Dec. 20, 1927. 1,653,023

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PROCESS OF MAKING NITRIC ACID

Filed Aug. 5. 1925

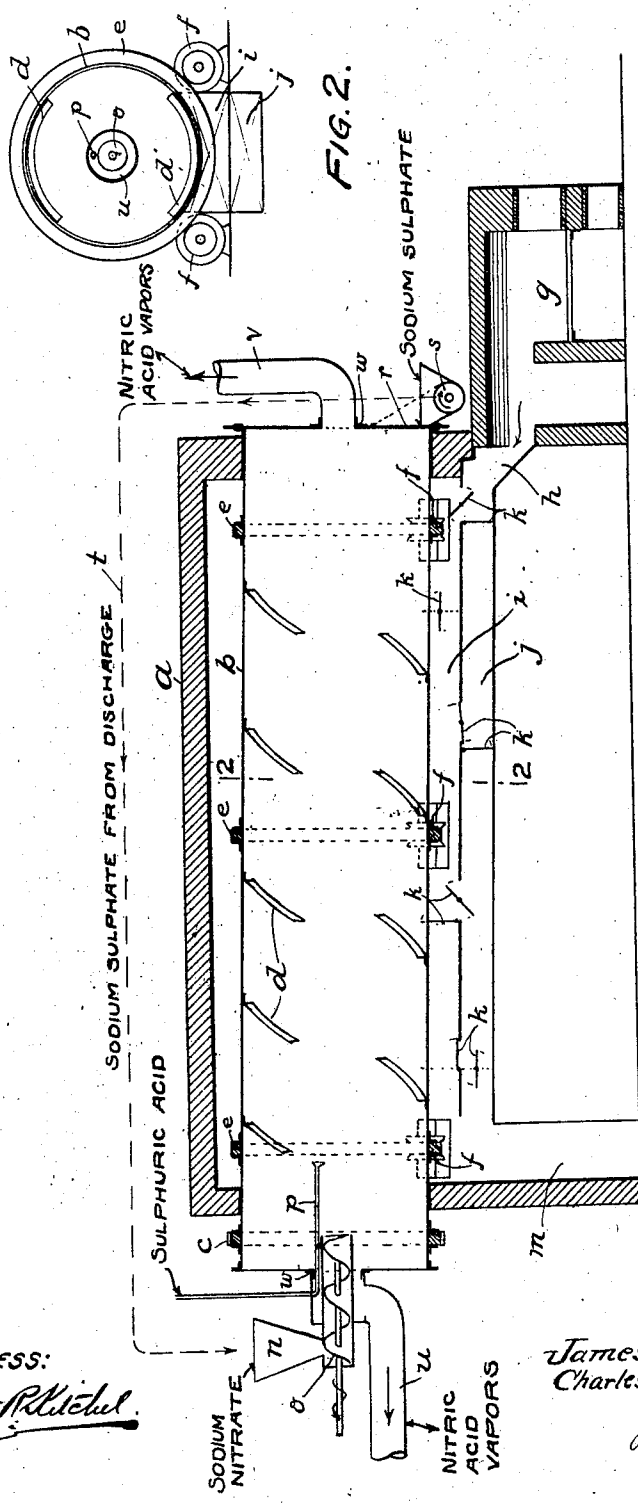


FIG. 2.

FIG. 1.

WITNESS:

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Patented Dec. 20, 1927. 1,653,023

UNITED STATES PATENT OFFICE.

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PROCESS OF MAKING NITRIC ACID.

Application filed August 5, 1925. Serial No. 48,216.

The object of our invention is to provide a new method of manufacturing nitric acid.

