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METHOD OF HANDLING PHOSPHORIC ACID

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1 Claim. (Cl. 23—165)

The present invention relates to the handling and shipping of phosphoric acid. In particular, the instant discovery concerns minimizing problems attending the handling of phosphoric acid by reducing the corrosivity of the acid to a substantial degree.

In the past years the use of wet process phosphoric acid, for example, in the manufacture of complete mixed granulated fertilizer has increased tremendously. In order to provide the manufacturer of these fertilizers with bulk quantities of the acid it is accepted practice to ship and store the wet process phosphoric acid in rubber-lined tanks, or the like. The object of the lining is to cope with the extreme corrosivity of the acid, since conventional tanks or storage containers, such as steel tank cars, are rapidly and extensively attacked by the corrosive acid. Of course, the inevitable, adulteration of the acid as well as eventual destruction of the tank, ensues unless a protective lining is used. On the other hand, the use of protective linings or other similar expensive measures seriously cripples sales volume.

The present invention, however, handily and very surprisingly overcomes the difficulties attending the prior art. Whereas wet process phosphoric acid, for example, of conventional commercial grade contains, generally, from 53 to 56 percent by weight P_2O_5 and from 15 to 20 percent by weight H_2O, it has been found, pursuant to the instant discovery, that by maintaining the P_2O_5 concentration of the acid above about 57 percent by weight, preferably in the range of 58 percent to 69 percent, basis the total weight of the wet acid, and the H_2O content below about 12.5 percent by weight, basis the total weight of the wet acid, corrosivity of the wet acid is diminished to such an extent that mild steel tanks or containers, for instance, may be employed for handling and storing the acid. Hitherto this was unheard of, and for that very reason, among others, the present invention represents a significant forward stride in the art.

Furthermore, increasing the P_2O_5 concentration of the wet acid and decreasing its water content was by no means an obvious solution to the corrosivity problem. In fact, the results achieved by the instant discovery are entirely unexpected, as will be seen hereinafter.

A typical teaching in the art which would direct anyone away from the practice suggested herein may be found in "Corrosion Data Survey" (1954 edition) published by thet Shell Development Company, Emeryville, California. Therein it is stated unequivocally that aqueous phosphoric acid at all concentrations corrodes steel, cast iron, and the like, at a rate greater than 0.05 inch per year, and implicitly suggests the use of glass, platinum, gold, rubber, stoneware, or the like, to minimize corrosion. As will be seen hereinafter from comparative data, wet process phosphoric acid of commercial grade corrodes steel at a rate which is 5 or 6 times greater than 0.05 inch per year.

Generally speaking, therefore, the present invention comprises a novel method of handling and shipping aqueous phosphoric acid, such as wet process phosphoric acid, aqueous relatively-pure phosphoric acid, such as "furnace acid," and mixtures of these aqueous acids with sulfuric acid, and the like, by maintaining the water concentration of said acids or mixtures below about 12.5 percent by weight, basis the total weight of the acid solution or mixture.

The moisture content of the acids herein contemplated may be reduced by any conventional means, such as by subjecting the mixture to heat, drying agents, or the like, or by adding more acid to the mixture to decrease the water content.

By wet process phosphoric acid herein is intended commercial grades aqueous phophoric acid which may have the following typical analysis:

	Percent by weight [1]
P_2O_5 [2]	56.0
H_2O	17.0
H_2SO_4	4.0
Al_2O_3	2.3
Fe_2O_3	1.8
F	0.7

[1] Based upon total weight of the solution.
[2] Phosphoric acid (H_3PO_4) computed as P_2O_5.

Wet process phosphoric acid is usually prepared by aqueous H_2SO_4 digestion of low-grade phosphate rock having the following typical analysis:

	Percent by weight [1]
CaO	46.5
P_2O_5	31.0
CO_2	3.0
F	3.5

[1] Based upon total weight of phosphate rock.

The digested material is filtered and washed to remove gypsum ($CaSO_4 \cdot 2H_2O$), and the resulting wet phosphoric acid evaporated to desired concentration, generally from 53 to 56 percent P_2O_5 by weight and from 15 to 20 percent H_2O by weight, as indicated above.

A representative relatively-pure phosphoric acid contemplated herein is that commonly prepared by an electrothermal process and known as "furnace acid." This acid has only a small amount, if any, of the impurities, such as aluminum, iron and fluorine, generally found in wet process phosphoric acid.

Pursuant to the instant discovery, and as will be seen hereinafter, P_2O_5 concentrations above about 63 percent by weight (87 percent H_3PO_4 by weight) and H_2O concentrations below about 12.5 percent by weight give best results against corrosion in the case of furnace acid-type phosphoric acid.

