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## Neutralization of free acid ( $\text{H}_3\text{P O}_4$ ) in commercial mono-calcium phosphate ( $\text{Ca H}_4 (\text{PO}_4)$ )

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**THESIS**  
FOR  
Bachelor of Science Degree  
in  
Chemistry and Metallurgy

Subject: — Neutralization of Free Acid ( $H_3P O_4$ )  
in Commercial Mono-Calcium  
Phosphate ( $Ca H_4 (P O_4)$ )

J. W. Harris .

1904

H. A. Grine .

## Introduction.-

The manufacture of phosphates, while a comparatively old industry, is one in which advancement in the methods of manufacturing has been slow. Most of the earlier plants worked more or less empirically, not basing their operations on exact chemical principles. In the last ten years however rapid strides have been made towards increasing and improving the products.

Those most extensively manufactured are the sodium compounds, di-sodium and tri-sodium phosphates used in cleansing preparations and in boiler compounds, commercial ortho phosphoric acid ( $H_3PO_4$ ), used in manufacture of C.P. phosphoric acid and as an extract, and the acid salt mono-calcium phosphate  $CaH_4(PO_4)_2$ , used principally as the acid in the manufacture of baking powder.

The last mentioned has received the most attention towards its improvement and purification. The object of this thesis has been a systematic research based on the characteristic properties and reactions of mono-calcium phosphate,  $Ca H_4(PO_4)_2$ , tending towards the development of a process for neutralizing the free phosphoric acid,  $H_3PO_4$  formed during its manufacture.

### Commercial Mono-calcium Phosphate.

Our efforts have not aimed at the production of a chemically pure mono-calcium phosphate, which is obtained only by crystallization from alcoholic solution, but towards the production of this salt free from phosphoric acid, low in insoluble calcium phosphates,  $(Ca H PO_4)$  and  $Ca_3(PO_4)_2$  iron and aluminum phosphates and calcium sulphate.

The acid salt  $\text{CaH}_4(\text{PO}_4)_2$  as previously stated is used extensively in the baking powder industry, its neutralizing power is determined in terms of bi-carbonate of soda,  $\text{NaHCO}_3$  with which it is mixed in proper proportions to form a baking powder. The acid phosphate is used as a substitute for cream of tartar, alum, etc. Free phosphoric acid is the most objectionable impurity because it is generally considered to cause some decomposition in the baking powder, thus lowering its keeping qualities and efficiency.

#### Methods of Manufacture.-

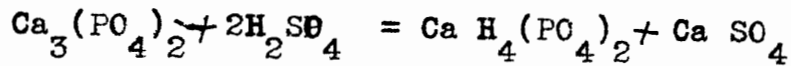
In order to make clearer the application of the improvements suggested by the results of this research, a brief description of present methods is here given.

The raw phosphate materials used in the manufacture of mono-calcium phosphate come mainly from two sources; first from animal charcoal which is a byproduct in the clarification of sugars, being used as a decolorizer. When it loses this decolorizing power it is washed and sold to the phosphate manufacturers. The second source is the amorphous phosphate rock deposits, occurring mainly in southeastern United States. This rock consists approximately of 75%  $\text{Ca}_3(\text{PO}_4)_2$ , the remainder being iron and aluminum phosphates and oxides, silica, carbonates, etc.

The acid used for the extraction of the phosphate from the crude material is commercial  $\text{H}_2\text{SO}_4$ .

The operations here described are those practiced at the Provident Chemical Works of St. Louis, which company has kindly furnished us with the material for carrying out our research.

The animal charcoal previous to grinding is heated in a furnace in order to burn off as much carboniferous matter as possible. It is then milled to pass 60 to 70 mesh. From the mill-room the pulverized material is conveyed to the mixing room where it is charged into lead lined vats, 6-8 feet in width and 12-15 feet in depth, provided with stirring apparatus. The charge is calculated from chemical analysis of animal charcoal. Allowing for the impurities  $H_2SO_4$  is added, as indicated by the following equation:



The charging is done by running into the vats the required amounts of  $H_2SO_4$  and water to make a 1 to 1 solution.

Animal charcoal being added gradually.

Extraction requires from thirty-four to forty-four hours, depending on completeness of extraction desired.

At the end of this time the whole mix is run into a series of leaching vats on the floor below.

