

United States Patent Office

3,698,862

Patented Oct. 17, 1972

1

3,698,862

METHOD FOR THE STORAGE AND SHIPMENT OF WET PROCESS PHOSPHORIC ACID

Jatinder Jolly, Metairie, La., assignor to Freeport Sulphur Company, New York, N.Y.

No Drawing. Filed July 17, 1970, Ser. No. 55,944

Int. Cl. C01b 25/18, 25/22

U.S. Cl. 23-165

19 Claims

ABSTRACT OF THE DISCLOSURE

The undesirable sludge which typically accumulates in shipped or stored wet process phosphoric acid is rendered flowable by the presence in the phosphoric acid of a polymer selected from the group consisting of polyacrylamides, hydrolyzed polyacrylonitriles and salts thereof, and polyethylene oxide, these polymers being present in an amount effective to render the sludge flowable. The flowability of the sludge facilitates unloading of the acid from the shipping or storage vessel in addition to providing other advantages to a shipper of the acid.

BACKGROUND OF THE INVENTION

This invention relates to an improved method of handling and transporting wet process phosphoric acid. More particularly, it relates to a method which renders flowable the solid impurities or sludge which typically accumulates in wet process phosphoric acid.

Phosphoric acid is generally produced by the wet process method. According to this method, phosphate rock is acidulated with a concentrated mineral acid such as sulfuric acid to produce a slurry containing diluted P_2O_5 solution and insoluble gypsum. The slurry is drawn off and filtered to produce phosphoric acid having a P_2O_5 content of 22 to 30% by weight. This acid is concentrated to a product containing 48-58% P_2O_5 and 1.0 to 6.0% solids by weight; 54% P_2O_5 acid containing from 2.0 to 4.0% solids is ordinarily produced. It is common practice to use centrifugation or decantation to remove a part of these solids, with the resultant acid being known as "run-of-plant" acid. The acid is then transferred to storage tanks or shipped directly.

The run-of-plant acid contains many soluble impurities which continue to precipitate from the acid with time. This phenomenon is referred to as post-precipitation. The precipitated impurities, commonly referred to as "sludge," include materials such as calcium sulfates (dihydrate, hemihydrate, and anhydrite), sodium and potassium silico-fluorides, potassium phosphates of iron and aluminum, ralstonite type compounds, and many others.

The wet process phosphoric acid, upon standing in storage tanks or during shipments in tank cars, trucks, or barges, deposits a layer of heavy sludge which can make handling of the stored or shipped acid exceedingly difficult and frequently unfeasible. Some producers prefer to pump run-of-plant acid to storage tanks where the acid is cooled and aged for several days, after which it is subjected to centrifugation to remove the post-precipitated impurities. Clarification through unassisted settling is also practiced. These methods, though successful in removing a part of the solid impurities, are uneconomical due to expensive storage capacity being tied up for a long period of time. Moreover, it entails a considerable loss of valuable P_2O_5 in the sludge at the bottom of the clarifier or the underflow from the centrifuge since these sludges normally contain 40 to 50% P_2O_5 . Furthermore, the impurities continue to precipitate in the clarified acid and present further handling problems.

It is the common practice in the industry for the cus-

2

tommer to pay only for the acid unloaded and not for the sludge left in the shipping vessel. Normally, the sludge left in the shipping vessel is very hard and does not flow by gravity. The nozzles become plugged during transit and extra manpower is required to loosen the sludge at the bottom in order to get the acid to flow. At times, the sludge is so hard that it requires hammering to open the plugged-up nozzle. It becomes all the more difficult when top-unloading tank cars using air are employed. This virtually makes it impossible to unload all of the acid, and normally 5 to 10% of the sludge is left in the shipping vessel. This accounts for about a 2 to 5% loss of P_2O_5 .

Since it is not practical to clean the shipping vessel after each trip, the manufacturer normally takes it out of service only after two or three trips. This results in accumulation of several tons of sludge. It becomes an item of expense because of unnecessary freight being paid on the undelivered acid. Moreover, this high-solids sludge is a loss to a producer not engaged in the fertilizer business, where this material might be utilized. It has been proposed to use agitated shipping vessels so that solids may be kept suspended during transit. However, the higher cost of installing, operating and maintaining the agitators does not justify their usage for trucks, tank cars, and medium-sized barges.

For these reasons, it is apparent that a method for preventing accumulations of this hard non-flowable sludge and thereby delivering more of the shipping vessel's contents to the customer would have considerable utility.

Numerous methods have been heretofore proposed to facilitate the problem of handling the sludge in wet process phosphoric acid. These methods fall into two general categories:

- (1) The mechanical removal of solids prior to storing or shipping; and
- (2) Inhibition of solids precipitation in the acid by the addition to the acid of various additives.

Mechanical separation, employing the techniques of clarification, filtration, and centrifugation, is the most common method being practiced in the industry. However, due to the nature of the solids and high viscosity of the acid, it is difficult to perform these operations efficiently. Moreover, because the rate of precipitation is slow, not only is a large storage volume required for settling, but this expensive storage volume also is tied up for a long period of time, since one month is usually accepted as the time required for post-precipitation to occur to the extent that additional precipitation will not greatly increase the solids content during transit or storage. The sludge formed via aging and settling is hard in nature and does not ordinarily flow by gravity.

The second category pertains to methods for inhibiting the post-precipitation of these solids by adding various additives such as, for example, certain polymers and chelating agents to the acid.

It should be noted that this latter method minimizes precipitation of the solids, whereas it has now been found, in accordance with this invention, that it is not necessary to inhibit post-precipitation in order to effectively handle the sludge problem. Instead an economical, unique, and improved method for treating wet process phosphoric acid has been found which makes no attempt to inhibit solids precipitation. Instead, the nature of the sludge solids is effectively altered so that the sludge formed is soft and flows freely.

It is therefore a general object of this invention to provide wet process phosphoric acid which can be shipped or stored over an extended time period economically and without the problems normally attendant with sludge formation.