

PATENT SPECIFICATION (11)

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- (21) Application No. 44924/75 (22) Filed 2 Oct 1972
(62) Divided out of No. 1436113
(23) Complete Specification filed 26 Apr 1973
(44) Complete Specification published 19 May 1976
(51) INT CL² CO1B 25/46
(52) Index at acceptance
CIA 11
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(54) CRYSTALLIZATION PROCESS

(71) We, Albright & Wilson Limited, a British Company of P.O. Box 3, Oldbury, Warley, West Midlands, England, formerly of P.O. Box 3, Oldbury, Warley, Worcestershire, England, do hereby declare the invention, for which we pray that a Patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to the purification of phosphoric acid obtained by the wet process by reaction of sulphuric acid with phosphate rock. Such acid will hereafter be termed "wet process phosphoric acid". In particular the present invention relates to purification of such acid by solvent extraction techniques.

Proposals for solvent extraction purification of wet process phosphoric acid date back at least 40 years. Initially the solvents suggested were water-miscible, for example alcohols and acetone, which required distillation in order to release the purified acid; alternatively there were suggested water immiscible short chain alcohols requiring many stages for effecting a satisfactory extraction.

In more recent years attempts to put into practice solvent extraction processes for wet process phosphoric acid have been made. However, these have largely been restricted to processes (such as those described in BP 805517 using butanol and BP 953378 using alkyl phosphates), in which either chloride ions are especially added to the acid or chloride ions are present as a result of using hydrochloric acid instead of sulphuric acid in the production of the phosphoric acid. The presence of chloride ions promotes a salting out effect which assists in promoting transfer of the phosphoric acid species to the organic phase.

A group of recent proposals is concerned with the use as solvents of certain ethers which extract the phosphoric acid present in aqueous solutions at concentrations above a certain threshold value, quoted as 35% H_3PO_4 , but do

not extract any acid at concentrations below the threshold value. The first of these proposals is contained in BP 1,112,033 which, in addition to the ethers referred to above, also mentions a number of other possibilities including ketones. The method disclosed required a substantial temperature differential between extraction and release of the acid, the former being carried out at a relatively low temperature and the extract being heated, with or without the addition of a little water, to effect release of the acid. BP 1,240,285, which is a patent of addition to BP 1,112,033 describes the same process but using a mixture of solvents, one such mixture being an ether and a ketone, of which cyclohexanone is specifically mentioned. The third proposal in the group concerned with solvents having a threshold value quoted as 35% H_3PO_4 is USP 3,556,739 which described the use of a wide range of aliphatic esters, aliphatic and cycloaliphatic ketones and glycol ethers. While the specific description is directed only to the same type of process as that of BP 1,112,033 in which the extract is heated in order to release the acid, reference is also made to the possibility of effecting release of the acid by an isothermal route involving one stage contact of the solvent extract with water. However no information is given as to which of the many solvents referred to in connection with the temperature-raising process may be employed or as to the temperatures appropriate to it.

A process has also been described in BP 1063248 for removing nitric acid from the aqueous phosphoric nitric acid mixture obtained by decomposing phosphate rock with nitric acid. In this process a ketone is used to extract the nitric acid, leaving the phosphoric acid in its impure form in the aqueous phase. Such acid could only be used for fertiliser production.

We have found that wet process phosphoric acid which has been purified by solvent extraction can be further purified, eg. to render it suitable for use in foodstuffs, by

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concentrating the acid to an H_3PO_4 content of 84.9–92% and then cooling to produce crystals of $H_3PO_4 \cdot \frac{1}{2}H_2O$. The production of phosphoric acid crystals has been described in the past where a suggestion has been made to up-grade by crystallisation wet process phosphoric acid which has previously been desulphated and defluorinated. This proposal is not in fact practicable as a method of producing pure phosphoric acid crystals since it results in inclusions in the crystals of for example, iron phosphates. Moreover the crystals are difficult to separate from the mother liquor since this is very viscous. Although it is known that by cooling aqueous acid of concentration below 92% H_3PO_4 it crystallises as $H_3PO_4 \cdot \frac{1}{2}H_2O$ (see Thorpe's Dictionary of Chemistry, Fourth Edition, Volume IX, page 503) this knowledge relates to thermal acid and hence is only of academic interest, thermal acid requiring no purification.

The present invention provides a process for purifying wet process phosphoric acid, which comprises subjecting it to extraction with an organic solvent to give a solvent extract containing phosphoric acid, contacting the extract with water and producing an aqueous purified phosphoric acid, and then concentrating the aqueous acid to give a concentrated acid of H_3PO_4 content (by weight) of 84.9%–92%, eg. 85–88%, then cooling the concentrated acid, eg. to 8–12°C to bring about formation of crystals of the formula $H_3PO_4 \cdot \frac{1}{2}H_2O$ and a mother liquor, and separating the crystals from the mother liquor.