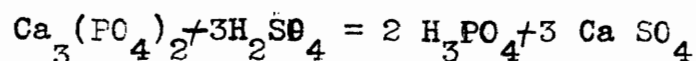
From these the clear liquid drains into troughs leading to a storage vat. After all the phosphate liquid has been leached out the vat residue consisting mainly of  $CaSO_4$ , with small amounts of phosphates are hauled to the dump. After drying these residues are sometimes used as adulterants in fertilizers.

The phosphate liquid of about 9-12 degrees Beaume, is pumped from the storage vat into the boiling or evaporating room, where it is boiled down in lead lined vats to the consistency of a thin paste while hot.

The boiling is done by superheated steam passing through lead coils, at temperatures ranging from 100 degrees C., when boiling begins to 111 degrees, when the paste is withdrawn from vats.

(4)

The liquid before being boiled down is tested for free phosphoric acid, which forms together with the acid salt according to the following equation:



The determination of  $\text{H}_3\text{PO}_4$  is made by titration with NaOH solution, using methyl orange as indicator.

Calcium Carbonate is used for the neutralization of this free acid and the amount required is calculated from the above titration.

The neutralization in this plant is carried on in large revolving lead-lined pans, provided with stirring apparatus. A measured amount of the paste, while still hot is treated with pulverized marble mixed with water. During action of the marble the whole mass is cooled by wind blast from a fan. After action of the marble has ceased starch enough is added to make it friable when dried.

The treatment of rock material, with exception that the rock is not burned before crushing is practically the same.

#### Experimental Work and Results.

According to process just outlined the free  $\text{H}_3\text{PO}_4$  was not completely eliminated. Attempts at complete elimination yield a product below the required acid strength i.e. 100 parts of acid salt shall neutralize 50 parts bicarbonate of soda.

Our first work tending towards an improved process was upon phosphate liquid itself before boiling down. The liquid was treated with pulverized marble until completely neutral, as regards free acid, and filtered from insoluble  $\text{CaHPO}_4$ , which is always formed under such conditions, partially by the action of marble on some of the acid salt and partially

by free acid and marble.

Part of this liquid was boiled down over direct flame and part in a vacuum at a temperature of 50-60 degrees C. The idea of boiling in vacuum was to avoid decomposition of the acid salt into free acid and insoluble  $\text{CaH PO}_4$  which we found took place in boiling down over a direct flame.

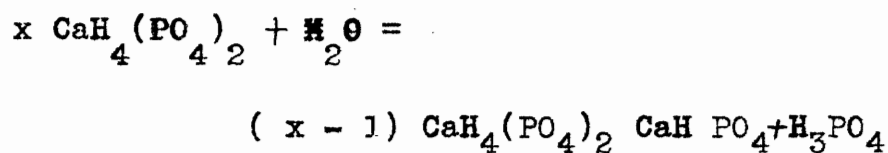
While this tended to reduce greatly the amount of decomposition there still formed sufficient  $\text{H}_3\text{PO}_4$  to required subsequent treatment.

However the results obtained indicate that the substitution of low temperature vacuum evaporators for the boiling vats described in previous process would largely decrease the amount of insoluble  $\text{CaH PO}_4$  and free  $\text{H}_3\text{PO}_4$  formed by high temperatures in vats which cause decomposition of acid salt.

The acid salt being insoluble in alcohol and the free acid being freely miscible in alcohol our attention was next turned to attempts to apply these facts as a means for extracting free acid from the acid salt.

While this gave good results it was found impracticable commercially owing to the cost of the alcohol and the increased danger due to fire.

The next probable solution was suggested by the equation:



(Watts. Vol. 11. Page 109 - Edition 1894)

This shows action of small amounts of water in decomposing the acid salt, when the ratio of the acid salt to water is as one to two hundred. (Same reference as above).

We attempted to apply these facts by avoiding the presence of water when the neutralization was complete. A sample of phosphate liquid from Provident Chemical Works, containing 2.8% of  $\text{H}_3\text{PO}_4$  was evaporated on a

water bath almost to dryness, barely enough moisture remaining to cause action between marble and  $H_3PO_4$ . By this means we were able to completely neutralize the free  $H_3PO_4$  with formation of a comparatively small amount of insoluble  $CaHPO_4$ . Marble was here added dry and not only did it neutralize the free acid but its drying effect was such that by the time the action between the marble and free  $H_3PO_4$  was completed the product was pulverizable in a mortar.