In our specified and preferred process, which comprises features all of which are of advantage and importance, but not all of which are essential to the successful execution of the process, there are continuously fed to one end of an elongated retort about equal quantities of sodium sulfate and sodium nitrate and the amount of sulfuric acid required to react with the sodium nitrate to form nitric acid gases and convert the sodium nitrate to sodium sulfate with no, or a minimum, production of sodium acid sulfate. The retort is so differentially heated that the material relatively near the feed end of the retort will be subjected to a relatively low heat with resultant production of a maximum proportion of gases yielding, on condensation, strong nitric acid, while the material relatively near the discharge end of the retort will be subjected to the relatively high heat required to complete the reaction of sulfuric acid and sodium nitrate, with resultant production of gases (largely oxides of nitrogen from decomposition due to high temperature) adapted, on condensation, to yield weak strength nitric acid. The different evolved gases are preferably separately withdrawn from the retort and separately condensed and absorbed. Inasmuch as the different gases are evolved in a single retort, the proportions of different gases that are separately withdrawn may be regulated by applying suction at the separate gas outlets and varying the suction. The originally introduced sodium sulfate and the non-gaseous products of the reaction between the sulfuric acid and the sodium nitrate (which, if the process is carefully conducted, will comprise mainly or wholly normal sodium sulfate) are continuously discharged from the retort, and a part of this discharged material (about one-half) is conveyed back to the feed end of the retort and is used as the source of supply of the sodium sulfate which, together with the sodium nitrate, is continuously fed into the retort. The retort is preferably heated by means of hot gases that are first brought into heat exchange relation with the retort at its discharge end and which flow along the retort in a direction opposite to the direction of movement of the salts in the retort; more or less of the heating gases being by-passed during their flow along the retort so as to provide heat zones in the retort of substantially different temperatures, as above stated. The salts entering the retort should be preheated, and the waste heating gases may be utilized for this purpose. However, if, as above described, the sodium sulfate discharged from the retort be utilized as the source of supply of the sodium sulfate which is continuously being fed to the retort, such sodium sulfate may be utilized to preheat the sodium nitrate with which it is mixed before entering to the retort, and the waste heating gases may therefore be used to supply any additional heat which it may be desirable or necessary to impart to the entering sodium nitrate. The salts that travel through the retort should be agitated so as to maintain them in mixed condition and establish the most favorable conditions for reaction between the sodium nitrate and the sulfuric acid.

Different apparati may be employed to carry out our process. While, therefore, it should be understood that the successful execution of the process is not dependent on the employment of any particular apparatus, we herein disclose an apparatus which is well adapted to carry on the process with a high degree of efficiency and economy.

In the drawings:

Fig. 1 is a diagrammatic view, in sectional elevation, of such an apparatus.

Fig. 2 is a cross-section on the line 2—2 of Fig. 1, also diagrammatic.

Through a brick setting *a* extends a rotatable cylinder *b* which serves as a retort. The retort is provided with a drive gear *c* which is driven from driving means not shown. Within the retort are angle plates *d* or other means for imparting additional agitation to the contents of the retort during its revolution. The retort is provided with rings *e* which revolve on trunnions *f* with water cooled bearings within the setting *a*. The retort may be inclined somewhat to the horizontal to effect a forward feed of the material, and internal contriv-

ances may be provided to push the material forward during the rotation of the retort. If the angle plates *d* are arranged spirally, as shown, they will operate to push the material forward, even though the cylinder be positioned exactly horizontally. The retort need not be rotated at all if internal contrivances be provided to push the material forward. This could be effected by rotating the angle plates *d*.

A fire box *g* is located beyond the exit end of the retort. From the fire box extends a gas passage *h* leading to two control flues, one (*i*) being adjacent to and extending along the shell of the retort and the other (*j*) extending along and adjacent to the flue *i*. By means of dampers *k* the hot flue gas may be directed into flue *i* and into contact with the shell of the retort along any or all of its length, or the gas may be by-passed through part or all of the length of flue *j*. Both flues communicate with a gas flue *m* leading to a stack (not shown).

By means of these flues and dampers, different "zones" of the retort may have imparted to them different temperatures. Temperature control of this character is an important feature of our process, although, obviously, it may be secured by other means than those described.

In front of the entrance end of the retort is a hopper *n* for supplying the retort with the solid materials (i. e. sodium nitrate and sodium sulfate). Beneath the hopper is a conveyor *o* for feeding those materials continuously into the retort. A feed pipe *p* for sulfuric acid has a perforated end through which sulfuric acid is continuously sprayed into the retort. At the exit end of the retort is an outlet for discharging solids (i. e. sodium sulfate), which outlet is provided with a swing door *r*. From this outlet extends a conveyor *s* for carrying away the discharged material. Part of this material, as hereinafter explained, may be conveyed back to the hopper *n*, the return feed path being indicated by the letter *t*.

An outlet flue *u* for strong gases is provided at the front of the retort; conveyor *o* and feed pipe *p* extending through the mouth of flue *u*. An outlet flue *v* for weak strength gases is provided at the rear of the retort. Revolving joints *w* between the retort and flues *u* and *v* are made sufficiently tight to prevent, as far as possible, gas leakage from, or air leakage into, the retort.

Balls may be placed in the retort to assist in preventing the balling of the material therein. The balls may be allowed to circulate along with a portion of the salt cake or they may be prevented from longitudinal movement by any appropriate means.

