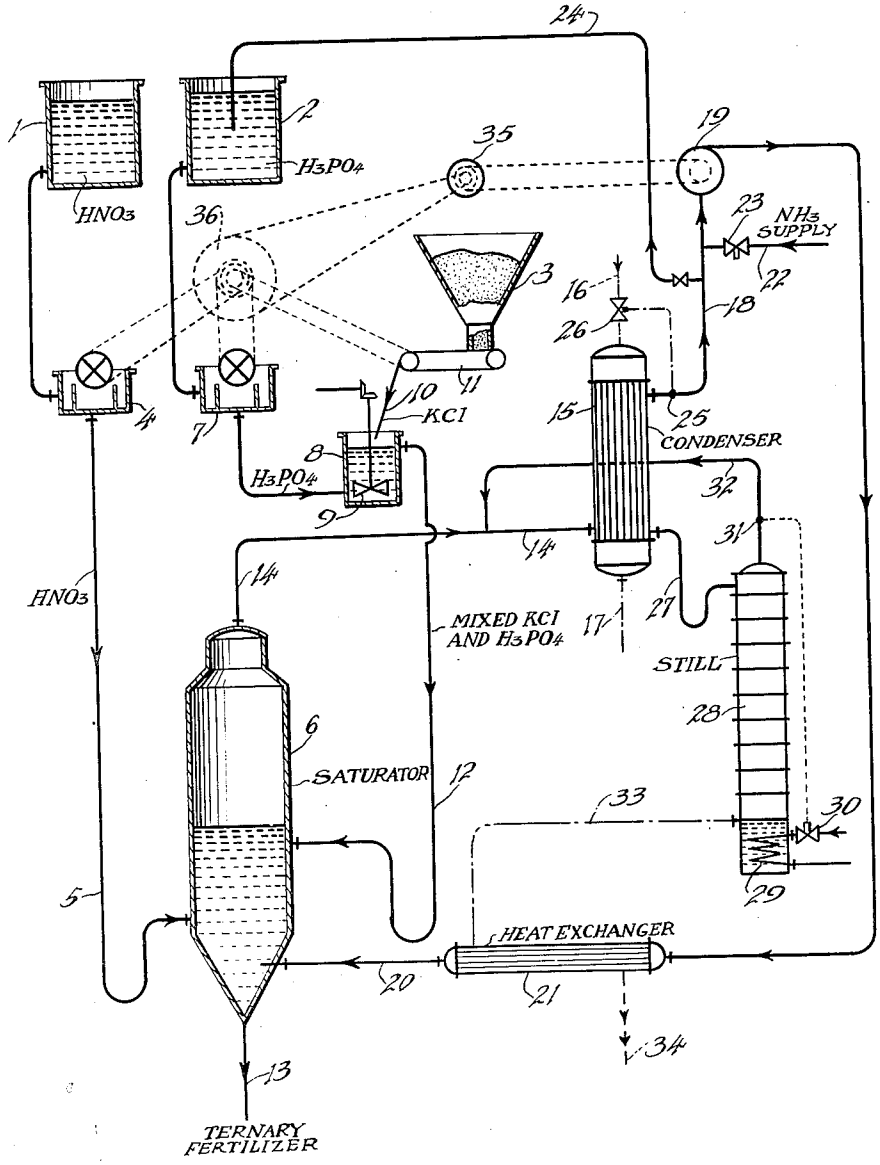
Oct. 14, 1952 P. KAIKINGER 2,614,040

METHOD OF AMMONIZATION

Filed May 1, 1947



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Patented Oct. 14, 1952 2,614,040

UNITED STATES PATENT OFFICE

2,614,040

METHOD OF AMMONIZATION

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Application May 1, 1947, Serial No. 745,189
In France February 12, 1947

2 Claims. (Cl. 71—36)

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The present invention relates to a general method of ammonization, more particularly applicable to the preparation of soluble compound fertilizer with high fertilizing material contents from starting materials of current manufacture.