Preferably the concentration of the aqueous purified acid from the solvent extraction is raised by use of vacuum evaporators such as forced circulation evaporators or alternatively, P_2O_5 obtained by burning elemental phosphorus may be dissolved in the solvent extracted purified acid or concentrated thermal phosphoric acid may be admixed with the purified acid to produce an acid of the desired concentration.

Preferably the aqueous purified phosphoric acid obtained from the solvent extraction has a metal content of less than 100 ppm, as can be the case when methyl isobutyl ketone is the solvent. Often scrubbing of the extract containing impurity acid is needed to obtain this highly purified acid. Since the acid used to produce the initial wet process phosphoric acid from phosphate rock is sulphuric acid, the solvent extracted acid contains a substantial proportion of sulphuric acid, eg. of the order of 0.5–1.0% H_2SO_4 on a 85% H_3PO_4 basis. We have found that the presence of this impurity does not interfere with the crystallisation. If, however, an unduly large amount of liquor, resulting in a high impurity content, adheres to the crystals when they are separated, eg. by centrifuging from the mother liquor, it can readily be removed by washing.

The mother liquor from the crystallization

after dilution with water to an appropriate strength may advantageously be used as the liquor for scrubbing the extract, integrating the solvent purification and crystallization processes.

Any organic solvent capable of extracting phosphoric acid from wet process phosphoric acid may be used in the initial solvent extraction. Thus the solvent may be tributyl phosphate, butanol, isoamyl alcohol or diisopropyl ether.

However preferably the solvent is an unsubstituted acrylic dialkyl ketone of 5 or 6 carbon atoms, eg. methyl isobutyl ketone, which is most preferred, diethyl ketone and methyl n propyl ketone.

Thus the present invention preferably comprises contacting wet process phosphoric acid with said acrylic ketone to give a ketone phase containing at least some of the phosphoric acid extracted from the wet process acid, optionally scrubbing the ketone phase, then contacting the ketone phase with water to produce aqueous phosphoric acid of increased purity having regard to the feed wet process acid, and then raising the concentration of the aqueous acid to 84.9 to 92%, crystallising the hemihydrate crystals and separating the latter from the mother liquor.

The solvent extraction with the acrylic ketone, scrubbing and release are described in the complete Specifications of our cognate Applications 19476/72 and 45380/72, (Serial No. 1436113) and 44924/75 (Serial No. 1436115).

In the Complete Specification of Cognate Application 19476/72 and 45380/72 we describe and claim a process for purifying crude wet process phosphoric acid obtained from contact of sulphuric acid and phosphate rock which comprises contacting said crude wet process phosphoric acid with an unsubstituted acrylic dialkyl ketone containing five or six carbon atoms, to give an organic extract containing at least some of the H_3PO_4 in the crude acid, and subsequently contacting the extract with water or an aqueous solution of a base to produce an aqueous phase consisting essentially of purified aqueous phosphoric acid or comprising a phosphate salt, the purified acid or salt being of increased purity having regard to the feed wet process acid and separating said aqueous phase from a ketone phase containing no more than 3% of the H_3PO_4 present in the extract, with the provisos (a) that when the ketone is a hexanone the acidity (as hereinafter defined) of the crude acid is at least 65%, (b) when the ketone is methyl isobutyl ketone at least one of the contact of crude acid and ketone, and extract and water or base, is in more than 1 stage, and (c) when the ketone is a pentanone, the acidity of the crude acid is at least 50% and also, when the pentanone extract contacts water to produce an aqueous phase consisting essentially of aqueous purified phosphoric acid, the contact

of extract and water is in more than one countercurrent stage.

In the complete Specification of Application 44924/75, (Serial No. 1436115) we describe and claim a process for purifying wet process phosphoric acid from crude wet process acid of acidity (as hereinafter defined) at least 65% obtained by the action of sulphuric acid on phosphate rock which comprises contacting the crude wet process phosphoric acid in one stage with methyl isobutyl ketone to give an organic extract containing at least some of the H_3PO_4 in the crude acid, subsequently contacting the extract in one stage with water or an aqueous solution of a base to produce an aqueous phase consisting essentially of aqueous phosphoric acid or comprising a phosphate salt, said aqueous phosphoric acid or said phosphate salt being of increased purity having regard to the feed wet process acid and separating said aqueous phase from a ketone phase containing less than 3% of the H_3PO_4 present in the extract.

With the acrylic ketone as solvent for the solvent extraction it is possible to carry out an efficient initial purification of wet process acid at the commercially available concentrations, operating both the extraction and release at a temperature which is at or relatively near ambient temperature. This obviates the need either to refrigerate the acid for extraction step or raise the temperature of the extract for the release step, and also ensures that the acid/solvent system is at a suitable viscosity for carrying out the process.