In utilizing the above apparatus to carry on our process, the retort, which may be assumed to be about twenty feet in length and about five feet in diameter, is filled, to a depth of about a foot or so, with dry sodium sulfate, say, for example, 4000 pounds. The fire is started, before or after loading, and the flue dampers are adjusted so as to produce the desired reaction temperatures in different zones of the retort. For example, the retort may be so differentially heated that the charge adjacent the feed end of the retort will be at approximately 300° F., while the charge in succeeding zones will be heated to progressively higher temperatures, until, in the final zone, the charge will be heated to a temperature of approximately 550° F. These examples are merely preferential. The possible extreme range of temperature of the charge would be probably from substantially cold at the feed end to almost any temperature short of the melting point of sodium sulfate at the discharge end. The number of heat zones and the temperatures in the several zones are matters for determination by those practicing the process. These factors may vary with the strength of acid desired to be produced, the amount of salts in the retort at any one time, the rate of feed of salts and sulfuric acid into the retort, the length of the retort, the temperature of the material when it enters the retort, and the length of time required for the material to traverse the retort. In the example which we are giving, the salts, sodium sulfate and sodium nitrate, are continuously fed into the retort at the rate of about 500 pounds of each salt per hour. The salts are preferably mixed before entry into the retort and they are preferably preheated, by means hereinafter described, to any suitable temperature, as, for example, a temperature approximating the temperature in the first zone of the retort, so that an immediate reaction occurs within the retort when the acid comes in contact with the nitre. Sulfuric acid is sprayed into the retort, near its feed end, at the rate of about 288 pounds per hour and in such manner that it is distributed in the salt mixture. This amount of sulfuric acid specified is about that theoretically required to react with the specified amount of sodium nitrate to produce nitric acid and normal sodium sulfate.

Since the sodium nitrate is initially at a good reaction temperature, nitric acid gas is given off rapidly at the start. As the rate at which the nitric acid gas is driven off decreases, the progressively higher temperature zones offset largely the rate reduction. Further, the sodium sulfate acts as a diluent and, together with the quick reaction rate, keeps the mass in a relatively dry state and more or less free from balling, whereby a conversion of the sodium nitrate to normal sodium sulfate instead of sodium acid sulfate, is insured. The use of balls is

unnecessary, but is advisable in that they complete the pulverization and improve the product.

As the mixture nears the end zone, or hottest zone, the reaction is relatively complete, the sodium nitrate is converted to normal sodium sulfate, and normal sodium sulfate is discharged from the retort. A part of the discharged material, for example, one half, is returned to the feed end of the retort and serves, through its heat content, to economically heat the ingoing sodium nitrate. As hereinbefore stated, waste heat from the flue gas is also available to supplement the heating action of the sodium sulfate.

Assuming that the initial charge of material is about 4000 pounds, that this amount of material is maintained in the retort, and that the material is fed into the retort at the rate specified, the length of time required for material to traverse the retort will be about four hours.

The bulk of the reaction takes place near the feed end and at relatively low temperatures, giving a high percentage of strong acid. Further toward the discharge end, and under the higher temperature conditions required to complete the reaction of sodium nitrate to sodium sulfate, the nitric acid dissociates, producing weak strength acid.

All the nitric acid may be taken from a single exit, but this is highly inadvisable, and therefore separate gas exit flues *u* and *v* are provided near or at the feed end and discharge end respectively. Thereby mixing of nitric acid gases of widely different temperatures is avoided. The number of gas exit flues and their location are matters for the judgment of those operating the apparatus. By applying suction to the gas exit flues and controlling the relative amounts of suction in the two flues, the amount of gas delivered at each end may be accurately controlled.

From the foregoing description it will be understood that by regulating the factors of rate of feed, temperature, etc., nitric acid may be continuously distilled with direct production, as a by-product, of normal sodium sulfate (which has a substantial market value) in contrast to the production, as in the usual process, of sodium acid sulfate (a product of low value), and without waste of sulfuric acid, as in the usual process. Even if the process be not carried out with the highest skill or under the best conditions, so that some acid sodium sulfate may be formed, the process presents advantages with respect to economy and continuity.

Due to the zones of progressively increasing and readily controllable temperature, the nitric acid produced is of desirable strength and quality.

The use of sodium sulfate in the reaction mixture is a factor that materially contributes to the success of the process.

The utilization of waste heat and of the heat of the discharging and re-used sodium sulfate make the fuel economy high.

After the process has continued for a short time, and if the desired differential temperature conditions are maintained, the conditions within the retort remain fixed. The proportion of sodium sulfate in the retort is maintained at from about fifty per cent at the feed end to one hundred per cent at the discharge end. At any given point along the length of the retort, the composition of the mixture (amount and proportion of each salt), the temperature, and the gas composition remain unchanged. Once started, therefore, the operation requires a minimum of labor.

There is, of course, heat transfer from one zone of the retort to another, the effect of which, however, if the dampers are properly adjusted, is not to create, within the retort, a uniform temperature, but a gradual increase of temperature from one zone to the next. In other words, instead of distinct zones of different temperatures, there is a more or less gradual increase of temperature from one zone to another, which is a condition more favorable to an economical and efficient practice of the process than distinct zones with abrupt temperature rises from one to another.

