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PROCESS FOR SIMULTANEOUS PRODUCTION OF AVAILABLE PHOSPHORIC ACID AND AVAILABLE LESS COMMON ELEMENTS

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This invention relates to improvements in the manufacture of phosphatic fertilizers, and particularly to fertilizers which have in mixture, a proportion of one or more of the less commonly used elements such as manganese, zinc, copper and magnesium, etc.

It is only within the last few years that the agronomic value of these less commonly used elements, of which manganese may be considered an example, has been investigated, and although it has been proven that manganese plays an important part, either directly or catalytically, as a fertilizing element, antiseptic, anticryptogamis, accelerator of germination and maturation, and in increasing the yield and quality of the crop, little or nothing has been done in the way of developing this phase of the fertilizing industry, except to purchase the manganese in plant-available form, generally as a by-product of some phase of the manganese industry, and transport it to the fertilizer manufactory, mixing it directly with the available phosphatic fertilizer.

The present invention has for its general object the provision of a wet process for the simultaneous production, in a single reaction, of a mixture of available phosphoric acid having available compound or compounds of manganese or other of the aforementioned less commonly used fertilizing elements.

Other objects of the invention will appear as the following description of the process unfolds.

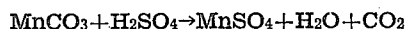
The present invention has its inception in the similarity of the reactions for producing super-phosphate and for obtaining of plant-available manganese compounds.

Those manganese compounds which may be looked to as source materials, either occur as natural products or as the by-products of industry, among which are manganese phosphate (mineral triplite or triploidite), manganese carbonate, manganese oxides and by-product sludge such as of the well known Parker rust-proof process, in which the manganese occurs as a phosphate.

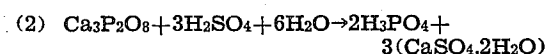
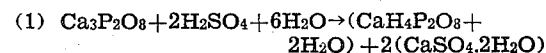
In general, it may be stated that it is not possible to utilize many of the impure manganese ores, manganese bearing slags, or other insoluble manganese compounds without previous treatment with acids to convert the insoluble manganese into soluble manganese, available to plants. None of the natural occurring manganese materials, insofar as they have been tested, have given any appreciable response in combating the symptoms of manganese deficiency in plants.

Up to the present time it is found that manganese sulphate is the cheapest as well as the

most advantageous plant-available compound of manganese, and in general, the natural and by-product compounds of manganese may be converted into the sulphate, sulpho-phosphate, or other similar complexes, by the simple reaction involved in treating said compounds with sulphuric acid. In illustrating this invention, manganese carbonate or rhodochrosite has been selected as the optimum manganese source compound. The reaction of treating this compound with sulphuric acid is illustrated as follows:



The common reaction involved in making super-phosphate from phosphatic rock is illustrated in the two equations:



Whether reaction (1) or (2) takes place, depends upon the proportion of volume of sulphuric acid used, or the strength of the same. In the first instance, an available phosphatic compound primarily in the form of monocalcium phosphate is formed; while in Equation (2) free phosphoric acid is formed. Incidental to both reactions is calcium sulphate.

The significant analogy of these reactions to the reaction for the production of manganese sulphate is that it involves merely the conversion of the source material into the plant-available compound by the addition of sulphuric acid to the manganese or the phosphatic compound.

This analogy gave rise to the concept of producing the super-phosphate as well as the available manganese sulphate, sulpho-phosphate, or other similar complexes simultaneously and in a single reaction by first mixing the proper proportions of phosphatic material, such for example, as phosphate rock and the manganese compound, such as rhodochrosite, and adding the proper quantity of sulphuric acid to complete the combined reaction.

While the prime purpose in combining the two reactions was in the interest of economy, in dispensing with the necessity of purchasing the manganese sulphate at a distant point of production and of conserving factory space, materials and labor, the invention accomplished far more than was expected, since it produced a mixed fertilizing compound which is superior in

its physical characteristics to any mixture produced by separate and distinct reactions.

