratio of ~ 1.93-3.15:1. Solids are separated, washed with enough solvent to remove H_3PO_4, and dried. They then are dissolved in mineral acid to recover U. Miscible solvent and H_2O are distilled from the H_3PO_4. The distillate is rectified to recover solvent for recycle. Thus, to 100 g of black wet process H_3PO_4 (P_2O_5 53.8, Fe 0.65, Al 0.53, Mg 0.16, F 0.43, SO_4- 3.73, and U 0.0209 wt %) were added 0.40 g of powdered Zn and 2.99 g of NH_4HCO_3. The mixture was held at 65° for 15 minutes with stirring to dissolve the Zn and NH_4HCO_3. Then 144 g methanol was added and the mixture was refluxed for 30 minutes. The precipitated solids were filtered, washed with 150 mL of methyl alcohol, and dried in air. The solid contained 0.0031 g of U or 15% of input. When 11.97 g of NH_4HCO_3 was used, the dried solid contained 0.0209 g of U or 100% of input.

74 Process for Concentrating Wet-Process Phosphoric Acid. J. G. Getsinger and W. C. Scott. *U.S.* 3,317,306, May 2, 1967, Appl. Sept. 16, 1964; 7 pp. A process is described for the production of a fluid, highly concentrated wet-process H_3PO_4 substantially free of FeAl tripolyphosphate. Wet-process H_3PO_4 containing ~ 30-54 wt % P_2O_5 is fed into an evaporator where it is maintained at ~ 450-600°F for ~ 1- < 20 minutes. The product acid contains in solution the impurities originally present in the feed acid and is substantially free of solids. The P_2O_5 concentration is ~ 60-76 wt %. The concentrated acid contains substantial proportions of pyrophosphoric acid, tripolyphosphoric acid, and higher polymers of polyphosphoric acid.

CALCIUM PHOSPHATES

MONO-, DI-, TRIPLE-, AND CONCENTRATED CALCIUM PHOSPHATES

75 Production of Phosphatic Fertilizers. G. L. Bridger. *U.S.* 2,522,500, Sept. 19, 1950, Appl. Apr. 20, 1949; 5 pp. Granular phosphatic fertilizer is manufactured by mixing an aqueous solution of H_3PO_4 with phosphate rock and dispersing the mixture in droplets into the upper part of a vertical heated zone. The droplets are dropped downward through the heated zone countercurrently to a stream of heated gas. The resulting fertilizer is withdrawn from a lower part of the heated zone. The process is improved by diluting superphosphoric acid containing ~ 75-87% P_2O_5 with H_2O to a P_2O_5 concentration of ~ 43-57% and maintaining the diluted acid at ~ 100-140°F for ≤ 30 minutes before mixing with finely divided phosphate rock. The acid and rock are mixed in proportions to give a CaO:P_2O_5 mole ratio of ~ 1:1. The mixture is maintained at ~ 100-140°F for ~ 1-1½ minutes from the time of mixing and then sprayed into an upper part of the heated zone. A stream of gas at ~ 250-1800°F is passed upward through the heated zone.

76 Making Calcium Phosphate Fertilizer. W. H. MacIntire. *U.S.* 2,086,565, July 13, 1937, Appl. Aug. 23, 1935; 3 pp. Calcium phosphate fertilizer is prepared from a Ca-containing material, $CaSiO_4$, and dilute H_3PO_4 (30-40 wt %). The Ca-containing material is mixed with dilute H_3PO_4 to form a thin slurry. Fine $CaSiO_4$, in an amount sufficient to desiccate the mixture, is mixed with the slurry until a plastic state is reached. The plastic mixture is cured until an apparently dry product results. For example, 407 wt parts of Tennessee brown phosphate rock containing 76.22% $Ca_3(PO_4)_2$ equivalent and 2.9% $CaCO_3$ equivalent were mixed with 1235 wt parts of 40 wt % H_3PO_4 to form a thin slurry. To this was added 81 wt parts of fine, unquenched slag (85%-200 mesh and 65%-325 mesh). Mixing continued until the plastic stage was reached. After curing the plastic mass for 1 month the apparently dry product contained: total P_2O_5 46.8, H_2O-soluble P_2O_5 40.25, citrate insoluble P_2O_5, 3.25 available P_2O_5 43.55, and moisture 4.36%.

77 Making Superphosphate. H. A. Curtis. *U.S.* 2,070,582, Feb. 16, 1937, Appl. Oct. 9, 1935; 3 pp. A process is described for the manufacture of superphosphate which requires a minimum expenditure of power and which reduces to a minimum the time required to bring the superphosphate to a granular condition. Phosphate rock (-100 mesh) is treated with 75-85% H_3PO_4 in proportions to form monocalcium phosphate. Mixing is accomplished in a paddle type mixture operated at a sufficiently high speed to insure thorough mixing of the charge while in a highly fluid condition. Mixing is continued for the duration of the fluid state, ~ 1 minute. It is discharged onto a conveyor and conveyed away without further agitation for a sufficient period of time for the mixture to pass through the plastic stage and crumble on disturbance, ~ 2-3 minutes. The material is discharged onto a second conveyor in such a manner that the material is broken up. It remains on the second conveyor without further agitation for ~ 8-12 minutes. This is long enough for the reaction to continue further and the mixture to form lumps which do not

agglomerate in storage.

78 Manufacture of Granular Calcium Phosphates. H. A. Curtis. *U.S.* 2,072,980, May 9, 1937, Appl. June 4, 1934; 4 pp. Limestone or phosphate rock is treated with concentrated H_3PO_4 containing ≥ 65 wt % H_3PO_4 to form a granular Ca phosphate which is essentially monocalcium phosphate. Fine limestone or phosphate rock and H_3PO_4 are contacted in a high speed paddle mixer. Size of the rock, concentration and temperature of the acid, and the time of contact are controlled to produce a fluid, partially reacted mixture which will set in a few seconds after dispersion. The mixture is dispersed through a fluid distributor into a tower. The dispersed particles are contacted countercurrently with a gas, such as air, heated to ≥ 200° to produce a solid, substantially completely reacted product.

79 Making Monocalcium Phosphate. R. H. Newton. *U.S.* 2,143,025, Jan. 10, 1939, Appl. Mar. 2, 1936; 4 pp. A process is described for reducing the setting time of a reaction mixture of concentrated H_3PO_4 and fine phosphate rock to ~ 1/3-1/6 of that required when all the reactants are added simultaneously. Substantially all of the phosphate rock is -200 mesh. The concentration of the acid is ≥ 65%, preferably 75-90%, H_3PO_4. A portion of phosphate rock in an amount required to react with ≤ 20% of the H_3PO_4 is dispersed in the acid in a mixer capable of thorough homogenization. The remainder of the fine phosphate rock required to react with the H_3PO_4 to form monocalcium phosphate is added immediately to the solution of Ca phosphate in concentrated H_3PO_4.

80 Manufacture of Calcium Phosphates. H. A. Curtis. *U.S.* 2,053,266, Sept. 8, 1936, Appl. May 21, 1934; 3 pp. Finely divided limestone and concentrated H_3PO_4 are contacted continuously in a paddle type mixer in a process for the manufacture of mono- or dicalcium phosphate. The mixer is operated at a sufficiently high speed to insure thorough mixing while the charge is in a fluid condition. After the fluid state has passed, the material is transferred to a second paddle type mixer which operates at a substantially lower speed than the first. Mixing is continued until the plastic mixture breaks up into agglomerated masses. The masses are heated until the chemical reaction between the constituents is substantially complete. The agglomerated masses are ground Thus, to manufacture monocalcium phosphate 50 mesh limestone 190 lb/hr and 83% H_3PO_4 364 lb H_3PO_4/hr were fed into a high speed mixer operating at 150 rpm. The partially reacted mixture, while still fluid, was discharged into a low speed mixer operating at 40 rpm from which it was delivered to storage in the form of small lumps. These were subsequently ground in a hammer mill to -10 mesh.

81 Production of Fertilizer. F. T. Nielsson. *U.S.* 2,879,153, Mar. 24, 1959, Appl. Nov. 7, 1951; 7 pp. Fertilizer is produced by mixing phosphate rock with at least enough HNO_3 to convert the Ca phosphate content of the rock to monocalcium phosphate and adding NH_3. A soluble sulfate is added in sufficient quantity to convert all $Ca(NO_3)_2$ present after ammoniation to $CaSO_4$ and the slurry is dried. The process is improved by adding ~ 1.0-1.2 times the amount of NH_3 theoretically required to precipitate all phosphate present as dicalcium phosphate and all F as CaF_2. The slurry is ammoniated in the presence of enough K_2SO_4 to give a $K_2O:P_2O_5$ mole ratio of ~ 0.2-0.55:1. Some of the Ca precipitates as citrate-soluble phosphate compounds with $CaO:P_2O_5$ mole ratios higher than that of dicalcium phosphate. The resulting slurry is dried to a moisture content of ~ 4-8% at a temperature high enough to keep it fluid. Enough K_2SO_4 is mixed with the hot, fluid slurry to react with all $Ca(NO_3)_2$ present. The resulting mixture is cooled and granulated.

82 Manufacture of Dicalcium Phosphate. H. A. Curtis. *U.S.* 2,043,238, June 9, 1936, Appl. July 2, 1934; 2 pp. Dicalcium phosphate is made from limestone and concentrated (≥ 65 wt %) H_3PO_4. Ground limestone is separated into a coarser fraction and a finer fraction. The coarser fraction is reacted with concentrated H_3PO_4 to form monocalcium phosphate. The finer fraction is mixed with H_2O to make a slurry. The amount of H_2O used is equivalent to that required for hydration of dicalcium phosphate subsequently produced. The monocalcium phosphate and limestone slurry are contacted to produce dicalcium phosphate. Alternately, finely ground phosphate rock is reacted with H_3PO_4 to produce dicalcium phosphate. This is contacted with an aqueous slurry of a Ca compound, rich in $CaCO_3$, to produce dicalcium phosphate. Thus, 302 wt parts of 50-100 mesh limestone were mixed with 336 wt parts of 87.5% H_3PO_4 to form monocalcium phosphate. A slurry was made from 302 wt parts of -100 mesh limestone and 85 wt parts of H_2O. The monocalcium phosphate and limestone slurry were mixed to react and form dicalcium phosphate.

83 Process for Making Dicalcium Phosphate. W. H. MacIntire. *U.S.* 2,108,940, Feb. 22, 1938, Appl. May 3, 1934, 3 pp. Dicalcium phosphate of ~ 95% purity is prepared from high grade limestone, comminuted to -100 mesh, 85% H_3PO_4, and H_2O. The reactants are added in amounts of 294 parts of H_3PO_4, 300 parts of $CaCO_3$, and 25-50 wt % H_2O based on wt of limestone. The mixture is agitated vigorously until it reaches a granular condition.

84 Preparation of Dicalcium Phosphate from Phosphate Rock by the Use of Sulfur Dioxide, Water, and Carbonyl Compounds. J. F. McCullough, J. F. Phillips Jr., and L. R. Tate. *U.S.* 4,113,842, Sept. 12, 1978, Appl. Oct. 6, 1976; 12 pp. Dicalcium phosphate is prepared from beneficiated or unbeneficiated phosphate ore by use of SO_2, H_2O, and an organic carbonyl compound. The carbonyl compound is selected from aldehydes, methyl alkyl ketones, cycloketones, and mixtures thereof. Phosphate ore is treated with a mixture of SO_2, H_2O, and organic carbonyl compound and the resulting slurry is maintained at < 50° for ~ 0.5-10 hr. The mixture is filtered and the filter cake is washed with a mixture of SO_2, H_2O, and organic carbonyl compound. The wash effluent may be recycled or combined with the filtrate. The filter cake is heated to recover organic carbonyl compound and SO_2 which are recycled. Sulfur dioxide is distilled from the filtrate to precipitate dicalcium phosphate. The resulting slurry is filtered to recover the product dicalcium phosphate. The filtrate is recycled.

85 Process for Making Double or Treble Calcium and Magnesium Superphosphate. W. H. MacIntire. *U.S.* 2,137,674, Nov. 22, 1938, Appl. Feb. 14, 1934; 3 pp. A process is described for the preparation of a fertilizer product containing substantially equivalent quantities of H_2O-soluble Mg phosphate and H_2O-soluble Ca phosphate intimately mixed. Dolomitic limestone, preferable comminuted to -100 mesh, is added to H_3PO_4, preferable of ~ 85% concentration, while

the mixture is agitated. The dolomitic limestone preferably has a neutralizing value equivalent to ≥ 95% $CaCO_3$ and a Ca:Mg molar ratio of ~ 5:4. Agitation is continued until the mixture reaches the condition of a viscous sludge (~ 10-20 minutes). The viscous sludge is transferred to bins or piles for curing.

86 Making Tricalcium Phosphate. W. H. MacIntire. *U.S.* 2,095,994, Oct. 19, 1937, Appl. July 29, 1935; 2 pp. Tricalcium phosphate of high purity is prepared from sucrose, lime, and H_3PO_4. An aqueous sugar solution containing 20-25 wt parts of sucrose is treated with fine, granular, unslaked lime to produce a solution containing 5-6 wt parts of CaO equivalent. The solution is filtered to separate undissolved material, and 80-90 wt % H_3PO_4 in a 2:3 molar ratio with the CaO is added to the filtrate. The solution is agitated vigorously during addition of the acid. A gelatinous mass forms. Agitation is continued until the gelatinous mass is converted into a fine, white precipitate of tricalcium phosphate. The solution is filtered to separate the precipitate which then is washed and dried. The filtrate is recycled to the first step.

87 Process for Making Double or Treble (Calcium) Superphosphate. W. H. MacIntire. *U.S.* 2,067,538, Jan. 12, 1937, Appl. Jan. 5, 1934; 2 pp. Double or triple superphosphate is prepared by mixing high-grade comminuted dry limestone with 85% H_2PO_4. The reactants are added in a $CaCO_3$: H_3PO_4 ratio of ~ 100:230. The mixture is agitated for ~ 2.25 minutes, permitted to stand for ~ 8-10 minutes, and agitated again until granulation occurs. During the mixing operation the temperature is 45-50°; it rises to 75-80° during the aging period. At the end of the aging period the material is a dry granular mass that contains meager residues of the initial limestone and free H_3PO_4.

88 Preparation of Concentrated Superphosphate. R. D. Young, F. G. Heil, Jr., and A. B. Phillips. *U.S.* 3,074,792, Jan. 22, 1963, Appl. Apr. 23, 1959; 5 pp. Finely divided phosphate rock is introduced into a mixing zone where it is mixed with H_3PO_4 containing ~ 72-76% P_2O_5, preferably 74% P_2O_5. The acid is heated to ~ 180-250°F before mixing. Fresh superphosphate is withdrawn from the mixing zone with the heat of reaction conserved. The fresh superphosphate is cured for ~ 1 hr at ~ 270-400°F with substantially all the heat required to maintain the curing temperature supplied from the heat of reaction. The material is cooled at a slowly decreasing temperature due to radiation of heat from the curing superphosphate. Enough F is evolved during the mixing and curing steps to yield a product containing < ~ 0.7% F. Curing is completed within 24 hr.

89 Production of Granular Superphosphate Fertilizer. T. P. Hignett, A. B. Phillips, and R. D. Young. *U.S.* 3,034,883, May 15, 1962, Appl. Sept. 30, 1957; 4 pp. Granular superphosphate fertilizer is prepared continuously by reacting phosphate rock with H_2SO_4 and/or H_3PO_4 in an inclined rotating drum. Fine phosphate rock is introduced continuously into the upper end of the drum in which a bed of rolling discrete particles is maintained. Acidulating material is introduced continuously in sufficient quantity to react with the rock to form superphosphate beneath the bed at a plurality of locations extending the length of the drum. The temperature within the drum is maintained at ~ 160-220°F. Moisture is controlled by adding H_2O or steam beneath the surface of the bed in an amount sufficient to maintain a tendency of the particles to coalesce. A strong, porous, and dry granular superphosphate product containing < ~ 4.5 wt % moisture is withdrawn from the lower end of the drum.

90 Calcium Polyphosphate from Concentrated Superphosphate. J. R. Lehr, J. M. Potts, and L. D. Hand, Jr. *U.S.* 3,208,821, Sept. 28, 1965, Appl. Nov. 20, 1961; 4 pp. Phosphate rock (> ~ 70% -200 mesh) is reacted with H_3PO_4 containing ~ 52-55% P_2O_5. The resulting concentrated superphosphate, either cured for ~ 30 days, granulated, or fresh material preheated to ~ 150°F, is heated at a rate of ~ 6-12°F/minute to ≤ ~ 400-575°F. The treated Ca phosphate material is recovered as product. It contains ~ 60-65% P_2O_5 of which ~ 96-99% is in available form. The problems of severe stickiness, ball formation, and reversion to an unavailable form are eliminated by slow and uniform heating.

SUPERPHOSPHATES AND AMMONIATED SUPERPHOSPHATES

91 Method for the Manufacture of Superphosphate. S. A. Harvey and G. L. Bridger. *U.S.* 2,528,514, Nov. 7, 1950, Appl. Dec. 20, 1947; 9 pp. Superphosphate is prepared continuously in an apparatus with no moving parts by a method which is operable over wide ranges of temperature, acid concentration, and acid:rock ratio. A stream of finely divided phosphate rock is introduced continuously into a cone-shaped mixing zone which has its apex at the bottom. The rock stream is directed vertically downward to a central location adjacent to the bottom of the zone. A plurality of H_3PO_4 streams are introduced into an upper part of the mixing zone. The acid streams are directed downward at an acute angle to the axis of the frustum and tangential to the side of the zone. The flow rate and velocity of the acid streams are controlled to maintain a thick layer of rapidly moving liquid which swirls as it descends spirally along the inside walls of the cone. The rock flow rate is controlled in conjunction to the acid rate of descent to maintain a swirling, turbulent pool of fluid acid-rock mixture in the lower part of the mixing zone. The rock is dropped directly into the pool without contact with the acid higher in the mixing zone. The resulting intimate mixture of acid and rock is withdrawn by gravity from the lower part of the zone while still fluid.

92 Production of Ordinary Superphosphate with Strong Sulfuric Acid. L. B. Hand, Jr. *U.S.* 3,170,784, Feb. 23, 1965, Appl. Nov. 6, 1961; 4 pp. Granular ordinary superphosphate is produced by acidulating fine phosphate rock (> ~ 90% -200 mesh) with H_2SO_4 of a concentration > 96% H_2SO_4. The (P_2O_5 + SO_3):lime mole ratio is ~ 1:1. A powdery acidulate results. This acidulate is held in a second vessel for ~ 30 minutes until ≥ 50% of the F originally present in the rock is evolved. Enough H_2O is added to the powdery acidulate to dilute the acid to ~ 80% H_2SO_4. Total H_2O added including that present in the H_2SO_4 and that added to the acidulate is sufficient to yield a product with a moisture content of ~ 4-8 wt %. The acidulate is granulated and the granules are transferred to storage for ~ 3-7 weeks until final equilibrium conditions are attained. The granules have a P_2O_5 availability > ~ 96 wt %.

93 Manufacture of Ammoniated Superphosphates. H. A. Curtis. *U.S.* 2,037,706, Apr. 21, 1936, Appl. June 16, 1934; 5 pp. Ammoniated superphosphates are prepared continuously from limestone or phosphate rock, H_3PO_4, and anhydrous NH_3. Limestone or phosphate rock are contacted with concentrated H_3PO_4 (65%) to form a fluid, partially reacted mixture. The mixture is sprayed into a tower to form spherical particles. The particles fall through the tower countercurrent to a rising column of a heated inert gas, such as air, to form substantially completely reacted spherical particles. These are contacted with a mixture of NH_3 and air. When the partial pressure of NH_3 in the mixture is > the vapor pressure of NH_3 above monoammonium phosphate (MAP) and < the vapor pressure of NH_3 above diammonium phosphate (DAP) at the temperature of the reaction zone, MAP is formed. DAP is formed when the partial pressure of NH_3 is > the vapor pressure of NH_3 above DAP and < the vapor pressure of NH_3 above triammonium phosphate, at reaction temperature.

94 Ammoniation of Superphosphate. F. T. Nielsson. *U.S.* 2,729,554, Jan. 3, 1956, Appl. Dec. 26, 1952; 5 pp. Superphosphate is introduced continuously into an upper end of an inclined rotating drum to form a bed of rolling discrete particles of superphosphate with a depth of ~ one fourth to two fifths of the drum diameter. The surface of the bed is maintained at an inclination of ~ 30-45° to the horizontal diameter of the drum. Each of the particles passes through the bed from end to end of the drum in a continuous curved path approximating a flatten helix of many turns. Ammoniating fluid is introduced continuously beneath the surface of the bed in a broad steam countercurrent to the upward movement of the superphosphate particles. The breadth of the stream extends about the full length of the bed. The flow rate in the center part of the stream of ammoniating fluid is substantially greater than in the edges of the stream. Anhydrous NH_3, aqua NH_3, or ammoniating solution can be used. A current of air is passed over the surface of the bed continuously. Ammoniated product is withdrawn from the lower end of the drum.