Over the batch process that is in general use, our process has distinct advantages other than those hereinbefore pointed out. It is devoid of "critical" points such as "primes" and hence does not require "nursing", like the batch system. The latter requires very careful heat regulation and an experienced fireman for "pushing" and "holding" the fires, whereas in our process the temperature conditions, once properly adjusted, need only be maintained constant. The alternate heating and cooling of the batch system is a serious source of heat waste. Not only does our process avoid this waste of heat, but the residual heat of the flue gases and the absorbed heat of the discharging sodium sulfate are both availed of to preheat the entering salts.

By reason of the continuity of the process, great economy may be attained in the installation of condensers and towers for handling the nitric acid.

While we have described, and hereinafter claim, the continuous feeding of salts and sulfuric acid into the retort and the continuous discharge therefrom of sodium sulfate, and while absolute continuity is contemplated where it can be conveniently maintained, we do not mean to limit the process to absolute continuity as distinguished from such substantial continuity as would be afforded by intermittent admission and discharge, but intend, in referring to the process as continuous, to exclude batch treat-

ments and such substantial departures from literal continuity as would maintain substantially variable, as distinguished from substantially fixed and constant, conditions in the retort.

While we prefer to feed into the retort about equal quantities of the two salts, and while the feed of sodium nitrate and the feed of sulfuric acid should be so proportioned as to insure the conversion of the highest possible proportion of sodium nitrate to nitric acid and sodium sulfate, the proportions of sulfate relative to nitrate that should be fed into the retort may be varied from that specified within rather wide limits.

Having now fully described our invention, what we claim and desire to protect by Letters Patent is:

1. The process of making nitric acid which comprises continuously feeding sodium nitrate, normal sodium sulfate and uncombined sulfuric acid to and along a confined path, subjecting said salts during their travel along said path to agitation and to differential heating varying from a relatively low temperature relatively near the feed end of the path to a relatively high temperature relatively near the discharge end of said path, continuously discharging from said confined path the sodium sulfate admitted thereto and the sodium sulfate produced by the reaction of the sulfuric acid with the sodium nitrate, the proportion of sulfuric acid fed to said path being not substantially in excess of the proportion theoretically required to produce nitric acid and normal sodium sulfate and the proportion of normal sodium sulfate fed to said path being sufficient to provide the conditions required to prevent conversion of substantial amounts of sodium sulfate to sodium acid sulfate, and controlling said temperature to produce, by the reaction of the sulfuric acid with the sodium nitrate, gases, relatively near the feed end of the path, adapted to yield on condensation relatively strong nitric acid and gases, relatively near the discharge end of the path, adapted to yield on condensation relatively low strength nitric acid.

2. The process defined in claim 1 comprising also the utilizaton of the discharged salt as a source of supply of the sodium sulfate that is fed to said confined path.

3. The process of making nitric acid which comprises continuously feeding sodium nitrate, normal sodium sulfate and uncombined sulfuric acid to and along a confined path, subjecting said salts during their travel along said path to agitation and to differential heating varying from a relatively low temperature relatively near the feed end of the path to a relatively high temperature relatively near the discharge end of said path, continuously discharging from said confined path the sodium sulfate admitted thereto and the sulfate produced by the reaction of the sulfuric acid with the sodium nitrate, controlling said temperatures to produce, by the reaction of the sulfuric acid with the sodium nitrate, gases, relatively near the feed end of the path, adapted to yield on condensation relatively strong nitric acid and gases, relatively near the discharge end of the path, adapted to yield on condensation relatively low strength nitric acid, and utilizing hot gases from a single source to supply heat to the material in said confined path, conveying a portion of said hot gases into heat exchange relation with said material and by by-passing the remainder, a predominant proportion of the first named portion of gases being conveyed into heat exchange relation with the material relatively near the discharge end of said path.

4. The process of making nitric acid which comprises continuously feeding sodium nitrate, normal sodium sulfate and uncombined sulfuric acid to and along a confined path, subjecting said salts during their travel along said path to agitation and to differential heating varying from a relatively low temperature relatively near the feed end of the path to a relatively high temperature relatively near the discharge end of said path, continuously discharging from said confined path the sodium sulfate admitted thereto and the sulfate produced by the reaction of the sulfuric acid with the sodium nitrate, controlling said temperatures to produce, by the reaction of the sulfuric acid with the sodium nitrate, gases, relatively near the feed end of the path, adapted to yield on condensation relatively strong nitric acid and gases, relatively near the discharge end of the path, adapted to yield on condensation relatively low strength nitric acid, and separately withdrawing gases produced relatively near the feed end of said path and gases produced relatively near the discharge end of said path.

5. The process defined in claim 1 comprising also the regulation of the relative proportions of the separately withdrawn gases by applying suction to the gas outlets and controlling the degrees of suction.

In testimony of which invention, we have hereunto set our hands at Philadelphia, Penna., on this 29th day of July, 1925.

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