The preferred ketone is one unmentioned in USP 3556739 namely methyl isobutyl ketone. This is contrary to expectation, since this ketone is known to be useful for extracting from acid for analytical purposes the very metal impurities which remain in the aqueous phase in this solvent extraction process. We have found however, that methyl isobutyl ketone has the advantage of being able to extract substantially all the H_3PO_4 values from a commercial wet process phosphoric acid of 70–85% acidity as defined below. Ketones of higher molecular weight require a higher concentration of phosphoric acid in the feed before they will extract this amount of H_3PO_4 and it would therefore be necessary to institute a further difficult concentration stage of the acid prior to using such a ketone. Methyl isobutyl ketone further has the advantage of having a higher flash point as compared to ketones of lower molecular weight but forming an azeotrope having a boiling point sufficiently low to enable easy solvent recovery by distillation. Furthermore methyl isobutyl ketone has low solubility (of the order of 1–2%) in aqueous H_3PO_4 thus permitting the final product of the release stage to have only a low ketone content which may be removed with comparative ease as compared to other ketones as a result of the composition and boiling

point of the azeotrope formed. It further permits the production of an aqueous raffinate having an H_3PO_4 content in the range 55–65% which after removal of the small amount of methyl isobutyl ketone present is suitable for use as such in fertiliser production, unlike the raffinate produced by using ketones of lower molecular weight.

The fact that phosphoric acid of normal merchant grade acidity may have substantially all of its H_3PO_4 content extracted into methyl isobutyl ketone at temperatures at which it is normally convenient and desirable to work (i.e. in the range 25–50°C, at which the system has a suitable viscosity) would normally require that a little water be added in order to produce a handlable raffinate. This may be accomplished either by adding water with or to the feed or more preferably by feeding aqueous phosphoric acid, which has been employed in a scrubbing operation to reduce the impurity content of extract, into the initial operation where wet process acid is contacted with the ketone.

It is also preferred, contrary to the teaching of USP 35567/39, that either or both of the extraction of H_3PO_4 from the wet process phosphoric acid into the five or six carbon atom-containing ketone and the release of purified acid, if carried out into water, is carried out in more than one stage. The reason for this is that we have found a greater concentration of H_3PO_4 occurs in the raffinate for a given impurity content for a one stage extraction than for a two stage extraction. Thus less H_3PO_4 is lost in the raffinate if the extraction is carried out in two stages. The two stage extraction is conveniently accomplished by introducing the feed acid into one mixer unit of a two stage counter current mixer-settler extractor unit and the ketone into the other. If a scrubbing stage is employed the recycled scrub liquor is fed into the same unit as the feed acid. The use of a multistage release permits an aqueous phosphoric acid of higher H_3PO_4 content to be obtained.

When an acid of lower concentration than merchant grade acid is available, eg. acid of acidity in the range 50–70%, it may be preferred, rather than concentrating the acid, to employ a pentanone such as diethyl ketone or methyl n propyl ketone as the solvent, using both a two stage extraction into the ketone of H_3PO_4 and a 2 stage release into water, normally after a scrubbing operation has been effected. The concentration of phosphoric acid which is used to obtain most beneficial results according to the process of the invention will vary depending upon the ketone employed. If pentanones are employed an acid of an acidity as hereinafter defined of at least 40% and normally below 65% (preferably an acid of acidity from 50–55% as for example is obtained by the process described in BP 1209911) is desirably employed. In such processes it is normal that instead of producing $CaSO_4 \cdot 2H_2O$

as the by product of the reaction of H_2SO_4 on phosphate rock $CaSO_4 \cdot \frac{1}{2}H_2O$ is formed, either in one stage from the attack or two stages, e.g. as a result of recrystallizing the slurry obtained from a conventional process. If hexanones, such as methyl isobutyl ketone, are employed the acid is desirably of an acidity of at least 65%, frequently in the range 70 to 85% preferably 74–79% expressed as H_3PO_4 and H_2SO_4 . The acidity of the acid is herein defined as the total weight percentage of H_3PO_4 and H_2SO_4 species present therein, this simple addition being possible as a result of H_3PO_4 and H_2SO_4 both having a molecular weight of 98. Thus an acid having an H_3PO_4 total of 74% and an H_2SO_4 content of 5% would have an acidity of 79%.

Use of such solvents will permit the production of purified acids after one stage of release into water at about 33% H_3PO_4 if pentanones are employed as the extractants, and about 45% H_3PO_4 if hexanones are used. The strengths of the acid obtainable can be increased if multi-stage releases are employed. For example an acid of concentration 55–58% H_3PO_4 can be obtained from an extract in methyl isobutyl ketone if such techniques are employed.

Phosphoric acid for purification according to the invention is obtained by filtration or other separation of calcium sulphate from the slurry obtained by the attack of sulphuric acid on phosphate rock. In such a state it contains a wide range of impurities, some of which such as fluorides and sulphate and dissolved organic material may if desired be removed from the acid prior to the solvent extraction of the present invention; other impurities such as iron, chromium, magnesium and other metallic cations, however, are not removable by such a pre-treatment.

Conventionally the acid from the attack stage is cooled as much as possible in order to induce post precipitation of the impurities present. The acid will normally be cooled to about 25–30°.