The application of this method would require a mixing machine capable of giving a very intimate mixture of the marble with the acid salt. Many such machines are now on the market.

Besides the great advantage of the small amount of insoluble  $CaHPO_4$  formed by this process two others of considerable importance are also secured namely, the exceedingly small amount of drying required after neutralizing and the avoidance of the use of starch as an aid in drying the product before removal from mixing pans. This would seem to be important as there appears to be some tendency towards decomposition in phosphate baking powders, generally ascribed to the free  $H_3PO_4$  but which might be caused equally by the practice of adding starch to the acid salt while still wet.

The following is a complete analysis of a sample made by the above method

	Percentage.
Free Phosphoric Acid $P_2O_5$	0.00
Acid Phosphate of Ca, $CaH_4(PO_4)_2$	72.74
Insoluble Phosphate of Ca, $CaHPO_4$	9.43
Sulphate of Ca $CaSO_4$	0.95
Phosphates of Iron and Aluminum, $FePO_4$ $AlPO_4$	1.74
Acid Phosphate of Mg . $MgH_4(PO_4)_2$	4.97
Water of Crystallization, moisture, etc.	<u>10.17</u>
	100.00



100 parts neutralize 69.6 parts of sodium bicarbonate cold : 75.2 parts hot.

The magnesium phosphate appearing in the above is accounted for by the fact that the  $\text{CaCO}_3$  used in neutralizing contained a small percentage of  $\text{MgCO}_3$ .

The above method was found inapplicable to bone phosphate liquid (animal charcoal) containing more than 3% free acid, and to that obtained by treatment of rock phosphate which usually runs high in free acid,  $\text{H}_3\text{PO}_4$ .

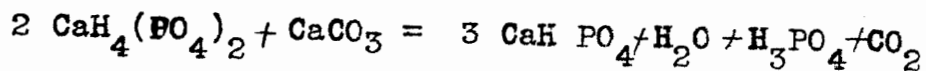
In order to overcome these limitations and to secure a process which could be carried out with but slight additions to present equipment at Provident Chemical Works our research was carried still further on samples of paste made from both bone and rock phosphate.

Attempts to neutralize free  $\text{H}_3\text{PO}_4$  with alkali salts, such as  $\text{Na}_2\text{P}_2\text{O}_7$ ,  $\text{Na}_2\text{HPO}_4$  were found inapplicable: because, while they accomplished the neutralization of  $\text{H}_3\text{PO}_4$  they caused the product to work up wet, owing to their hygroscopic nature. Therefore attempts along this line were abandoned.

Experimenting with the carbonates, results obtained indicate that the action between  $\text{MgCO}_3$  and  $\text{H}_3\text{PO}_4$  was such that the  $\text{H}_3\text{PO}_4$  was neutralized with formation of a very slight amount of insoluble phosphate.  $\text{MgCO}_3$  seems to have little or no action on the acid salt.

The use of  $\text{MgCO}_3$  however when added to wet paste was found to give a wet product very difficult to dry. This was overcome by partially neutralizing the  $\text{H}_3\text{PO}_4$  with dry  $\text{CaCO}_3$ , which partially dried the paste, then completing the neutralization with  $\text{MgCO}_3$ .

By repeated experiment we are led to conclude that the action of marble is forming insoluble  $\text{CaH PO}_4$  at the end of the neutralization is due to the fact that when the free  $\text{H}_3\text{PO}_4$  falls below a certain strength the strength of the acid salt,  $\text{CaH}_4(\text{PO}_4)_2$  is the greater, giving a reaction between the acid salt and the  $\text{CaCO}_3$  forming insoluble phosphates. The following reaction illustrates this point:



The action of  $\text{MgCO}_3$  may be explained by the fact that it is less energetic in its reaction with  $\text{H}_3\text{PO}_4$  than  $\text{CaCO}_3$  and has little tendency to attack the acid salt  $\text{Ca H}_4(\text{PO}_4)_2$  while there is the slightest trace of  $\text{H}_3\text{PO}_4$  present with which to combine.

Results of experiment seem to indicate that  $\text{Mg H}_4(\text{PO}_4)_2$  is almost exclusively formed by the reaction between  $\text{H}_3\text{PO}_4$  and  $\text{MgCO}_3$  in the absence of much water.