It is well known that the neutralization of phosphoric acid through ammonia up to the second valence inclusive requires, if it is desired to realize it with the use of heat in order that the heat evolved in the reaction may be used at the utmost for vaporizing the water brought in with the acid, that the saturation of said acid should be achieved in the presence of a certain excess of ammonia the object of which is to create a tension opposing the hydrolysis. Now, the neutralization of phosphoric acid up to the above mentioned stage is desirable, more particularly in the manufacture of fertilizers, insofar as it would provide at no increase of cost a carrier for a supplement or increased concentration of nitrogen.

If the reaction is achieved in a single step and in a continuous manner as, for example, by causing a regular current of ammonia to bubble through a saturator of rather large capacity receiving a constant flow of phosphoric acid in a quantity which is stoichiometrically less than that of the delivered ammonia, the products which are collected are, on the one hand, a thin crystalline, concentrated and hot paste and, on the other hand, a vapour containing the ammonia in excess diluted in the quantity of steam which represents, the yield being accounted for, the calorific equivalent of the energy freed by the conversion. The weight ratio (ammonia): (water) in the vapour phase depends, therefore, on the excess of ammonia and increases therewith. If the operation is achieved with a constant total pressure, the steam partial pressure will be the lower the higher the pressure of the ammonia is; consequently, the working temperature in the vapour phase will be the lower the larger the excess of ammonia is. With a constant total pressure and for a given conversion characterized by an acid having a predetermined initial concentration and a prescribed saturation rate, the relative excess of ammonia will, therefore, condition the working temperature of the steam i. e., the higher the relative quantity of ammonia, the lower the steam temperature.

This temperature cannot be chosen arbitrarily. As a matter of fact, it is connected with that of the obtained paste through a certain parallelism. Now, the hotter the paste, the higher its coefficient of hydrolysis. Consequently, in order to obtain the desired saturation rate, that is to say, as above mentioned, a hundred percent of both the first valences, it is necessary, the total working pressure having been chosen, to arrange that the partial pressure of the ammonia is sufficient, that is, in practice, higher than the tension of hydrolysis.

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Finally, for each total pressure, the excess of ammonia should be determined by experiment, and thus the regime of the temperatures, which, from an acid of a given concentration, leads to the desired saturation rate.

By operating under the above mentioned conditions the ammonization of the phosphoric acid is obtained in an alkaline medium and at a reduced temperature.

Such a method can be applied not only to the phosphoric acid alone but also to mixtures of said acid with other substances such as, for example, sulphuric acid.

Thus, it can be applied with advantage to the ammonization of mixtures which, without the particular precautions which characterize it, i. e. in a non-alkaline medium and at the normal boiling temperature, would give rise to secondary reactions of decomposition or volatilization and submit the equipment used for effecting the reaction to an excessive corrosion. For instance, by using the above mentioned method, it is possible to ammonize very readily a mixture of phosphoric and nitric acids or nitric acid at the same time as phosphoric acid in which a potassium salt, preferably potassium chloride, has previously been dissolved or stirred in order to prepare a well homogeneous fertilizer in which all the necessary fertilizing substances appear in the desired quantities.

An object of the present invention is to provide a method using the above explained principle and making it possible to perform commercially and economically the ammonization of substances such as, for example, phosphoric acid in the presence or in the absence of other acids with or without the previous incorporation of potash in order to manufacture a homogeneous concentrated compound fertilizer which is perfectly soluble in water.

Said method fundamentally consists in introducing in a continuous manner into a reaction chamber in which a constant or substantially constant pressure is maintained, on the one hand, the substance or substances to be ammonized and, on the other hand, a current of gaseous ammonia brought into an intimate contact

in said chamber with said substance or substances, in extracting the ammonized products from said chamber in a continuous or discontinuous manner, and in collecting, in the upper part of said chamber, the mixture of steam and ammonia which escapes and which is submitted to a condensation, possibly accompanied by a distillation, for separating the steam from the ammonia which is recycled into the chamber after the addition, thereto, of a quantity of fresh ammonia equal to the quantity consumed by the reaction, the respective quantities of the ammonized product or products and of ammonia introduced at every moment into the reaction chamber being maintained constant with a proportion of ammonia calculated in order that the partial pressure of said gas in the chamber is decidedly higher than the tension of hydrolysis of the substances which are formed.