In the ordinary manufacture of super-phosphate, as soon as the sulphuric acid has been mixed with the ground or pulverized phosphatic material, the mixture is run into an acid-proof receptacle where the principal reactions are permitted to take place. Considerable heat is developed, accompanied by the escape of various gases incident to the reaction and dependent upon the nature of the impurities which the mixture may contain. As the reaction progresses, the mass becomes stiff and finally solidifies, forming a cake. This cake is characterized by a certain degree of "honey-comb" or porosity, the extent and fineness of which affects the subsequent steps of the process and determines, in a measure, the value and perfection of the final product. After the mass has solidified, the cake is broken up, dried and then powdered in a disintegrating mill. If the "honeycomb" is of fine texture, the pulverizing of the fertilizer is facilitated and the uniformity of the pulverized product is enhanced. If, on the other hand, the "honey-comb" is coarse or non-uniform, or the cake unduly hard, the grinding is more difficult and the final product is less perfect.

When the manganese compound and phosphatic rock are first mixed and treated together with sulphuric acid, the presence of the manganese compound in the mixed mass produces an optimum condition of "honey-comb" and a friability of the cake which facilitates the subsequent pulverization.

Furthermore, the simultaneous reaction of the sulphuric acid upon the manganese compound and the phosphatic rock tends to inhibit the "reversion" of the super-phosphate.

Example No. 1

A mixture was made of:

	Grams.
Phosphate rock—31.25% P_2O_5	950
Manganese carbonate—44.69% Mn.....	160
Sulphuric acid—50° Bé. x 60° F.....	1150

in which by analysis the proportion of manganese is 3.58% by weight of the reaction mixture. On account of the evolution of carbon dioxide from the manganese carbonate, it was necessary to add the sulphuric acid more slowly to avoid excessive frothing of the mix than would have been the case in the manufacture of the super-phosphate per se; otherwise, mixing conditions would be considered ideal and after aging of the mass, an unusually fine "honey-comb" was developed.

It is conceivable that the phosphatic and manganese compounds in water- or citrate-insoluble form may be obtained already in mixture as a by-product of industry, as for instance, the by-product sludge from the Parker rust-proofing process, which sludge is a mixture of iron and manganese phosphates. By simple treatment of this sludge with sulphuric acid, the phosphatic and manganese compounds are in one and the same reaction transmuted into plant-available compounds as per the following:

Example No. 2

	Grams
Parker sludge—29.72% P_2O_5 =10.70% Mn.	1500
Sulphuric acid—50° Bé. x 60° F.....	650

in which by analysis the proportion of manganese is 8.03% by weight of the reaction mixture.

The mixing conditions were somewhat difficult on account of the stiff plastic condition of the mix, there was no evolution of gas and after a setting period of twenty-four hours, the eventuating product was hard and cement-like with heavy density and which could be satisfactorily ground in an impact mill. While quality of the "honey-comb" was not optimum, the economies made possible by the utilization of the sludge bring the process within the purview of commercial practicability.

Natural or chemically produced compounds of these less common elements possessing the phosphate radical, in forms not readily available as plant foods, may be treated similarly Example No. 2, which describes reacting conditions with Parker by-product sludge.

It will be understood that while the above examples involve the employment of a manganese compound in mixture with the phosphate, there are other less commonly used elements besides manganese, which have been found to have agronomic value when presented to the soil in plant-available form and which can be substituted in the above reactions without transcending the scope of the invention.

What I claim is:

1. Process for the simultaneous production in a single reaction of a mixed fertilizer of available phosphoric acid, and available compounds of elements in the following group, manganese, zinc, copper and magnesium, comprising mixing phosphate rock and a carbonate of an element or elements selected from the said group in which carbonate or carbonates the content of the said selected element or elements is sufficient to give a proportion by weight of said element or elements of 3.58% of the reaction mixture, and treating the mixture with a re-agent commonly effective in combining both constituents of the mixture into plant available compounds.

2. Process for the simultaneous production in a single reaction of a mixed fertilizer of available phosphoric acid, and available compounds of elements in the following group: manganese, zinc, copper and magnesium, comprising mixing phosphate rock and a carbonate of an element or elements selected from the said group in which carbonate or carbonates the content of the said selected element or elements is sufficient to give a proportion by weight of said element or elements of 3.58% of the reaction mixture, and converting both constituents of the mixture into plant available compounds of the respective elements by treating the mixture with sulphuric acid.

3. Process for the simultaneous production in a single reaction of a fertilizer having available phosphoric acid and an available carbonate of manganese in which the manganese content is sufficient to give a proportion by weight of manganese of 3.58% in the reaction mixture, comprising mixing phosphate rock and carbonate of manganese having the requisite manganese content both in comminuted form, and converting both constituents of the mixture into plant available compounds of the respective elements by treating the mixture with sulphuric acid.

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