

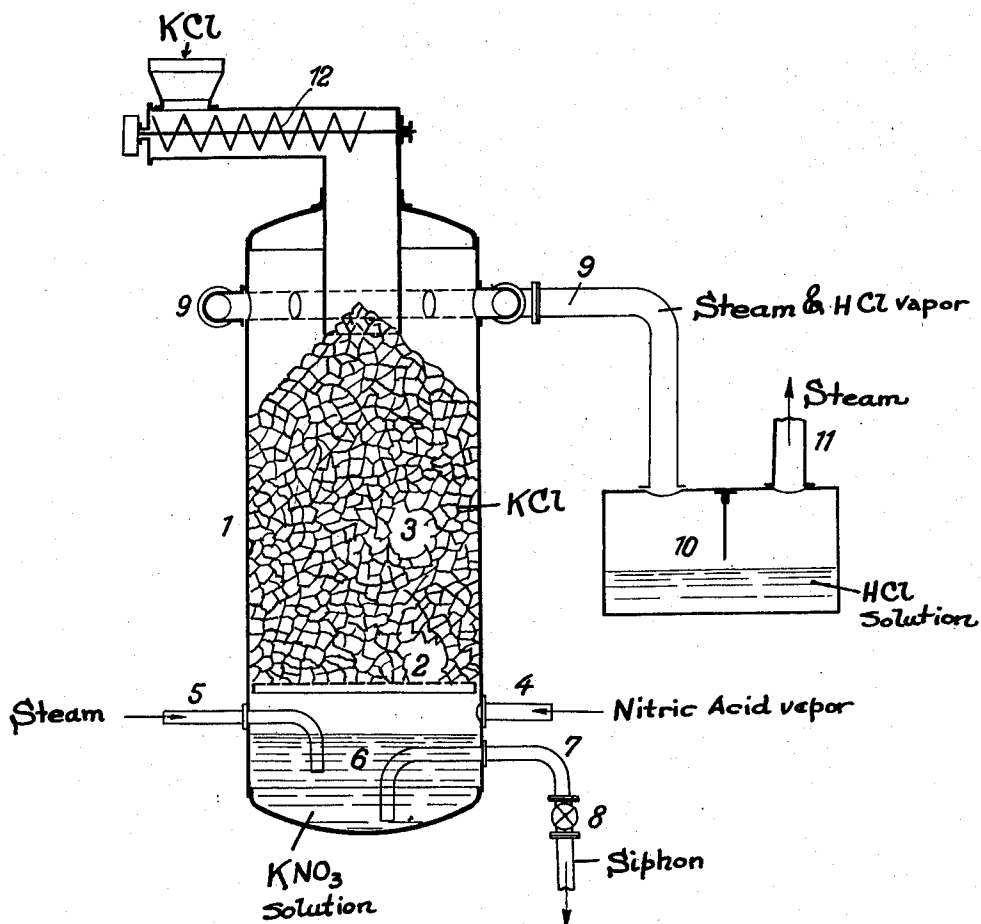
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PROCESS FOR MANUFACTURING NITRATES

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UNITED STATES PATENT OFFICE

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PROCESS FOR MANUFACTURING NITRATES

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The present invention relates to the conversion of chlorides of alkali-forming metals, more particularly of sodium chloride and potassium chloride, into nitrates by treatment with nitric acid.

It is true that it has already been proposed to obtain nitrates in the above manner, for instance by treating solutions of potassium chloride or of sodium chloride with nitric acid, and by crystallizing out the nitrates produced. It has been also attempted to distill off the hydrochloric acid liberated in the process, which however means considerable losses of nitric acid.

It has now been ascertained that chlorides of alkali-forming metals can be easily converted into nitrates by treating these chlorides with vapors of nitric acid or with nitric oxides which are strongly diluted with steam. For the purpose in question there is preferably used an apparatus according to the accompanying drawing.

