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# PROCESS FOR THE DISINTEGRATION OF CRUDE PHOSPHATES WITH MINERAL ACIDS

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The invention to which the following specification relates is the process for the disintegration of crude phosphates, particularly uncalcined crude phosphates, with mineral acids.

When disintegrating crude phosphates, particularly uncalcined crude phosphates with 50 to 60% nitric acid, such as is obtained by burning ammonia on a large commercial scale, it is a known fact that, in the case of discontinuous working methods, considerable losses in nitrogen occur, which amount to 4 to 6% of the quantity of $HNO_3$ employed. Furthermore the losses in nitrogen increase considerably when the disintegration is carried out with both nitric acid and sulphuric acid, the losses becoming the greater the higher is the concentration of the sulphuric acid and the greater is its proportion of the total quantity of disintegrating acid.

Continuous processes are known for disintegrating raw phosphates with nitric acid alone or in combination with sulphuric acid or phosphoric acid or both together, in which, by suitable measures, the above mentioned high nitrogen losses are reduced. This is effected, on the one hand, by avoiding the detrimental increase in temperature of the reaction mixture by cooling and, on the other hand, by carrying out the disintegration while maintaining a certain quantitative proportion, for example, in a large available volume of disintegrating mixture ready for use.

In the known continuous methods of operation the nitrogen losses are certainly reduced as compared with the discontinuous methods of operation but, as the inventors have discovered, the continuous methods of operation are open to the serious objection that the nitric acid alone or mixed with sulphuric acid is fed, undiluted, at the same time with the crude phosphates to the stock solution of the disintegrating vessel or—if there are several such vessels—in the first or the second such. This causes streams of concentrated acid to form in the reaction mixture which, as streams of increased temperature, immediately exert an oxidizing effect on the components of the crude phosphate with the result that increased nitrogen losses are caused.

A continuous process for disintegrating crude phosphates, and in particular uncalcined crude phosphates with nitric acid together with sulphuric acid or phosphoric acid or both together, has now been discovered which, while avoiding the last mentioned disadvantages, enables the nitrogen losses to be still further reduced to 0.2 to 0.5% of the quantity of $HNO_3$ employed. The process according to the invention is carried out in several, preferably 2 or 3 agitator containers arranged in sequence, through which the disintegration mixture flows. Each successive container is, according to working requirements, connected by return pipe lines to one or more of the preceding containers, so that it is possible to return such a quantity in counterflow into the containers as actually desired.

The essential feature of the present invention consists in that the crude phosphate is introduced into the first or second container or both such containers, whereas the quantity of nitric acid required for disintegrating the crude phosphate is, according to the rate of the crude



phosphate feed, introduced in the return flow between the last or one of the preceding containers and the first or second container, or both such containers. The chief effect is, as has already been mentioned above, that the nitrogen losses are reduced to a minimum quantity. This is obviously due to the fact that the concentrated nitric acid comes into contact with the crude phosphate only after considerable dilution and mixture with the disintegrating solution which consists chiefly of phosphoric acid, calcium nitrate and water, and possibly also of free nitric acid and calcium sulphate in suspension.

When sulphuric acid is used in combination with nitric acid for disintegrating the crude phosphate, the procedure according to the invention preferably consists in feeding the sulphuric acid separately or mixed with the nitric acid into the return flow between the last or one of the later containers and the first or second container, or both such containers. However, the procedure may be such that the sulphuric acid is introduced into the first container or second container, or both such containers directly either alone or mixed with the crude phosphate. The addition of the nitric acid, if it is not mixed with the sulphuric acid, is then carried out in the manner above described.

Furthermore, when phosphoric acid is used in combination with nitric acid for the disintegration of the crude phosphate, the procedure may consist in feeding the phosphoric acid, if desired mixed with the nitric acid, to the return flow between the last or one of the later containers and the first or the second container, or both such containers. However, the phosphoric acid, either alone or mixed with the crude phosphate might also be fed directly into the first or second container, or both such containers. The introduction of the nitric acid, if it is not mixed with the phosphoric acid, then takes place in the manner above described.

If all three of the acids mentioned are used for the disintegration of the phosphate, the sulphuric acid is preferably first mixed with the phosphoric acid and the mixture obtained is then added to the return flow between the last or one of the later containers and to the first or second container, or both such containers. The mixture may also be introduced directly into the first or second container or both such containers. In this case the introduction can also take place mixed with the crude phosphate. The addition of the nitric acid, if desired mixed with the sulphuric acid or/and phosphoric acid, is carried out in the manner above.