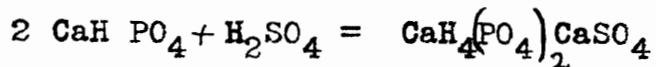
Feeling that there must be some conditions under which marble would give results similar to those obtained by use of  $\text{MgCO}_3$  we carried our research further, obtaining good results in following manner: Some of the bone past as received from Provident Chemical Works was redissolved in water, filtered and the filtrate boiled down until the acid salt commenced to crystallize out in cooling. Pulverized marble moistened with water was then quickly added with energetic stirring until neutral. On testing this we found that it contained a small excess of marble and a small amount of insoluble phosphate.

This product was sprayed with a very dilute solution of  $\text{H}_2\text{SO}_4$  and again stirred. This left the product in a somewhat wet condition.

The removal of this excess of water was accomplished by use of a filter press. It is necessary to remove this water in accordance with the principle

first established concerning the formation of the free  $H_3PO_4$  and insoluble phosphates by the decomposition of the acid salt when heated in the drying room while still containing much water.

When taken from the filter press the product crumbled in the fingers and when dried in the air bath at 60 degrees C. showed to decomposition, being almost entirely soluble in cold water and containing no free acid. A probable explanation for the action of dilute  $H_2SO_4$  may be found by assuming that the following reaction takes place between the insoluble phosphate and  $H_2SO_4$



This assumption was corroborated by treating with dilute  $H_2SO_4$  a sample of acid phosphate, previously made, containing a large excess of insoluble phosphate and running less than 30 in neutralizing strength. After  $H_2SO_4$  treatment it tested over 60 in neutralizing strength and still contained no free acid.

Our research on the bone phosphate was completed by an attempt at the mechanical removal of a large percentage of free  $H_3PO_4$  by means of a filter press.

The liquid was evaporated to such a consistency that it was capable of being pressed when cold.

The success of this treatment was indicated by the large percentage of  $H_3PO_4$  found in liquid from filter press. The comparatively dry paste, when treated with dry marble, gave a product of high solubility and acid strength, containing no free acid.

Owing to the large amount of free  $H_3PO_4$  contained in paste from rock liquid we were able to apply successfully only the last mentioned of the methods used in bone paste. The rock paste furnished us contained a large percentage of insoluble phosphates of Ca, Fe and Al and  $CaSO_4$ ,

mainly insoluble Ca Phosphates, caused by use of too high a temperature in boiling. In order to remove this insoluble matter the original paste was dissolved in water and the insoluble filtered out. The filtrate thus obtained was boiled down to form a paste when cold of such consistency that it could be pressed between ordinary filter cloths, thus removing the liquid still contained in it without allowing the solid matter to pass through.

By this pressing the greater portion of the free  $H_3PO_4$  was carried out in the liquid. When the percentage of free acid was very large we found it advantageous to thoroughly wet the pressed paste and repeat the pressing operation. The liquid obtained from the press was a brown syrup, consisting mainly of  $H_3PO_4$  and suitable for working up as commercial  $H_3PO_4$ .

The paste which is gummy and sticky before pressing is almost dry and mealy after this operation. This mechanical removal of the large excess of free  $H_3PO_4$  enabled us to obtain a comparatively dry paste to which we could apply the first method applied to the bone paste, namely, that of neutralizing when almost dry.

Experimenting along this line we were led to a consideration of the relative merit of pulverized marble and slaked lime as neutralizing agents.

We found that  $CaCO_3$  required the presence of considerable moisture in order to react with the small amount of free acid present.

Also when marble enough to secure neutralization had been added the addition of water to a test portion caused evolution of  $CO_2$ , proving the presence of an excess of marble which was now reacting with the acid salt.

Repeated experiments with slaked lime.  $Ca(OH)_2$  gave the best of results, requiring less than of marble and the neutralization going to

completion without the addition of a large excess of  $\text{Ca}(\text{OH})_2$

The product obtained showed no free acid.  $\text{H}_3\text{P}\overset{\text{O}}{\text{O}}_4$  was almost completely soluble in water and 100 parts neutralized 73 parts  $\text{NaH CO}_3$  both hot and cold.

