

UNITED STATES PATENT OFFICE.

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PROCESS OF MAKING SUPERPHOSPHATES.

No Drawing.

Application filed May 20, 1922. Serial No. 562,557.

To all whom it may concern:

Be it known that I, HYLEMAN ALISON WEBSTER, a citizen of the United States, residing at Columbia, in the county of Maury and State of Tennessee, have invented certain new and useful Improvements in Processes of Making Superphosphates; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to a process of making superphosphate and double superphosphate from low grade phosphate rock, and has for its object to provide a procedure which will be more efficient and less costly than those heretofore proposed.

With these and other objects in view, the invention consists in the novel steps and combinations of steps constituting the process, all as will be more fully hereinafter disclosed and particularly pointed out in the claims.

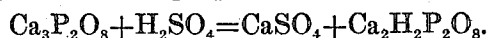
In order that the precise invention may be the more clearly understood, it is said: According to the prior processes of making what is commercially known as super phosphates from phosphate rocks, it has been customary to employ relatively high grade Tennessee ores, or those carrying say 72% tri-calcium phosphate $\text{Ca}_3\text{P}_2\text{O}_8$, and with not more than 5% of iron and aluminum oxides combined. These processes also require for each 1000 pounds of rock about 1000 pounds of sulphuric acid, H_2SO_4 , having a strength of say 52° Bé. In the case of Florida proosphate rock, a somewhat lower grade is used owing to the fact that the iron and aluminum oxides present are somewhat less, and therefore a less quantity of acid may be used, or say about 900 pounds of acid to each 1000 pounds of rock.

These relatively high grade phosphate ores, however, are getting more and more scarce, and the cost of acid phosphate is consequently getting higher and higher.

In carrying out this invention, on the other hand, I may proceed as follows: I take a relatively low grade of phosphate rock or phosphorite, having, say, 65% of tri-calcium phosphate and as high as, say, 8% of iron and aluminum oxides, and grind the same very fine, or to such a degree that, say, 95% of it will pass a screen having 200 meshes to the linear inch, so that all the par-

ticles of the rock will have substantially the same size. To this finely divided rock is added a quantity of sulphuric acid, if super phosphate is to be made, and of phosphoric acid, H_3PO_4 , if double super phosphate is desired. The H_2SO_4 may be of say 52° Bé. strength and of a quantity less than that theoretically required to convert all the tri-calcium phosphate present into mono-calcium phosphate. The strength and relative quantity of the phosphoric acid may be the same as that of the sulphuric or the H_3PO_4 may be used in quantities as low as 400 pounds of acid to each 1000 pounds of rock, depending upon the grades of the final product desired. That is, in the case of H_2SO_4 , for each 1000 pounds of finely divided low grade rock, I may use, say, 750 pounds of sulphuric acid of 52° Bé.

As a consequence of this deficiency of acid and of this unusually fine subdivision of the rock, the resulting product is found to be a mixture of di-calcium phosphate $\text{Ca}_2\text{H}_2\text{P}_2\text{O}_8$ and of mono-calcium phosphate, $\text{CaH}_4\text{P}_2\text{O}_8$, with a greater quantity of the former present than of the latter, provided the mixing of the ingredients is properly carried out. The importance of a proper mixing will be appreciated when it is said: Theoretically, available phosphoric acid, P_2O_5 , can be produced with less than one half the quantity of sulphuric acid ordinarily used, as shown by the following equation:



That is, 310 pounds of tri-calcium phosphate is theoretically required to only 98 pounds of concentrated sulphuric acid, but in practice it is well known that much more than double this quantity of acid is required, due to the physical difficulties that are encountered, which involve the action of the acid unequally on different portions of the mass when it is not ground finer than for 90% of it to pass through a 100 mesh screen.

In other words, the prior processes place the rock ground to 60 to 100 mesh in a mixer, and they feed acid gradually thereto, whereupon the acid first attacks the finer particles, and liberates water which accumulates. This water dilutes the oncoming acid which now only has the coarser particles to attack, and the result is a very slow and imperfect conversion of the insoluble phosphate into the soluble form, all as is well known. Furthermore, that portion of the acid which

reacts upon the smaller particles of rock, combines with the calcium present, so completely as to produce phosphoric acid, H_2PO_4 , which is a much weaker acid than sulphuric, and also is much slower in acting upon the coarser particles present.

In mixing the acid and rock according to this invention, on the other hand, a stream of rock powder proportional in quantity to the amount of acid used is fed into the mixer along with a stream of acid, with the result that the plows or blades of the mixer effectually bring the two constituents together into the most intimate contact. This kind of mixing action constitutes an important feature of this invention, as a little consideration will show. That is, if one attempted to get an intimate contact between the acid and powdered rock, by first placing the rock powder in a mixer and then introducing a stream of acid, the rock powder would speedily form into ball like masses containing no acid in the center, and the same troubles, due to imperfect reactions would result as in the prior procedures. In such cases, the centers of these ball like masses could not be attacked by the acid until the balls were broken up, and then the acid would be in the weakened or dilute condition above mentioned, as being the case in the prior processes. In other words, my finished product notwithstanding my finer subdivision of the rock, would not under such procedure be much better than the product of said prior procedures. But when the acid and rock powder are brought together in two streams of predetermined proportions, as above indicated, each portion of the acid acts upon a fresh portion of the rock powder, which is not the case in the prior processes. Further, it is found that the coarser particles of this said rock powder will readily pass a 150 mesh screen, so that the fresh acid acts upon them as completely and as satisfactorily as it does upon the average size of the finer particles of the prior processes. The result is, I find from operations on a commercial scale, that I can successfully treat high grade rock with a quantity of acid very much less than has heretofore been thought possible, and I can successfully treat low grade rock that is ordinarily considered impossible commercially.