The carrying out of the method according to the invention will be explained more particularly in the following description in which reference is made to the appended drawing which shows, by way of example, the diagram of a plant for the application of the invention to the manufacture of ternary fertilizer, starting from phosphoric acid, nitric acid and potassium chloride.

Said plant comprises supply vats 1 and 2 adapted for receiving nitric acid and phosphoric acid respectively, and a supply silo 3 adapted for rereceiving finely ground potassium chloride. The vat 1 is connected, through a volumetric measuring device 4 of any known type and a siphon 5, to the lower part of an autoclave saturator 6 which is heat-insulated and provided with an inner acid-proof coating. The vat 2 is connected, through a volumetric measuring device 7 similar to the device 4, to a mixer 8 provided with a stirring device 9 and to which leads a conduit 10 coming from a weight measuring device 11 insuring the regular and controlled delivery of the potassium chloride contained in the silo 3. The mixer 8 is itself connected to the middle part of the saturator 6 through a siphon 12.

The bottom of the saturator 6 is provided with a pipe branch 13 for the removal of the reaction products and its upper part is provided with a piping 14 for the removal of the vapours, which piping is connected to a reflux condenser 15 in which a circulation of cooling water is insured through pipings 16 and 17.

The condensation elements of the condenser 15 are connected in their upper part through a piping 18 to a volumetric booster 19 which discharges into a piping 20 connected, with interposition of a heat exchanger 21, to the lower part of the saturator 6. A drain piping 24 leading to the supply vat 2 is connected with the piping 18, into which opens a piping 22 supplying gaseous ammonia and provided with an adjustable reducing valve 23 which can be calibrated to reduce the pressure to that in pipe 18 which is at a pressure value chosen in advance. Furthermore, said piping 18 is provided at 25 with a pyrometer which controls, in a manner known per se, a delivery regulator 26 inserted in the piping 16 which supplies the condenser 15 with cooling water, said pyrometer and said regulator being combined in order that the quantity of cooling water delivered to the condenser 15 increases directly proportionally to the temperature in the piping 18.

From the lower part of the condensation elements of the condenser 15 starts a siphon piping 27 which opens into the upper part of a distillation column 28 heated through a steam coil 29.

The admission of the steam to the coil 29 is controlled by a governor 30 itself controlled by a pyrometer arranged at 31 on a piping 32 starting from the upper part of the column 28 and opening into the piping 14 upstream of the condenser 15. Finally, a piping 33 connects the lower part of the distillation column 28 to the heat exchanger 21 inserted in the piping 20, the liquid brought to said exchanger through said piping being discharged at 34.

The volumetric measuring devices 4 and 7, the weight measuring device 11 and the booster 19 are driven through a common motor 35, a system of counter-gears 36 insuring the transmission of the movement to the measuring devices 4, 7 and 11.

The said measuring devices are arranged so that the quantities of materials which they deliver respectively are at every moment in a ratio corresponding to the desired proportioning of the quantities of substances to be introduced into the saturator 6.

The so delivered phosphoric acid and potassium chloride are mixed in the mixer 8 from which the mixture is poured through the siphon 12 into the saturator 6 to which the nitric acid delivered through the measuring device 4 is also supplied by the siphon 5. The ammonia which arrives at the saturator 6 through the piping 20 in a hot and practically dry state, as will be seen later on, reacts with the phosphoric and nitric acids and a thin crystalline, homogeneous and hot paste is formed which is taken off in a continuous or non-continuous manner through the bottom pipe branch 13 in order to be granulated and dried through the usual means. The heat evolved through the reaction determines the vaporization of a part of the water supplied by the acids and freed in the course of the neutralization. The quantity of ammonia to be introduced into the saturator at every moment is determined by calculation and by experience in order to permit the neutralization of the phosphoric acid up to the second valence inclusive, which supposes that the partial pressure of the ammonia in the gaseous phase which is proportional together to the total pressure, to the quantity of injected ammonia and to the delivered quantity of acids, is at every moment higher than the tension of hydrolysis of the bath which is proportional to the temperature.

