LIQUID FERTILIZERS

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FOREWORD

The detailed, descriptive information in this book is based on U.S. patents since 1960 relating to the manufacture and application of liquid fertilizers. Where it was necessary to round out the complete technological picture, some earlier but very relevant patents were included, as were reissues and British patents of importance.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced, commercially oriented review of liquid fertilizer manufacture and technology, together with the underlying chemical and biochemical principles.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development. One should have to go no further than this condensed information to establish a sound background before launching into research in this field.

Advanced composition and production techniques developed by Noyes Data Corporation are employed to bring these durably bound books to you in a minimum of time. The shortest possible production time is necessary to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, printing, binding and shipping methods can render a technical or scientific book quite obsolete before the potential user gets to see it.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

15 Reasons Why the U.S. Patent Office Literature Is Important to You—

(1) The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical commercial process information assembled here than is available from any other source.

(2) The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."

(3) The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.

(4) An important feature of the patent literature is that it can serve to avoid duplication of research and development.

(5) Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.

(6) It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.

(7) Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.

(8) Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.

(9) Can aid in process design by providing a selection of alternate techniques. A powerful research and engineering tool.

(10) Obtain licenses — many U.S. chemical patents have not been developed commercially.

(11) Patents provide an excellent starting point for the next investigator.

(12) Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.

(13) Patents offer a most valuable method of keeping abreast of latest technology, serving an individual's own "current awareness" program.

(14) Copies of U.S. patents are easily obtained from the U.S. Patent Office at 50¢ a copy.

(15) It is a creative source of ideas for those with imagination.

CONTENTS AND SUBJECT INDEX

INTRODUCTION

Liquid mixed fertilizer use is expected to continue to grow rapidly through this decade. The ability of fluid fertilizers to chelate micronutrients and supply appreciable quantities of iron in chelated form to the soil leading to good crop yields is an important factor. The major advantage is their demonstrated convenience in handling, processing and application that further underscores their selection by agronomists and farmers over solid fertilizers.

This book presents a comprehensive survey of liquid mixed fertilizer technology. The term fluid fertilizer, as used in the book, encompasses both liquids and slurries. The major portion of the work in the field is concerned with fluid and slurry fertilizer production from wet process phosphoric acid. Within this broad category this review covers the production technology of the foremost producers and the industry-wide search for solutions to some of the production problems involved, i.e., solids settling and equipment corrosion.

Apparatus used in application techniques is also covered. Included is information on specialty fertilizers both with regard to sources other than wet process phosphoric acid and unusual applications for fluid fertilizers.

Fertilizers account for one-third to one-half of crop production in the U.S. The high agricultural productivity enjoyed as a result is testament to the need for fertilizers and to their continued use. This book should therefore serve as a useful guide to a major U.S. industry.