The temperature at which the solvent extraction is optimally carried out may vary according to the concentration of acid. However, we have found that a temperature equal to or below 50°C e.g. of 25 to 50°C is normally convenient for all concentrations of acid and one in the range 35–40°C for methyl isobutyl ketone using an acid of an acidity in the range 65–85% is particularly useful.

The acid to be employed in the present process will either be obtained direct at the required concentration, or will be concentrated up to this level e.g. by vacuum evaporation before purification. Acid of an acidity in the range 74–79% is the most commonly available commercial acid at the present time. Thus, for example, when methyl isobutyl ketone is employed it is common to employ an acid of about 79% acidity, for example 75% H_3PO_4

and 4% H_2SO_4 or 78% H_3PO_4 and 1% H_2SO_4 .

The wet process acid is preferably contacted with a ketone having five or six carbon atoms, such as methyl n propyl ketone, diethyl ketone, and methyl isobutyl ketone. The extracting ketone may be contacted with the aqueous wet process phosphoric acid in weight ratio of above 0.3:1 preferably in the range 0.5 to 2.0:1, and in the case where the ketone is methyl isobutyl ketone, more preferably in the range 1.0 to 1.3:1, optimally 1.2 to 1.4:1 for one stage extractions. A ratio greater than 2.0:1 may be employed but would result in a requirement for larger vessels. If a 2 stage extraction is employed a slightly higher ratio e.g. 1.3 to 1.6:1 of ketone feed may be employed. We have found that aqueous phosphoric acid of the highest purity in a plant of the minimum size per unit H_3PO_4 throughput may be obtained if the ketone phase contains from 28 to 40% by weight of H_3PO_4 .

The contacting of the acid with the ketone is carried out in conventional equipment such as mixer-settlers and counter current packed columns. Normally an extractor with two or three actual or theoretical counter current stage, preferably two stages, is employed for the reasons explained previously, although a one stage operation is possible.

Alternative apparatus for carrying out the contact such as sieved plate, rotating disc or pulsed column extractors of the desired number of theoretical stages may be employed.

If a phosphoric acid of high purity is required the extract containing the H_3PO_4 is then scrubbed by repeatedly contacting it with a small amount of scrub liquor which is preferably an aqueous solution of phosphoric acid of a high degree of purity in order to extract the cationic impurities into the aqueous phosphoric acid phase. Alternatively water can be used which re-extracts some H_3PO_4 in the first contact to give an aqueous phosphoric acid which may then be used as scrub liquor to impure extract. The phosphoric acid used for scrubbing should have an impurity content sufficiently low to enable it to extract impurities from the ketone extract. It should preferably also have an H_3PO_4 content of less than 45% for pentanones and less than 56% for hexanones in order to avoid transfer of H_3PO_4 from the scrub liquor into the extract. It may either be acid obtained by the thermal process or by a wet process fulfilling the above conditions. Conveniently it is recycled purified acid from the release operation of the process. The amount of phosphoric acid used or produced by the partial extraction of H_3PO_4 into water and employed as the liquor to scrub the organic extract will normally be at least in amount of 10% of the amount of H_3PO_4 present in the organic phase. Preferably it is in the range 30–50%. That is to say the weight ratio of scrubbing liquor to extract is normally from 0.25 to 0.5:1 of the acid which has an

H_3PO_4 content of about 56% if a hexanone such as methyl isobutyl ketone or about 45% if a pentanone is employed.

After scrubbing the phosphoric acid is released from the organic ketone phase by contacting it with water. This may be accomplished in one stage if desired. However, more commonly a multistage release, normally using 2 actual or theoretical stages is employed. The amount of water employed should be such that substantially all of the phosphoric acid passes into the aqueous phase from the organic. Desirably no more than 3% preferably no more than 1% of the H_3PO_4 values will be retained in the organic phase. The H_3PO_4 content of the aqueous phosphoric acid in a one stage release operation will be in the range 44 to 48% H_3PO_4 if the ketone employed is methyl isobutyl ketone depending upon the temperature employed; for example using water introduced at a temperature of 20°C an acid of H_3PO_4 content 45% may be obtained. Using a 2 counter current stage extraction, higher concentrations eg. in the range 55–59% may be obtained, for example 56% using water at 20°C . For pentanones such as diethyl ketone and methyl propyl ketone, a 2 stage release will provide an acid of about 43–48% H_3PO_4 . If desired water at other temperatures for example condensates obtained from a heat exchanger such as used for vacuum concentrators may be employed. Typically temperatures in the range 20 – 40°C for the release step will be employed. For a 2 stage release the extract is fed to one mixer unit of a 2 stage counter current mixer settler unit and the water to the other mixer section. Although acid of these concentrations may be used direct for a number of applications it will normally be desirable to concentrate it if it is to be transported. When employing methyl isobutyl ketone as the solvent the amount of water employed for satisfactory one stage release is normally in the range 0.2 to 0.4:1 based on the weight of extract, whereas for two stage release an amount of water in the range 0.10–0.13 may be employed. For pentanones a ratio of 0.4–0.6:1 for a one stage and 0.05–0.3 for two stage release suffices. It should be understood however that if a more dilute acid is desired more water may be employed.

