

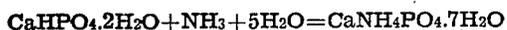
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it may be added to the semisolid or slurry type of concentrated fish solubles, above described, in a completely anhydrous form or in the largely anhydrous form containing two molecules of water ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$). These anhydrous and partially hydrated forms take up water of crystallization to yield the heptahydrate



As a consequence, the anhydrous form takes up 7 molecules of water and the dihydrate takes up 5 molecules of water. It is preferred to employ the anhydrous form because of its greater water-combining property, each pound of such anhydrous form being capable of binding 0.89 pound of water to form the heptahydrate. While disodium phosphate will bind 12 molecules of water as water of crystallization at lower temperatures, it nevertheless loses 5 molecules of water at temperatures a little above normal (about 85° F. to 105° F.) which would be objectionable under some storage conditions. However, the heptahydrate is desirable because it is then stable up to around 115° F. to 120° F.

From the standpoint of the use of the calcium ammonium phosphate, the hydrated dicalcium phosphate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) is required either as a starting material or as an intermediate material. Either this dicalcium phosphate may itself be added to the wet mixture or wet concentrate herein described, or formed in the wet mixture or otherwise from tricalcium phosphate, monocalcium phosphate, calcium pyrophosphate, calcium carbonate and phosphoric acid or phosphoric anhydride, or calcium oxide and phosphoric acid or phosphoric anhydride, as will be apparent to the skilled chemist. Upon supplying dicalcium phosphate with ammonia in the wet mixture or slurry, either by addition thereto or formation therein of the dicalcium phosphate, the previously mentioned heptahydrate of calcium ammonium phosphate forms in accordance with the following formula:

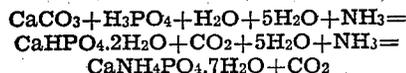


As is made evident by the above equation, the formation of the calcium ammonium phosphate results in the taking up of 5 molecules of water as water of crystallization.

From the standpoint of the calcium ammonium phosphate, some of the ammonia often will be supplied by the fish solubles which have an ammonia constituent (e. g. ammonium sulfate) in amounts varying up to about 1%. When the ammonia content of the fish solubles is too low, ammonia will be added as required, and this applies also to the fish granular hydrolysates previously mentioned. When one pound of dicalcium phosphate is converted to calcium ammonium phosphate, 0.52 pound of water is taken up as water of crystallization in the form of the calcium ammonium phosphate heptahydrate. Thus, assuming no addition of ammonia and the treatment of concentrates containing 50% water, one pound of dicalcium phosphate will take up all of the water from 1.04 pounds of the concentrate, or, in other words, about 49% of the product represents dicalcium phosphate and 51% of the product represents the original fish solubles and their water content, the water content being now combined in the hydrated calcium ammonium phosphate, such water content being about 25.5% of the dry product, of which the fish constituents, on a water-free basis, constitute about 25.5% of the dry product.

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From the standpoint of the production of dicalcium phosphate, or equivalent, in the wet fish concentrate represented either by fish solubles or fish glandular hydrolysates, the following equations are indicative of the method of procedure where calcium carbonate and phosphoric acid are used:



On a theoretical basis, 100 pounds of fish concentrate containing 50% water, in order to take up all of the water as water of crystallization, will require about 46 pounds of calcium carbonate, about 45 pounds of phosphoric acid, and about 8 pounds of ammonia for the reaction to go to completion. This amount of ammonia ordinarily is more than that naturally found in the concentrate. Therefore, some ammonia usually must be added. In the resultant product, about 42% is the calcium ammonium phosphate, figured without its water content, about half of the remaining 58%, i. e. about 29%, being the water of crystallization of the heptahydrate, and the other 29% being the dry fish constituent.

While the above figures indicate the use of phosphate in quantities sufficient to take up all of the water of the fish concentrate, it will be appreciated that absolute dryness ordinarily will not be required, and that from 5% to perhaps 15% or 20% of free moisture content, for example 10%, will ordinarily be preferable.

It is to be appreciated that all percentages are on a weight basis.

Since the initial mixture of the fish concentrate, represented by either of the previously mentioned fish solubles or fish glandular hydrolysates, is a rather sloppy slurry following addition of the edible phosphate salt, a rather long standing period or "curing" time, such as two or three days, is required unless some step is taken to accelerate the hydration process.

The curing time for the hydration stage may be desirably accelerated, and a more uniform product obtained, by adding an edible wetting agent, of which there are many. One such wetting agent is a sulfonated fish oil; again, any sulfonated edible liquid animal or vegetable oil may be used. Of course, these wetting agents must be stable under the acidic conditions normally existing in the fish concentrates, for example pH 4.5 to pH 5.5, or within the range of pH 4 to pH 6. About 1/20% to 1/4% of such a wetting agent is employed, and an optimum percentage is in the order of 1/16%. This reduces the curing time to about one-half or two-thirds the time otherwise required, and it results in uniform combining of the water of crystallization throughout the mass after hydration has been completed. The resultant hard mass or cake is ordinarily ground to produce a meal of appropriate fineness.

It may also be desirable to add some agent to the prepared meal which will prevent subsequent lumping. Any material capable of performing such a function may be employed, and calcium stearate is an example of appropriate substances. It will ordinarily be used to the extent of about 1/2% by weight, and 1% may be considered an upper limit. Also, as little as 1/4% is quite effective. Other anti-lumping agents which might be used are other water-insoluble salts of saponifiable fatty acids, such as the calcium soaps thereof, these including oleates for example, and such soaps of other appropriate metals, such as