95 Apparatus for Ammoniation of Superphosphate. F. T. Nielsson. *U.S.* 2,741,545, Apr. 10, 1956, Nov. 18, 1953; 5 pp. Continuation in-part of *U.S.* 2,729,554. The title apparatus is a rotary cylindrical drum with open ends and retaining rings singly disposed at the ends. The length of the drum is substantially equal to its diameter and its axis is inclined ~ 3° from the horizontal. A stationary manifold is along the axis within the drum. A valved conduit introduces ammoniating fluid into the manifold at a controlled rate. The ammoniating fluid can be anhydrous NH_3, aqua NH_3, or ammoniating solution. Ammoniating fluid is distributed through a pipe substantially equal in length to the length of the drum between the retaining rings. The pipe is located within the drum parallel to the axis. It is near the inner surface of the drum ~ 20-40° from the intersection of a vertical diameter with the bottom of the drum in the direction of rotation. The pipe has closed ends and a series of openings along its side opposite to the direction of rotation. The area of the series of openings increases from the ends to the center of the pipe. Two opposed plates the same length as the pipe are attached to the pipe on either side of the openings at converging angles to form a slot along the pipe opposite to the direction of rotation. Supply tubes connect the distribution pipe to the manifold. A fan is used to pass a current of air through the drum.

NITROGEN PHOSPHATES

NITRIC PHOSPHATES

96 Recycling Ammonium Sulfate in Nitric Phosphate Processing. O. W. Livingston. *U.S.* 3,515,534, June 2, 1970, Appl. Feb. 19, 1968; 11 pp. Particulate phosphate rock is acidulated with ~ stoichiometric amounts of ~ 50-65% HNO_3 to form an acidulate of $Ca(NO_3)_2$ and H_3PO_4 together with dissolved impurities, principally Fe and Al. The acidulate is reacted in a precipitator vessel with an $(NH_4)_2SO_4$ solution (~ 20-40%) to form a slurry containing $CaSO_4$, NH_4NO_3, and H_3PO_4. The slurry is filtered to remove gypsum. Filtration is improved when a portion of the $(NH_4)_2SO_4$ is added to the extraction vessel. The filtrate is ammoniated to pH ~ 5-6 while being heated to 220-235°F. Residence time is ~ 0.5-1 hr. The slurry is passed to a second reactor where it is cooled to ~ 60-85°F and ammoniated to pH ~ 9-9.9. Residence time is 0.5-1.5 hr. The slurry is filtered to remove a filter cake containing ~ 91- > 99% of the P_2O_5 present in the phosphate rock. The cake is dried to obtain a stabilized solid product consisting essentially of ammonium phosphate, NH_4NO_3, and minor amounts of Ca phosphate. The $N:P_2O_5$ ratio is ≥ 1:1.5. The filtrate is essentially NH_4NO_3 with unprecipitated P_2O_5. The gypsum is slurried and treated with $(NH_4)_2CO_3$ solution to produce $CaCO_3$ and $(NH_4)_2SO_4$ solution. The latter is recycled. Use of minimum agitation results in the growth of $CaCO_3$ agglomerates which are highly filterable.

97 Method of Preparing Ammoniated Nitric Acid-Phosphate Rock Extracts. A. V. Slack. *U.S.* 3,477,843, Nov. 11, 1969, Appl. Jan. 16, 1967; 20 pp. Ammoniation characteristics of HNO_3-phosphate rock extracts are improved by the addition of at least one soluble acyclic polyphosphate compound as a reaction inhibitor. The inhibitor is added to the slurry after it has been ammoniated to a pH of ~ 1.9-2.5 and is added in quantity sufficient to supply ~ 10-20 wt % of the total P_2O_5 content in the nitric phosphate fertilizer. It is selected from polyphosphates of ammonium, Na, K, Ca, Mg, and mixtures thereof, such as ammonium polyphosphate containing ~ 11-15% N and ~ 33-45% P_2O_5. Ammoniation of the slurry is continued to a terminal pH of ~ 6-8. The resulting ammoniated HNO_3-phosphate rock slurry is suitable for use as nitric phosphates and nitric phosphate suspensions. The formation of apatite is inhibited and the Ca phosphate content is substantially all in the form of $CaHPO_4$. The P_2O_5 solubility in both neutral citrate and alkaline citrate is > 90%.

98 Production of Carbonated Nitric Phosphate Fertilizer. F. T. Nielsson. *U.S.* 2,738,265, Mar. 13, 1956, Appl. May 25, 1953; 4 pp. Phosphate rock is extracted with HNO_3 and the slurry is treated with enough NH_3 to precipitate substantially all the P_2O_5 as dicalcium phosphate. Then the slurry is treated with NH_3 and CO_2 simultaneously to convert $Ca(NO_3)_2$ to NH_4NO_3 and $CaCO_3$. Before the $NH_3:NO_3$ mole ratio reaches 0.5:1 a sulfate is added in amounts to give a SO_4:CaO wt ratio of 0.07-0.15:1 in the slurry. The SO_4 can be provided by H_2SO_4, $(NH_4)_2SO_4$, K_2SO_4, $MgSO_4$, $CaSO_4$,

Na_2SO_4, gypsum, glaserite, langbeinite, kainite, and mixtures thereof. The addition of small amounts of SO_4 eliminates the necessity of careful distribution of NH_3 introduced into the slurry and permits rapid ammoniation. This increases production rate. The power of the slurry to absorb CO_2 is increased also so that complete carbonation can be attained with the use of ~ one seventh to one fourth of the CO_2 otherwise required.

99 Method of Manufacturing Fertilizers by Evaporating Slurries Containing Fertilizer Constituents. J. L. Graham. *U.S.* 2,857,262, Oct. 21, 1958, Appl. Sept. 11, 1952; 6 pp. Fertilizer is produced from phosphate rock, HNO_3, and NH_3 with the addition of KCl if desired. A slurry containing ~ 20-40% NH_4NO_3, ~ 16-24% dicalcium phosphate, ~ 1-4% monoammonium phosphate, 0- ~ 16% $CaSO_4$, 0- ~ 3% $Ca(NO_3)_2$, 0- ~ 11% KNO_3, ~ 1-4% acid insoluble material, and ~ 30-36% H_2O is produced and dried. The drying process is improved by introducing this slurry, without addition of KCl, into an evaporating zone where it is agitated and intimately contacted with hot combustion gases at ~ 400-2500°F. A fluid slurry containing < 1-15% moisture is withdrawn. When the moisture content is ≤ 2-3%, the concentrated slurry is introduced into a granulating zone, other fertilizer materials are added, and the resulting mixture is cooled and granulated with further evaporation of H_2O. At slurry moisture contents of ~ 3-6.5 % of the granules are dried by direct contact with combustion gases which are at temperatures below the softening point of the granules. The concentrated fluid slurry has a moisture content of 6.5-15% and enough previously dried product is added to reduce the moisture content of the mixture to 6.5%. The mixture is granulated and dried.

100 Nitric Phosphate Process. David McKnight, F. P. Achorn, and R. S. Meline. *U.S.* 3,005,697, Oct. 24, 1961, Appl. Apr. 9, 1958; 5 pp. Granular nitric phosphate fertilizers of various grades are produced by a process in which ammoniation can be carried out to a high degree without undue reversion of phosphate to an unavailable form. Difficulties caused by a mud stage at a transition point between fluid and solid stages are eliminated, and there is very little loss of N during drying. Phosphate rock (-20 mesh) is extracted with ~ 57-60% HNO_3 for ~ 20-30 minutes. Enough HNO_3 is used to form a fluid slurry. Cool, dry recycle fines are introduced into a rotating drum and if desired potash salts are added. A bed of rolling solid particles is maintained. Enough rock-HNO_3 slurry is distributed on the full length of the bed in a reciprocating spray to moisten the solid particles. Anhydrous NH_3 or an NH_3-containing solution is introduced beneath the particle bed to neutralize the slurry. Heat of reaction raises the bed temperature to ~ 130-150°F. The temperature is controlled by controlling the proportion of fines recycled. The nitric phosphate fertilizer is withdrawn from the drum, dried, cooled, and sized, and the fines are recycled to the rotating drum.

101 Nitric Phosphate Process. J. C. Brosheer. *U.S.* 3,028,230, Apr. 3, 1962, Appl. June 24, 1959; 4 pp. A nitric phosphate fertilizer low in apatite content is prepared in a two-step ammoniation process. Phosphate rock is extracted with HNO_3, a mixture of HNO_3 and H_2SO_4, or a mixture of HNO_3 and H_3PO_4. The extract is partially neutralized with NH_3; 45-60% of the total required for neutralization. The NH_3 is added at a rate of ~ 0.7-2.0% of the total NH_3/minute. A precipitate forms which contains > 90% of the F present in the phosphate rock. This precipitate is removed by filtering and the remaining extract is ammoniated to a pH of ~ 3.5-4.0. The resulting product is dried and preferably granulated.

102 Method for the Production of Granular High-Nitrogen and Mixed Fertilizers. I. W. McCamy, J. L. Graham, and M. R. Siegel. *U.S.* 3,165,395, Jan. 12, 1965, Appl. Apr. 4, 1962; 6 pp. A stream of acidulating material selected from H_3PO_4, H_2SO_4, HNO_3, and mixtures thereof and a stream of gaseous and/or liquid NH_3 are introduced simultaneously into a first-stage neutralization zone. The ratio of reactants is controlled to maintain a pH of 1-4. The temperature is maintained at 250-320°F. The partially neutralized acid stream is transferred to an evaporator where it is concentrated to > 90 wt %. A stream of concentrated material and a stream of NH_3 are introduced simultaneously into a second-stage neutralization zone in a ratio to maintain a pH of 4.5-6.0. The temperature is ~ 300-370°F. If desired, a K_2O source selected from KCl, KNO_3, and K_2SO_4 is added to the second-stage neutralization zone also. Material from this zone has essentially the same composition on a dry basis as the final product. A bed of recycle fines is maintained in a horizontally inclined rotating pan in continuous and alternate rising and cascading motion. Material from the second-stage neutralization zone is sprayed onto the cascading portion of the bed of fines. A granular high-analysis fertilizer is discharged continuously over the lower rim of the rotating pan. The material is sized and the onsize portion is withdrawn as product. The undersize and crushed oversize material are returned to the upper rim of the rotating pan. This process is applicable to a great variety of high-N and high-analysis complex fertilizers.

103 Process for Producing Granular Nitric Phosphate Fertilizer with High Phosphate Availability. C. H. Davis. *U.S.* 3,436,205, Apr. 1, 1969, Aug. 26, 1965; 9 pp. Phosphate rock ground to -10 mesh is extracted with HNO_3 with supplemental quantities of H_3PO_4 and/or H_2SO_4 for ~ 5-60 minutes. The extraction slurry is reacted with ~ 85% of the total NH_3 to be used in a preneutralizer tank. Recycled fines from a sizing step are introduced into a rotating drum to maintain a bed of rolling discrete particles in the drum. Slurry from the preneutralizer is sprayed onto the recycle bed in quantity sufficient to moisten the particles. The remainder of the NH_3 is fed beneath the bed of particles. The at least partially granulated nitric phosphate fertilizer is dried, cooled, and sized. Fines and crushed oversize are recycled to the drum. Potash can be fed to the drum to produce an N-P-K fertilizer. Detailed pilot-plant data are tabulated for the production of 20-20-0, 15-15-15, 26-13-0, and 14-28-0 grades, all having a P_2O_5 water-solubility of 40%.

AMMONIUM PHOSPHATES

104 Method of Preparing Purified Phosphates from Impure Phosphoric Acid. R. C. Sheridan. *U.S.* 3,920,796, Nov. 18, 1975, Appl. Feb. 23, 1973; 9 pp. Purified alkali metal or ammonium orthophosphates are prepared by mixing impure wet-process H_3PO_4 containing P_2O_5 ~ 10-60 and impurities ~ 1-10 wt % with melamine at a P_2O_5:melamine mole ratio of ~ 1:2-3.25:1 to produce crystals of melamine orthophosphate which then are separated from the mother liquor. The crystals are treated with an aqueous solution of alkali metal hydroxide, NH_4OH, or mixtures thereof at a hydroxide:melamine ortho-

phosphate mole ratio of ~ 1-8:1. Crystals of melamine precipitated in the reaction are separated and recycled for mixing with the impure H_3PO_4. Purified alkali metal or ammonium orthophosphate is recovered as product from the remaining filtrate. In another embodiment, purified alkali metal or ammonium pyrophosphates are prepared by heating the melamine orthophosphate crystals prepared as above, at ~ 170-325° for ~ 1-4400 minutes thereby converting them to melamine pyrophosphate. The crystals of melamine pyrophosphate are treated with an aqueous solution of alkali metal hydroxide, NH_4OH, or mixtures thereof at a hydroxide: melamine pyrophosphate mole ratio of ~ 2-10:1. Crystals of melamine are separated and recycled as above and the purified alkali metal or ammonium pyrophosphate recovered as product from the remaining filtrate.

105 Manufacture of Ammonium Phosphates. H. A. Curtis. *U.S.* 2,051,029, Aug. 18, 1936, Appl. May 21, 1934; 3 pp. A process for the manufacture of an ammonium salt of a mineral acid is described. Gaseous NH_3 and an inert gas are mixed in such proportions that the partial pressure of NH_3 in the mixture is greater than the vapor pressure of NH_3 above the ammonium salt at the reaction zone temperature. The partial pressure is less than the vapor pressure of NH_3 over the next compound in the series if additional compounds can be made from NH_3 and the mineral acid at the reaction zone temperature. The amount of NH_3 in the mixture is at least that required to form the ammonium salt. The gaseous mixture is contacted countercurrently and continuously with a spray of the mineral acid. Contact time is sufficient to achieve equilibrium between the reactants. For example, 90% H_3PO_4, 98 wt parts/unit of time, was admitted continuously and uniformly to the top of a reaction tower. Gaseous NH_3, 17 wt parts/ unit of time, in an NH_3:air vol ratio of 25:735 was added from near the bottom of the tower. The gaseous mixture passed up the tower counter-current to the fall acid. The reaction zone was maintained at 125°. Monoammonium phosphate was removed from the bottom of the tower and contacted countercurrently with air in a finishing tower to remove excess NH_3.

106 Manufacture of Fertilizer from Wet Process Phosphoric Acid and Ammonia. J. G. Getsinger and R. L. Haunschild. *U.S.* 2,891,856, June 23, 1959, Appl. Dec. 12, 1955; 6 pp. Wet process H_3PO_4 may be used to manufacture fertilizers in which both purified acid and precipitated impurities are present. Alternately, compounds containing the impurities Fe, Al, and Ca are precipitated leaving an acidic solution that may be used for crystallization of diammonium phosphate. The acid concentration is adjusted to ~ 20-28% P_2O_5 and NH_3 is introduced at a rate < 15 lb of $NH_3/hr/ft^3$ of acid. The temperature of the acid solution is raised to its boiling point before rapid precipitation occurs. Ammoniation is discontinued at a suspension pH of ~ 4.5-5.5 The resulting easily separable precipitate is separated from the solution without strong agitation. The solution is ammoniated to a pH of ~ 6.0 at boiling temperature under vacuum. Diammonium phosphate is crystallized from the solution. It is separated from mother liquor and dried. The mother liquor is recycled to the precipitation and crystallization steps.

107 Production of Granular Diammonium Phosphates. F. P. Achorn, R. D. Young, and G. C. Hicks. *U.S.* 3,153,574, Oct. 20, 1964, Appl. Dec. 8, 1960; 8 pp. In a process for the production of high-analysis granular diammonium phosphate, wet-process H_3PO_4 containing ~ 30-76 wt % of P_2O_5 is ammoniated continuously in a preneutralizer vessel. A slurry of ammonium phosphate with an NH_3:H_3PO_4 mole ratio of ~ 1.3-1.5:1 is produced. A stream of slurry, a stream of ammoniating fluid, and undersize product particles are introduced into the upper end of an inclined rotating drum. A bed of rolling discrete particles of diammonium phosphate is maintained in the drum. Additional ammoniating fluid is introduced continuously beneath the surface of the bed in a broad stream extending the length of the bed. An NH_3:H_3PO_4 mole ratio of ~ 2:1 is maintained in the drum. Evolved NH_3 is recovered in a scrubber and returned to the preneutralizer. Diammonium phosphate material is withdrawn from the lower end of the drum, cooled, and sized. Undersize material is recycled into the feed end of the drum. Oversize is crushed and rescreened. Substantially all heat needed for drying is supplied by chemical heat of reaction so the need for supplying external heat to the system is eliminated.

108 Process for Production of Ammonium Phosphate Fertilizers. T. P. Hignett, M. R. Siegel, R. S. Meline, and G. M. Blouin. *U.S.* 3,005,696, Oct. 24, 1961, Appl. Dec. 6, 1957; 6 pp. Granular, high-analysis fertilizers which have ammonium phosphate as their principle phosphatic component are produced in a horizontally inclined rolling drum by a one-step, continuous process. Such fertilizers also may contain NH_4NO_3, $(NH_4)_2SO_4$, urea, K salts, and trace elements. Fines, sized < 12 mesh, are introduced into the upper end of the drum together with one or more of NH_4NO_3, $(NH_4)_2SO_4$ and, if desired, K salts. Impure H_3PO_4 is introduced into the upper end of the drum. Enough ammoniating fluid is added to neutralize the H_3PO_4 to such a degree that proportions of monoammonium phosphate and diammonium phosphate are formed. The ammoniating fluid used may be anhydrous NH_3, concentrated aqueous NH_3, a concentrated aqueous solution of NH_3 and NH_4NO_3, or a concentrated aqueous solution of NH_3, urea, and ammonium carbonate. A bed of rolling discrete particles is maintained in the drum. Granulated material is withdrawn from the lower end of the drum at ~ 150-210°F and a moisture content of ~ 1.5-7.0%. The material is sized and at least a portion of product-size material is withdrawn. The remaining product-size material and the oversize are crushed, mixed with the fines, and recycled.

109 Pipe Reactor-Continuous Ammoniator Process for Production of Granular Phosphates. G. C. Hicks and F. E. Lancaster, Jr. *U.S.* 3,985,538, Oct. 12, 1976, Appl. Oct. 24, 1974; 6 pp. Commercial-grade wet-process H_3PO_4 containing ~ 50-58% P_2O_5 and NH_3 are fed simultaneously into a reactor to yield an NH_3:H_3PO_4 mole ratio of ~ 0.3-0.5:1. The resulting partially neutralized acid and a second stream of NH_3 are fed simultaneously to an inline pipe-type reactor to maintain an NH_3:H_3PO_4 mole ratio of ~ 0.9-1.2:1 at ~ 400-500° and 1 atm, thereby producing an ammonium phosphate melt containing ~ 5-50% of its P_2O_5 as polyphosphate. The melt is atomized by reaction steam pressure and sprayed through a plurality of apertures of predetermined size in the side wall of the inline reactor onto the upper end of a rolling bed of solids in an inclined rotary drum. Simultaneously, recycled fines from the process and other raw materials are fed to the drum. Granular product leaving the drum is cooled and sized. Crushed oversize and fines are recycled to the granulator. The ammonium phosphate melt is essentially anhydrous and the granules of mixed fertilizers do not require drying. Raw materials fed to the drum along with the recycled fines

consist of solids or concentrated solutions of fertilizer materials selected from KCl, urea, $(NH_4)_2SO_4$, NH_4NO_3, superphosphate, and mixtures thereof. A pugmill or blunger may be used instead of a rotating drum for granulation.

110 Production of Fertilizer from High-Alumina Phosphate Ores. T. P. Hignett, M. R. Siegel, R. S. Meline, and T. M. Kelso. *U.S.* 2,783,140, Feb. 26, 1957, Appl. Mar. 14, 1955; 8 pp. A process is described for the production of fertilizers from phosphate ore in which ⩾ 15% of the P_2O_5 is in the form of Al phosphate minerals. The ore is completely calcined at ~ 800-1200° and the calcined ore is crushed to -1/2 in. The crushed ore is extracted at ~ 80-100° with an aqueous solution of H_2SO_4, HNO_3, or a mixture of the two. Enough acid is used to provide an acid:P_2O_5 mole ratio of 2.0-10.0:1 and a slurry containing 5-75% solids. The slurry temperature is reduced to ~ 50-70° and the slurry is filtered. The filtrate is ammoniated to a pH of 3.0-9.0 and the resulting material is granulated and dried. A homogeneous, granular, noncaking fertilizer product is produced which has a high proportion of its phosphate content in citrate-soluble form.