The final product obtained from the ketone extraction and release process may contain a small amount of the ketone solvent employed. This can be released for example by distillation if desired. The process of the invention therefore normally produces two streams of phosphoric acid, one obtained via the solvent which contains approximately 50–70% of the H_3PO_4 present in the starting material and having a total metallic content less than 100 ppm relative to H_3PO_4 , and a less pure one containing phosphate not extracted into the organic phase which is suitable for use in fertiliser production. Alternatively a less pure

purified stream containing eg. 95% of the initial H_3PO_4 content may be produced by using a high concentration of feed acid and little or no scrubbing.

In a preferred embodiment of the invention, the solvent purification process with the pentanone or hexanone is integrated with the crystallization process. Thus a preferred process comprises (a) contacting wet process phosphoric acid of acidity 65–85% with methyl isobutyl ketone in a solvent : acid weight ratio of 0.5:1 to 2:1 to form an organic extract containing H_3PO_4 and an aqueous raffinate, (b) separating the extract from the raffinate, (c) scrubbing the extract, (d) contacting the scrubbed organic extract with water in two or more countercurrent stages to effect release to give an aqueous purified phosphoric acid containing less than 100 ppm metal impurities and an organic layer, (e) separating the aqueous acid and the organic layer, (f) raising the concentration of the aqueous phase to give a concentrated acid of 84.9–92% H_3PO_4 content (g) cooling said concentrated acid to bring about the crystallization of crystals of $\text{H}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ from the mother liquor and separating the crystals, (h) recycling said mother liquor after dilution with water for use as the scrub liquor in stage (c). A further preferred process comprises (a) contacting wet process phosphoric acid with a pentanone to form an organic phase containing at least some of the H_3PO_4 content and an aqueous raffinate, (b) separating said organic phase and said aqueous raffinate, (c) scrubbing the organic extract, (d) contacting the scrubbed organic extract with water in two or more countercurrent stages to effect the release to give an aqueous purified acid containing less than 100 ppm metal impurities and an organic layer, (e) separating the aqueous acid and organic layer, (f) raising the concentration of the aqueous phase to give a concentrated acid of 84.9–92% acidity content, (g) cooling said concentrated acid to bring about the crystallization of crystals of $\text{H}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ from the mother liquor and, (h) recycling the mother liquor after dilution with water for use as the scrub liquor in stage (c).

The process of the invention is illustrated by the following Examples 1 and 2; Examples A–H described solvent purifications which can be used to make the purified aqueous acid which can be concentrated and crystallized in an analogous manner. In each of the Examples 1, 2, A and B, the feed phosphoric acid employed was of the following composition.

Specific gravity	1.66
H_3PO_4	77.4%
H_2SO_4	1.6%
Fe	0.23%
Mg	0.25%

In examples 1, 2, A and B the extracting solvent was methyl isobutyl ketone.

EXAMPLES A, B and 1(a)

Example A is herein described with reference to the flow diagram Figure 1. This illustrates a process in which both the initial extraction of the H_3PO_4 into methyl isobutyl ketone and the final release into water are both accomplished using one stage mixer settlers (1 and 2 respectively in the figure). The solvent extract is separated from the aqueous raffinate and scrubbed by being passed through a series of mixer settlers, 3, to extract cationic impurities from the solvent extract. The scrub liquor employed is the purified acid obtained from the release mixer settler 2.

The feed acid is introduced to the first mixer settler at a temperature of about 25°C. The temperature rises as a result of the release of heat of extraction of the H_3PO_4 into the ketone.

The exact details of the conditions pertaining at each stage of the process are shown on the flow diagram.

The product had an analysis of

25	H_3PO_4	45%
	H_2SO_4	0.65%
	Fe	25 ppm
	Al	< 5 ppm
	Mg	< 5 ppm
30	Ca	< 5 ppm
	Na	< 1 ppm
	V	< 2 ppm
	Cr	< 2 ppm
	Cu	< 2 ppm
35	Ni	< 1 ppm
	Pb	< 1 ppm
	Cd	< 1 ppm

Example B is illustrated by Fig. 2.

In this example the 1 stage mixer settler employed for the release of the H_3PO_4 from the ketone phase into the water was replaced by a 2 stage operation. The temperature of the feed acid was again 25°C. The exact conditions pertaining at different stages and the compositions of the streams are shown in Fig. 2.

The first stage of Example 1, Ex.1(a) is illustrated by Fig. 3. In this example 2 stage mixer settlers are employed both for the extraction of the H_3PO_4 into the ketone and for the release of H_3PO_4 into water. Figures for the conditions pertaining at various points and the compositions of the various streams are shown on the figure.