A tower-shaped container 1 of earthenware or some other acid-proof material, provided at a certain distance from the bottom with a perforated bottom or grate 2 is filled with pieces of potassium chloride 3. Under the grate open several pipe branches. Through the pipe branch 4 are continuously admitted vapors of water-containing nitric acid, and through the pipe branch 5 is continuously admitted slightly superheated steam. The steam and the nitric acid could however be brought together beforehand and introduced through a common pipe.

It has now been ascertained that as the nitric acid vapor enters the potassium chloride charge, potassium nitrate is formed even within the lower layers of the charge. As it is much more soluble in hot water than potassium chloride, the potassium nitrate thus formed will be dissolved much sooner by hot water (from the steam), and the hot solution of almost pure potassium nitrate 6 will collect under the grate 2: it is intermittently or continuously discharged by means of a siphon 7 which is provided with a valve 8. This solution of potassium nitrate is concentrated to such a degree that on cooling it becomes a crystalline paste. By suit-

ably dimensioning the height of the charging vessel 1, which must be adapted to the resistance to passage offered at the time by the charge and determined experimentally, it is possible to ensure that the mixture of steam and hydrochloric acid vapors escaping through 9 will be completely, or practically completely, free from nitric acid or nitric oxides. If the escaping acid vapors are given an opportunity to condense, there will be left already in the first condensing vessel a hydrochloric acid with about 15% HCl, and the escaping steam will be practically free from acid; by raising it to about 130° C., it can be used again in the process, with the addition of fresh steam. This steam here functions so to say as a vehicle, as at first it conveys the nitric acid, then lixiviates the potassium nitrate and finally further conveys the hydrochloric acid. Only as much steam is consumed as required for dissolving potassium nitrate and nitric acid, the remaining steam (65 to 75%) is left in circulation and merely requires always to be heated again to about 130° C.

The process may be rendered a continuous one. The charging with solid potassium chloride may be effected by the well-known combination of a hopper with a worm conveyor 12 or by means of similarly acting auxiliary devices.

As a rule the proceeding must be such that there should be under the grate 2 a mixture of vapors which consists of about one part by weight of nitric acid and ten to fifteen parts by weight of water. It has been found that a temperature of 120–130° C. is very favorable. At this temperature any slight quantities of potassium chloride that may be contained in the solution 6, are decomposed by the nitric acid atmosphere, and on the other hand the risk of the solution 6 retaining free nitric acid, is avoided as at this temperature it already distills off.

This process is not limited to the use of solid potassium chloride. If a mixture of nitric acid and steam of about 130° C. is passed through a solution containing potassium chloride, the whole nitric acid can be separated in this manner, without any percep-

tible losses of nitric acid taking place. This process may likewise be converted into a continuous one, for instance by filling the tower 1 with acid-proof pieces or rings of ceramic material and by causing a more or less concentrated lye containing potassium chloride to trickle down. The rising mixture of nitric acid vapors and steam decomposes this lye in the same way as it does solid potassium chloride. With this method of working, it is true that it is as a rule necessary to have the tower a little higher, and it is moreover advisable to introduce the nitric acid vapors and steam mixture into the bath 6 in order to decompose any potassium chloride that may be contained therein.

In working with salt brine it is advisable to keep the steam as hot as the nitric acid can stand without decomposing, and moreover to protect the reaction tower from loss of heat externally. The quantity of steam can be reduced, for instance to eight parts by weight of steam to one part by weight of nitric acid. Sometimes it is advisable to use for filling the reaction tower, salt in pieces or briquetted, over which the salt brine trickles down. In this way the capacity of the tower is increased, and steam is economized as a consequence.

The hot solution which collects under the charging grate and consists chiefly or exclusively of dissolved nitrates is siphoned off and crystallized whether at rest or in motion. The siphoning can also be done continuously. The remaining mother-lye is either evaporated or, in the event of its still containing chlorides, used again for charging the reaction tower.

The method of working which has been described here with reference to the treatment of potassium chloride, can also be used for the conversion of sodium chloride into sodium nitrate. The process can also be extended to the treatment of crude potassium salts as will be described further on.