POLYPHOSPHATES

111 Monocalcium Diammonium Pyrophosphate. E. H. Brown. *U.S.* 3,053,623, Sept. 11, 1962, Appl. June 3, 1959; 3 pp. Finely divided vitreous Ca metaphosphate is soaked with H_2O in a reaction vessel to promote hydrolysis. A mixture of hydrated polymers in relatively long-chain molecules of Ca metaphosphate is formed which contains ~ 30-60 wt % of $Ca(PO_3)_2$. An extract is produced which contains a heavy viscous phase substantially immiscible with H_2O and a supernatant aqueous solution of short-chain molecular degradation products of vitreous Ca metaphosphate. The supernatant solution is withdrawn continuously during extraction. An excess of concentrated NH_4OH is added to the viscous phase in a closed vessel. The mixture is held until spherulitic crystals form. Crystals of monocalcium diammonium pyrophosphate with the formula $Ca(NH_4)_2P_2O_7 \cdot H_2O$ are withdrawn as product.

112 Tricalcium Diammonium Pyrophosphate. E. H. Brown. *U.S.* 3,028,217, Apr. 3, 1962, Appl. June 3, 1959; 3 pp. Finely divided vitreous Ca metaphosphate is soaked with H_2O in a reaction vessel to promote hydrolysis. An extract consisting of two phases is produced: (1) a heavy, substantially H_2O-insoluble viscous phase, and (2) a supernatant aqueous solution of H_2O-soluble degradation product of vitreous Ca metaphosphate. The supernatant solution is withdrawn continuously leaving the viscous phase which is a sirupy mixture of hydrated polymers of Ca metaphosphate containing 30-60% $Ca(PO_3)_2$, polymerized in relatively long-chain molecules. The viscous material is held in a closed vessel until crystallization occurs. The crystalline material is tricalcium dihydrogen pyrophosphate, $Ca_3H_2(P_2O_7)_2 \cdot 4H_2O$, mixed with some orthophosphate. Orthophosphate is removed by washing with H_2O. Crystalline $Ca_3H_2(P_2O_7)_2 \cdot H_2O$ is digested at ~ 20-35° with an excess of the theoretical quantity of concentrated NH_4OH to form crystalline tricalcium diammonium pyrophosphate with the formula $Ca_3(NH_4)_2(P_2O_7)_2 \cdot 6H_2O$. This is a new material suitable for fertilizer and other uses.

113 Production of Ammonium Pyrophosphates and Byproduct Calcium Fluoride. J. R. Lehr. *U.S.* 3,362,785, Jan. 9, 1968, Appl. Apr. 20, 1964; 5 pp. Ammonium pyrophosphates are prepared by reacting Ca pyrophosphate or Ca ammonium pyrophosphate with an aqueous solution of NH_4F. The NH_4F is used in an amount sufficient to provide a F:Ca molar ratio of 2:1. A mixture is formed which consists of a solution of ammonium pyrophosphate with a pH of ~ 2-7 and suspended CaF_2 byproduct. The CaF_2 is recovered by filtering and the ammonium pyrophosphate may be recovered by precipitation with ethanol or by evaporation and crystallization. For example, 55.0 g $CaH_2P_2O_7$ and 18.8 g NH_4F was added to 100 m of H_2O at room temperature with only enough stirring to ensure dissolution of the NH_4F and mixing of the reactants. The CaF_2 precipitated rapidly and the reaction was complete in 5-10 minutes. The mixture was filtered, and the filtrate was treated with ~ an equal volume of ethanol which caused $(NH_4)_2H_2PO_7$ to precipitate, first as an oil which crystallized later. Other examples describe the preparation of $(NH_4)_3HP_2O_7 \cdot H_2O$ and $(NH_4)_4P_2O_7$ by similar methods.

114 High-Analysis Ammonium Polyphosphate Fertilizer. T. P. Hignett and J. G. Getsinger. *U.S.* 3,171,733, Mar. 2, 1965, Appl. Sept. 8, 1961; 7 pp. A new composition of matter is described which is readily soluble in H_2O and useful as a starting material for the production of high-analysis liquid fertilizers. The N + P_2O_5 content is ~ 73-82 wt %. The composition consists essentially of a solid mixture of solid H_2O-soluble salts of ⩾ ~ 50% $NH_4H_2PO_4$, ⩾ ~ 38% $(NH_4)_4P_2O_7$, and ⩾ ~ 2% higher ammonium polyphosphates. The latter are polymers of ammonium phosphate more highly condensed than $(NH_4)_4P_2O_7$. For example, superphosphoric acid (76% P_2O_5) 2.6 and NH_3 0.7 lb/hr were fed to a reactor. The vol of liquid retained in the reactor was 0.7 gal and the retention time was 168 minutes. The temperature was controlled at 380°F by regulating the flow of H_2O through a cooling coil. Liquid product was discharged at a rate of 3.3 lb/hr. The liquid product was agitated with a propeller-type stirrer for 15 minutes until it solidified and then was crushed. The solid product contained 17.9% N and 60.8% P_2O_5. It was hard, dry, and free-flowing.

115 High-Analysis Ammonium Polyphosphate Fertilizer. T. P. Hignett and J. G. Getsinger. *U.S.* 3,228,752, Jan. 11, 1966, Appl. Sept. 8, 1961; 9 pp. Division of *U.S.* 3,171,733. A solid, high-analysis ammonium polyphosphate fertilizer containing ~ 80% available plant food (N + P_2O_5) is prepared from anhydrous NH_3 and superphosphoric acid. Superphosphoric acid containing ~ 74-85% P_2O_5 and NH_3 are reacted to form a mass of molten material of low viscosity. This mass is maintained in a closed reaction vessel at ~ 325-475°F at a constant pressure of ~ 10-1000 psi. Relatively small streams of superphosphoric acid and NH_3 are combined with the molten mass continuously. The material is vigorously and continuously agitated causing immediate ammoniation of the incoming acid. Molten ammonium polyphosphate is withdrawn from the bottom of the vessel. The product material either may be applied directly to the soil in dry form or dissolved in an aqueous medium for preparation of high-analysis liquid fertilizers.

116 High Analysis Ammonium Pyrophosphate Process and Product. T. P. Hignett and J. G. Getsinger. *U.S.* 3,264,085, Aug. 2, 1966, Appl. Sept. 8, 1961; 9 pp. Continuation-in-part of *U.S.* 3,228,752. Division of *U.S.* 3,171,733. Anhydrous

NH_3 and H_3PO_4 containing ~ 78-80 wt % P_2O_5 are reacted in a closed reaction vessel to form a mass of molten material. This material is maintained in the vessel at ~ 300-500°F and ~ 10-1000 psi. The mass is agitated vigorously while small streams of NH_3 and acid are added continuously, thus effecting immediate ammoniation of inflowing acid. Molten ammonium phosphate material is withdrawn from the bottom of the mass and combined with aqueous medium to form a slurry. The pH of the slurry is adjusted to 5.0-6.3 by ammoniation. The diammonium pyrophosphate phase is recrystallized to triammonium pyrophosphate monohydrate in the form of easily filterable crystals. These are separated as product.

117 High Analysis Ammonium Polyphosphate Fertilizer. T. P. Hignett and J. G. Getsinger. *U.S.* 3,336,127, Aug. 15, 1967, Appl. Feb. 28, 1966; 8 pp. Continuation-in-part of *U.S.* 3,264,085, Continuation-in-part of *U.S.* 3,228,752, division of *U.S.* 3,171,733. A new composition of matter produced by the reaction of NH_3 and superphosphoric acid at elevated temperature and pressure contains ~ 72-84 wt % N + P_2O_5. The N:P_2O_5 ratio (where N is 1 lb NH_3 and P_2O_5 is 20 lb P_2O_5) is ~ 5.2-9.5:1. The composition consists essentially of an equilibrium mixture of $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_3HP_2O_7$, and $(NH_4)_4P_2O_7$. The material is H_2O-soluble and may be applied directly to the soil or dissolved in aqueous medium for preparation of high-analysis liquid fertilizers.

118 Ammonium Polyphosphate Produced at Atmospheric Pressure. T. D. Farr, H. K. Walters, Jr., and J. D. Fleming. *U.S.* 3,484,192, Dec. 16, 1969, Appl. Aug. 24, 1967; 20 pp. Solid and liquid ammonium polyphosphate fertilizers are produced at atmospheric pressure in a fully integrated continuous process. A stream of superphosphoric acid (~ 76-80% P_2O_5) and streams of anhydrous NH_3 and H_2O are introduced into a first reaction zone and mixed rapidly. Proportions are controlled so the reaction product is at ~ 50-80°, has a pH of ~ 5-7, and contains > 33 wt % (N + P_2O_5). A stream of reaction product is withdrawn and introduced into a second reaction zone together with streams of anhydrous NH_3 and makeup H_2O. Enough H_2O is added to adjust the viscosity and to maintain the H_2O content at ~ 20-47%. The proportions of NH_3 and reaction product are controlled to raise the pH to ~ 7.4-8.9 and form a slurry containing > 45 wt % total (N + P_2O_5), preferably > 50 wt %. The temperature is maintained at ~ 20-70° and retention time is > 5 minutes. A stream of slurry is withdrawn and the liquid and solid phases are separated. The solid phase is granulated and dried to produce a solid product which is substantially ammonium orthophosphate and ammonium pyrophosphate and contains ~ 17-21 wt % N ~ 52-60 wt % P_2O_5. The liquid phase can be recovered as a product containing ~ 9-12 wt % N and ~ 29-34 wt % P_2O_5 or it can be recycled to the first reaction zone. For example, superphosphoric acid (77% P_2O_5), NH_3, and H_2O were combined at 70°, forming a stock solution at pH 5.8, containing 11.1% N and 37.6% P_2O_5. The P_2O_5 was present as 37% ortho-, 46% pyro-, 15% tripoly-, and 2% tripolyphosphate. Part of this solution was ammoniated at 15-20°, to prepare a slurry having a pH of 8.5 and a viscosity of 600 cps. The slurry was vacuum filtered at a rate of 100 lb/hr/sq ft. The solids were dried. The filtrate was mixed with a portion of the stock solution and the mixture was ammoniated as before, to pH 8.5, and filtered. The cycle was repeated three times. The four solid products contained 20.6-20.9% N and 55.4-57.0% P_2O_5; the P_2O_5 was present as 34-42% ortho-, 48-56% pyro-, 8-10% tripoly-, and 1% tetrapolyphosphate. The four filtrates contained 11.2-11.5% N and 30.4-30.9% P_2O_5.

119 Ammonium Polyphosphate Produced at Atmospheric Pressure. T. D. Farr and H. K. Walters. *U.S.* 3,508,865, Apr. 28, 1970, Appl. Sept. 12, 1968; 8 pp. Continuation-in-part of *U.S.* 3,484,192. In a continuous process for the production of granular ammonium polyphosphate, superphosphate (~ 76-80% P_2O_5) is ammoniated in two steps to a pH of ~ 7.4-8.9. A slurry is produced which contains ~ 20-47% and > 45 wt % total (N + P_2O_5). The slurry is fed to an ammoniator-granulator where it is mixed with recycle product fines, NH_3, and additional superphosphoric acid. The heat of ammoniation is sufficient to evaporate the free H_2O and produce a dry granular product containing 17-21% N and 52-60% P_2O_5, distributed as ammonium ortho-, pyro-, and tripolyphosphates.

120 Ammonium Polyphosphate Produced at Atmospheric Pressure. T. D. Farr and H. K. Walters, Jr. *U.S.* 3,520,652, July 14, 1970, Appl. Oct. 2, 1968; 6 pp. Division of *U.S.* 3,484,192. Superphosphoric acid containing > 80 wt % P_2O_5, anhydrous NH_3, and H_2O are introduced into reaction zones at rates and proportions such that the retention time is ~ 5 minutes, the temperature is ~ 70-110°, the pH is ~ 0.1-4. The resulting slurry contains > 33 wt % total (N + P_2O_5) and ≤ ~ 30% of the phosphate is more condensed than tripolyphosphate. The slurry is introduced into a second reaction zone which is composed of 1-3 batch reactors with a total capacity sufficient to handle the continuously produced slurry from the first stage. Anhydrous NH_3 and makeup H_2O are added to produce a slurry with a pH of ~ 6 and a H_2O content of ~ 20-47 wt %. The temperature is maintained at ~ 70-110° and ≤ 15% of the phosphate is more condensed than tripolyphosphate. Reaction product is introduced into a third reaction zone together with NH_3 and makeup H_2O to adjust the viscosity and maintain a H_2O content of ~ 20-47 wt % and a pH of ~ 7.4-8.9. Temperature is ~ 50-110° and retention time is > 5 minutes. The slurry has a gross concentration of > 45 wt % (N + P_2O_5), ~ 13-16% N, and ~ 35-42% P_2O_5. It is granulated and dried to produce a product containing ~ 17-21 wt % N and ~ 52-60% P_2O_5, distributed as ammonium ortho-, pyro-, and tripolyphosphates.

121 Ammonium Polyphosphate Produced at Atmospheric Pressure. T. D. Farr and J. D. Fleming. *U.S.* 3,533,737, Oct. 13, 1970, Appl. Aug. 24, 1967; 10 pp. Division of *U.S.* 3,484,192. Superphosphoric acid containing 74-76 wt % P_2O_5 is combined with NH_3 and H_2O in proportions to raise the pH to ~ 4-7.8 while maintaining the temperature at < 70°. The solid and liquid phases are separated. The solid phase is granulated and dried to form a material containing ~ 12-21 wt % N and ~ 54-63% P_2O_5, distributed as ammonium ortho-, pyro-, and tripolyphosphates. The liquid phase is ammoniated to a pH of ~ 8-9 and the phases are separated. The solid phase is dried at ~ 50-110° and granulated to recover a material containing ~ 19-22% N, ~ 53-59% P_2O_5, and consisting substantially of diammonium orthophosphate and tetra-

ammonium pyrophosphate. A liquid phase is recovered which contains ~ 9-12% N and ~ 27-34% P_2O_5. Approximately one-half of the P_2O_5 from the feed acid is in this liquid which may be recycled, used as a liquid fertilizer, or processed further.

122 Ammonium Polyphosphate Produced at Atmospheric Pressure. T. D. Farr and H. K. Walters, Jr. *U.S.* 3,537,814, Nov. 3, 1970, Appl. Aug. 24, 1967; 9 pp. Division of *U.S.* 3,484,192. Anhydrous NH_3 and H_2O vapor are added to superphosphoric acid containing > 70% P_2O_5 in a reaction zone. The amount of NH_3 is controlled to raise the pH to ~ 5-6 within 10-150 minutes. The amount of H_2O vapor is 100-3000% of that theoretically required to hydrolyze long-chain polyphosphates to pyrophosphate. The temperature is maintained at ~ 125-200°. An intermediate melt is produced which contains ~ 15-17% N and ~ 58-64% P_2O_5. The pyrophosphate content is ~ 40-90% of the total phosphate. The melt is granulated with recycle fines and dried to produce a solid product containing a mixture of ortho-, pyro-, and tripolyphosphates with ammonium pyrophosphate the predominate form. It contains ~ 15-17% N and ~ 58-64% P_2O_5. Alternately the intermediate melt is reacted in a second stage with additional NH_3 and H_2O to produce granular or liquid fertilizer.

123 Ammonium Polyphosphate Produced at Atmospheric Pressure. T. D. Farr and H. K. Walters, Jr. *U.S.* 3,572,990, Mar. 30, 1971, Appl. Aug. 24, 1967; 6 pp. Division of *U.S.* 3,484,192. Superphosphoric acid containing > 80 wt % P_2O_5, NH_3, and H_2O are mixed rapidly and thoroughly in a reaction zone. Rates and proportions of the reactants are controlled so the retention time is > 5 minutes, the temperature is ~ 70-110°, and the pH is ~ 0.1-4.0. The slurry contains > 33 wt % total (N + P_2O_5) and phosphates more condensed than tripolyphosphate are reduced to ~ 15% of the total phosphate. A stream of first reaction slurry is introduced into a second reaction zone together with NH_3 and makeup H_2O in proportions to maintain a temperature of 50-110°, a H_2O content of ~ 20-47 wt %, and a pH of ~ 7.4-8.9. A slurry is formed which contains > 45 wt % total (N + P_2O_5). After a retention time of > 5 minutes, a stream of slurry is withdrawn, granulated, and dried. A solid product is recovered which ~ 17-21 wt % N and ~ 52-60 wt % P_2O_5. Ammonium ortho-, pyro-, and tripolyphosphate are present in ~ equal proportions.

124 Production of Ammonium Polyphosphates from Wet-Process Phosphoric Acid. J. G. Getsinger. *U.S.* 3,382,059, May 7, 1968, Appl. July 2, 1964; 7 pp. Stable liquid and solid mixed fertilizers containing ≤ 45% total (N + P_2O_5) in the liquids and ~ 70% in the solids by ammoniation of wet-process H_3PO_4. The acid contains ~ 1-10 wt % of metallic and other impurities which normally cause the formation of precipitates and gelatinous bodies in ammonium phosphates. Wet-process H_3PO_4 containing ≤ 54% P_2O_5 and off gas from a later mentioned reaction vessel are introduced simultaneously into a scrubbing vessel. The offgas is composed of H_2O and unreacted NH_3 vapors which heats and preneutralizes the H_3PO_4. A stream of partially neutralized H_3PO_4 from the scrubber and a stream of anhydrous NH_3 are introduced simultaneously into a reactor vessel. The reactor contains a melt of ammonium polyphosphate which is agitated continuously. It is maintained at ~ 15-1000 psi and ~ 300-600°F. A melt of ammonium polyphosphates is withdrawn from the bottom of the reactor and may be granulated to form a solid product or dissolved in aqueous solutions to produce liquid fertilizers. Typical composition of the solid product is 11.8% N and 60.8% P_2O_5. Chromatographic analysis showed that of the total P_2O_5, 57% was orthophosphate, 33% was pyrophosphate, 10% was tripoly- through nonapolyphosphate, and < 1% was higher than nonapolyphosphate. Dissolution of the solid in aqueous NH_3 solutions produced liquid fertilizers of 8-24-0 and 10-34-0 grades in which the impurities were well sequestered. These liquids did not salt out on storage at 75°F or 32°F for 30 days. Operating data are shown.

125 Process for the Production of Ammonium Polyphosphate. J. M. Stinson. *U.S.* 3,540,874, Nov. 17, 1970, Appl. May 6, 1968; 12 pp. Ammonium polyphosphates are produced in a form suitable for the manufacture of high-analysis solid or liquid fertilizer by ammoniating wet-process H_3PO_4. The acid contains ~ 1-10 wt % of metallic and other impurities, such as Fe and Al. Wet-process acid containing ~ 50-58% P_2O_5 is introduced into a reaction vessel simultaneously with offgas (unreacted NH_3 and H_2O vapors) from a second reactor. The offgas partially neutralizes the acid and heats it to 200-400°F. Preneutralized acid and anhydrous NH_3 are introduced simultaneously into the second reactor which contains a melt of ammonium polyphosphate formed by the acid-NH_3 reaction. Urea (solid or solution) is added to give a urea N:P_2O_5 mole ratio of ~ 0.01-0.5:1. The urea ensures a P_2O_5 availability of ≥ 99% by effecting in part and complementing the conversion of orthophosphates to essentially H_2O-soluble polyphosphates and the formation of relatively short chain acyclic polyphosphates.

126 Ammonium Polyphosphate. M. R. Siegel and H. C. Mann. *U.S.* 3,562,778, Feb. 9, 1971, Appl. Aug. 7, 1967; 15 pp. In production of ammonium polyphosphate fertilizer by reacting wet-process H_3PO_4 with NH_3, the solubility and fertilizer effectiveness of the phosphate is likely to be reduced if the R_2O_3:P_2O_5 mole ratio in the acid is > ~ 0.04:1. The process is improved, adding most of the NH_3 before a high degree of polyphosphate formation from orthophosphate has taken place. Thus, ammonium polyphosphate is produced in a three-stage continuous flow reactor in which wet-process H_3PO_4 containing about 55% P_2O_5 is fed to the first stage and the feed NH_3 to the second stage. Ammonium polyphosphate melt flows from the third stage and the gaseous NH_3 evolved in and released from this stage bypasses the second stage and passes back to the first stage. Other configurations are also possible, all aimed at getting most of the ammoniation completed in the early stages before the high polyphosphate formation and high temperature in the last stage. The method gives almost complete phosphate availability even at R_2O_3:P_2O_5 ratios of 0.09:1, whereas with simple two-stage ammoniation, availability as low as 95% is obtained.