Still another embodiment of the instant discovery which is alluded to just briefly hereinabove is the reduction of the corrosivity of phosphoric acid—sulfuric acid mixtures. It has been found that mixtures of wet process phosphoric acid and/or furnace acid and sulfuric acid may be handled and shipped with a minimum of corrosion by maintaining the P_2O_5 concentration of the mixtures at at least about 30 percent by weight, basis the total weight of the mixture, and the water concentration

below about 12.5 percent by weight, basis the total weight of the mixture.

Generally, P_2O_5 concentrations on the order to 30 to about 58 percent by weight and H_2SO_4 concentrations in the range of about 50 to about 10 percent by weight, based upon the total weight of the mixtures, are contemplated.

Good resistance to mild steel corrosion is manifested, for example, by a mixture comprising 45 percent P_2O_5 by weight, 30 percent H_2SO_4 and about 7 percent H_2O.

The following examples will best illustrate the present invention:

EXAMPLE I

Six samples of identical volumes of wet process phosphoric acid having the H_2O and P_2O_5 concentrations given in the table below are prepared from a bulk amount of process acid having the analysis given above (see typical analysis). The corrosion rate of each of these samples with respect to mild steel (SAE 1010) is tested under identical conditions and over the same period of time. The following results are achieved:

Table I

Sample No.	P_2O_5 Concentration (percent by weight)	H_2O Concentration (percent by weight)	Overall[1] Rate of Corrosion (inches per year)	Steady State[2] Corrosion Rate After Passivation (inches per year)
1	47.6	27.0	0.300	>0.300
2	51.3	21.8	0.310	>0.300
3	58.0	12.8	0.050	<0.0002
4	60.3	10.1	0.006	<0.0002
5	63.3	5.4	0.0005	<0.0002
6	66.0	1.7	0.0005	<0.0002

[1] Includes initial high rates of corrosion before "passivation" (before steady state corrosion rates are attained).
[2] By passivation is intended the leveling off of corrosion rate which is exhibited by Sample Nos. 3–6. On the other hand, Sample Nos. 1 and 2 left the range of the corrosometer and did not passivate.

Each of the above samples is tested by a conventional electrical resistance measurement method. To begin with, each sample of the aqueous acid is placed in a separate glass container having therein a mild steel corrosion meter probe. The containers are placed in a rack on a rotator to provide mild agitation. Readings are taken at predetermined intervals, usually hourly, until a steady state corrosion rate is obtained. The rate of corrosion is determined from a graph on which is recorded the extent of corrosion at different time intervals. The slope of the curve of corrosion versus time indicates the rate of corrosion.

Comparing samples 2 and 5, for instance, in Table I, above, it is obvious that substantially more corrosion (approximately 600 times more, even before passivation) takes place at the higher water concentration.

EXAMPLE II

Tests similar to those in Example I, above, are made on various furnace acid solutions having the concentrations given in Table II, below, the results being as shown:

Table II

Sample No.	Components[1]				Penetration Before Passivation[2]	Steady State Corrosion Rate After Passivation[4]
	H_2O	P_2O_5	H_2SO_4	HF		
7	6.0	68.1			0.045	0.0002
8	15.0	61.5			[3] 1.600	
9	6.0	64.5	5.0		0.230	0.0002
10	15.0	58.0	5.0		[3] 1.600	
11	6.0	67.4		1.0	0.120	0.0002
12	15.0	60.9		1.0	[3] 1.600	

[1] Given in percent by weight based on total weight of solution.
[2] Given in mils (1000 mils=1 inch).
[3] Corrosion measured to slightly above 1.600 but "Passivation" not achieved; by passivation as is indicated in Table I, above, is intended the leveling off of corrosion rate which is exhibited by Sample Nos. 7, 9 and 11. In other words, Sample Nos. 8, 10 and 12 left the range of the corrosometer in 12–24 hours and did not passivate.
[4] Given in inches per year.

Clearly, the instant discovery encompasses numerous modifications within the skill of the art. Consequently, while the present invention has been described in detail with respect to specific embodiments thereof, it is not intended that these details be construed as limitations upon the scope of the invention, except insofar as they appear in the appended claim.

We claim:

In a process for treating a wet-process phosphoric acid comprising less than 58% P_2O_5 and more than 12.5% water for incorporation into a mild steel container comprising essentially iron to minimize both corrosion of said container and iron contamination of said phosphoric acid, the improvement which consists essentially in the steps of:

(*a*) establishing the P_2O_5 concentration of the phosphoric acid at a level between 58% and 69% and the water content therein at a level between 1.7% and 12.5%, said P_2O_5 and water content levels being based on the weight of said acid, and

(*b*) incorporating said acid in a mild steel container, whereby corrosion of said container does not exceed about 0.05 inch per year.

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