The process described may be modified in various ways. Thus for instance it is known that by simply pouring nitric acid over a potassium chloride solution, a crystalline paste is obtained which already contains nearly 80% of the nitric acid bound to potassium. If this crystalline paste is drawn off or centrifuged, a liquid will be left which contains about 20% undecomposed potassium chloride and an acid mixture of 20% nitric acid and 80% hydrochloric acid. In certain cases it may be economical to combine the processes in such a manner that the solution which is separated from the crystalline paste and contains about 20% nitric acid, is carried together with fresh salt lye or pieces of salt, in the opposite direction to the rising nitric acid vapor-steam mixture. In this case however the solution

which contains a mixture of free acids, must be admitted through a separate branch at about the middle of the height of the charging column.

If the working is done with crude potassium salts, the process may be carried out in two ways:

The reaction tower described is charged with solid crude salt or with a solution of crude salt, or with both, for instance by causing a crude salt lye to trickle down over crude salt pieces. If the speed of the rising mixture of nitric acid vapors and steam is low, it is possible to ensure that all the constituents of the crude potassium salts (potassium, sodium, calcium, magnesium) will be converted to a greater or less extent into nitrates. The solution of all these nitrates, collecting under the grate of the reaction tower, can then be mixed in crystallization vessels with fresh crude salt, potassium nitrate being chiefly crystallized out, and the other nitrates formed, being converted back to their chlorides. As a rule it is however preferable to so work that the rising mixture of steam and nitric acid converts only, or chiefly, potassium chloride alone into nitrate. This can be done by coordinating the temperature, concentration and velocity of flow of the nitric acid vapor mixture in such a manner that the dissolving action of this mixture is stronger than the nitrating action. In this way the salt to be treated will be dissolved to a greater extent than nitrated. Consequently in the trickling liquid, partly even before it reaches the grate 2, there takes place already the reaction between any other nitrates carried by it and the potassium chloride that may still remain.

In all these processes, the degree of concentration of the original nitric acid is of little importance as it comes into action only after a strong dilution with steam. It is not therefore absolutely necessary to cause nitric acid in the form of vapors mixed with steam to act on the chlorides to be converted. Diluted nitric acid can be introduced, for instance in the middle of the reaction tower, whilst from the bottom would be supplied only superheated steam, owing to which losses by decomposition of nitric acid will also be avoided. Instead of pure or finished nitric acid, there may also be used suitable nitric oxides with air or with oxygen, that is to say mixtures produced in the burning of atmospheric nitrogen in electric arc furnaces or in the catalytic burning of ammonia. The presence of oxygen or air does not affect the process described. In connections herewith it may however be stated that although dilution of the nitric acid or nitric oxides is not excluded, in connection with the process of this invention, such dilution is not adapted to substitute the

dilution with copious quantities of steam. Experience has shown that nitric acid when brought to reaction with alkali metal chlorides, if used in a concentrated condition or diluted with air, tends to react with the formed hydrochloric acid, so as to liberate chlorine. Thereby the process is made not only uneconomical but above all the hydrochloric acid is spoiled and there results a highly deteriorating effect on the reaction vessels. This drawback can only be avoided by dilution of the nitric acid (or oxides) with copious quantities of steam as taught by this invention.

If it is found that the finished product, in the present case saltpeter, contains some free acid which is chiefly injurious to the durability of the packing, it is advisable to neutralize the free acid by the addition of tiny quantities of lime or alkalies or carbonates. As the nitrates thus produced are chiefly used for manuring, slight admixtures of other salts or of undecomposed chlorides are of no importance.

The economic importance of the present process for agriculture is that it makes it possible to obtain directly such high grade manures as sodium nitrate (Chile saltpeter) and potassium nitrate (potash saltpeter) from their chlorides or brines or from crude salt without any loss of nitric acid.