127 Process for the Production of Ammonium Polyphosphate. R. S. Meline and R. G. Lee. *U.S.* 3,733,191, May 15, 1973, Appl. Mar. 25, 1968; 18 pp. High-analysis solid and fluid ammonium polyphosphate fertilizers of high P_2O_5 availability and high polyphosphate content are produced directly by ammoniating wet-process H_3PO_4 containing ~ 30-58% P_2O_5 and 1-10 wt % of metallic and other impurities, principally Fe and Al. The process employs simultaneous ammoniation, dehydration, and polyphosphate formation in an in-line reactor. The polyphosphate foam produced is

passed into a disengaging vessel designed to allow escape of free H_2O from the foam before cooling, thereby preventing hydrolysis and maintaining the polyphosphate content at a high level. Melt discharged from the disengaging vessel has a specific gravity of ~ 1.6-1.7. Steam and NH_3 vapors expelled from the disengaging vessel are scrubbed with feed H_3PO_4 prior to its entry into the reactor. A small relatively negative pressure of ~ 1-10 in. of H_2O is maintained in the disengaging vessel and in the scrubber. The ammonium polyphosphate melt of substantially 100% availability is suitable for the production of solid, clear liquid, or suspension fertilizers by conventional methods. In an example, wet-process H_3PO_4 made from uncalcined phosphate rock and containing 52.3 wt % P_2O_5 was preheated to 300°F and fed to the scrubber at 567 lb/hr. Gaseous anhydrous NH_3 preheated to 310°F and the partially neutralized melt were reacted in the in-line reactor to produce a foamy melt at 445°F. After treatment in the disengaging vessel for ~ 2 minutes, using a foam breaker speed of 1150 rpm, the ammonium polyphosphate melt product was discharged at 500 lb/hr. It contained N 12.7 and P_2O_5 59.4%. All of the P_2O_5 was citrate soluble and 46% of the P_2O_5 was in a polyphosphate form.

128 Ammonium Polyphosphates. J. F. McCullough and R. C. Sheridan. *U.S.* 3,912,802, Oct. 14, 1975, Appl. Apr. 20, 1970; 6 pp. A process is described for the manufacture of long-chain crystalline ammonium polyphosphates having the general formula $(NH_4)_mH_{(n-m)+2}P_nO_{3n+1}$, where n is > ~ 50 and the ratio *m:n* is ~ 1.04-0.85:1. The process consists of heating ammonium ortho-, pyro-, or tripolyphosphates in NH_3 at 1 atm and ~ 250-400° for a time sufficient to convert the reactants to a long-chain crystalline ammonium polyphosphate, usually ~ 1-16 hr. No condensing agent is added. The atmosphere of NH_3 is maintained by continuously sweeping the area with a gas containing ~ 10-100 vol % of NH_3. The product consists of the crystalline modification forms I, II, III, IV, or V, and mixtures thereof and contains N ~ 12.5-14.5 and P_2O_5 ~ 69-73 wt %. Conversion of the short-chain products to the long-chain crystalline ammonium polyphosphates is ~ 100%. For example, 20 g of crude $NH_4H_2PO_4$ prepared by ammoniation of wet-process H_3PO_4 was heated at 250° for 8 hr in a slow stream of NH_3 at 1 atm. A crystalline product (13.4 g) was obtained which contained 12.5% N and 69.2% P_2O_5. X-ray analysis showed that it was a mixture of forms I, II, and V of ammonium polyphosphate.

129 Slowly Soluble Ammonium Polyphosphate and Method for Its Manufacture. A. W. Frazier. *U.S.* 3,342,579, Sept. 19, 1967, Appl. Oct. 12, 1964; 7 pp. A high-analysis, slowly soluble ammonium polyphosphate fertilizer containing > 87 wt % (N + P_2O_5) is produced from anhydrous NH_3 and concentrated superphosphoric acid (83-92% P_2O_5). A mass of molten material formed by combining the reactants is maintained in a closed vessel at ~ 300-600°F and under a constant pressure of ~ 10-1000 psi. Small streams of acid and NH_3 are added continuously. The mass is agitated vigorously continuously thus effecting immediate ammoniation of incoming acid. Surplus ammonium polyphosphate material is removed from the lower portion of the reactor and cooled down to 100-0°F. The resulting gelatinous-like mass is contacted with H_2O. A long-chain ammonium polyphosphate salt precipitates and is recovered as product. The empirical formula of the fertilizer product is $(NH_4)_{n+2}P_nO_{3n+1}$, where the average n is 51. Its solubility is ~ 0.1 g/100cc of H_2O/24 hr at 25°.

130 Method for Urea-Ammonium Polyphosphate Production. G. A. Bottai and J. M. Stinson. *U.S.* 3,578,433, May 11, 1971, Appl. Aug. 5, 1968; 13 pp. High-analysis urea-ammonium phosphate prills are produced with good handling and storage qualities without high recycle rates of the addition of mechanical shear energy. Molten ammonium polyphosphate containing ~ 25-98% of the total P_2O_5 as polyphosphate and urea solution containing > 97 wt % urea are mixed at ~ 190-325°F. The urea:ammonium polyphosphate wt ratio is ~ 85:15-25:75. The mixture is transferred to a rotating cylindrical cup with holes in the side walls through which droplets of melt are thrown. The drops fall into a body of oil containing ≥ 0.25% Formalin solution. The oil is maintained at ~ 32-175°F and the drops cool and solidify. The prills thus formed are separated by centrifuging.

131 Urea-Ammonium Polyphosphate Production. R. G. Lee and R. D. Mitchell. *U.S.* 3,825,414, July 23, 1974, Appl. Apr. 1, 1971; 9 pp. Strong crystalline granular high-analysis urea-ammonium polyphosphate fertilizers are produced in a pugmill mixer. A 95-99.5 wt % urea solution at ~ 250-325°F and molten ammonium polyphosphate at ~ 270-600°F containing ~ 10-65% of its P_2O_5 as polyphosphate are added to recycled undersize solids in the pugmill. The urea:ammonium polyphosphate wt ratios are 20:80-80:20. The ammonium polyphosphate is fed to the pugmill ≥ 12 in. downstream of the urea to prevent hydrolysis of the urea and the resultant foaming and gas evolution. Product temperature at the pugmill discharge is maintained at ~ 130-250°F. The mixture is cooled and screened to remove product-size material. Crushed oversize and fines are recycled to the pugmill at 70-180°F at recycle:product wt ratios of 0.5-10:1. Typical product grades are 30-30-0, 28-28-0, 22-44-0, 21-42-0, 36-18-0, and 34-17-0.

132 Production of Urea-Ammonium Polyphosphates from Urea Phosphate. J. M. Stinson, H. C. Mann, Jr., and J. F. McCullough. *U.S.* 4,217,128, Aug. 12, 1980, Appl. Oct. 3, 1977; 17 pp. Continuation-in-part of Defensive Publication T973,004. High-purity urea-ammonium polyphosphate liquid fertilizers containing ≤ ~ 45 wt % (N + P_2O_5) or solid fertilizers containing ≤ ~ 70 wt % (N + P_2O_5) are produced by a process in which urea is used as a condensing agent in urea phosphate. Solid urea orthophosphate is heated at atmospheric pressure to ~ 260-350°F to form a melt. The melt is agitated continuously to ensure control of foam produced in the melt by evolution of CO_2 and to release the CO_2 from the foam to the atmosphere. The melt is maintained at reaction temperature for 1-30 minutes to simultaneously effect the pyrolysis of a portion of the urea component and to condense a portion of the orthophosphate component of the urea orthophosphate. For liquid and solid fertilizers respectively, ~ 0.05-0.578 and ~ 0.05-0.248 moles of urea/mole H_3PO_4 are pyrolyzed and ~ 8-90 and ~ 8-45% of the orthophosphate is condensed. Melts are produced which are mixtures of urea and ammonium polyphosphate. The general formula of the ammonium polyphosphate is $(NH_4)_nH_2P_nO_{3a+1}$, where n is the average chain length and ranges from > ~ 1.05- < ~ 3 and > ~ 1.05- < ~ 1.4 for liquid and solid fertilizers, respectively.

133 Production of Oil-Prilled Fertilizer Materials. J. E. Jordan. *U.S.* 3,703,364, Nov. 21, 1972, Appl. Aug. 28, 1970; 10 pp. An improved process is described for the production of strong crystalline high-analysis urea-ammonium polyphosphate

prills. Molten ammonium polyphosphate and urea solution are mixed and discharged as droplets into a body of oil as in *U.S.* 3,578,433. The improvement is a method for reducing the oil content of the recovered urea-ammonium polyphosphate product. A prilling oil of low viscosity composed of naphthenic and/or isoparaffinic hydrocarbons is treated with ~ 0.01-5.0 wt %, preferably ~ 0.25-1.0 wt % of fatty acid chosen from lauric, myristic, octanoic, palmitic, stearic, oleic, linoleic, and mixtures thereof. During the subsequent separation of oil from the product, the prills are washed with 0.1 lb of methanol, H_3PO_4, or mixtures thereof/lb of product. Examples indicate that the fatty acid additive reduces the oil content of the prills to ~ 30-40% of the value obtained when the fatty acid is omitted. After the washing step, ~ 80-90% of the oil had been removed from the prills.

134 Potassium Ammonium Polyphosphates. R. C. Sheridan and J. F. McCullough. *U.S.* 3,911,086, Oct. 7, 1975, Appl. Feb 4, 1971; 5 pp. A process is described for the manufacture of long-chain crystalline potassium polyphosphates with the general formula $K_x(NH_4)_yP_nO_{3n+1}$, where n is > 50, x + y = n + 2, and y/x is ~ 0.25-4.0. An ammonium phosphate selected from ortho-, pyro-, tripoly-, tetrapoly-, tetrameta-, long-chain polyphosphates, and mixtures thereof is heated with a K salt selected from K orthophosphate, metaphosphate, carbonate, chloride, and mixtures thereof in a stream of NH_3 vapor at 200-400° for 1-16 hr. For example, 13.6 g of KH_2PO_4 and 11.5 g of $NH_4H_2PO_4$ were mixed and heated at 210° for 16 hr in a slow stream of NH_3 at 1 atm. A homogeneous crystalline product was obtained which weighed 21.4 g and contained 6.3% N, 63.0% P_2O_5, and 21.8% K_2O. The major x-ray powder diffraction lines at d spacings were 6.54, 3.454, 5.51, and 5.290 Å.

VAPOR PHASE AND OTHER NITROGEN PHOSPHATES

135 Nitrogen-Phosphorus Compounds. H. T. Lewis. *U.S.* 3,539,328, Nov. 10, 1970, Appl. Sept. 17, 1968; 8 pp. New high-analysis NP compositions suitable for fertilizer use are prepared by vapor phase reaction of NH_3, O_2, and elemental P in a two-stage reactor. The temperature in the first stage is 950-1065°F and that in the second stage is 1200-1600°F. In the first stage, vapors of NH_3, O_2 (as dry air), and P are introduced at rates to provide a > 120- ≤ 300 wt % excess of O_2 over that required to give an O_2:P_4 mole ratio of 5:1. The NH_3 is introduced at a rate to provide ~ 60-280% of that required to give an N:P atomic ratio of 2:1. The residence time in the first reactor is 1-7 seconds. The reaction gases from the first reactor are fed to the second stage where the residence time is 0.5-4 seconds. The product from the second stage is cooled, and collected in the form of an amorphous, white, particulate solid which is substantially nonhygroscopic. The degree of H_2O-solubility can be regulated between 20 and 95%. The N content is 12-20% and the P content is 34-41%.

136 Production of Nitrogen-Phosphorus Compounds. H. T. Lewis, Jr. and J. G. Getsinger. *U.S.* 3,922,157, Nov. 25, 1975, Appl. Mar. 16, 1973; 13 pp. A vapor phase reaction process is described for the production of concentrated N-P fertilizer compositions. Vapors of NH_3, O_2, and elemental P are fed simultaneously into a single-stage tubular reaction zone having a maximum surface area:vol ratio of ~ 0.8 in^2:1 in^3 and maintained at ~ 400-1350°F. The flows of the NH_3, O_2, and elemental P vapors are controlled and proportioned to maintain an O_2 level of ~ 120-800 wt % of that required to yield an O_2:P_4 mole ratio of 5:1 and an NH_3 level of ~ 50-80 wt % of that required to yield an N:P atomic ratio of 2:1. Retention time of the vapors in the reactor is ~ 0.1-4 sec. The reaction product is a substantially nonhygroscopic, amorphous, white, particulate N-P product of predetermined H_2O solubility with N:P_2O_5 wt ratio of ~ 0.19-0.23:1. Products contain 14-16% N and 31-33% P; H_2O solubility of the solid product is 90-100%.

137 Production of Nitrogen-Phosphorus Compounds. J. C. Driskell. *U.S.* 2,713,536, July 19, 1955, Appl. Jan. 7, 1955; 4 pp. Air is dried to a moisture content of < 0.00008 lb H_2O/lb of dry air. Elemental P is oxidized with the dry air and the products of combustion are cooled to 450-950°F. The P_2O_5 vapor in the cooled combustion products is reacted with anhydrous NH_3 in an NH_3:P_2O_5 molar ratio of 2.1-2.7:1. A solid, finely divided product is obtained. The product consists of 60-79% ammonium metaphosphate, 1.5-19.0% phosphoronitridic acid, and 10-30% ammonium phosphoronitridate in intimate mixture. The N:P atomic ratio is 1.05:1.35 and 60-75% of the N is in ammoniacal form.

138 Nitrogen-Phosphorus Compounds. T. P. Hignett, J. M. Stinson, N. A. Brown, and M. C. Nason. *U.S.* 2,856,279, Oct. 14, 1958, Appl. Dec. 19, 1955; 4 pp. An intimate mixture of ammonium metaphosphate, phosphoronitridic acid, and ammonium phosphoronitridate is introduced into a hydrolysis zone. The mixture has a N:P atomic ratio of 1.05-1.35:1 and 60-75% of its N is in ammoniacal form. It is hydrolyzed with H_2O to an extent that 80-95% of its N content is in ammoniacal form. The material is maintained within the temperature range of ~ 200°F to the decomposition point of the material during hydrolysis. The product is cooled, crushed, and sized to give a fertilizer material of high bulk density and low hygroscopicity.

139 Making Alkali Metal Phosphate. G. R. Pole. *U.S.* 2,280,848, Apr. 28, 1942, Appl. Dec. 15, 1939; 5 pp. An alkali metal phosphate is formed from an alkali metal compound, such as KCl or NaCl, and H_3PO_4. A hot gaseous mixture containing metaphosphoric acid is formed in a heating zone in which the lowest temperature is above the melting point of the alkali metal phosphate to be formed. The alkali metal phosphate is admitted to the heating zone. Phosphoric acid and vaporized alkali metal compound are separated from the gaseous mixture outside of the heating zone. The liquid H_3PO_4 and alkali metal compound are brought into contact by returning them to the heating zone. The temperature in the heating zone is maintained so that a substantial portion of the alkali metal compound and H_3PO_4 react to form fused alkali metal phosphate. The process is adaptable for the production of orthophosphates, metaphosphates, and pyrophosphates. To produce Ca alkali metal phosphate, phosphate rock or other Ca containing material which is reactive with metaphosphoric acid is admitted to the heating zone with the alkali metal compound.

POTASSIUM, SECONDARY NUTRIENT, AND MICRONUTRIENT CONTAINING

140 Production of Chloride-Free Potassium Phosphates. T. P. Hignett and A. J. Smith. *U.S.* 3,832,154, Aug. 27, 1974, Appl. Oct. 10, 1972; 12 pp. Solid KCl and a recycled depleted brine solution from the process are fed simultaneously into a saturator maintained at ~ 55°. The resulting brine saturated with KCl is introduced into an electrolytic cell together with a stream of Hg, which flows in juxtaposition with the cathode. Direct current is applied across the electrolytic cell of voltage and amperage sufficient to electrolyze the saturated KCl brine therein; the cell is operated at a current density of ~ 0.2-0.7 amp/cm^2. Gaseous Cl_2 formed at the anode is removed and the depleted brine solution returned to the saturator. The Hg-K amalgam formed at the cathode is removed and introduced, together with a recycled K phosphate solution from the process, into a decomposer operating at ~ 35-100°. Mercury stripped of K is removed from the decomposer and recycled to the electrolytic cell, gaseous H_2 is evolved, and the resulting K-enriched, H_2O-depleted phosphate solution is introduced into a mixer together with H_3PO_4 and makeup H_2O. The resulting chloride-free K phosphate solution is removed from the mixer, a portion recycled to the decomposer, and the remainder collected as product. Alternately a portion of the K phosphate solution may be recovered as a solid product.

141 Process of Making a Granulated, Homogeneous Phosphate Rock Sulfur Fertilizer. T. P. Hignett and George Hoffmeister, Jr. *U.S.* 3,177,062, Apr. 6, 1965, Appl. June 17, 1963; 6 pp. Pulverized phosphate rock, elemental S, and a binding agent such as clay are dry blended and granulated. Proportions of 10-30 parts of S/100 parts of rock are used. The granules are sized and those in the -10 +20 mesh range are stabilized by heating to ~ 300°F for ~ 1-2 hr and recovered as product. Undersize and crushed oversize are returned to the blending step.

142 Production of Nitrogen-Phosphorus-Sulfur Compounds. J. C. Driskell and H. T. Lewis, Jr. *U.S.* 3,411,893, Nov. 19, 1968, Appl. Aug. 30, 1965; 9 pp. A highly concentrated, H_2O insoluble, nonhygroscopic fertilizer intermediate is produced from NH_3, P, and S by vapor phase reaction. The vapors are introduced into the reactor vessel at an N:P:S molar ratio of ~ 10-19:4:9-10. They are heated at ~ 660-1100°F to form an intermediate product which is easily handled, stored, and shipped in open containers without deleterious effect such as caking or hardening. To produce a H_2O-soluble fertilizer the intermediate is hydrolyzed by steam treating at 435-525°F and ~ 380-900 psi for ~ 0.5-2 hr. The recovered fertilizer product contains ~ 12-16% N, ~ 49-55% P_2O_5, and ~ 1-3% S.

143 Granular Ammonium Phosphate Sulfate and Monoammonium Phosphate Using a Common Pipe-Cross-Type Reactor. F. P. Achorn and J. S. Lewis, Jr. *U.S.* 3,954,942, May 4, 1976, Appl. Sept. 16, 1974; 13 pp. High-analysis, granular, substantially dust-free ammonium phosphates and ammonium phosphate sulfates are produced from H_3PO_4, H_2SO_4, NH_3, and H_2O in a pipe-cross reactor. Liquid anhydrous NH_3 and a small amount of H_2O are fed into a common pipe and are mixed downstream with H_3PO_4 and H_2SO_4 which is introduced to the pipe through a pipe cross. The acids and NH_3 react in the pipe cross and extension of the pipe beyond the cross. Overall length of the pipe reactor is 7 feet. It is cooled by a H_2O jacket or the reaction tube is made of either Hastelloy C metal or Teflon-lined mild steel pipe and the H_2O jacket is omitted. Slurry from the reactor is fed directly into the upper end of an inclined rotating drum in which a bed of recycle fines is maintained. Additional NH_3 and H_2SO_4 are fed beneath the surface of the bed in a broad stream extending the entire length of the bed. Additional H_3PO_4 is introduced above the surface of the bed in a stream extending the length of the bed. Product from the granulator is cooled and screened for product size removal. The proportions of raw materials fed to the process are specified. Typical products include ammonium phosphate sulfate grades such as 6-24-24, 12-12-12, 8-32-16, and 8-22-11, and monoammonium phosphate of grade 12-48-0.

144 Granular Ammonium Phosphate Sulfate and Urea-Ammonium Phosphate Sulfate Using a Common Pipe-Cross Reactor. M. M. Norton and B. R. Parker. *U.S.* 4,134,750, Jan. 16, 1979, Appl. July 25, 1977; 18 pp. Granular, substantially dust-free ammonium phosphate sulfates of a particle size distribution suitable for bulk blending are produced using a common pipe-cross reactor. A stream of anhydrous NH_3 is introduced into the common pipe section of a pipe-cross reactor; simultaneously a stream of H_3PO_4 containing 30-52 wt % of P_2O_5 and a stream of 78-98 wt % H_2SO_4 are supplied to the cross section of the pipe-cross reactor. The acids are contacted with NH_3 at the cross section at a temperature high enough to eliminate the need of additional H_2O to maintain continuous operation. The reaction product flows through a vapor tube extention to ensure continued intimate contact between the reactants. The essentially anhydrous molten ammonium phosphate sulfate is discharged into the upper end of an inclined rotating drum which contains a bed of recycle fines. Additional NH_3 can be added to the drum beneath the surface of the bed and additional H_3PO_4 can be sprayed onto the surface of the bed. The material is cooled, granulated, and sized. Moisture evaporates during the cooling stage. Urea-ammonium phosphate sulfate can be produced by adding either particulates solid urea, concentrated urea solution, or anhydrous urea melt to the material in the drum or by adding concentrated urea solution or anhydrous urea melt to the stream of anhydrous NH_3 fed to the pipe-cross reactor. Ammonium phosphate sulfate grades of 12-48-0, 6-24-24, 13-13-13, 10-40-10, a monoammonium phosphate grade of 11-55-0, a diammonium phosphate and diammonium phosphate sulfate grade of 18-46-0, and urea-ammonium phosphate sulfate grades of 33-11-0, 17-17-17, and 20-10-10 have been produced with this process.