Instead of feeding the above mentioned mixtures containing crude phosphate and sulphuric acid, crude phosphate and phosphoric acid or crude phosphate, sulphuric acid and phosphoric acid directly into the first or the second container, the reaction products obtained from the above-mentioned mixtures can be added directly to the first or to the first two containers.

The quantity of disintegration mixture fed per unit of time into the return flow depends upon the kind, concentration and quantity of disintegrating acid fed per unit of time. Regarding the desired dilution and rapid mixture of the disintegrating acid which it is desired to attain, this is generally greater the higher the concentration and the greater is the quantity of disintegration acid fed per unit of time. As the fore-mentioned factors depend in every case upon the composite fertilizer to be produced from the disintegration mixture and there are many different kinds of composite fertilizers on the market, according to the invention the quantity of disintegration mixture fed per unit of time into the return flow can be varied within a wide range in the process.

If for example, it is desired to produce a composite fertilizer containing 18% N and 18% $P_2O_5$ or 12% N, 12% $P_2O_5$ and 20% $K_2O$ by ammoniating the disintegra-

tion mixture obtained by the disintegration of crude phosphate with nitric acid, sulphuric acid and phosphoric acid and by the appropriate addition of potash salt to the ammoniating product, the quantity of disintegration mixture fed to the return flow per unit of time preferably amounts to

9 to 18 times the quantity of $HNO_3$ (anhydrous) per unit of time

80 to 160 times the quantity of $H_2SO_4$ (anhydrous) per unit of time

40 to 80 times the quantity of $H_3PO_4$ (anhydrous) per unit of time

the concentration of the nitric acid used being 56%, that of the sulphuric acid 80% and that of the phosphoric acid 69%.

The temperature of the disintegrating mixture is, according to the invention, maintained at 50° to 70° C., without the introduction of special cooling measures. It can, however, also be lowered to 20° to 50° C. by suitable means, if the calcium fluoride is to remain unchanged.

The foam formation, such as is known to occur when disintegrating uncalcined crude phosphates, is effectively suppressed in the process according to the invention by suitable measures, for example, by the employment of intensive agitators, preferably in the first or in the first and second containers, also by using foam centrifuges, built-in units and the like, without the intensive agitation causing a prohibitive increase in nitrogen losses. Moreover, the turbulence and rapid mixture produced in the reaction mixture by the intensive stirring, furthers the conversion of the crude phosphate by the disintegrating acid.

What we claim is:

1. In a process for the disintegration of crude phosphates with a mixed acid containing nitric acid and at least one acid from the group consisting of sulphuric acid and phosphoric acid by agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the later vessels to the initial vessels, and continuously feeding crude phosphates to the initial vessels, the method of preventing nitrogen losses which comprises continuously adding fresh mixed acid above identified to the returning mixture before said mixture reaches the initial vessels.

2. In a process for the disintegration of crude phosphates with a mixed acid containing nitric acid and at least one acid from the group consisting of sulphuric acid and phosphoric acid by agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the last vessel to the first vessel, and continuously feeding crude phosphates to the initial vessel, the method of preventing nitrogen losses, which comprises continuously adding fresh mixed acid above identified to the returning mixture before said mixture reaches the first vessel.

3. In a process for the disintegration of crude phosphates with a mixed acid containing nitric acid and at least one acid from the group consisting of sulphuric acid and phosphoric acid by agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the later vessels to the initial vessels, and continuously feeding crude phosphates and fresh sulphuric and phosphoric acids to the initial vessels, the method of reducing the nitrogen losses, which comprises continuously adding fresh nitric acid to the returning mixture before said mixture reaches the initial vessels.

4. In a process for the disintegration of crude phosphates with a mixed acid containing nitric acid and at least one acid from the group consisting of sulphuric acid and phosphoric acid by agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the later vessels to the initial vessels, and continuously feeding crude phosphates mixed with fresh sulphuric and phosphoric acids to the initial vessels, the method of reducing the nitrogen losses, which comprises continuously adding fresh nitric acid to the returning mixture before said mixture reaches the initial vessels.

5. In a process for the disintegration of crude phosphates with a mixed acid containing nitric acid and at least one acid from the group consisting of sulphuric acid and phosphoric acid by agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the last vessel to the first vessel and continuously feeding crude phosphates and fresh sulphuric acids to the first vessel, the method of reducing the nitrogen losses, which comprises continuously adding fresh nitric acid to the returning mixture before said mixture reaches the first vessel.