EXAMPLE 1(b)

Product phosphoric acid from the solvent extraction operation described in Example 1(a) of 7.4 gph, is steam stripped countercurrently in a packed column yielding 7.0 gph at SG = 1.43, containing 42.0% P_2O_5 and less than 50 ppm ketone, and recovering 0.2 gph each of ketone and water mutually saturated.

This essentially solvent free phosphoric acid is concentrated in a forced circulation evaporator at 80°C under reduced pressure to produce

4.0 gph containing 62.0% P_2O_5 (85.6% H_3PO_4)

1.0% SO_3
40 ppm Fe
less than 10 ppm Mg
less than 50 ppm F
SG = 1.70/20°C.

which after cooling to 30°C is fed to a continuous crystalliser operating at 8–12°C. The slurry produced is centrifuged to produce 31.5 lb/hr of crystalline phosphoric acid hemihydrate ($2H_3PO_4 \cdot H_2O$) of analysis

66% P_2O_5
less than 500 pm SO_3
less than 5 ppm each of Fe, Mg, F

and also 36 lb/hr of aqueous phosphoric acid of analysts

58% P_2O_5
1.9% SO_3
less than 100 ppm each of Fe, Mg and F.

The purity of the crystalline product can be further improved by washing it with a solution of a portion of the crystals in water. This of course reduced the yield of crystals.

The crystals are melted by adding them to a stirred vessel in which the contents are maintained above 30°C to provide a liquid phosphoric acid suitable for transporting. The acid forming the mother liquor is suitable for sale as produced.

EXAMPLE 2

In this example the object was to recover the total "upgraded" phosphoric acid in the form of crystals. Phosphoric acid produced as in Example 1(a) from the solvent extraction operation, 14.7 gph, was steam stripped and concentrated to produce 8.0 gph containing 61.5% P_2O_5 (84.9% H_3PO_4)

1.55% SO_3
25 ppm Fe
10 ppm Mg
less than 50 ppm F
SG = 1.70/20°C

which after cooling to 30°C was fed to a crystalliser comprising a stirred tank and a recirculation loop via a scraped surface heat exchanger, a temperature of approximately 10°C being maintained with brine circulating at -5°C.

The slurry produced was centrifuged yielding 1 64 lb/hr of phosphoric acid hemihydrate crystals and 72 lb/hr of aqueous phosphoric acid. 11 lb/hr of the crystals were dissolved in water to yield 12 lb/hr of aqueous phosphoric acid to be used for washing the crystals on the centrifuge.

The washings were combined with the separated aqueous phosphoric acid and diluted with 3.1 gph water to yield 8.1 gph acid to be used for scrubbing the solvent extract. This acid contained 41.0% P_2O_5 and 2.1% SO_3 .

The resultant 53 lb/hr of crystals were melted in a stirred tank, the contents of which were maintained at 30–40°C, to provide aqueous phosphoric acid for sale containing 66% P_2O_5

TABLE I

Example or Experiment No.	Solvent	EXTRACTION			RAFFINATE			RELEASE			PRODUCT ACID			Yield
		Volume cm ³	No. of counter-current stages	Amount cm ³	H ₃ PO ₄ %	Fe%	S.G.	Volume of water cm ³	No. of counter-current stages	Amount cm ³	S.G.	H ₃ PO ₄ %	Fe%	
Example D	diethyl ketone	1525	2	460	52.5	0.39	1.42	235	2	995	1.34	52.5		67%
Example F	diethyl ketone	1525	2	460	52.5	0.39	1.42	495	1	1185	1.29	45.5		67%
Example G	diethyl ketone	1400	1	485	55.0	0.31	1.44	470	1	1110	1.29	45.5		63%
Example E	methyl n-propyl ketone	1400	1	220	52.5	0.44	1.44	460	2	1385	1.31	48	0.09	84%
Example H	methyl n-propyl ketone	1400	1	220	52.5	0.44	1.44	810	1	1740	1.26	40	0.08	84%

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less than 200 ppm SO_3
and less than 5 ppm each of Fe, Mg and F.

EXAMPLE C

5 1000 cm^3 wet process phosphoric acid derived
from Moroccan phosphate rock having a
specific gravity of 1.54, an H_3PO_4 content
of 67% and H_2SO_4 content of 1.96% and an
iron content of 0.23% was fed into one mixer
10 unit of a two stage countercurrent mixer settler
at 25°C where it was mixed with 425 cm^3 of
recycled scrub liquor of SG 1.34. Into the other
mixer unit was fed 2000 cm^3 of diethyl ketone
of SG 0.82. 535 cm^3 of a raffinate of SG 1.43
15 having an H_3PO_4 content of 53.5% an iron
content of 0.46% and containing 6.5% ketone
was taken from one settler unit. The ketone
extract of the other settler unit was fed to a
three stage countercurrent mixer-settler series
20 in which it was scrubbed with 52 cm^3 of
water. The scrub liquor was recycled to the
initial mixer-settler of the extraction unit and
the scrubbed organic phase passed on to a mixer
in a two stage countercurrent mixer-settler
25 employed for the release. Into the other mixer
of the two stage mixer-settler was fed 205 cm^3
water. From one settler there was taken
1830 cm^3 a product acid of specific gravity
1.34, or H_3PO_4 content of 54%, a ketone
30 content of 7% and 125 ppm of iron was
obtained.