145 Making Manganese Phosphate Fertilizer. W. H. MacIntire. *U.S.* 2,093,460, Sept. 21, 1937, Appl. June 22, 1935; 2 pp. Phosphate fertilizer containing Mn as an essential element is prepared from phosphate rock or other Ca compound reactive with H_3PO_4, rhodochrosite, and H_3PO_4. Fine phosphate rock is mixed with fine (-300 mesh) rhodochrosite and the mixture is contacted intimately with 75-90% H_3PO_4. The resulting mixture is cured at atmospheric temperature until the product contains the Mn substantially as $MnH_4(PO_4)_2 \cdot 2H_2O$.

146 Making Manganese Phosphate. W. H. MacIntire. *U.S.* 2,093,461, Sept. 21, 1937, Appl. June 22, 1935; 2 pp. The title fertilizer is prepared by mixing fine (-300 mesh) rhodochrosite with 80-90% H_3PO_4 until the mixture forms a creamy suspension. The mixture is cured at $\leqslant 100°$ until the product is substantially fine crystalline $MnH_4(PO_4)_2 \cdot 2H_2O$. For example, 672.4 wt parts of 87.5% H_3PO_4 was added to 338.5 wt parts of rhodochrosite, sized -300 mesh. The rhodochrosite

contained $MnCO_3$ 84.3, $MgCO_3$ 8.91, $CaCO_3$ 3.57, Fe_2O_3 + Al_2O_3 2.06. and SiO_2 0.65%. The mixture was agitated vigorously for 10-15 minutes until a creamy suspension was formed. This suspension contained some partially reacted material mixed with unreacted rhodochrosite and concentrated H_3PO_4 impregnated with CO_2. The gas-distended body collapsed in < 16 hr into a mass containing crystals of mono-manganese phosphate, some undecomposed rhodochrosite, and some free H_3PO_4. After 3 weeks curing time 900 wt parts of a slightly hygroscopic mixture consisting substantially of crystalline mono-manganese phosphate were obtained. The product was in a condition suitable for admixture with other fertilizer materials.

147 Manganese Phosphate Fertilizer. W. H. MacIntire. *U.S.* 2,095,993, Oct. 19, 1937, Appl. June 22, 1935; 2 pp. A superphosphate fertilizer containing Mn as an essential element in the form of an available Mn phosphate is described. The superphosphate contains ⩾ 16% P_2O_5 and the Mn is present in a form such as $MnH_4(PO_4)_2 \cdot 2H_2O$, $MnHPO_4 \cdot 3H_2O$, and $NH_4MnPO_4 \cdot H_2O$. An example is given which is the same as that for *U.S.* 2,093,461.

148 Fertilizers Containing Micro- and Macronutrients. O. D. Philen, Jr., Julius Silverberg, and M. M. Norton. *U.S.* 3,423,199, Jan. 21, 1969, Appl. Sept 29, 1965; 7 pp. Micronutrients are added to macronutrient-containing fertilizer granules by coating the granules with pulverized compounds of the desired micronutrients selected from Zn, Cu, Fe, Mn, Co, B, Mg, Mo, S, and mixtures thereof. The particles are sprayed with H_2O or steam forming a surface film of fertilizer solution. This binds the micronutrient-containing compound either mechanically or by chemical reaction. For example, a blended fertilizer (16-16-16) composed of ammonium phosphate nitrate, diammonium phosphate, and KCl, all granular, was mixed with MnO (4%) and ZnO (2.3%) for 1 minute in a rotary drum. The mixture was sprayed with H_2O (1.5%) and mixing was continued for 1 minute. Adherence of the micronutrient compounds was 98% as compared to an adherence of 63% without H_2O.

149 Fertilizers Containing Micro- and Macronutrients. O. D. Philen, Julius Silverberg, and M. M. Norton. *U.S.* 3,520,651, July 14, 1970, Appl. Sept. 29, 1965; 7 pp. Division of *U.S.* 3,423,199. The compound $3Zn(OH)_2 \cdot NH_4NO_3$ is claimed as a new composition of matter. The compound can be formed *in situ* on the surface of granular fertilizers in a process for the incorporation of micronutrients intimately into the structure of the granule surface rather than in a shell surrounding the granule.

150 Fertilizers Containing Micro- and Macronutrients. O. D. Philen, Jr., Julius Silverberg, and M. M. Norton. *U.S.* 3,523,019, Aug. 4, 1970; Appl. Sept. 29, 1965; 7 pp. Division of *U.S.* 3,520,651, Division of 3,423,199. A process is described for the incorporation of micronutrients selected from Zn, Cu, Fe, Mn, Co, B, Mg, Mo, S, and mixtures thereof into macronutrient-containing fertilizers. Granules of hygroscopic fertilizer salts are coated with pulverized micronutrients which, when wetted with H_2O and/or steam, react to form *in situ* stable compounds such as $Zn_3(NH_4)_2(P_2O_7)_2 \cdot 2H_2O$ or complex zinc ammonium hydroxy nitrates. The complex fertilizer compounds maintain good physical properties of the fertilizers in addition to providing available micronutrients.

151 Incorporation of Micronutrients in Fertilizers. J. M. Stinson and H. C. Mann, Jr., *U.S.* 3,244,500, Apr. 5, 1966, Appl. July 25, 1963; 11 pp. Anhydrous NH_3 and highly concentrated H_3PO_4 are combined in a closed reaction vessel to form a mass of molten material of low viscosity. This material is maintained at ~ 300-500°F and ~ 10-1000 psig. Small streams of acid and NH_3 are added continuously while the mass is agitated vigorously. Incoming acid is ammoniated immediately. Ammonium polyphosphate is withdrawn from the bottom of the mass. Micronutrients are incorporated by adding oxides of Fe, Cu, Zn, Mn, or mixtures to the acid before its introduction into the reaction vessel. The oxides are added in such proportion that the final product will contain ~ 0.05-0.9 wt % of micronutrient expressed as Fe, Cu, Zn, and Mn. Normally H_2O-insoluble micronutrient sources are converted to a H_2O-insoluble form by this process. Similarly, micronutrients are incorporated into liquid mixed fertilizers by mixing H_2O, NH_3, and superphosphoric acid containing oxides of the desired micronutrients. Proportions of H_2O, NH_3, and acid introduced into the reaction zone are controlled so that the pH and specific gravity of the solution are ~ 5-7 and ~ 1.25-1.5 at 80°F, respectively. The temperature is maintained at ~ 55-210°F during mixing. A stable fertilizer solution is produced which contains > 33 wt % total N + P_2O_5 and ~ 0.05-0.9 wt % of each micronutrient expressed as Fe, Cu, Zn, and Mn.

FLUID FERTILIZER

SOLUTION

152 Production of Liquid Fertilizer. M. M. Striplin, Jr., J. M. Stinson, and J. M. Potts. *U.S.* 2,950,961, Aug. 30, 1960, Appl. Nov. 23, 1956; 6 pp. A liquid mixed fertilizer with a total plant food content > 33% is prepared by mixing rapidly H_2O, NH_3, and superphosphoric acid containing 75-77 wt % P_2O_5 in a reaction zone. The proportions are controlled so that the pH and sp gr of the solution are 5.0-6.65 and 1.26-1.45 at 80°F respectively. The temperature of the solution is maintained at 55-125°F during mixing. A stable fertilizer solution containing 33-60 wt % total (N + P_2O_5) is withdrawn from the mixing zone. Enough NH_4NO_3 or urea may be added to the withdrawn solution to adjust the N:P_2O_5 wt ratio to 1:3. An aqueous solution of KCl can be added to form a complete NPK fertilizer.

153 Process for Preparing Stable Liquid Fertilizer and Product Thereof. M. M. Striplin, Jr., J. M. Stinson, and J. A. Wilbanks. *U.S.* 3,015,552, Jan. 2, 1962, Appl. June 9, 1958; 5 pp. Ammonium salts of unhydrolyzed superphosphoric acid are introduced into a mixing vessel in such quantities that 5-25% of the total P_2O_5 in the fertilizer to be produced is supplied. The salts are in an aqueous solution of ~ 11-33-0 to 13-46-0 grade. The quantity of salts is sufficient to maintain the congeneric impurities of wet process H_3PO_4 in solution. Wet process H_3PO_4 and NH_3 are introduced into the mixing vessel simultaneously and the materials are mixed intimately. The H_3PO_4 and NH_3 rates are controlled to maintain a pH of 4.0-7.0 and a temperature of ⩽ 200°F during mixing. A clear, stable, noncorrosive concentrated liquid fertilizer is withdrawn

from the mixing vessel.

154 Concentrated Liquid Fertilizers from Superphosphoric Acid and Potassium Hydroxide. J. M. Potts, H. W. Elder, and J. F. Anderson, Jr. *U.S.* 3,022,154, Feb. 20, 1962, Appl. May 6, 1960; 7 pp. Superphosphoric acid (~ 75-77% P_2O_5) and aqueous KOH (40-67%) are introduced simultaneously into a reaction zone maintained at ~ 80-240° and pH ~ 7.0-11.5 and agitated vigorously. A temperature-stable fertilizer solution with a salting-out temperature < 32°F is withdrawn from the reaction zone. Total $P_2O_5 + K_2O$ content is ~ 46-63 wt % with units of available K_2O at least equal to units of P_2O_5. The solution is essentially composed of K salts of superphosphoric acid with the P_2O_5 distributed as follows: 56-40% as K orthophosphate, 39-47% as K pyrophosphate, 5-11% as K tripolyphosphate, and ≤ 2% as K tetrapolyphosphate. A NPK fertilizer solution can be made by adding NH_4NO_3, diammonium phosphate, urea, or a combination of these.

155 Liquid Fertilizer from Batchwise Ammoniation of Wet-Process Phosphoric Acid. A. V. Slack and D. W. Rindt. *U.S.* 3,264,087, Aug. 2, 1966, Appl. June 24, 1963; 8 pp. The concentration of wet-process H_3PO_4 is adjusted to a P_2O_5 content of ~ 20-28%. Ammonia is added until the pH reaches 6.0-6.6. The temperature of the acid solution is raised to about its boiling point before rapid precipitation of impurities in the wet-process acid occurs. This is usually accomplished by heat of reaction during ammoniation; however, the acid may be preheated. The improvement consists of the control of the rate of NH_3 addition. It is introduced at the relatively high rate of ~ 15-50 lb NH_3/hr/ft^3 of acid solution until the pH is ~ 2.8. Subsequently, the NH_3 rate is reduced to ~ 2-5 lb/hr/ft^3 of acid solution until the pH reaches ~ 4.2. This low rate causes the formation of a granular, easily separable precipitate. The remaining NH_3 is added at ~ 15-50 lb/hr/ft^3 of solution to adjust the pH to ~ 6.0-6.6. The precipitate is separated leaving a clear fertilizer product.

156 Production of Potassium Ammonium Polyphosphate Solution. J. M. Potts and A. V. Slack. *U.S.* 3,347,656, Oct. 17, 1967, Appl. May 28, 1964; 7 pp. A high-analysis liquid fertilizer is prepared by reacting KCl and H_3PO_4 in a P_2O_5:K_2O wt ratio of ~ 2:1 at ~ 500-600°F for ~ 15-90 minutes. The temperature and time ranges are dependent and inversely proportional to one another. The resulting mixture of K polyphosphate and H_3PO_4 is cooled to ~ 300-400°F and H_2O at ~ 150-212°F is added. The solution is cooled to ≤ 180° and ammoniated to a pH of ~ 6.5-7. The aqueous potassium ammonium polyphosphate product has an N:P_2O_5:K_2O ratio of ~ 1:6:3. The grades fall between the range of ~ (1-6-3) to ~ (6-36-18). The Cl content is < ~ 2%. For example, wet-process H_3PO_4 (54% P_2O_5) was mixed with KCl (62% K_2O) in a wt ratio of 2:1. The mixture was heated to 550°F over a period of 1 hr and held at 550° for an additional 30 minutes. Boiling H_2O was added to the mixture at 300°F; all of the solids dissolved in 10 minutes. After cooling, the solution was ammoniated with gaseous NH_3, holding the temperature < 150°F. The resulting solution was 6.30-30.25-14.80 grade, containing 1.85% Cl. About 56% of the P was in polyphosphate form. The solution remained free of crystals for 14 days at 80°F.

157 Stabilization of Polyphosphate Fertilizer Solutions. A. W. Frazier. *U.S.* 3,711,268, Jan. 16, 1973, Appl. Apr. 20, 1970; 7 pp. A process is described for the stabilization of ammonium polyphosphate fertilizer solutions of grades ≤ ~ 11-37-0, containing ~ 50% of the P content as polyphosphate, and at least partly derived from wet-process H_3PO_4. The solutions are treated with a soluble F source selected from NH_4F, NH_4HF_2, $(NH_4)_2SiF_6$, KF, KHF_2, K_2SiF_6, NaF, $NaHF_2$, Na_2SiF_6, HF, H_2SiF_6, and mixtures thereof to precipitate Mg and Al impurities as $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$. The F is added in an amount equivalent to a sequestration ratio of 0.2:0.3 based on the empirical formula:sequestration ratio = wt % F/wt % MgO + 3 wt % Al_2O_3 + 1/3 wt % Fe_2O_3. The precipitate is removed by filtering.

158 Stabilization of Polyphosphate Fertilizer Solutions. A. W. Frazier. *U.S.* 3,861,897, Jan. 21, 1975, Appl. Apr. 20, 1970; 9 pp. Continuation- in-part of *U.S.* 3,711,268. Ammonium polyphosphate fertilizer solutions containing ≤ 11 wt % N and ≤ 37 wt % P_2O_5 with ~ 50% of the P_2O_5 as polyphosphate are stabilized against post-precipitation of dissolved impurities by addition of F. The impurities, principally Mg, Al, and Fe are derived from wet-process H_3PO_4 used in producing the fertilizer solutions. The F is added as a fluoride or fluosilicate in amounts sufficient to provide a sequestration ratio of ~ 0.4:0.5 as determined by the empirical formula:sequestration ratio = wt % F/wt % MgO + 3 wt % Al_2O_3 + 1/3 wt % Fe_2O_3. Effectively, this amount of excess F shifts the solution composition from a region where the H_2O-insoluble precipitate $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ is stable to a region where the H_2O-soluble form, dimorph II, is stable; the metallic cations are sequestered.

159 Ammonium Polyphosphate Solutions from Super Wet Acid. R. S. Meline. *U.S.* 3,775,534, Nov. 27, 1973, Appl. Mar. 22, 1971; 11 pp. Ammonium polyphosphate melts suitable for preparing fertilizer base solutions are produced from wet-process superphosphoric acid, NH_3, and H_2O. The base solution has improved self-sequestering properties. Wet-process superphosphoric acid having ~ 10-50% of its P as polyphosphate is contacted with NH_3 in a pipe reactor at atmospheric pressure and > 630°F. An ammonium polyphosphate melt is formed wherein ≥ 80% of the P is in the polyphosphate form.

160 Production of Ammonium Polyphosphates from Melamine Phosphates. J. F. McCullough and R. C. Sheridan. *U.S.* 4,017,587, Apr. 12, 1977, Appl. Oct. 6, 1975; 6 pp. Short-chain ammonium polyphosphates are manufactured from melamine orthophosphate prepared from wet-process H_3PO_4. The melamine orthophosphate is heated in a sweep of NH_3 to 150-210° for ~ 10-90 minutes to convert it to crystalline melamine and ammonium polyphosphates. The mixture is treated with H_2O or a dilute solution of ammonium polyphosphate to dissolve the product ammonium polyphosphates. The slurry is filtered and a relatively pure liquid ammonium polyphosphate product is recovered. The insoluble melamine is recycled.

161 Removal of Carbonaceous Matter from Ammonium Polyphosphate Liquids. J. M. Stinson, H. C. Mann, Jr., and D. H. Johnson. *U.S.* 3,969,483, July 13, 1976, Appl. Nov. 7, 1974; 21 pp. An improved process is described for the removal of carbonaceous matter from ammoniated polyphosphate solutions of pH ~ 5.5-6.5, grade ~ 8-27-0 to 11-37-0, and containing ~ 50-90 wt % of the total P_2O_5 as nonorthophosphate. The solutions are prepared by molecular dehydration and ammoniation of wet-process H_3PO_4 containing ~

50-72% P_2O_5. The carbonaceous matter which results from organic impurities in the acid chars during dehydration of the acid. The ammonium polyphosphate solution is mixed intimately with ~ 0.015-0.075 wt % of a H_2O-insoluble primary amine or a H_2O-insoluble acetic acid salt of a primary amine and ~ 0.005-0.075 wt % of a H_2O-insoluble quarternary ammonium chloride. These have lower densities than and are insoluble with the ammonium polyphosphate solution. The primary amine has alkyl groups with hydrocarbons with chain lengths of ~ 12-20 C atoms, the acetic acid salt of the primary amine has alkyl groups with hydrocarbons with chain lengths of ~ 12-18 C atoms, and the quarternary ammonium chloride is a dialkyl dimethyl ammonium chloride having hydrocarbon chain lengths of ~ 16-18 C atoms. Agitation is equivalent to that produced by ~ 20-250 passes through a centrifugal pump having a closed impeller. The resulting solution is held in a separation vessel until the solids flocculate and float to the surface. Clarified solution containing essentially no particulate carbonaceous matter is withdrawn from the bottom of the vessel.

SUSPENSION

162 Manufacture of Fluid Fertilizer from Wet-Process Phosphoric Acid. H. K. Walters. *U.S.* 3,019,099, Jan. 30, 1962, Appl. June 10, 1959; 3 pp. A stable suspension fertilizer of high sedimentation volume, low viscosity, and good pour characteristics is produced from wet process H_3PO_4 and NH_3. A stream of NH_3 is added to wet-process H_3PO_4 at a rate to maintain a temperature of > 150°F and in an amount to raise the pH to 7.5-8.5 in the suspension. Additional wet-process H_3PO_4 is mixed intimately with the suspension to lower the pH to 5.5-7.3, and a stable suspension is withdrawn as product. For example, concentrated wet-process H_3PO_4 (55% P_2O_5) and NH_3 were fed into a reaction vessel at a rate to produce a suspension with a pH of 8.0. Good mixing was maintained. Acid was added to lower the pH to 6.0-6.8. The resulting suspension showed no settling after standing for 1 week at room temperature. The sedimentation volume was 100 and the viscosity was 68 cP. Pour properties were acceptable after standing a week followed by slight agitation. The suspension was thixotropic. The test was repeated using acid containing 30% P_2O_5. The sedimentation volume was 100, the viscosity was 130 cP, and the pour properties were better after standing for 1 week than when concentrated acid was used. The suspension was not thixotropic.

163 High-Analysis Fertilizer Suspensions. A. V. Slack, J. D. Hatfield, and H. K. Walters, Jr. *U.S.* 3,109,729, Nov. 5, 1963, Appl. June 10, 1959; 4 pp. A high-analysis, stable, suspension-type fertilizer with desirable flow properties and low viscosity is produced by ammoniating strong H_3PO_4, preferably containing ~ 76% P_2O_5, at > 20°. The H_2O content is controlled to effect a supersaturated solution during a subsequent cooling step. An impalpable clay material, either attapulgite or bentonite, is mixed into the solution in an amount sufficient to furnish ~ 1-5 wt % of the impalpable material based on total fertilizer wt. If desired, additional fertilizer material, such as NH_4NO_3, urea, NH_4Cl, KCl, and K_2SO_4, can be added to the solution. The resulting material is cooled rapidly to ~ 20° to effect the formation of minute crystals of fertilizer salts in a saturated aqueous solution of the salts. The numerous particles of impalpable material act as nuclei for these minute crystals. The resulting stable suspension is withdrawn as product. At least one-third of the total quantity of fertilizer material is present in the form of these crystals.