6. In a process for the disintegration of crude phosphates with a mixed acid containing nitric acid and at least one acid from the group consisting of sulphuric acid and phosphoric acid by agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the last vessel to the first vessel, and continuously feeding crude phosphates mixed with fresh sulphuric acid and phosphoric acids to the first vessel, the method of reducing the nitrogen losses, which comprises continuously adding fresh nitric acid to the returning mixture before said mixture reaches the first vessel.

7. The process for the disintegration of crude phosphates with a mixed acid consisting of nitric acid and sulphuric acid which consists of agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the later vessels to the initial vessels, continuously adding fresh nitric acid and sulphuric acid to the returning disintegration mixture and continuously feeding crude phosphates to the initial vessels.

8. The process for the disintegration of crude phosphates with a mixed acid consisting of nitric acid and sulphuric acid which consists of agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the last to the first vessel, continuously adding fresh nitric acid and sulphuric acid to the returning disintegration mixture and continuously feeding crude phosphates to the first vessel.

9. The process for the disintegration of crude phosphates with a mixed acid consisting of nitric acid and sulphuric acid which consists of agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the last to the first vessel, continuously adding fresh nitric acid to the returning disintegration mixture and continuously feeding fresh sulphuric acid and crude phosphates to the initial vessels.

10. The process for the disintegration of crude phosphates with a mixed acid consisting of nitric acid and sulphuric acid which consists of agitating the crude phos-

phates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the last to the first vessel, continuously adding fresh nitric acid to the returning disintegration mixture and continuously feeding crude phosphates mixed with fresh sulphuric acid to the initial vessels.

11. The process for the disintegration of crude phosphates with a mixed acid consisting of nitric acid and sulphuric acid which consists of agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the last to the first vessel, continuously adding fresh nitric acid to the returning disintegration mixture and continuously feeding fresh sulphuric acid and crude phosphates to the first vessel.

12. The process for the disintegration of crude phosphates with a mixed acid consisting of nitric acid and sulphuric acid which consists of agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the last to the first vessel, continuously adding fresh nitric acid to the returning disintegration mixture and continuously feeding crude phosphates mixed with fresh sulphuric acid to the first vessel.

13. In a process for the disintegration of crude phosphates with a mixed acid consisting of nitric acid and phosphoric acid by agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the later vessels to the initial vessels, and continuously feeding crude phosphates to the initial vessels, the method of reducing the nitrogen losses which comprises continuously adding fresh nitric acid and phosphoric acid to the returning mixture before said mixture reaches the initial vessels.

14. In a process for the disintegration of crude phosphates with a mixed acid consisting of nitric acid and phosphoric acid by agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the last to the first vessel, and continuously feeding crude phosphates to the first vessel, the method of reducing nitrogen losses which comprises continuously adding fresh nitric acid and phosphoric acid to the returning mixture before said mixture reaches the first vessel.

15. In a process for the disintegration of crude phosphates with a mixed acid consisting of nitric acid and phosphoric acid by agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the last to the first vessel, and continuously feeding fresh phosphoric acid and crude phosphates to the initial vessels, the method of reducing the nitrogen losses which comprises continuously adding fresh nitric acid to the returning mixture before said mixture reaches the initial vessels.

16. In a process for the disintegration of crude phosphates with nitric acid together with phosphoric acid by agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the last to the first vessel, and continuously feeding crude phosphates mixed with fresh phosphoric acid to the initial vessels, the method of reducing the nitrogen losses which comprises continuously adding fresh nitric acid to the returning mixture before said mixture reaches the initial vessels.

17. In a process for the disintegration of crude phosphates with a mixed acid consisting of nitric acid and phosphoric acid by agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the last to the first vessel, and continuously feeding fresh phosphoric acid and crude phosphates to the first vessel, the method of reducing the nitrogen losses which comprises continuously adding fresh nitric acid to the returning mixture before said mixture reaches the first vessel.

18. In a process for the disintegration of crude phosphates with a mixed acid consisting of nitric acid and phosphoric acid by agitating the crude phosphates with a solution of said acids in the disintegration mixture in a sequence of connected vessels through which said mixture is passed continuously, continuously returning a portion of said mixture from the last to the first vessel, and continuously feeding crude phosphates mixed with fresh phosphoric acid to the first vessel, the method of reducing the nitrogen losses which comprises continuously adding fresh nitric acid to the returning mixture before said mixture reaches the first vessel.

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