It should be noted that a purer acid could
be obtained by increasing the number of stages
of the scrubbing operation.

EXAMPLES D and E, F, G, and H

In these examples the scrubbing operation was
omitted. In each case 1000 cm^3 /wet process
phosphoric acid as above was extracted into
40 a ketone and subsequently released into water
in accordance with the conditions set out in
Table 1. The nature of the raffinate and the
purified material is also set out in the table.

WHAT WE CLAIM IS:—

45 1. A process for purifying wet process
phosphoric acid, which comprises subjecting
it to extraction with an organic solvent to give
a solvent extract containing phosphoric acid,
contacting the extract with water and producing
50 an aqueous purified phosphoric acid, concen-
trating the aqueous acid to give a concentrated
acid of H_3PO_4 content (by weight) of 84.9–
92%, cooling the concentrated acid to bring
about formation of crystals of $\text{H}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
55 and a mother liquor, and separating the crystals
from the mother liquor.

2. A process according to Claim 1 wherein
the aqueous purified phosphoric acid obtained
60 from the solvent extraction and release contains
less than 100 ppm of metal impurities.

3. A process according to Claim 1 or 2,
wherein the concentrated acid has an H_3PO_4
content of 84.9–88%.

4. A process according to any one of the
65 preceding claims wherein the crystals are melted

to produce an aqueous phosphoric acid having
a P_2O_5 content of 66%.

5. A process according to any one of the
preceding claims wherein the concentrated acid
is cooled to $8-12^\circ\text{C}$.

6. A process according to any one of the
preceding claims wherein the concentrated acid
is obtained by vacuum evaporation of the
aqueous purified phosphoric acid obtained
75 from the solvent extraction and release.

7. A process according to any one of the
preceding claims wherein the solvent is an
unsubstituted acrylic dialkyl ketone of 5 or 6
carbon atoms, butanol, isoamyl alcohol, tributyl
phosphate or diisopropyl ether.

8. A process according to Claim 7 wherein
the solvent is a dialkyl ketone of 5 or 6 carbon
atoms.

9. A process according to Claim 8 wherein
the solvent is methyl isobutyl ketone.

10. A process according to Claim 9 wherein
the solvent extract is scrubbed with purified
phosphoric acid before release to give the
aqueous acid.

11. A process according to Claim 10
wherein the purified phosphoric acid used for
scrubbing is derived by adding water to the
mother liquor obtained from the crystallization.

12. A process according to Claim 9 which
comprises:

a) contacting wet process phosphoric acid
of acidity 65–85% with methyl isobutyl ketone
in a solvent: acid weight ratio of 0.5:1 to
2:1 to form an organic extract containing
85 H_3PO_4 and an aqueous raffinate

b) separating the extract from the raffinate

c) scrubbing the extract

d) contacting the scrubbed organic extract
with water in two or more counter current
stages to effect release to give an aqueous
purified phosphoric acid containing less than
100 ppm metal impurities

e) separating the aqueous acid and the
organic layer

f) raising the concentration of the aqueous
phase to give a concentrated acid of 84.9–92%
 H_3PO_4 content

g) cooling said concentrated acid to bring
about the crystallisation of crystals of
 $\text{H}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ from the mother liquor and
separating the crystals

h) recycling said mother liquor after dilution
with water for use as the scrub liquor in
stage (c).

13. A process as claimed in Claim 8 which
comprises:

a) contacting wet process phosphoric acid
with a pentanone to form an organic phase
containing at least some of the H_3PO_4 content
and an aqueous raffinate

b) separating said organic phase and said
aqueous raffinate

c) scrubbing the organic extract

d) contacting the scrubbed organic extract
with water in two or more counter current

less than 200 ppm SO_3
and less than 5 ppm each of Fe, Mg and F.

EXAMPLE C

5 1000 cm^3 wet process phosphoric acid derived
from Moroccan phosphate rock having a
specific gravity of 1.54, an H_3PO_4 content
of 67% and H_2SO_4 content of 1.96% and an
iron content of 0.23% was fed into one mixer
10 unit of a two stage countercurrent mixer settler
at 25°C where it was mixed with 425 cm^3 of
recycled scrub liquor of SG 1.34. Into the other
mixer unit was fed 2000 cm^3 of diethyl ketone
of SG 0.82. 535 cm^3 of a raffinate of SG 1.43
15 having an H_3PO_4 content of 53.5% an iron
content of 0.46% and containing 6.5% ketone
was taken from one settler unit. The ketone
extract of the other settler unit was fed to a
three stage countercurrent mixer-settler series
20 in which it was scrubbed with 52 cm^3 of
water. The scrub liquor was recycled to the
initial mixer-settler of the extraction unit and
the scrubbed organic phase passed on to a mixer
in a two stage countercurrent mixer-settler
25 employed for the release. Into the other mixer
of the two stage mixer-settler was fed 205 cm^3
water. From one settler there was taken
1830 cm^3 a product acid of specific gravity
1.34, or H_3PO_4 content of 54%, a ketone
30 content of 7% and 125 ppm of iron was
obtained.