164 Method of Producing High-Analysis Fertilizer Suspensions. A. V. Slack and H. K. Walters, Jr., *U.S.* 3,113,858, Dec. 10, 1963, Appl. June 26, 1961; 4 pp. Continuation-in-part of *U.S.* 3,109,729. A stable suspension-type fertilizer with high plant-food content, good flow properties, and low viscosity is produced by reacting NH_3 and either wet-process or electric-furnace type H_3PO_4. The heat of solution is utilized and an ammonium phosphate solution is produced at ~ 200°F. The hot solution is cooled to ~ 140-160°F. Attapulgite or bentonite clay is added in an amount to furnish ~ 1-5 wt % of clay in the product. Urea or NH_4NO_3 is added to the partially cooled solution. The resulting suspension is cooled to ~ 80°F through addition of solid fertilizer salts selected from K_2CO_3, KNO_3, and KCl. The salts are sized to ~ -20 mesh. The resulting suspension is withdrawn as product. At least one-third of the total quantity of fertilizer material is present as minute crystals in suspension.

165 Suspension Fertilizers from Concentrated Superphosphates. H. K. Walters, Jr. *U.S.* 3,326,666, June 20, 1967, Appl. June 29, 1964; 6 pp. A stable suspension type fertilizer with high plant food content, good flow properties, and low viscosity is prepared from concentrated superphosphate added in two stages. Water and ~ 10-40% of concentrated superphosphate is mixed and agitated for ~ 1-10 minutes. Supplemental N source materials [urea, $(NH_4)_2SO_4$, NH_4NO_3, or ammonium phosphates], K supplying material (KCl, K phosphate, K_2SO_4, or KNO_3), and NH_3 (anhydrous or aqueous) are added in that order. Subsequently, the remaining superphosphate is added and the suspension is agitated for 5-10 minutes. A fertilizer suspension is withdrawn which is characterized by the formation of a stable gel precipitated during the mixing steps. The gel has suspending properties such that the addition of a foreign suspending agent is unnecessary. For example, a 12-12-12 suspension was prepared by mixing the required H_2O with 20% of the required concentrated superphosphate (46% P_2O_5, -20 mesh). Subsequently a urea-NH_4NO_3, potash (-20 mesh KCl), NH_3 (28% aqueous solution) to supply 6 lb NH_3/20 lb P_2O_5, and the remainder of the superphosphate were then added in the order given, and mixing was continued for 4 minutes. After storage for one day the settled volume was 8% and the apparent viscosity was 302 cP.

166 Production of Suspension Fertilizers from Wet-Process Orthophosphoric Acids. L. A. Kendrick, Jr. *U.S.* 3,813,233, May 28, 1974, Appl. Aug. 28, 1972; 12 pp. Stable suspension-type fertilizers containing ≤ ~ 14 wt % N and ≤ 41 wt % P_2O_5 and with substantially all the P_2O_5 as orthophosphate are prepared from wet-process H_3PO_4 in a two-step process. The H_3PO_4, NH_3, and H_2O are fed simultaneously into a first reactor maintained at ~ 160-230°F to produce a slurry with a pH of ~ 2.0-5.5. The H_2O rate is adjusted to produce a product suspension of specific gravity 1.48 at 160°F. Retention time in the reactor is ~ 15-75 min. Partially ammoniated H_3PO_4 from the first reactor is fed into a second reactor maintained at 100-230°F where sufficient additional NH_3 is added to raise the pH to ~ 5.4-6.5 together with a predetermined amount of a gelling-type clay. After a retention time of 5-30 minutes the suspension product, which contains the congeneric impurities originally present in the wet-process

acid, is removed from the reactor. The product has a pourability of substantially 100%, expressed as % of total vol. Viscosity is at ~ 500 cP at 80°F. Both the pourability and viscosity are maintained after storage for up to ~ 90 days at ~ 100°F. Alternately, the process may be carried out batchwise in a single reactor by stopping the flow of H_3PO_4 and H_2O after the first ammoniation step and continuing ammoniation with addition of the gelling-type clay to produce the final suspension product.

167 Production of Suspension Fertilizers from Wet-Process Orthophosphoric Acids. T. M. Jones. *U.S.* 4,066,432, Jan. 3, 1978, Appl. July 2, 1976; 12 pp. Stable suspension-type N-P_2O_5 fertilizers containing ≤ ~ 14 wt % N and ≤ ~ 41 wt % P_2O_5 are prepared from wet-process H_3PO_4. The product also contains the impurities originally present in the H_3PO_4. The pourability is good and the viscosity is 500-1000 cP at 80°F. Both characteristics are maintained after storage for ≤ 90 days and after vibration equivalent to that which is experienced in railroad tank cars. The process comprises three-stage ammoniation. Streams of NH_3, H_2O, and H_3PO_4 are added simultaneously to the first reactor to produce an N:P_2O_5 mole ratio of ~ 0.20-0.25:1. In the second reactor the N:P_2O_5 mole ratio is raised to ~ 0.27-0.34:1, and in the third reactor to ~ 0.34-0.37:1. In addition to the NH_3, small amounts of gelling type clay are added in the third reactor. The retention times are 15-75 min, 10-90 min, and 15-60 min and the temperatures are 220-225°F, 180-220°F, and 90-120°F in the first, second, and third reactors, respectively. The procedure produces small, thin crystals of $(NH_4)_2HP_2O_4$ which resist settling.

168 Calcium Ammonium Polyphosphate—A Suspending Agent for Liquid Fertilizers. O. D. Philen, Jr. and A. W. Frazier. *U.S.* 3,526,495, Sept. 1, 1970, Appl. Aug. 1, 1967; 7 pp. Stable suspension-type fertilizers with plant food contents of ~ 40-60% total (N + P_2O_5 + K), good flow properties, and low viscosity are prepared from highly concentrated ammonium polyphosphate solutions containing pyrophosphate, with or without K. A Ca source such as Ca silicate slag (-100 mesh size) is added to the ammonium polyphosphate liquid fertilizer whereby a reaction occurs forming small $Ca(NH_4)_2P_2O_7 \cdot H_2O$ crystals in dendritic clusters. These crystals are an effective agent for keeping solids in suspension. Also formed in the reaction are hydrated silica gel and metal silicates, both of which are also good suspending agents. In an example, Ca silicate slag was added to 12-40-0 grade ammonium polyphosphate liquid fertilizer. The mixture was stirred at 170-180°F for 23-30 minutes to complete the reaction.

169 Self-Suspending Ammonium Polyphosphate Suspension Fertilizer. F. D. Nix. *U.S.* 3,676,101, July 11, 1972, Appl. June 25, 1969; 13 pp. Stable, clayless suspensions with grades as high as 14-47-0 are prepared by rapidly reacting superphosphoric acid containing 80-81 wt % P_2O_5 with NH_3 and H_2O. The H_2O content is controlled to effect a highly supersaturated solution. The solution is quick-cooled by discharging as an air-atomized mist into a body of cool oil in which the fertilizer is insoluble. The quick cooling causes formation of a suspension of fine ammonium polyphosphate crystals which has good storage properties. All the components of the suspension are H_2O soluble so clear solutions of grade 11-37-0 can be made by dissolving the suspensions in H_2O.

170 Elimination of Magnesium Gels in Liquid and Suspension Fertilizers Derived from Wet Acid. T. M. Jones and A. W. Frazier. *U.S.* 3,697,247, Oct. 10, 1972, Appl. Oct. 16, 1970; 5 pp. Gels form in ammonium polyphosphate fertilizer solutions and suspensions prepared from wet-process H_3PO_4 containing normal congeneric impurities. These include Al, Fe, Mg, and F in amounts such that the Mg:Al wt ratio is ~ 1.4-5.0:1. Formation of this gel is avoided by adding enough Al to form an Al_2O_3:MgO wt ratio of ≥ 0.9:1 before ammoniating the H_3PO_4.

171 Ruminant Direct Feeding Suspension Supplement. F. P. Achorn and J. F. Anderson, Jr. *U.S.* 3,794,740, Feb. 26, 1974, Appl. Oct. 22, 1971; 10 pp. A ruminant direct feeding supplement contains significant amounts of Mg, Ca, and/or S, which is particularly useful in treating the symptoms of grass tetany. The supplement is low in cost and may be fed directly without dilution or adulteration. It is liquid at about neutral pH and is highly stable during storage and handling. It is suitable for direct feeding such as by a licking pot. The supplement contains in wt %:H_2O ~ 10-20; urea ~ 5-25; ammoniated superphosphoric acid ~ 3-30 (≥ 70% of P_2O_5 as condensed ammoniated polyphosphoric acid including pyro-, tripoly-, and more condensed polyphosphoric acid); aqueous soluble ruminant edible sucrose material including molasses (based on 7% protein content) ~ 20-65; overfeeding preventative selected from $(NH_4)_2SO_4$ and NaCl 0.2-3.0; and MgO, part of which is in suspension, ~ 0.5-2.0. At least 20% of the total P_2O_5 present in the ammoniated superphosphoric acid is present as tripolyphosphoric acid. Nonprotein N totals ~ 2.6-14.8 wt %. This level is compatible with the metabolic characteristics of the ruminant.

CONTROLLED RELEASE

172 Method of Making Sulfur-Coated Fertilizer Pellet Having a Controlled Dissolution Rate. G. M. Blouin and D. W. Rindt. *U.S.* 3,295,950, Jan. 3, 1967, Appl. May 3, 1965; 8 pp. A process is described for the treatment of solid fertilizer particles to make them H_2O resistant, reduce caking tendencies, reduce hydroscopicity, and to produce a fertilizer product which has a controlled rate of dissolution when applied to the soil. The treating agent serves to supply a secondary nutrient as well as a pellet coating. An oily subcoating material selected from petrolatums, petroleum softwaxes and oils, wood rosins, and paraffins is applied to fertilizer particles in quantities of 1-8 wt % based on fertilizer wt. This quantity is sufficient to fill surface voids, cracks, and capillaries of the fertilizer particles. A coating of elemental S is applied to the oil-coated fertilizer in amounts of ~ 5-50 wt % based on the finally coated fertilizer. A topcoating with additional subcoating material is applied in amounts of 1-5 wt %. The viscosity of molten S is decreased and spraying and spreading characteristics are enhanced by the addition of halogens in amounts of 1-5 wt %. The addition of 1-10 wt % of powdered siliceous material to the molten S increase plasticity and strength. If desired, 1-30 wt % of powdered compounds of the micronutrients Fe, Zn, Cu, Mn, Mg, Mo, and Bo may be added to the molten S. In some instances the subcoating and/or the topcoating may be omitted.

173 Sulfur-Coated Fertilizer Pellet Having Controlled Dissolu-

tion Rate and Inhibited Against Microbial Decomposition. G. M. Blouin and D. W. Rindt. *U.S.* 3,342,577, Sept. 19, 1967, Appl. Dec. 12, 1966; 9 pp. Continuation-in-part of *U.S.* 3,295,950. A coating of elemental S is applied to fertilizer pellets in an amount to provide ~ 5-50 wt % of the coated fertilizer pellet wt. The coated pellets are topcoated with an oily selant selected from petrolatums, petroleum softwaxes and oils, wood rosins, paraffins, and mixtures thereof. The quantity of oily material is sufficient to impregnate any cracks and voids in the S coating. It provides ~ 1-8 wt % of the total wt. The process is improved by dissolving in the sealant ~ 0.1-4 wt % (based on total wt) of a microbially-toxic agent such as pentachlorophenol, coal tar oil, camphor, cresol, or mixtures thereof. This addition reduces the harmful microbiological activity on the coating when the fertilizer is in the soil. A subcoating of the sealant material may be added prior to the S coating.

174 Sulfur-Coated Urea by Improved Method. A. R. Shirley, Jr. and R. S. Meline. *U.S.* 3,903,333, Sept. 2, 1975, Appl. July 3, 1972; 33 pp. A slow-release N fertilizer is produced by applying a coating of commercial grade S on commercial-grade granular urea in a continuous process. A precisely uniform solid coating of fluid S is sprayed onto the surface of solid urea granules at 170-203.9°F in a horizontal rotary coating drum of length ~ 1.5-10 times its diameter filled to ~ 3-10% of its capacity, and rotating at ~ 30-80% of its critical speed. In one embodiment the surface of the granular urea is preheated and smoothed by superficial fusion and rolling in a rotary drum. Multiple, thin, concentrically formed layers of fluid S then are applied by cascading the urea granules beneath a plurality of sequentially applied, closely controlled pneumatic sprays of the fluid S in the rotary drum. In a second embodiment, hydraulic spray nozzles are utilized in a manner wherein preheating is not required. Special operating conditions are specified which allow the production of a slow-release urea fertilizer coated only with S. Proper temperature control is maintained during the process to assure that the S solidifies in the proper crystalline structure to impart significantly improved tensile strength characteristics to the coating. Each embodiment has characteristically different operating conditions, specifically temperatures, which result in decisively different coating characteristics.

175 Guanidine Phosphate Fertilizer. H. A. Curtis. *U.S.* 2,070,581, Feb. 16, 1937, Appl. Aug. 23, 1935; 2 pp. An improved superphosphate is produced which contains N as an essential element in the form of a guanidine salt. For example, a triple superphosphate, essentially monocalcium phosphate, was treated with a nitrifying compound containing ~ 23 wt % NH_3 and 27 wt % guanidine. The inorganic N:organic N was 1:1. The principle constituents of the resulting product were monocalcium phosphate, dicalcium phosphate, monoammonium phosphate, diammonium phosphate, and guanidine phosphate.

176 Method of Nitrifying Superphosphate. H. A. Curtis. *U.S.* 2,075,801, Apr. 6, 1937, Appl. Aug. 23, 1935; 2 pp. An improved liquid superphosphate nitrifying agent contains both inorganic and organic N. The organic N is derived from free guanidine or a guanidine salt of a mineral acid. Ammonia is the inorganic source of N. For example, a nitrifying composition with an inorganic N:organic N ratio of 1:1 was produced by absorbing NH_3 in an aqueous solution of crude guanidine, containing 39-40 wt % of the free base. The resulting solution contained 23 wt % NH_3 and 27 wt % guanidine.

177 Making Guanidine Salts. J.W.H. Aldred. *U.S.* 2,114,280, Apr. 19, 1938, Appl. Aug. 23, 1935; 2 pp. A process is described for the preparation of guanidine sulfate from Ca cyanamide. A mixture of Ca cyanamide, $(NH_4)_2SO_4$, NH_3, and H_2O is formed in amounts of each sufficient to produce a $H_2CN_2:H_2SO_4:NH_3$ mole ratio of 2:1:> 2. The mixture is heated in an autoclave at 130-180° to form a product rich in guanidine sulfate. Other guanidine salts are formed similiarly. The fixed N is available as a plant food in a form less toxic than Ca cyanamide. For example, crude Ca cyanamide was extracted with 5 times its wt in H_2O for 2 hr with frequent stirring. The resulting slurry was filtered and the Ca in the filtrate was precipitated by adding enough 20% H_2SO_4 to give a pH of 7. This mixture was filtered to remove $CaSO_4$ leaving a filtrate containing ~ 3% cyanamide N with small quantities of cyanamide derivatives. The pH was adjusted to 5 by adding H_2SO_4 and the solution was concentrated at < 70°. An autoclave was charged with 780 wt parts of concentrated solution (487 wt parts of cyanamide), 320 wt parts of monoammonium phosphate, 350 wt parts of H_2O, and 255 wt parts of NH_3. The total charge was heated to 150° and maintained for 1 hr. The resulting product of 1473 wt parts contained 19.8% guanidine N, which was equivalent to a 60% conversion of cyanamide to guanidine.

178 Preparation of Oxamide. E. H. Brown and W. D. Wilhide. *U.S.* 3,281,346, Oct. 25, 1966, Appl. June 28, 1963; 7 pp. A process is described for the direct production of oxamide by the glow-discharge electrolysis of formamide or alkaline cyanide solutions without the use of catalysts. Liquid formamide or an aqueous alkaline solution of an alkali metal cyanide (NaCN + NaOH) is introduced into a glow-discharge electrolytic cell. The glow-discharge electrolytic cell is of the double-compartment type so the compartment housing the anode is separated from the compartment housing the cathode by a porous membrane. A high-voltage direct current source is supplied to the glow-discharge electrolytic cell. The voltage (~ 500 V) is sufficient to initiate and maintain a glow-discharge between the anode of the cell and the upper surface of the liquid. A vacuum is applied to the cell such that a pressure of > ~ 50 mm Hg is maintained. The material is subjected to the glow-discharge treatment for 3-6 hr at ~ 0-25°. Solid oxamide forms and is recovered by filtering. The process is characterized by an electrical efficiency of ~ 1-3 equivalents/Faraday.

SULFURIC ACID AND SULFATES

179 Making Sulfuric Acid. J. H. Walthall. *U.S.* 2,188,324, Jan. 30, 1940, Appl. May 10, 1938; 5 pp. An aqueous solution of $Al_2(SO_4)_3$ and $MnSO_4$ containing 0.1-1 wt % Al and 0.05 wt % Mn is prepared. A stream of gas containing SO_2 and O_2 is passed in intimate contact with and counter-current to the flow of the aqueous solution in a closed gas absorbing zone. An aqueous solution containing ≤ ~ 40 wt % H_2SO_4 is withdrawn from the absorbing zone.

180 Making Sulfuric Acid. M. M. Striplin. *U.S.* 2,342,704, Feb. 29, 1944, Appl. Feb. 27, 1943; 4 pp. Sulfur dioxide is recovered from a gaseous mixture by conversion to H_2SO_4.

An aqueous absorbent solution containing $MnSO_4$ and material selected from alkyl naphthalene sulfonic acid and the alkali metal salts thereof, both in relatively small amounts, is passed through a gas absorbing zone. A stream of gas containing SO_2 and O_2 is passed through the absorbing zone in intimate contact with and countercurrent to the stream of absorbent solution. An aqueous solution of $\leqslant$ 40 wt % H_2SO_4 is withdrawn.

181 Recovery of Sulfur Dioxide from Waste Gases. Grady Tarbutton, J. C. Driskell, T. M. Jones, and C. M. Smith. *U.S.* 2,926,999, Mar. 1, 1960, Appl. Feb. 24, 1958; 5 pp. Sulfur dioxide is recovered from waste gases containing $<$ 1% SO_2 and at least enough O_2 to convert the SO_2 to SO_3. The gaseous mixture is free from substantial amounts of Cu and phenolic compounds. The mixture is cooled to a temperature a little above its dew point and 20-80 ppm of O_3 are added. The resulting mixture is passed upward through a packed absorption tower countercurrent to and in intimate contact with a liquid absorption medium. This medium is composed of an aqueous solution containing ~ 0.03-0.3% Mn ion and ~ 0.0-30% H_2SO_4. A gas-liquid contact time of ~ 8-36 sec is maintained. The tower temperature is held at ~ 55-75°. A liquid effluent containing ~ 16-30% H_2SO_4 is withdrawn from the tower. The SO_2 may be recovered as $(NH_4)_2SO_4$ instead of H_2SO_4 by introducing NH_3 into the tower at a rate sufficient to neutralize H_2SO_4 formed to a slight degree of acidity.

182 Fertilizer Process Incorporating Scrubbed Flue Gas Sludge Byproduct. J. J. Schultz and V. J. Van Pelt. *U.S.* 4,028,087, June 7, 1977, Appl. Feb. 23, 1976; 8 pp. Granular fertilizer is prepared from waste sludge discharged from boiler flue gas scrubbing processes. Waste sludge containing $\leqslant$ ~ 50 wt % H_2O is fed to a preneutralizer along with controlled amounts of NH_3, H_2SO_4, and/or H_3PO_4 to form a partially neutralized $(NH_4)_2SO_4$ and/or ammonium phosphate slurry of N:P ratio 0.5-0.7:1. The retention time in the preneutralizer is ~ 5-25 minutes. Heat of reaction serves to evaporate a substantial part of the excess H_2O from the sludge. Preneutralizer slurry, ammoniating fluid, and recycled fines are fed to an inclined rotating drum for further ammoniation to an N:P mole ratio of ~ 1-2:1 and granulation. The resulting product is dried, cooled, and screened to obtain the desired H_2O content and particle size. Alternatively, the N:P ratio in the preneutralizer is maintained at ~ 1.4-1.5:1. In either case, less than ~ 50% of the $CaSO_3$ in the waste sludge is converted to $CaSO_4$; by adding a strong oxidizing agent to the preneutralizer $>$ 50% of the sulfite can be converted to the sulfate. Ammonia evolved from the rotating drum is recovered by scrubbing and returning the resulting liquor to the preneutralizer.