The obtained vapours which are formed mainly of a mixture of water and ammonia are led to the condenser 15 through the piping 14. This condenser, which works with reflux, discharges through the piping 18 a gaseous and cooled fraction of practically dry ammonia and through the piping 27 a slightly ammoniacal condensate which passes to the distillation column 28. Said column delivers, on the one hand, a phlegm which is enriched in ammonia and which is returned to the condenser 15 through the piping 32 and, on the other hand, a totally exhausted liquor which is removed through the piping 33 and through the exchanger 21. Owing to said arrangement the whole quantity of water vaporized in the saturator is found again at 34 while the whole excess of ammonia which is practically free from moisture leaves through the piping 18. This ammonia receives through the reducing valve 23 an added portion of fresh gas corresponding exactly to what was absorbed in the saturator, then returns to the saturator through the piping 20 after compression in the volumetric booster 19 and preheating in the exchanger 21. Finally, the con-

tinuous draining 24 makes it possible to remove the uncondensable portions, the ammonia which is so carried forth being recovered through bubbling through the phosphoric acid contained in the vat 2.

When the range of temperatures which under the total pressure which has been chosen makes it possible to obtain the desired ammonization rate for the mixture which is treated has been determined experimentally as explained in the introduction to the present description, the control of the operation essentially consists in maintaining constant the pressure which has been chosen and the temperature of the vapour leaving the saturator.

The pressure will be maintained automatically irrespectively of the rate of working owing to the presence of the reducing valve 23 calibrated to hold the pressure in the system to that previously chosen.

On the other hand, the temperature of the atmosphere of the saturator is automatically maintained constant owing to the fact that, on the one hand, the booster 19 which controls the rate of circulation is driven through the same motor 35 which drives the measuring devices 4, 7 and 11—which, once the transmission ratio between said motor and the booster has been adjusted so that the quantity of ammonia forced into the piping 20 at every moment corresponds in the required ratio to the quantities of materials delivered by the measuring devices while taking into account the necessary excess, insures the invariability of said ratio—and that, on the other hand, the governor 26 controlled by the pyrometer 25 makes it possible to maintain constant the composition of the gaseous fraction leaving the condenser 15, the combination of both said arrangements making it possible to keep an invariable composition ratio (ammonia):(water) in the atmosphere of the saturator.

The steam governor 30 acting according to the indications of the pyrometer 31 facilitates the working of the system: pyrometer 25-governor 26 and makes it possible simultaneously to reduce the consumption of steam to a minimum.

Through operating according to the invention, it has been possible, while using the starting materials in the following proportions:

161 kilograms of anhydrous ammonia,
405 kilograms of nitric acid of normal concentration,
515 kilograms of phosphoric acid produced by the attack of phosphate through sulphuric acid, and
310 kilograms of rich potassium chloride,

to obtain a thin paste which, after dehydration, leaves 1,000 kilograms of a ternary fertilizer titrating:

18% of partly ammoniacal and partly nitric nitrogen,
18% of water soluble P_2O_5,
18% of K_2O.

For this operation the temperature of the bath was maintained in the neighborhood of 120° C.

When operating according to the invention, the following advantages are obtained:

(1) The proportioning and the addition of the starting materials to be ammonized being effected at the head of the plant, the final thin paste reproduces at every moment the proportions which were delivered without it being necessary to perform any analytic control or any adjustment of the titrations in the course of the manufacture. Consequently, any variation in the rate of the drawing off operation with respect to that of the saturation brings no change in the composition of the thin paste which is drawn off except a slight fluctuation of the moisture, which is of no importance. It is thus possible to interrupt completely the drawing off operation, for instance for the periodical cleaning of the granulating and drying apparatus without modifying in anything the working regime of the saturator, which would not be possible if the addition of potash were effected after the ammonization.

(2) Immediately after their introduction into the saturator, the starting materials are diluted in a large mass of saturated product; the acidity disappears immediately and the conversion is so to say instantaneous. The speed of the reaction is the best obstacle to the natural development of the crystals so that the obtained thin paste is homogeneous and fluid, which circumstance is favourable to its later granulation.

(3) Owing to the operation in an alkaline medium and at a reduced temperature no decomposition is to be feared. There is no evolution of fluorinated compounds supplied through the phosphoric acid nor nitrous decomposition nor reaction of the nitrate which has formed on the chloride, nor volatilization of ammonium chloride nor any other similar prejudicial reaction. Correlatively, the vapour phase contains only ammonia and water which makes it possible to construct the equipment following the saturator with ordinary materials.