Where the term "oxides of nitrogen" is used in the appended claims, we mean to comprise the hydrates thereof or in other words the acids directly derived from said oxides as well as the oxides themselves. Furthermore, in the accompanying claims by the term "alkali-forming metals" we mean to include the alkali metals and alkaline earth metals.

What we claim is:—

1. Process of manufacturing nitrates comprising treating chlorides of alkali-forming metals with oxides of nitrogen in the presence of copious quantities of steam.

2. Process of manufacturing nitrates comprising treating chlorides of alkali-forming metals with a mixture of vapors of nitric acid and of steam, the quantity of steam being a multiple by weight of the quantity of the vapors of nitric acid.

3. Process of manufacturing nitrates comprising reacting on pieces of salt comprising chlorides of alkali-forming metals wetted by salt brine with nitric acid in the presence of copious quantities of steam.

4. Process of manufacturing nitrates comprising reacting on crude salt containing chlorides of alkali-forming metals with oxides of nitrogen in the presence of copious quantities of steam.

5. Process of manufacturing nitrates comprising reacting on chlorides of alkali-forming metals with nitric acid, recovering the nitrate formed thereby and treating the

mother liquor in counter-current with a mixture of nitric acid and copious quantities of steam.

6. Process of manufacturing nitrates comprising reacting on chlorides of alkali-forming metals with oxides of nitrogen in the presence of copious quantities of steam and neutralizing the excess acid in the formed nitrate with an alkaline substance.

7. Process of manufacturing nitrates comprising introducing oxides of nitrogen and copious quantities of steam near the bottom of a reaction tower filled with solid chlorides of alkali-forming metals supported on a grate, removing the exhaust gas at the top of the tower and recovering nitrate solution collecting at the bottom of the tower.

8. Process of manufacturing nitrates comprising treating chlorides of alkali-forming metals with oxides of nitrogen in the presence of copious quantities of steam at a temperature above the boiling point of aqueous hydrochloric acid of highest possible concentration.

9. Process of manufacturing nitrates comprising treating alkali metal chlorides with oxides of nitrogen in the presence of copious quantities of steam.

10. Process of manufacturing nitrates comprising treating alkali metal chlorides with a mixture of nitric acid vapors and steam, the quantity of steam being a multiple by weight of the quantity of nitric acid vapors.

11. Process of manufacturing nitrates comprising reacting on pieces of alkali metal chlorides wetted by alkali metal chloride brine with nitric acid in the presence of copious quantities of steam.

12. Process of manufacturing nitrates comprising reacting on crude alkali metal chlorides with oxides of nitrogen in the presence of copious quantities of steam.

13. Process of manufacturing nitrates comprising reacting on alkali metal chlorides with nitric acid, recovering the nitrate formed thereby and treating the mother liquor in counter-current with a mixture of nitric acid and copious quantities of steam.

14. Process of manufacturing nitrates comprising reacting on alkali metal chlorides with oxides of nitrogen in the presence of copious quantities of steam and neutralizing the excess acid in the formed nitrate with an alkaline substance.

15. Process of manufacturing nitrates comprising introducing oxides of nitrogen and copious quantities of steam near the bottom of a reaction tower filled with solid alkali metal chlorides supported on a grate, removing the exhaust gas at the top of the tower, and recovering nitrate solution collecting at the bottom of the tower.

16. Process of manufacturing nitrates comprising treating alkali metal chlorides

with oxides of nitrogen in the presence of copious quantities of steam at a temperature above the boiling point of aqueous hydrochloric acid of highest possible concentration.

6 17. Process of manufacturing nitrates which comprises treating an alkali metal chloride with oxides of nitrogen in the presence of copious quantities of superheated steam.

10 18. Process of manufacturing nitrates which comprises treating an alkali metal chloride with oxides of nitrogen in the presence of copious quantities of superheated steam at a temperature of about 120-130° C.

15 In testimony whereof I affix my signature.
JEGOR ISRAEL BRÖNN.

In testimony whereof I affix my signature.
DR. GEORG FISCHER.

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