EQUIPMENT USING WET PROCESS PHOSPHORIC ACID

PHILLIPS PETROLEUM

Predetermined Nitrogen-Phosphorus Pentoxide-Water Ratio

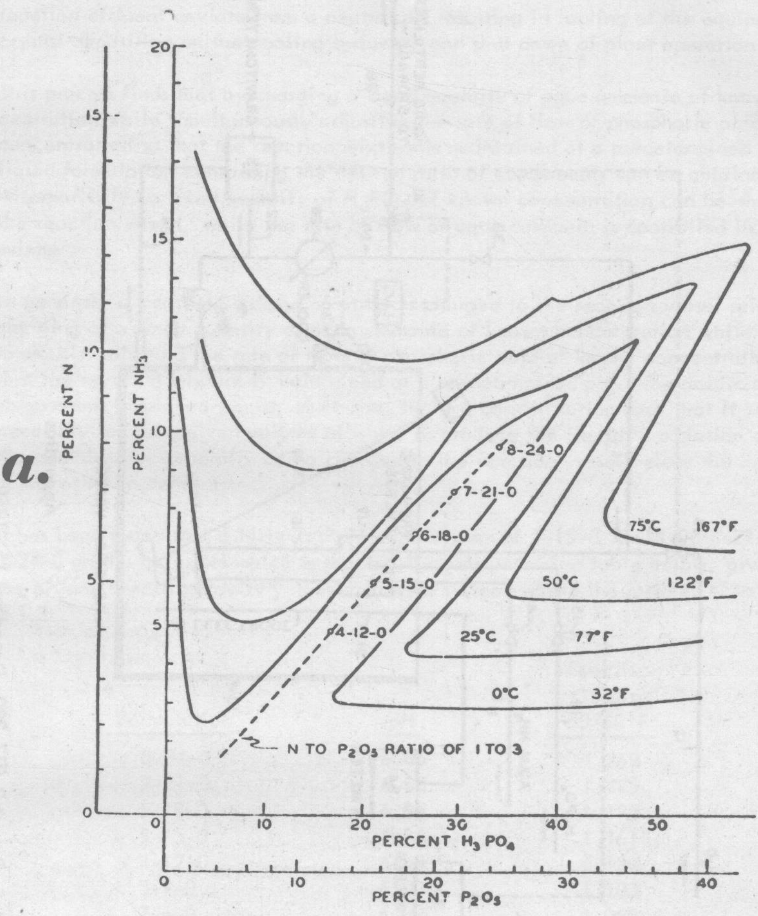
C.E. Franklin; U.S. Patent 2,917,380; December 15, 1959; assigned to Phillips Petroleum Company discusses the production of a liquid fertilizer with a predetermined nitrogen-phosphorus pentoxide-water ratio. The procedure is explained with reference to Figure 1.1 which shows the solubility isotherms in the systems at various temperatures.

The solubility isotherms for the system NH_3-H_3PO_4-H_2O have been plotted at 32°, 77°, 122°, and 167°F. Double axes of ordinates are shown where percent nitrogen is plotted on one axis, and percent ammonia is plotted on the other axis. Double axes of abscissas are also shown with percent phosphorus pentoxide plotted on one abscissa axis and percent phosphoric acid on the second abscissa axis. The area below any particular curve is a liquid phase, the area above is the region of crystal formation. The ammonia, phosphoric acid and water content of any liquid formulation, for example, an 8-24-0 grade, can be determined by quantitative analysis in the laboratory.

However, the final desired formulation would not be produced merely be charging fixed quantities of ammonia, phosphoric acid and water into a reaction vessel since the reaction of ammonia and phosphoric acid is highly exothermic, and the reaction mixture temperature rises considerably resulting in appreciable loss of ammonia by evaporation.

In addition, in the production of a liquid fertilizer comprising NH_3-H_3PO_4-H_2O, commercial phosphoric acid is employed, and consequently, the uniformity of concentration of the phosphoric acid will vary from batch to batch. As such, predetermined quantities of H_3PO_4 necessary to give a particular grade of liquid fertilizer will often be inaccurate. Moreover, in the production of a neutral (pH 7) liquid fertilizer such as an 8-24-0 grade it is desirable to maintain the ratio of nitrogen to P_2O_5 close to 1:3 to keep from forming crystals or balls of ammonium phosphate