This successful treatment of low grade rock enables me to produce an acid phosphate of a grade as high as that produced from average high grade rock, because I add less acid and therefore do not lessen the percentage of phosphoric acid in the phosphate to the same degree as heretofore. With high grade rock, my process, of course, raises the percentage of the phosphoric acid content of the product above that ordinarily obtained by the prior processes.

In addition to this, my process provides in all cases a more perfect physical condition for the product than heretofore. That is, in the prior processes the product due to the above mentioned imperfect reactions, is often found to be pasty or gummy, even after prolonged storage, and will not readily pass through the drills used in applying fertilizers to the soil. The product resulting from my process, on the other hand, is entirely free from these objections owing to the more perfect reaction between the rock and the sulphuric acid, as well as to the absence of free acids and a very low content of free water.

Another reason for a better physical condition of my finished product resides in the fact that since my reactions are more complete, more heat is liberated, the mass is heated to a higher degree, more of the water present is evaporated, and a drier product is had.

While the temperature of the reacting mass is lowering from, say, $250^{\circ} F.$ to about $212^{\circ} F.$ the material is mechanically elevated and aerated to eliminate any water vapor that may be present. In this way, I get rid of the necessity of the tedious drying by ordinary methods, and am enabled to ship the product within, say, two weeks time instead of having to wait a period of from 90 to 100 days, as heretofore.

In addition to the foregoing, the escape of the water vapor in the manner above described at once leaves any free acids that may be present in the mass in a more concentrated condition than in the prior procedures. Accordingly, any phosphates that have not been acted upon are at once attacked by these free acids and thus are they all eliminated from the mass, and further hygroscopic troubles due to them are avoided.

It will now be clear that by following the above disclosure, I am enabled to accomplish the following advantageous results:

(a) One is enabled to utilize commercially lower grades of the phosphorite than has heretofore been customary;

(b) One is enabled to employ a less quantity of sulphuric and of phosphoric acid than heretofore;

(c) One is enabled to produce a finished salable product in much less time than heretofore;

(d) The finished product is not sticky or gummy as in the prior products, and does not become so when stored in any climate, due to an absence of free acids and abnormally small quantities of water and mono-calcium phosphate. That is to say, in the prior products, there is usually some free sulphuric acid present, as well as an excess of mono-calcium phosphate, both of which will hold the water that has not been driven

off. In my product, on the other hand, there is no free sulphuric present, the mono-calcium phosphate is present in a less quantity than is the di-calcium phosphate, and the water that was present has been almost eliminated.

It is obvious that those skilled in the art may vary the details of the procedure without departing from the spirit of the invention, and therefore I do not wish to be limited to the foregoing disclosure, except as may be required by the claims.

What is claimed is:

1. The process of making super phosphates which consists in finely subdividing phosphate rock to form a powder; flowing said powder into a mixer; flowing an acid into said mixer simultaneously with said powder, the weight of said acid being less than that theoretically required to convert all the tri-calcium phosphate present into mono-calcium phosphate; mixing said powder and acid into a mass; and eliminating free water present in the mass, substantially as described.

2. The process of making super phosphate which consists in forming a powder from phosphorite; flowing said powder in a predetermined quantity into a mixer; simultaneously delivering a predetermined proportional quantity of acid to said mixer, the weight of said acid being less than that theoretically required to convert all the tri-calcium phosphate present into mono-calcium phosphate; and intimately mixing said acid and powder as they enter said mixer, substantially as described.

3. The process of making super phosphate which consists in forming a powder from phosphorite; flowing said powder in a predetermined quantity into a mixer; simultaneously delivering a predetermined proportional quantity of acid to said mixer, the weight of said acid being less than that theoretically required to convert all the tri-calcium phosphate present into mono-calcium phosphate; intimately mixing said acid and powder as they enter said mixer; and aerating the resulting mass to free it from water, substantially as described.

4. The process of making super phosphate which consists in forming a powder from phosphorite; flowing a stream of said powder into a mixing device; simultaneously flowing a stream of acid into said device, the quantity of said powder having a weight more than one and one fourth that of said acid when diluted to 52° Baumé; and eliminating free water present in the mass, substantially as described.

5. The process of making super phosphates which consists in forming a powder from phosphorite; flowing a stream of predetermined proportions of said powder into a mixing device; simultaneously flowing a stream of predetermined proportions of acid into said device, the weight of said acid being less than that theoretically required to convert all the tri-calcium phosphate present into mono-calcium phosphate; mixing said acid and powder together to form said super phosphate; moving the mass thus produced; and aerating said mass at a temperature above 212° Baumé to remove a portion of the free water present, substantially as described.

6. The herein described new article of manufacture consisting of a mixture of mono-calcium phosphate and di-calcium phosphate, the latter being present in greater quantity than the former; and said mixture being devoid of free acids and of sticky constituents, substantially as described.

7. The process of making superphosphate which consists in forming a powder of phosphorite; flowing a stream of said powder into a mixing device; simultaneously flowing a stream of acid into said device, the quantity of said powder having a weight in excess of the weight of the acid when diluted to 52° Bé.; maintaining the prescribed proportions of phosphorite powder and acid throughout the mixing procedure; creating a temperature sufficiently high to free the mass of water present; and aerating the mass at a temperature sufficiently high to liberate the remaining excess water as vapor, substantially as described.

In testimony whereof I affix my signature.

HYLEMAN ALISON WEBSTER.