It should be noted that a purer acid could
be obtained by increasing the number of stages
of the scrubbing operation.

EXAMPLES D and E, F, G, and H

In these examples the scrubbing operation was
omitted. In each case 1000 cm^3 /wet process
phosphoric acid as above was extracted into
40 a ketone and subsequently released into water
in accordance with the conditions set out in
Table 1. The nature of the raffinate and the
purified material is also set out in the table.

WHAT WE CLAIM IS:-

45 1. A process for purifying wet process
phosphoric acid, which comprises subjecting
it to extraction with an organic solvent to give
a solvent extract containing phosphoric acid,
contacting the extract with water and producing
50 an aqueous purified phosphoric acid, concen-
trating the aqueous acid to give a concentrated
acid of H_3PO_4 content (by weight) of 84.9-
92%, cooling the concentrated acid to bring
about formation of crystals of $\text{H}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
55 and a mother liquor, and separating the crystals
from the mother liquor.

2. A process according to Claim 1 wherein
the aqueous purified phosphoric acid obtained
from the solvent extraction and release contains
60 less than 100 ppm of metal impurities.

3. A process according to Claim 1 or 2,
wherein the concentrated acid has an H_3PO_4
content of 84.9-88%.

65 4. A process according to any one of the
preceding claims wherein the crystals are melted

to produce an aqueous phosphoric acid having
a P_2O_5 content of 66%.

5. A process according to any one of the
preceding claims wherein the concentrated acid
is cooled to $8-12^\circ\text{C}$.

6. A process according to any one of the
preceding claims wherein the concentrated acid
is obtained by vacuum evaporation of the
aqueous purified phosphoric acid obtained
75 from the solvent extraction and release.

7. A process according to any one of the
preceding claims wherein the solvent is an
unsubstituted acrylic dialkyl ketone of 5 or 6
carbon atoms, butanol, isoamyl alcohol, tributyl
phosphate or diisopropyl ether.

8. A process according to Claim 7 wherein
the solvent is a dialkyl ketone of 5 or 6 carbon
atoms.

9. A process according to Claim 8 wherein
the solvent is methyl isobutyl ketone.

10. A process according to Claim 9 wherein
the solvent extract is scrubbed with purified
phosphoric acid before release to give the
aqueous acid.

11. A process according to Claim 10
wherein the purified phosphoric acid used for
scrubbing is derived by adding water to the
mother liquor obtained from the crystallization.

12. A process according to Claim 9 which
comprises:

a) contacting wet process phosphoric acid
of acidity 65-85% with methyl isobutyl ketone
in a solvent: acid weight ratio of 0.5:1 to
2:1 to form an organic extract containing
100 H_3PO_4 and an aqueous raffinate

b) separating the extract from the raffinate

c) scrubbing the extract

d) contacting the scrubbed organic extract
with water in two or more counter current
stages to effect release to give an aqueous
purified phosphoric acid containing less than
105 100 ppm metal impurities

e) separating the aqueous acid and the
organic layer

f) raising the concentration of the aqueous
phase to give a concentrated acid of 84.9-92%
 H_3PO_4 content

g) cooling said concentrated acid to bring
about the crystallisation of crystals of
115 $\text{H}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ from the mother liquor and
separating the crystals

h) recycling said mother liquor after dilution
with water for use as the scrub liquor in
stage (c).

13. A process as claimed in Claim 8 which
comprises:

a) contacting wet process phosphoric acid
with a pentanone to form an organic phase
containing at least some of the H_3PO_4 content
and an aqueous raffinate

b) separating said organic phase and said
aqueous raffinate

c) scrubbing the organic extract

d) contacting the scrubbed organic extract
with water in two or more counter current



stages to effect the release to give an aqueous purified acid containing less than 100 ppm metal impurities and an organic layer

5 e) separating the aqueous acid and organic layer

f) raising the concentration of the aqueous phase to give a concentrated acid of 84.9–92% H_3PO_4 content

10 g) cooling said concentrated acid to bring about the crystallisation of crystals of $\text{H}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ from the mother liquor and

h) recycling the mother liquor after dilution with water for use as the scrub liquor in stage (c).

15 14. A process according to Claim 12 or

13 wherein the acid content of the organic phase is 28–40%.

15. A process for purifying wet process phosphoric acid substantially described herein in Example 1 or 2.

16. Purified phosphoric acid obtained by a process as claimed in any one of Claims 1–15.

17. Purified phosphoric acid obtained by a process as claimed in any of claims 1–6, 8–11 and 15.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1976.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