FIGURE 1.1: PREDETERMINED NITROGEN-PHOSPHORUS PENTOXIDE-WATER RATIO

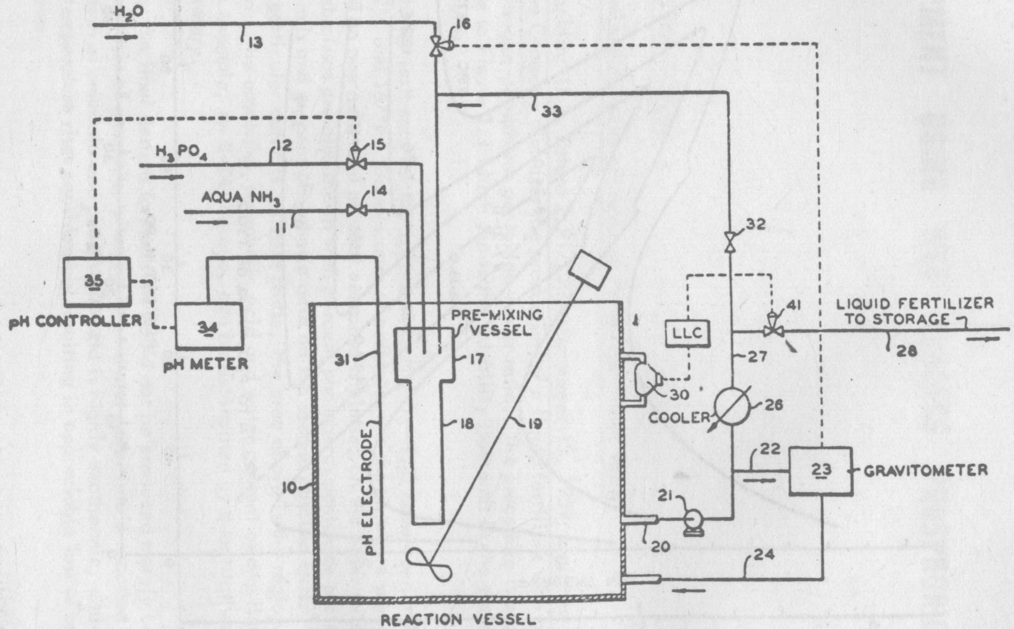


Solubility Isotherms for the System Ammonia-Phosphoric Acid-Water

(continued)

FIGURE 1.1: (continued)

b.



Apparatus

Source: C.E. Franklin; U.S. Patent 2,917,380; December 15, 1959 salts. This is difficult because the viscosity of the phosphoric acid varies considerably with the atmospheric temperature and consequently it is very difficult to charge the phosphoric acid at a constant rate. When aqua ammonia is employed, the concentration of the aqua will also vary due to ammonia vapor losses encountered in producing the aqua. Ammonia losses also occur during the storage of the aqua ammonia and phosphoric acid necessitates controlling the temperature of the reaction mixture by suitable cooling means. Crystal formation readily occurs should the reaction effluent deviate from a neutral pH resulting in fouling of the equipment, crystal deposition on the cooling surfaces, and shut down of plant operation.

This process finds that by charging a fixed quantity of aqua ammonia of known concentration while simultaneously adjusting the rate of flow of phosphoric acid of known concentration so that the reaction mixture is maintained at a predetermined pH, a liquid formulation containing the desired ratio of components can be obtained. Alternatively, a fixed quantity of H_3PO_4 of known concentration can be charged to the reaction vessel, while the rate of flow of aqua ammonia is controlled in the same manner.

In general, a measured volume of water is charged to the reaction vessel prior to the charging of a fixed quantity of aqua ammonia of known concentration while simultaneously adjusting the rate of flow of phosphoric acid of known concentration so that the reaction mixture is maintained at a predetermined pH. The acidic and basic components employed would, of course, be at a concentration such that it would be necessary to add a given volume of water to produce the liquid formulation desired, the added water generally being charged to the reaction vessel before the addition of the other ingredients.

It has been found that a NH_3-H_3PO_4-H_2O system of 5-15-0, 6-18-0, 7-21-0, and 8-24-0 grades has a pH which is practically constant. The table below, gives the the pH and specific gravity values for liquid systems where the ratio of N to P_2O_5 is 1:3.

Formulation	pH	Specific Gravity, 60/60°F.
8-24-0	6.85	1.269
7-21-0	6.85	1.225
6-18-0	6.85	1.193
5-15-0	6.86	1.161
4-12-0	6.90	1.128
3-9-0	6.95	1.103
2-6-0	6.99	1.063
1-3-0	7.08	1.031

Thus, it is readily apparent that if the pH of the reaction mixture is controlled at a predetermined pH of approximately 6.85 and at a predetermined specific gravity corresponding to the specific gravity of the liquid formulation desired, a liquid formulation of the 5-15-0, 6-18-0, 7-21-0, and 8-24-0 grades can be produced.