183 Process for Production of Granular Ammonium Sulfate. G. C. Hicks. *U.S.* 3,464,809, Sept. 2, 1969, Appl. July 14, 1966; 8 pp. In a process for the production of granular $(NH_4)_2SO_4$ fertilizer material 60-98% H_2SO_4 is ammoniated continuously in a preneutralizer vessel. An NH_3:H_2SO_4 mole ratio of ~ 0.9-1.5:1 is maintained. The resulting solution is cooled to ~ 250-400°F by adding H_2O. Streams of solution from the preneutralizer and of NH_3 together with recycled undersize product are introduced into the upper end of an inclined rotating drum. A bed of rolling discrete particles is maintained in the drum. Excess NH_3 evolved in the drum is recovered in a scrubber and returned to the preneutralizer. Dry granular $(NH_4)_2SO_4$ is withdrawn from the lower end of the drum. Substantially all the heat necessary to evaporate H_2O from the system to produce a dry product is supplied by the chemical heat of reaction. For example, 441 lb 98% H_2SO_4 was reacted with 34 lb NH_3 in the presence of 726 lb byproduct $(NH_4)_2SO_4$ in solution to produce a solution at 300°F with a pH of 0.8. The hot solution, 1201 lbs, was fed to a rotary drum with 125 lb NH_3, 660 lb byproduct $(NH_4)_2SO_4$, and 2512 lb recycled solids. The recycle ratio was ~ 1.3 lb/lb of product. The drum product was granular and the onsize product contained N 20.5, SO_3 60.0, and H_2O 0.1%. The N:SO_3 mole ratio was 1.95:1.

184 Production of Urea-Ammonium Sulfate. H. C. Mann, Jr. *U.S.* 3,785,796, Jan. 15, 1974, Appl. June 21, 1971; 10 pp. Strong, closely-sized granules of high-analysis granular urea-$(NH_4)_2SO_4$ fertilizers are produced from solid particulate $(NH_4)_2SO_4$ and molten urea in a horizontally inclined rotary pan granulator. Molten urea of 99-99.8% concentration is mixed at 270-325°F with $(NH_4)_2SO_4$ for 0.1-10 minutes and sprayed onto a circulating bed of recycled fines at 190-250°F in the pan granulator. The resultant product, containing discrete particles of $(NH_4)_2SO_4$ embedded in the matrix of urea, is cooled and screened to remove the product size fraction. Fines and crushed oversize are crushed and returned to the pan granulator as recycle. The urea-$(NH_4)_2SO_4$ feed constituents contain ~ 15-70 wt % $(NH_4)_2SO_4$. Typical product grades are 34-0-0-10 S and 40-0-0-5 S.

185 Manufacture of Urea-Ammonium Sulfate from Sulfuric Acid, Ammonia, and Urea. M. R. Siegel and O. E. Moore. *U.S.* 3,928,015, Dec. 23, 1975, Appl. Oct. 29, 1974; 7 pp. A direct process is described for the production of solid urea-$(NH_4)_2SO_4$ fertilizers from H_2SO_4, NH_3, and urea. Ammonia and 25-95% H_2SO_4 are fed simultaneously into a first stage reactor in amounts to yield an NH_3:SO_4 mole ratio of ~ 0.7-1.3:1. The resulting NH_4HSO_4 intermediate product is maintained at ~ 200-350°F for 1-15 minutes to remove a predetermined amount of H_2O vapor. At least a portion of this NH_4HSO_4 intermediate product together with NH_3 and molten 95-100 wt % urea at ~ 270-320°F are fed simultaneously into a second stage in proportions to give a NH_3:SO_4 mole ratio of ~ 1.7-2.0:1. The resulting homogeneous mixture of urea-$(NH_4)_2SO_4$ co-melt and particulate $(NH_4)_2SO_4$ are maintained at ~ 270-320°F for ~ 1-300 sec. The H_2O vapor evaporated from the first stage and NH_3 and H_2O vapor from the second stage, produced by the autogenous heat of reaction, are sufficient to yield on granulation a solid urea-$(NH_4)_2SO_4$ product with a moisture content of ~ 0.1-5 wt %. The offgases from the second stage may be scrubbed to recover the NH_3 for recycling to the first stage. Examples illustrate the production of fertilizers of grades 40-0-0-4S, 38-0-0-7S, 37-0-0-8S, and 36-0-0-9S.

MISCELLANEOUS

CRYSTALLIZATION, GRANULATION, AND COATING

186 Crystallization. W. C. Saeman. *U.S.* 2,567,968, Sept. 18, 1951, Appl. May 1, 1948; 10 pp. An apparatus and a method

are described for the production of NH_4NO_3 crystals suitable for fertilizer use. An aqueous NH_4NO_3 solution is withdrawn from the top of such solution contained in a crystallization vessel. The withdrawn solution is circulated through an evaporator where it is concentrated to a selected degree of supersaturation. A stream of the resulting supersaturated solution is introduced continuously into a lower part of the crystallizer which contains a suspension of crystals in a supersaturated solution. This stream is directed and its velocity is controlled to maintain two zones in the resulting rising suspension of crystals. The lower zone is one of crystal growth. A suspension of relatively coarser growing crystals is maintained in continuous, rapid, substantially vertical streamlined rotation by kinetic energy imparted by the entering stream. The upper, relatively quiescent zone contains a suspension of finer crystals. Fine crystals are transferred from the lower to the upper zone by upward flow of solution. A controlled stream of supersaturated solution is introduced into the upper zone continuously. The fine crystals are contacted with the supersaturated solution until their size is increased substantially. The resulting crystals of increased size are introduced into the lower zone as seed crystals. Strong mature crystals are withdrawn from a lower portion of the lower zone.

187 Crystallization. W. C. Saeman. *U.S.* 2,737,451, Mar. 6, 1956, Appl. Aug. 3, 1953; 5 pp. A process is described for the production of NH_4NO_3 crystals suitable for fertilizer use. A moving suspension of crystalline NH_4NO_3 in a solution of NH_4NO_3 is maintained within a crystallizing vessel. The average supersaturation is ~ 3 lb of NH_4NO_3/1000 gal of solution. The upper one sixth to one third of the suspension depth is divided vertically into two unequally sized zones. A stream of NH_4NO_3 solution having a supersaturation of ~ 8-14 lb of NH_4NO_3/1000 gal and carrying crystals of NH_4NO_3 in suspension is introduced into the lower part of the suspension. A suspension of coarse and medium-size crystals in a saturated solution is withdrawn from the smaller of the two upper zones at such a rate that the contents of the entire system are circulated 0.3-0.6 times/minute. The withdrawn suspension is introduced into an evaporator where it is concentrated to a supersaturation of ~ 8-14 lb/1000 gal. This concentrated suspension is reintroduced into the lower part of the crystallizing vessel. A suspension of relatively fine NH_4NO_3 crystals and saturated solution is withdrawn from the larger of the two upper zones. The fine crystals are dissolved in the suspension and the resulting solution is introduced into the evaporator. Makeup NH_4NO_3 solution is introduced into the evaporator. A suspension of relatively large crystals of NH_4NO_3 is withdrawn from a lower portion of the suspension within the crystallizing vessel.

188 Granulation and Coating by Improved Method of Heat Removal. A. R. Shirley, Jr. *U.S.* 4,213,924, July 22, 1980, Appl. Nov. 11, 1977; 12 pp. An improved process is described for granulation of materials in an enclosed vessel such as a rotating cylindrical drum equipped with lifting flights. These allow maximum mixing of the granules and the atmosphere enclosed in the vessel. Molten material is sprayed on rapidly moving granules of substrate. The granules are increased in size as molten material solidifies on the surface. The heat of crystallization and associated heat from cooling the material is removed by evaporation of H_2O in the enclosed vessel. The H_2O to be evaporated is atomized into droplets with a median vol diameter of $< 1.967 \times 10^4$ ft. The arc of the spray angle is $\geqslant 30°$. The H_2O evaporates within < 2 sec and no H_2O in the liquid state contacts either the molten material or the substrate granules. The moisture content of the air is controlled to below the dew point of the air to prevent H_2O condensation on any surface within the vessel or H_2O absorption by the granules. An equation is developed which mathematically represents the thermodynamics of the process. Specific values are presented for variables when granulating S or urea.

189 Apparatus for Applying Coatings to Solid Particles. G. M. Blouin. *U.S.* 3,877,415, Apr. 15, 1975, Appl. July 24, 1973; 10 pp. The title apparatus is a rotary cylindrical drum with open ends and a length at least equal to its diameter. Its axis is about horizontal. A plurality of equally spaced lifting flights are located on the inner peripheral surface and extend inwardly toward the axis. Retaining rings are positioned at the ends of the drum. Spray nozzles extend the length of the drum. A deflector pan is fixed in space inside the upper surface of the drum which deflects particles falling from the lifting flights to the side of the drum where they form a narrow, dense falling cascade. The coating material is sprayed onto the cascading particles. A uniform coating results regardless of size or shape of the particles.

190 Method for Applying Coatings to Solid Particles. G. M. Blouin. *U.S.* 3,991,225, Nov. 9, 1976, Appl. July 24, 1973; 10 pp. Division of *U.S.* 3,877,415. Coated rounded particles of substantially uniform size are formed in a rotating drum which is maintained in a generally horizontal position. Material to be coated is introduced into the inlet end of a rotating drum in which a bed of rolling discrete nuclei particles of the substance to be coated are in contact with each other. The rotating drum has lifting flights on the inner surface acting to elevate portions of the bed from the bottom to a higher point therein. The elevated portions of the bed on the lifting flights are released and cascade onto substantially the full upper surface of a deflector which is fixed in space in the upper hemispherical section of the drum and extends substantially there throughout. It comprises two generally horizontally inclined planes defining a generally inverted V configuration, moving the particles away from the apex of the inverted V and toward each of the two bottom edges. Each edge juxtaposed a sidewall of the drum wherefrom the particles free-fall back to the bed of nuclei juxtaposed the bottom of the chamber. Localized portions of the particles are sprayed after their release from the bottom edges of the inclined planes, thereby ensuring that at least a portion of the coating material so sprayed is directed upon a dense cascade of particles which are substantially homogeneous in particle size. At least a portion of the resulting spray-coated particle is removed from the outlet end of the drum. The process ensures that the localized portion of particles, which is sprayed to effect coating, is substantially homogeneous in particle size, thereby effecting substantially uniform coatings on each particle released from the lifting flights. In examples of coating granular urea with molten S, the use of this process and apparatus resulted in a 100% increase in capacity over equipment that did not include the cascading apparatus.

STACK GAS TREATMENT

191 Manganese Oxide Process for the Recovery of Sulfur

Dioxide from Waste Gases. Grady Tarbutton, T. M. Jones, J. C. Driskell, and C. M. Smith. *U.S.* 2,984,545, May 16, 1961, Appl. Feb. 27, 1958; 5 pp. A process is described for the substantially complete recover of SO_2 from waste gases containing < 1% SO_2, such as smelter gases, offgases from chemical processes, and stack gases from coal-burning furnaces. Dust or entrained solids in waste gases do not interfere. The waste gases containing SO_2 are passed in a scrubbing step upwardly through a scrubbing tower in intimate contact with a descending aqueous slurry of Mn oxides. The aqueous slurry is withdrawn from the lower part of the tower to a precipitation step. Precipitated $MnSO_4$ is calcined and the SO_2 product is separated. The regenerated Mn oxides are recovered for recycling to an aqueous slurry preparation step. The proportion of lower Mn oxides formed during calcination is controlled by subsequently cooling the hot mixture of Mn oxides formed with exposure to air. Thus, low slurry acidity is maintained in the scrubbing step. The regenerated Mn oxides are superior to other Mn compounds, such as pyrolusite ore or MnO_2, in SO_2 recovery.

192 Use of Potassium Polyphosphate in Sulfur Dioxide Recovery from Stack Gases. J. M. Potts. *U.S.* 3,630,672, Dec. 28, 1971; Appl. Mar. 14, 1969; 11 pp. Sulfur is recovered from the stack gases of fossil fuel fed power plants by scrubbing the gases with a 0-27-36 grade liquid fertilizer solution. The stack gases contain substantial amounts of fly ash, dust, and moisture, and < ~ 0.3% SO_2. The liquid fertilizer contains K_2HPO_4 and ≥ one-third of the K as $K_4P_2O_7$. The temperature in the scrubber is maintained at ~ 125°. Slurry from the scrubber containing precipitated $K_2S_2O_5$ is introduced into a gas stripper which is maintained at ~ 230-250°F. The $K_2S_2O_5$ is decomposed to K_2SO_3 and SO_2 vapor. The SO_2 vapors are recovered as product. Unreacted $K_4P_2O_7$ and K_2HPO_4 together with K_2SO_3 are recycled to the scrubber for contact with additional SO_2 in stack gas. The product SO_2 is reacted further to form elemental S.

193 Sulfur Dioxide Removal from Stack Gases. J. E. Jordan and G. M. Newcombe. *U.S.* 3,927,178, Dec. 16, 1975, Appl. Apr. 13, 1972. Flue gases containing SO_2, such as power plant stack gases, are scrubbed with an aqueous mixture of $(NH_4)_2SO_3$, NH_4HSO_3, and $(NH_4)_2SO_4$. The resulting liquor is transferred from the scrubber to a stripper where enough NH_4HSO_4 is added to remove SO_2 from the liquor and form $(NH_4)_2SO_4$ slurry. This slurry is mixed with gaseous NH_3 and a portion of the scrubber liquor in an absorber to depress the solubility of $(NH_4)_2SO_4$ and cause it to precipitate. Precipitation is effected without heating to evaporate H_2O. The slurry is cooled to precipitate additional $(NH_4)_2SO_4$ and the solid $(NH_4)_2SO_4$ and liquid component are separated. The liquid is recycled to the scrubber and the $(NH_4)_2SO_4$ is heated to give NH_4HSO_4 and gaseous NH_3 for recycle.

194 Removal and Recovery of Sulfur Oxides from Gas Streams with Melamine. J. J. Kohler, Joe Gautney, Y. K. Kim, and J. F. McCullough. *U.S.* 4,139,597, Feb. 13, 1979, Appl. May 5, 1977; 15 pp. Gas streams containing 1-100 vol % of SO_x, such as electric power plant stack gases or tail gases from roasting sulfide ores are treated to remove and recover the SO_x. The gas stream is contacted with an aqueous slurry of melamine containing paraphenylenediamine as an oxidation inhibitor at 20-70°. The free melamine in slurry:S in gas stream molar ratio is 1.5-2.5:1 and the melamine:slurry wt ratio is 0.01-0.5:1. A mixture of insoluble hydrated melamine sulfites and melamine sulfate is produced. The solids and liquid in the reaction slurry are separated and the liquid is recycled. The solids are dried at 70-105° to remove adhering liquid, part of the H_2O of hydration, and a small amount of SO_2. The vapors are recycled and the dried solids are heated at 105-200° to decompose melamine sulfite into solid, free melamine and gaseous H_2O and SO_2. The gaseous mixture of H_2O and SO_2 is withdrawn as product and the hot solids are cooled to ambient temperature and split into two unequal streams. The larger portion is recycled and the smaller portion contacted with a base stronger than melamine to convert melamine sulfate into free, solid melamine and a solution of a basic sulfate salt. Melamine is recycled and the sulfate solution is withdrawn as product.

OTHER

195 Process for Preparing Cyanogen. R. E. Isbeli. *U.S.* 3,302,996, Feb. 7, 1967, Appl. Jan. 27, 1965; 5 pp. An aqueous suspension of CuO is contacted in a reaction vessel with HCN. The reactants are maintained at 50-90° to form cyanogen and CuCN. A sweep gas, selected from air, N_2, CO, CO_2, and He, is introduced and exhaust gases are removed to a fractionating vessel. The exhaust gases contain sweep gas, cyanogen, and H_2O vapor. Cyanogen is separated as product and the remainder of the exhaust gas is returned to the reactor. A portion of the reacted slurry is removed from the reaction vessel and filtered to recover byproduct CuCN. The filtrate is returned to the reactor. This process is characterized by the fact that ~ one-half of the original cyanide is converted to cyanogen in one step. The other half is converted directly in one step to solid byproduct CuCN. The CuCN may be reduced to Cu and cyanogen, thus recovering the rest of the original cyanide.

196 Stabilization of Ammonium Carbamate for Fertilizer Use. A. V. Slack. *U.S.* 3,314,779, Apr. 18, 1967, Appl. May 5, 1964; 3 pp. Ammonium carbamate is produced for fertilizer use by reacting anhydrous NH_3 with CO_2. The resulting light crystalline ammonium carbamate material is compacted and pelletized at a pressure of ~ 40,000 lb/in^2. The material is sized and the -6 +10 mesh pellets are separated as product. The sized pellets are spray coated with a petroleum based oil which has a viscosity of ~ 200-215 Saybolt seconds at 130°F. The sprayed product is stored in containers, the walls of which are substantially impervious to the NH_3 vapor.

197 Ammonium Hydrogen Monoamidophosphate. R. C. Sheridan. *U.S.* 3,598,549, Aug. 10, 1971, Appl. Feb. 14, 1969; 4 pp. Ammonium hydrogen monoamidophosphate ($NH_4HPO_3NH_2$) is produced by reacting phosphoryl chloride ($POCl_3$) and aqueous NH_3 at -77 to + 90° and atmospheric pressure. The NH_3:phosphoryl chloride molar ratio is ~ 5-20:1 and the H_2O:phosphoryl chloride molar ratio is ~ 2-150:1. Acetone is added and the mixture is allowed to separate into two liquid phases. The upper phase is composed of acetone, ammonium diamidophosphate, diammonium orthophosphate, and NH_4Cl; and the lower phase is an aqueous solution of ammonium hydrogen monoamidophosphate and unreacted NH_3. The bottom layer is separated, neutralized with acetic acid, and cooled to induce crystallization of ammonium hydrogen monoamidophosphate. Crystallization

is increased by diluting the cooled and neutralized solution with ~ an equal vol of ethanol. For example, to 300 mL of 10% NH_4OH was added slowly, with stirring, 30.67 g $POCl_3$ at 0°. After stirring for 15 minutes the solution was mixed with 1000 mL of acetone. The aqueous phase was separated, neutralized with acetic acid, and diluted with an equal volume of ethanol, causing precipitation of crystalline $NH_4HPO_3NH_2$. The precipitate was separated to give 14.4 g product containing 24.5% total N and 27.0% P. The product is an excellent high-analysis (24-62-0 grade) fertilizer having good physical properties.

198 Making Phosphate Fertilizer and Nitric Acid. H. A. Curtis. *U.S.* 2,069,226, Feb. 2, 1937, Appl. June 6, 1935; 3 pp. Phosphate fertilizer and HNO_3 are made from phosphate rock and a mixture of N, CO_2, and P_2O_5 obtained from the combustion of P reduction furnace gases from which a substantial portion of the P has been removed. The gaseous mixture is passed through an electric arc to form NO. The phosphate rock is fused by heat from the electric arc and the fused rock is quenched to make the phosphate available as plant food. The hot gaseous mixture leaving the zone of the electric arc is partially cooled by countercurrent with the phosphate rock before fusion. Then, the gaseous mixture is cooled further, and the NO therein is oxidized and absorbed in H_2O to form HNO_3.

199 Separating Protein from Waste Material. E. R. Rushton. *U.S.* 2,379,929, July 10, 1945, Appl. June 22, 1942; 2 pp. A process is described for the separation of protein from aqueous sewage and industrial wastes, particularly those derived in the processing of milk. A finely divided solid Ca metaphosphate is mixed with the waste material. The material is digested for a time sufficient to precipitate a substantial proportion of the protein therein as a protein-phosphate complex which is separated. The protein-phosphate complex may be utilized either as livestock feed or as a fertilizer, depending on the character of the original waste material.

200 Ultrahigh-Frequency Apparatus. J. H. Christensen and A. J. Smith. *U.S.* 2,996,692, Aug. 15, 1961, Appl. May 2, 1960; 4 pp. An ultrahigh-frequency apparatus for detecting standing waves in an electromagnetic energy transmission system has a movable pickup device of the slotted-section type. Substantially all the slot is covered or closed in with a material which prevents radiation of energy through the slot. The detector is capable of increased reproducibility and accuracy in measuring standing wave ratios of voltage or current and points of maximum and minimum voltage within a length of transmission line.

