To all whom it may concern:

Be it known that I, LUDWIG SAARBACH, a citizen of the German Empire, and a resident of the borough of Manhattan, city, county, and State of New York, have invented a certain new and useful Improvement in Processes of Making Fertilizers, of which the following is a specification.

This invention relates to a process of treating mineral phosphates containing carbonates by exposing them to the action of nitrogen oxides for the purpose of obtaining fertilizers containing nitrates or nitrates, or both, and phosphoric acid in available form.

It has for its object the elimination of the labor and cost of concentrating and separating the nitric acid, nitrates and nitrates obtained by the utilization of the nitrogen of the air by processes hitherto practised, in case these products are intended for use in fertilizers.

I have found that nitrogen oxides (NO, N\textsubscript{2}O\textsubscript{5}, and N\textsubscript{2}O\textsubscript{4}) will in the presence of sufficient quantities of moisture and oxygen, for instance the oxygen of the air, react readily with for example insoluble calcium phosphates, containing calcium carbonate, forming a combination of nitrate or nitrite of lime with phosphoric acid in available condition, which ingredients are excellent plant foods.

The following formula will illustrate a characteristic reaction which may take place in the operation of my process:

\[
\text{Ca}_{3} (\text{PO}_4)_{2} + 3\text{CaCO}_3 + (\text{NO} + \text{NO}_2 + \text{NO}_3) + \text{H}_{2} \text{O} + \text{O}_2 = \text{Ca}_6 (\text{NO}_3)_{2} \cdot 4\text{Ca} \cdot \text{H}_2 \text{O} + \text{CO}_2.
\]

By the use of my process it is therefore possible to obtain a desirable compound fertilizer in one operation, thus obviating the necessity of first bringing the nitrogen compounds obtained from the furnace gases, or other sources of nitrogen oxides, into a more concentrated form.

It must, of course, be understood that the nitrogen oxides which I employ in my process may be produced in any suitable manner, for instance by the electric arc process or by the heat of explosive combustion or by a carbon monoxide flame, etc. It must also be understood that it is exceedingly difficult, if not impossible, to obtain any one of these nitrogen oxides separately from the others, as there is a constant mutation from one of them to another. Thus the nitric oxide (NO) primarily produced in the electric furnace begins to change to nitrogen peroxides (N\textsubscript{2}O\textsubscript{5}) when the temperature of the gas is reduced to about 600° C., taking up oxygen from the air with which it is diluted, and probably also to nitrogen trioxide (N\textsubscript{2}O\textsubscript{3}) (See Metallurgic and Chemical Engineering, Vol. IX, page 196, April, 1911.) Thus when these gases come in contact with the water there may be formed, and undoubtedly is formed in almost all cases, not only nitric acid but also nitrous acid, according to the formula,

\[
\text{SN}_2 + \text{H}_2 \text{O} = \text{HNO}_3 + \text{HNO}_2.
\]

The nitric acid will form nitrates, whereas the nitric acid will form nitrates. Moreover, when the nitrogen peroxides unite with the water to form the nitric acid of the above formulas, there is formed nitric oxide,

\[
\text{SN}_2 + 2\text{H}_2 \text{O} = \text{HNO}_2 + \text{HNO}_3 + \text{H}_2 \text{O}.
\]

which in turn unites with the oxygen of the air to form nitric peroxides for subsequent conversion into nitric acid. It will therefore be understood that my process contemplates the presence of oxygen, preferably that of the air, for its best operation.

My process is of particular value in making possible the working up of low-grade phosphates, particularly those which contain a large percentage of carbonate of lime. According to the method now in use a large quantity of sulfuric acid would be required to make the phosphoric acid available because a large amount of the sulfuric acid would be wasted in decomposing the carbonates, and the finished product would be overloaded with sulfate of lime. By my process these low-grade phosphates can be readily and cheaply converted into a fertilizer comprising two valuable constituents, namely available phosphoric acid and nitrates or nitrites of lime, or both, without the formation of calcium sulfate, a portion of the nitrates or nitrites of lime originating from the decomposition of the carbonate of lime where this substance is present.

According to the character of the phos- phoric raw material used, the fertilizer obtained by my process will contain variable amounts and proportions of phosphoric acid, nitrates or nitrites, or both. These may be mixed with other fertilizers or potash salts to suit the requirements of different soils or crops.
I claim:
1. The process of manufacturing a fertilizer, which consists in treating low grade phosphate minerals containing a carbonate, with nitrogen oxid in the presence of moisture, substantially as and for the purpose described.
2. The process of manufacturing a fertilizer, which consists in treating minerals which contain calcium phosphate and calcium carbonate, with nitrogen oxid in the presence of moisture, substantially as and for the purpose described.

In witness whereof, I have hereunto set my hand in the presence of two subscribing witnesses.

LUDWIG SAARBACH.

Witnesses:
JOHN A. FERGUSON,
JOHN A. KHELENBECK,