Example: A liquid fertilizer is prepared using the equipment in Figure 1.1b. Aqua ammonia (20 weight percent N), 75% phosphoric acid, and water are initially charged to a reaction vessel at a rate of 17.6, 11.5, and 6.2 gallons per minute, respectively. The reaction product is continuously monitored to maintain a predetermined pH of 6.85 and a specific gravity of 1.27; consequently the flow rates of the phosphoric acid and water are continually adjusted in relation to the predetermined pH and predetermined specific gravity of the reaction product. The reaction temperature is maintained between 50° to 150°F. by circulating a portion of the reaction mixture through an outside heat exchanger. An 8-24-0 grade is produced. The process is operated continuously; however, a batch process is equally operable.

Predetermined Ammonia Concentration

D.P. Bresee; U.S. Patent 2,952,531; September 13, 1960; assigned to Phillips Petroleum Company provides an apparatus which will produce an aqueous ammonia fertilizer with any desired concentration of ammonia. The process provides a closed tank with a conduit which admits water to the tank. A spray pipe is placed in the upper and normally vapor-containing space of the tank. Another conduit for passage of the liquid from the lower portion of the tank connected to a source of ammonia and a means for spraying the exterior wall of the tank with cooling water are also provided.

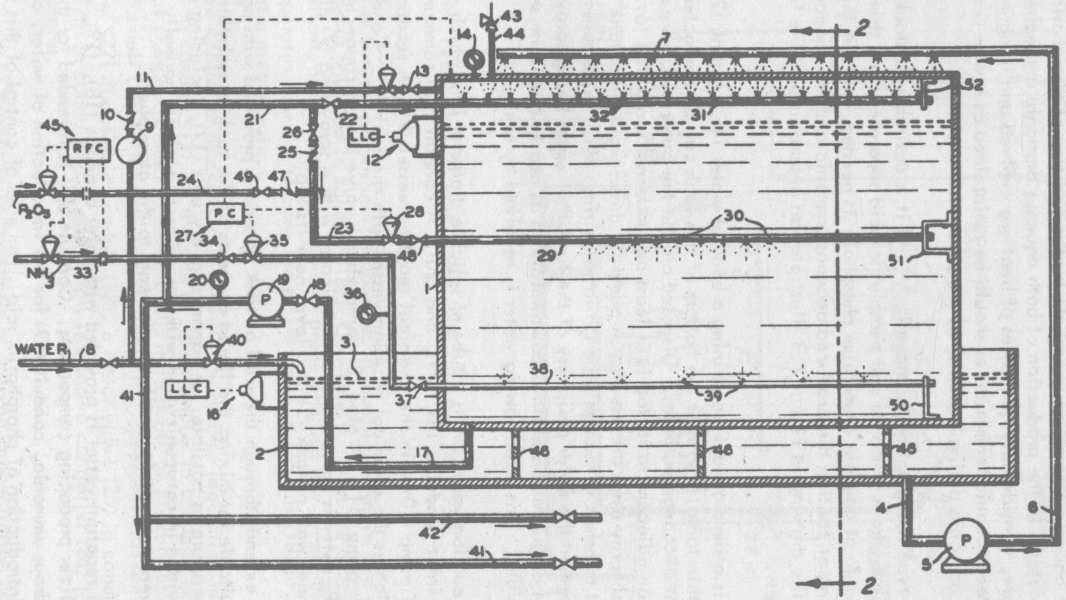
The process for producing these cooled aqueous fertilizers from reactants which, when mixed, evolve heat also consists of introducing a reactant into an aqueous medium in a mixing zone, withdrawing the aqueous medium from the lower portion of the zone. The aqueous medium is then sprayed on the inner surface of the upper walls of the zone and cooling water is sprayed on the outer surface of the zone to cool the aqueous contents of the tank.

Figure 1.2 is an illustration of such an apparatus. This apparatus and method have special application in the liquid fertilizer field in which liquid (anhydrous) ammonia is mixed with water to produce aqueous ammonia and in the production of aqueous ammonium phosphate by the addition of phosphoric acid and ammonia to water. In the production of both aqueous ammonia and aqueous ammonium phosphate, considerable quantities of heat are evolved and in aqueous solutions containing free ammonia temperatures should be maintained as low as possible to avoid loss of ammonia.