INVENTOR INDEX

ABRAMS

Abrams, A. J. 10
Achorn, F. P. 65, 100, 107, 171, 143
Aldred, J.W.H.. 177
Allgood, H. Y.. 66
Almond, L. H.. . . . . 8, 22, 53
Anderson, Jr., J. F. . . . 154, 171

Barber, J. C. . . 12, 23, 24, 25, 57
Baskerville, W. H.. 60
Blouin, G. M. . . . 108, 172, 173, 189, 190
Bottal, G. A.. 130
Bridger, G. L. . . . 30, 38, 75, 91
Brosheer, J. C.. 101
Brown, E. H.. . 50, 111, 112, 178
Brown, N. A. 138
Bundy, W. H. 19
Burt, R. B.. 57

Carroll, Frank 67
Christensen, J. H.. 200
Copson, R. L. 4, 15, 17, 47
Curtis, H. A.. . . 3, 9, 10, 13, 14, 15, 17, 21, 43, 45, 46, 48, 51, 59, 77, 78, 80, 82, 93, 105, 175, 176, 198

Darby, W. J.. 11
Davenport, J. E.. . . . . .2, 67
Davis, C. H. 103
DeWitt, T. W. 27
Driskell, J. C. 137, 142, 181, 191

Edwards, L. A. 42
Elder, H. W.. 154
Elmore, K. L. 5, 6, 55

Farr, T. D.. . . . 32, 33, 34, 118, 119, 120, 121, 122, 123
Fleming, J. D.. . . . . 118, 121
Fraser, L.H.D.. . . . . .35, 36, 37
Frazier, A. W. . . . 129, 151, 158, 168, 170
Frear, G. L. 54
Frederick, L. L.. 70

Gautney, Joe 194
Getsinger, J. G. . . .74, 106, 114, 115, 116, 117, 124, 136
Gilbert, Nathan 31
Graham, J. L. 99, 102

Hand, Jr., L. D. 68, 90, 92
Hardin, S. A.. . . . . .18, 19
Hartford, C. E. 61
Harvey, S. A. 91
Haseman, J. F.. 1
Hatfield, J. D.. . . . . 71, 163
Haunschild, R. L.. 106
Heaton, R. C. 45
Heil, Jr., F. G.. 88
Hein, L. B.. 58
Hendrix, Arnett. 26
Hicks, G. C. 107, 109, 183
Hignett, T. P. 7, 49, 68, 89, 108, 110, 114, 115, 116, 117, 138, 140, 141
Hobbs, I. A. 31
Hoffmeister, Jr., George . . . 141
Hubbuch, T. N. 7

Isbell, R. E. 195

Jerabek, H. S. 39
Johnson, D. H. 161
Jones, T. M. . . . 32, 33, 34, 167, 170, 181, 191
Jordan, J. E.. . . . . 133, 193
Junkins, J. N. 52

Kelso, T. M.. 110
Kendrick, Jr., L. A.. 166
Kim, Y. K.. . . . . 71, 194
Kohler, J. J. 194

Lancaster, Jr., F. E.. . . . 66, 109
Lee, R. G. 127, 131
Lehr, J. R.. . . . . 90, 113
Lewis, Jr., H. T.. . . . 32, 33, 34, 135, 136, 142
Lewis, Jr., J. S. 143
Livingston, O. W.. 96

MacIntire, W. H.. . . . 76, 83, 85, 86, 87, 145, 146, 147
Mann, Jr., H. C. . . 126, 132, 151, 161, 184
Marks, E. C. 63, 64
McCamy, I. W.. 102
McCullough, J. F.. . . 69, 70, 73, 84, 128, 132, 134, 160, 194
McFarlin, C. J.. 16
McKnight, David . . . 63, 64, 100
Megar, G. H.. . 12, 23, 24, 25, 26
Meline, R. S.. . . . 100, 108, 110, 127, 159, 174
Miller, Phillip 29, 44
Mitchell, R. D.. 131
Moore, O. E.. 185

Nason, M. C.. 138
Newcombe, G. M.. 193
Newton, R. H.. 79
Nielsson, F. T.. . . 81, 94, 95, 98
Nix, F. D. 169
Norton, M. M..144, 148, 149, 150

Parker, B. R.. 144
Philen, Jr., O. D. . 148, 149, 150, 168
Phillips, A. B. . . . 49, 50, 88, 89
Phillips, Jr., J. F. 73, 84
Pole, G. R.. . . . . 20, 139
Potts, J. M.. . . 68, 90, 152, 154, 156, 192

Rindt, D. W.. . 58, 155, 172, 173
Rushton, E. R. 199

Saeman, W. C.. . . . . 186, 187
Schultz, J. J.. 182
Scott, Jr., W. C.. . . . .40, 41, 74
Sheridan, R. C. . . .72, 104, 128, 134, 160, 197
Shirley, Jr., A. R.. . . . 174, 188
Shultz, J. R.. . . . . .56, 58
Siegel, M. R.. . . . 102, 108, 110, 126, 185
Silverberg, Julius . 148, 149, 150
Skolnik, Sol 30
Slack, A. V. . . 68, 97, 155, 156, 163, 164, 196

SLACK

Sloan, T. S. 12, 23, 24, 25
Smith, A. J. 140, 200
Smith, C. M. 181, 191
Stinson, J. M. . 40, 41, 125, 130, 132, 138, 151, 152, 153, 161
Stout, E. L. 40, 41
Striplin, Jr., M. M. . . 19, 61, 62, 63, 64, 65, 152, 153, 180
Tarbutton, Grady. . . 32, 33, 34, 58, 181, 191
Tate, L. R. 73, 84
Tusson, J. R. 28
Van Pelt, V. J. 182
Walters, Jr., H. K. . .71, 118, 119, 120, 122, 123, 162, 163, 164, 165
Walthall, J. H. 179
Wilbanks, J. A. 153
Wilhide, W. D. 178
Young, R. D. 49, 50, 88, 89, 107

SUBJECT INDEX

Alkali Metal Phosphate, manufacturing process, from phosphoric acid and alkali metal, 139
Ammoniated Superphosphate, manufacturing process, spherical, 93, rotating drum, 94, 95
Ammoniation, crystallization, equipment, 187
Ammonium Carbamate, granulation, pressure pelletization, 196
Ammonium Cryolite, manufacturing process, phosphate rock processing, 33
Ammonium Hydrogen Monoamidophosphate, manufacturing process, phosphoryl chloride-ammonia reaction, 197
Ammonium Nitrate, crystallization, equipment, 186
Ammonium Phosphate, manufacturing process, from crude phosphoric acid, 104, from high-alumina ore, 110, pipe reactor, 109, rotating drum, 108, solution, 153, 155, suspension, 162, 166, 167
Ammonium Phosphate Sulfate, manufacturing process, pipe cross reactor, 143, 144
Ammonium Polyphosphate
  manufacturing process, atmospheric pressure, 118, 119, 120, 121, 122, 123, base solution, 159, controlled release, 129, from wet process phosphoric acid, 124, from melamine orthophosphate, 160, granulated, 118, 119, 120, 121, 122, 123, high-analysis, 114, 115, 117, 127, liquid, 118, 121, 122, long-chain, 128, micronutrient containing, 151, suspension, 169, three-stage continuous, 126, urea-containing, 125
  purification, carbon removal, 161
  solution, stabilization, 157, 158
  suspension, gel prevention, 170
Ammonium Pyrophosphate, manufacturing process, calcium fluoride byproduct, 113, high-analysis, 116
Ammonium Sulfate, manufacturing process, rotating drum, 183
Calcium Ammonium Polyphosphate, suspension, silicate containing, 168
Calcium Carbonate, manufacturing process, nitric phosphate byproduct, 96
Calcium Fluoride, manufacturing process, byproduct of ammonium pyrophosphate production, 113, phosphate rock defluorination, 31
Calcium Magnesium Phosphate, manufacturing process from dolomite and phosphoric acid, 85
Calcium Metaphosphate
  granulation, complex fertilizer, 49, rotating drum, 50
  hydrolysis, monocalcium diammonium pyrophosphate, 111, tricalcium diammonium pyrophosphate, 112
  manufacturing process, phosphorus pentoxide, 43, 44, 45, phosphoric acid, 46, metaphosphoric acid, 47, 48
Calcium Phosphate, manufacturing process, ferrophosphorus oxidation, 38, from phosphate rock and phosphoric acid, 75, 76
Calcium Polyphosphate, manufacturing process, from concentrated calcium phosphate, 90
Ceramic Ware, manufacturing process, phosphate reduction furnace lining, 20
Coating
  equipment, rotating drum, 189, 190
  fertilizer granule, micronutrient addition, 148, 150, zinc, 149
  red phosphorus, phosphoric acid, 30
  sulfur, controlled release, 172, 173
Complex Fertilizer, manufacturing process, ammoniation of calcium phosphate, 81, calcium metaphosphate, 49, granulation, 99, 102, rotating drum, 103, 108, solution, 152, 154, sulfur-containing, 142, suspension, 163, 164, 165
Concentrated Calcium Phosphate
  heat treatment, calcium polyphosphate, 90
  manufacturing process, from phosphate rock and phosphoric acid, 88, granulated, 89
Controlled Release
  ammonium polyphosphate, long-chain, 128
  manufacturing process, ammonium polyphosphate, 129, micronutrient containing, 172, sulfur coated, 172, 173
  potassium ammonium polyphosphate, long-chain, 134
  sulfur-coated urea, rotary drum, 174
Cryolite, manufacturing process, phosphate rock processing, 32, 34
Crystallization
  ammonium hydrogen monoamidophosphate, technique, 197
  ammonium nitrate, equipment, 186, 187
Cyanogen, manufacturing process, hydrogen cyanide-cupric oxide reaction, 195
Diammonium Phosphate, manufacturing process, impurity separation, 106, rotating drum, 107
Dicalcium Phosphate, manufacturing process, from limestone and phosphoric acid, 80, 82, 83, 87, from phosphate rock, nitric acid, and ammonia, 81, from phosphate rock, sulfuric dioxide, and organic carbonyl, 84
Dolomite, reaction with phosphoric acid, calcium magnesium phosphate, 85
Environmental Control
  industrial waste treatment, protein separation, 199
  flue gas sludge, complex fertilizer, 182
  phosphate tailing, settling, 2
  phosphorus furnace condenser water, treatment, 26
  stack gas treatment, sulfur dioxide recovery, 191, 192, 193, 194
Equipment
  combustion chamber, calcium metaphosphate production, 45, phosphorus production, 16
  crystallizer, ammonium nitrate, 186, 187
  electric furnace, phosphorus production, 17, 18
  electrolytic cell, potassium phosphate production, 140
  furnace, defluorination of phosphate rock, 8
  mixing cone, superphosphate, 91
  phosphate reduction furnace, refractory lining, 20

phosphorus burner, phosphorus pentoxide production, 57
phosphorus oxidizer-hydrator, phosphoric acid production, 59
pipe cross reactor, ammonium phosphate sulfate, 143, 144, monoammonium phosphate, 143, urea ammonium phosphate sulfate, 144
pipe reactor, ammonium phosphate, 109, ammonium polyphosphate, 159
pugmill, urea-ammonium polyphosphate granulation, 131
rotating drum, ammoniated superphosphate, 94, 95, ammonium sulfate production, 183, coating, 189, 190, complex fertilizer, 103, 108, diammonium phosphate, 107, granulation, 188
rotating furnace, phosphorus production, 19
rotating pan, complex fertilizer granulation, 102, urea-ammonium sulfate, 184
spray tower, ammoniated superphosphate, 93, monoammonium phosphate, 105
ultrahigh-frequency apparatus, standing wave detection, 200
Expanded Slag, production, phosphate reduction byproduct, 40, 41, 42
Ferric Oxide, production, ferrophosphorus oxidation, 36
Ferrophosphorus
oxidation, calcium phosphate, 38, ferric oxide, 36, iron phosphate, 35, 37
utilization, metal alloy, 39
Flue Gas, treatment, ammonium phosphate, 182, ammonium sulfate, 182
Fluid Fertilizer
byproduct of phosphoric acid purification, urea and ammonium nitrate containing, 69
manufacturing process, ammonium polyphosphate, 124, micronutrient containing, 151, nitric phosphate suspension, 97, urea-ammonium polyphosphate, 132
starting material, ammonium polyphosphate, 114, 115, 117, ammonium pyrophosphate, 116
Fluorine
recovery, ammonium cryolite, 33, calcium fluoride, 31, cryolite, 32, 34
removal, phosphate rock, 3, 4, 5, 6, 7, 8
Granulation
ammoniated nitric phosphate slurry, complex fertilizer, 99
ammonium carbamate, pressure pelletization, 196
ammonium sulfate, rotating drum, 183
calcium metaphosphate, rotating drum, 50
complex fertilizer, calcium metaphosphate based, 49
concentrated calcium phosphate, rotating drum, 89
rotating drum, heat removal, 188
urea-ammonium polyphosphate, prilling, 130, 133, pugmill, 131
Guanidine Phosphate, manufacturing process, organic fertilizer, 175
Guanidine Sulfate, manufacturing process, from calcium cyanamide, 177
Iron Phosphate, production, ferrophosphorus oxidation, 35, 37
Limestone, reaction with phosphoric acid, dicalcium phosphate, 80, 82, 83, 87, monocalcium phosphate, 80, triple calcium phosphate, 87
Manganese Phosphate, manufacturing process, rhodochrosite containing, 145, 146, 147
Melamine, phosphoric acid purification, ammonium phosphate, 104
Melamine Orthophosphate, from wet process phosphoric acid, ammonium polyphosphate solution production, 160
Metal Alloy, corrosion resistant, ferrophosphorus, 39
Micronutrient
ammonium polyphosphate, incorporation, 151
fertilizer granule, coating, 148, 149, 150
fluid fertilizer, incorporation, 151
manganese, complex fertilizer, 145, 146, 147
zinc, granule coating, 149
Milk Processing Waste, treatment, protein separation, 199
Monoammonium Phosphate, manufacturing process, spray tower, 105, pipe cross reactor, 143
Monocalcium Diammonium Phosphate, manufacturing process, from calcium metaphosphate, 111
Monocalcium Phosphate, manufacturing process, from phosphate rock and phosphoric acid, 77, 78, 79, from limestone and phosphoric acid, 80
Nitogen-Phosphorus, manufacturing process, hydrolysis, 138
Nitric Acid, manufacturing process, electric ore fusion, 198
Nitric Phosphate, manufacturing process, ammonium sulfate recycle, 96, ammoniation, 100, 101, carbonated, 98, polyphosphate added, 97, rotating drum, 103
Nitrogen Phosphate, byproduct of phosphoric acid purification, acid impurity containing, 70
Nitrogen-Phosphorus, manufacturing process, vapor phase reaction, 135, 136, 137
Organic Fertilizer
guanidine, production, 177
manufacturing process, guanidine phosphate, 175
nitrified superphosphate, guanidine containing, 176
Oxamide
byproduct of phosphoric acid purification, from urea oxalate, 72
manufacturing process, electrolysis, 178
Phosphate Furnace, charge, agglomeration, 9, 11, 12, preparation, 10
Phosphate Rock
beneficiation, agglomeration, 9, defluorination, 3, 4, 5, 6, 7, 8, flocculation, 1
defluorination, calcium fluoride, 31
fusion, direct application, 13
granulation, sulfur-containing, 141
high-alumina, ammonium phosphate, 110
reaction with fuming sulfuric acid, concentrated phosphoric acid, 68
reaction with nitric acid, nitric phosphate, 98
reaction with phosphoric acid, calcium phosphate, 75, 76, monocalcium phosphate, 77, 78, 79, concentrated calcium phosphate, 88
reaction with phosphorus reduction gas, electric ore fusion, 198
reaction with sulfur dioxide and organic carbonyl, dicalcium phosphate, 84
reaction with sulfuric acid, superphosphate, 92
reaction with sulfuric and phosphoric acid, phosphoric acid, 67
reduction, phosphorus production, 14, 15, phosphorus recovery, 21
reduction byproduct, expanded slag, 40, 41, 42
reduction furnace gas, phosphorus recovery, 22
reduction furnace sludge, phosphorus recovery, 23, 24, 25
Phosphate Tailing
phosphate recovery, flocculation, 1
settling, shear, 2
Phosphoric Acid
concentration, superphosphoric acid production, 62, wet process phosphoric acid evaporation, 74
production, from acidulation of phosphate rock with fuming sulfuric acid, 68, hemihydrate process, 67, phosphorus oxidation, 58, 60, phosphorus oxidizer-hydrator, 59
purification, oxamide production, 72, uranium recovery, 73, with acetone

and ammonia, 71, with methanol and ammonia, 70, with urea and nitric acid, 69, with urea and oxalic acid, 72
reaction with phosphate rock, calcium metaphosphate, 46
Phosphorus
conversion, red phosphorus, 27
electric furnace charge, briquet, 11, 12
oxidation, burner assembly, 57, phosphoric acid production, 58, 59, phosphorus pentoxide production, 51, 52, 53, 54, steam, 55, 56, superphosphoric acid production, 61, 63, 64, 65, 66
production, charging stock, 9, combustion furnace, 16, condenser water treatment, 26, electric reduction furnace, 13, 14, 15, 17, 18, electric rotating furnace, 19, recovery, 21
recovery, phosphate furnace gas, 22, sludge, 23, 24, 25
reduction furnace charge, preparation, 10
separation, red phosphorus recovery, 28, 29
Phosphorus Pentoxide
production, phosphorus oxidation, 51, 52, 53, 54, 55, 56, phosphorus burner assembly, 57
reaction with phosphate rock, calcium metaphosphate, 43, 44, 45
separation, phosphorus combustion product, 60
Potassium Ammonium Polyphosphate, manufacturing process, long-chain, 134, solution, 156
Potassium Phosphate, manufacturing process, chlorine-free, 140, solution, 154
Red Phosphorus
production, nonagglomerated, 27
purification, nonautoinflammable, 28, 29
stabilization, phosphoric acid coating, 30
Ruminant Feed, manufacturing process, suspension, 171
Secondary Nutrient
sulfur, ammonium phosphate sulfate, 143, 144, complex fertilizer, 142, urea ammonium phosphate sulfate, 144
sulfur-phosphate rock, granulated, 141
Solution
manufacturing process, ammonium phosphate, 153, 155, ammonium polyphosphate, 160, complex fertilizer, 152, 154, potassium ammonium polyphosphate, 156, potassium phosphate, 154
purification, ammonium polyphosphate, 161
stabilization, ammonium polyphosphate, 157, 158
Stack Gas, sulfur dioxide recovery, manganese oxide, 191, melamine, 194, potassium polyphosphate, 192
Sulfur, phosphate rock mixture, granulation, 141
Sulfur Dioxide
oxidation, sulfuric acid production, 179, 180, 181
recovery, stack gas, 191, 192, 193, 194, waste gas, 181
Sulfur-Coated Urea, rotary drum, controlled release, 174
Sulfuric Acid, manufacturing process, from waste gas, 181, sulfur dioxide oxidation, 179, 180
Superphosphate
manufacturing process, granulated, 92, mixing cone, 91
nitrified, guanidine containing, 176
Superphosphoric Acid, production, phosphoric acid concentration, 62, phosphorus oxidation, 61, 63, 64, 65, 66
Suspension
feed supplement, ruminant, 171
gel prevention, ammonium polyphosphate, 170
manufacturing process, ammonium phosphate, 162, 166, 167, ammonium polyphosphate, 169, calcium ammonium polyphosphate, 168, complex fertilizer, 163, 164, 165
Technique
alkali metal phosphate production, reaction of phosphoric acid and alkali metal, 139
ammoniation, nitric phosphate slurry, 100, 101
ammonium polyphosphate production, atmospheric pressure, 118, 119, 120, 121, 122, 123, high-analysis, 127, three-stage continuous, 126, urea-containing, 125
concentrated phosphoric acid production, evaporation, 74
cyanogen production, hydrogen cyanide-cupric oxide reaction, 195
diammonium phosphate, impurity separation, 106
electric ore fusion, phosphate rock, 198
fused calcium metaphosphate, metaphosphoric acid, 47, 48, phosphoric acid, 46
glow-discharge electrolysis, oxamide production, 178
nitrogen-phosphorus compound, hydrolysis, 138
standing wave detection, ultrahigh-frequency apparatus, 200
urea-ammonium sulfate production, two stage process, 185
Tricalcium Diammonium Pyrophosphate, manufacturing process, from calcium metaphosphate, 112
Tricalcium Phosphate, manufacturing process, from sucrose, lime, and phosphoric acid, 86
Triple Calcium Phosphate, manufacturing process, from limestone and phosphoric acid, 87
Uranium, recovery, wet process phosphoric acid, 73
Urea Ammonium Phosphate Sulfate, manufacturing process, pipe cross reactor, 144
Urea-Ammonium Polyphosphate
granulation, prill, 130, 133
manufacturing process, granulated, 131, from urea orthophosphate, 132
Urea-Ammonium Sulfate, manufacturing process, rotary pan granulator, 184, two-stage ammoniation, 185
Vapor Phase
ammonia-phosphorus, concentrated nitrogen-phosphorus compound, 136, high-analysis, 135, nitrogen-phosphorus mixture, 137
ammonia-phosphorus-sulfur, complex fertilizer, 142

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