The better results obtained with  $\text{Ca}(\text{OH})_2$  are probably explained by the fact that sufficient water is formed in the reaction to carry neutralization to completion. The reaction between  $\text{CaCO}_3$  and  $\text{H}_3\text{PO}_4$  gives only one half as much water as that between  $\text{Ca}(\text{OH})_2$  and  $\text{H}_3\text{PO}_4$

In titrating the water solutions of some  $\text{CaH}_4(\text{PO}_4)_2$  products with  $\text{NaOH}$  solution, in order to determine their acid strength we found that some showed an acid strength somewhat higher when titrated after boiling over than that showed when titrated cold. In order to determine the cause of this action experiments were made with the various insoluble constituents which were likely to be contained in the acid salt, namely, —  $\text{Ca}(\text{OH})_2$ , free  $\text{CaCO}_3$ ,  $\text{CaHPO}_4$ ,  $\text{CaSO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ , etc. Only one of these was found to act in a way to indicate that it might be responsible for this.

When the normal salt,  $\text{Ca}_3(\text{PO}_4)_2$  was boiled in water a small amount of acid salt was formed.

Experiments with products made by some of the processes previously outlined show that the small amount of insoluble which is formed when the neutralization is completed while the paste is still very hot and wet is  $\text{CaH PO}_4$  as these products titrate practically the same both hot and cold. When the neutralization is carried out after the paste becomes cold the products titrate more hot than cold, indicating the formation of some  $\text{Ca}_3(\text{PO}_4)_2$ . The products obtained from  $\text{MgCO}_3$  titrate the same hot as cold, this is due to the fact that there is practically no soluble formed.

## Conclusions.

The following is a summary of the best methods of operation in order to secure a high class product from both bone and rock liquid, as based on results of this research.

First secure a liquid as low as possible in free acid by proper preparation of crude products. Where vacuum evaporators are not available evaporate liquid at a temperature not exceeding 100 degrees Cent. Where the desired output is great we would advise the use of vacuum evaporators. Evaporation at low temperature reduces largely the formation of insoluble phosphates.

If the Fe and Al phosphates exceed two percent they should be extracted from the liquid. Owing to the fact that they are less soluble in boiling solutions than in cold they will largely precipitate long before the liquid reaches a concentration at which any of the  $\text{CaH}_4(\text{PO}_4)_2$  crystallizes out.

Comey ( Ed. 1896).

Aluminum Ortho-phosphates (page 293)

This difference in solubilities could be practically applied by partially evaporating in large vats and filtering the liquid from the precipitated Fe and Al phosphates.

Evaporate the liquid to a very thin paste while hot, run into storage boxes and allow to cool and crystallize. Treat the cold paste in filter presses thoroughly wetting the paste and repeating the filtering operation if experience shows it to be advisable. Treat the pressed material with slaked lime in any machine which will give an intimate mixture without the addition of water.

While  $\text{MgCO}_3$  could be used here with good results, as regards neutralizing the free acid without forming insoluble phosphate, it is not to be commended because of its tendency to gum the product, thus making it

hard to dry and pulverize.

After treatment with slaked lime the product is pulverulent, and in such condition that drying can be completed in a short time at a temperature of 50 to 55 degrees C.

Following are analyses of products from bone and rock phosphate as we obtained them by application of above mentioned methods:

Acid Phosphate of Calcium from Rock.

	Percentage.
Free Phosphoric Acid, $P_2O_5$	00.00
Acid Phosphate of Ca, $CaH_4(PO_4)_2$	83.13
Insoluble Phosphates of Ca, $CaHPO_4$ etc.	0.15
Sulphate of Ca $CaSO_4$	5.93
Phosphates of Fe & Al, $FePO_4$ , $AlPO_4$	1.74
Moisture, etc.	<u>9.05</u>
	100.00

100 parts  $CaH_4(PO_4)_2$  neutralize 70.4 parts  $NaHCO_3$  both hot and cold

Acid Phosphate of Calcium from Bone.

	Percentage.
Free Phosphoric Acid $P_2O_5$	0.00
Acid Phosphate of Ca $CaH_4(PO_4)_2$	88.28
Insoluble Phosphates of Ca. $CaHPO_4$ , etc.	.32
Sulphate of Ca. $CaSO_4$	2.52
Phosphates of Fe and Al, $FePO_4$ , $AlPO_4$	1.66
Moisture, etc.	<u>7.22</u>
	100.00

100 parts  $CaH_4(PO_4)_2$  neutralize 71.2 parts  $NaHCO_3$  both hot and cold.