(4) No mother-liquor is produced and up to the drawing off operation, every operation is carried out in a closed vessel which makes it possible to obtain the highest yields.

(5) The calorific power of the acids is used to the utmost so that with starting materials of a current concentration a strongly dehydrated paste is obtained which is a chief condition for an economical drying operation.

(6) The consumption of energy even while taking into account the recompression of the ammonia and the consumption of vapour, which is practically limited to the exhausting of the condensate, are exceedingly reduced.

(7) The control is simple and can be rendered automatic which entails a saving of man power.

What I claim is:

1. A method of manufacturing concentrated and highly soluble ternary fertilizers from raw materials including phosphoric acid and nitric acid solutions, potassium chloride and gaseous ammonia, which comprises maintaining in a closed reaction container, at a temperature well above the normal boiling point of water and under a substantially constant pressure a large and relatively deep mass of a fluid aqueous paste previously formed by combining such materials therein, continuously combining relatively small streams of said materials into said mass by introducing potassium chloride with phosphoric acid solution into an upper zone of the mass, introducing nitric acid solution at a remote point into an intermediate zone of the mass, introducing the ammonia under pressure into a bottom zone of the mass and bubbling it through the mass at a rate exceeding that required to ammonize the nitric acid inflow and diammonize completely the phosphoric acid inflow, thereby keeping substantially the entire mass well agitated and distinctly alkaline and causing immediate ammonization of the inflowing acids so

as to avoid degradations within the mass, by regulating the excess ammonia inflow regulating the temperature of the mass and its steam pressure so that it forms continuously as a fluid aqueous paste of crystalline salts in a normally liquid aqueous medium, and withdrawing from the bottom of the mass surplus paste thus formed having its phosphate content completely diammonized.

2. A method of manufacturing concentrated and highly soluble ternary fertilizers from raw materials including phosphoric acid and nitric acid solutions, potassium chloride and gaseous ammonia, which comprises, while maintaining in a closed reaction container a large mass of a fluid aqueous paste previously formed by combining said materials and keeping the mass by the heat of reaction at a temperature well above the normal boiling point of water, continuously combining proportional streams of said material into said mass by introducing the potassium chloride with the phosphoric acid solution into an upper zone thereof, introducing the nitric acid solution into an intermediate zone thereof at a point remote from the inflow of potassium chloride, introducing the ammonia into a bottom zone of the mass and bubbling it through the mass at a rate substantially exceeding that required to ammonize the nitric acid inflow and diammonize completely the phosphoric acid inflow, continuously taking off from space in the container above said mass gases composed principally of ammonia and steam, in a closed circuit leading back to the ammonia intake continuously condensing steam from said gases and adding ammonia to the residual gas so as to provide enriched ammonia gas of substantially

uniform composition for the continuing ammonia inflow, by continuously regulating the pressure and flow rate of the enriched ammonia gas maintaining in the container a substantially constant pressure comprising a partial pressure of ammonia exceeding that required to diammonize the phosphoric acid inflow and so limiting the steaming rate that the reaction mass forms continuously as a fluid aqueous paste of crystalline salts in a normally liquid aqueous medium, and withdrawing surplus paste thus formed from the bottom of the mass with its phosphate content completely diammonized.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,322,758	Carpenter	Nov. 25, 1919
1,624,294	Wallace et al.	Apr. 12, 1927
1,625,807	Howard	Apr. 26, 1927
1,962,185	Fauser	June 12, 1934
1,971,563	Hirschkind et al.	Aug. 28, 1934
1,999,026	Tramm et al.	Apr. 23, 1935
2,024,480	Short	Dec. 17, 1935
2,025,916	Tramm	Dec. 31, 1935
2,033,388	Moose	Mar. 10, 1936
2,036,701	Kircher et al.	Apr. 7, 1936
2,086,808	Kallam	July 13, 1937

OTHER REFERENCES

Ross et al., Preparation and Properties of the Ammonium Phosphate, reprint from Ind. and Eng. Chem., vol. 21, page 286, March 1929.