The production of aqueous ammonia from water and anhydrous ammonia and aqueous ammonium phosphate from water, anhydrous ammonia, and phosphoric acid, in large commercial plants exhibits few cooling problems because an ample supply of cooling water and refrigeration is ordinarily available. However, in cases where it is desirable to stock anhydrous ammonia, or anhydrous ammonia and phosphoric acid separately and then produce aqueous ammonia or aqueous ammonium phosphate as needed, refrigerating or cooling the produced aqueous ammonia and the aqueous ammonium phosphate becomes a problem.

This apparatus operates to produce such products sufficiently cooled for storage and handling without undue vaporization loss and produces liquid fertilizer products, sufficiently cool for storage and handling. Aqueous ammonia is produced in any desired and suitable concentration for application to the soil. Similarly, aqueous ammonium phosphate with or without an excess of ammonia over that required to produce triammonium phosphate is produced for application to the soil by mechanical device or by irrigation water.

FIGURE 1.2: APPARATUS FOR PRODUCING LIQUID FERTILIZER



Source: D.P. Bresee; U.S. Patent 2,952,531; September 13, 1960

Cooled Aqueous Ammonium Phosphate

This process by A.W. Peck; U.S. Patent 2,969,280; January 24, 1961; assigned to Phillips Petroleum Company has special application in a liquid fertilizer field in which liquid ammonia is mixed with water to produce aqueous ammonia and in the production of aqueous ammonium phosphate by the addition of phosphoric acid and ammonia to water. In the production of both aqueous ammonia and aqueous ammonium phosphate, considerable quantities of heat are evolved and in aqueous solution containing free ammonia temperatures should be maintained as low as possible to avoid loss of ammonia during handling of the products.

Where plant-type refrigeration is unavailable and it is desirable to stock anhydrous ammonia, or anhydrous ammonia and phosphoric acid separately and then produce aqueous ammonia or aqueous ammonium phosphate as needed, there is the problem of refrigerating or cooling the produced aqueous ammonia and the aqueous ammonium phosphate. The drawing in Figure 1.3 illustrates an apparatus suitable for carrying out this process.

Numeral (1) is a sump or tank containing a body of water (4). A tank (2) is suitably supported within tank (1) so that the bottom of this tank can be contacted with the water for heat exchange purposes. Disposed around the outer periphery of tank (2) at an elevation adjacent to its top is at least one external spray ring (6). Two of these external spray rings are shown. A pump (3) draws water from tank (1) through pipe (16) and transfers it through pipe (5) to spray rings (6). These spray rings are so disposed around the outer periphery of the tank that water being sprayed then contacts the wall of the tank and flows downwardly in as nearly a uniform sheet of water as possible. This downflowing water is received by tank (1).

A chemical reaction vessel (9) is a tube of suitable diameter into which communicate reagent inlet conduits (18), (19), and (20). A conduit (12) communicates tank (2) by way of pump (10) with the chemical reaction vessel (9). A second conduit (13) communicates the chemical reaction vessel with the tank (2). Conduit (13) is provided with pump (11). A pipe (8) containing a valve (14) is connected with pipe (13). Pipe (8) extends upward and communicates with a spray ring (7) disposed around the inner wall of tank (2) at a level near its top.

Conduit (13) extends through the wall of tank (2) and is provided with agitation means (15) suitable for mixing the liquid contents of the tank to maintain as nearly uniform temperature as possible. A vapor recovery unit (17), including a water spray, is provided in communication with the space of tank (1) normally containing vapor to prevent escape of volatile components to the atomsphere.

The chemical reaction vessel is provided with inlet conduits (18), (19), and (20) for inlet of fertilizer producing components. Conduit (18) is intended for the introduction of anhydrous ammonia, conduit (19) for the introduction of water, and conduit (20) for the introduction of phosphoric acid. For ease of control of this system a temperature recorder controller apparatus (28) includes a temperature responsive device (33), such as a thermocouple, a motor valve in conduit (18) and a recorder-controller element. Such a temperature recorder-controller assembly can be set to operate a valve to regulate the flow of liquid in pipe (18) in response to changes in the temperature as indicated by the temperature responsive device (33). When the temperature of the liquid contents of tank (2) reaches a predetermined high