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(54) "PURIFICATION OF PHOSPHORIC ACID"

(71) We, ALBRIGHT & WILSON LIMITED, a British Company of P.O. Box 3, Oldbury, Warley, West Midlands, 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 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 (for example in U.S.P. 1968544) 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 ion are present as a result of using hydrochloric acid instead of sulphuric acid in the production of the phosphoric acid. The presence of chloride ion 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% H₃PO₄, 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% H₃PO₄ is USP 3,556,739 which describes 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 now found that if a specific ketone is used as the solvent it is possible to carry out an efficient purification of wet process acid at the commercially available concentrations, op-

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erating 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 the 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 present invention provides 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, the 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.

The use of methyl isobutyl ketone 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 about 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 fertilizer 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 of 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 the extract, into the initial operation where wet process acid is contacted with the ketone in order to promote the formation of an aqueous raffinate. The crude acid to be extracted is of an acidity of at least 65%, frequently in the range 70-85%, preferably about 74-79% expressed as $H_3PO_4 + H_2SO_4$. 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 content of 74% of an H_2SO_4 content of 5% would have an acidity of 79%.

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 25-30°C.

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. eg. of 25-50°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, 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 contacted with methyl isobutyl ketone. The extracting ketone

is preferably 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, more preferably in the range 1.0 to 1.5 : 1 optimally 1.2 to 1.4 : 1 for the one stage extraction. A ratio greater than 2.0 : 1 may be employed but would result in a requirement for larger vessels. 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% to weight of H_3PO_4 .

The contacting of the acid with the ketone is carried out in conventional equipment such as a mixer-settler.

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 contact further 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 also have an H_3PO_4 content of less than 56% 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%.

After scrubbing the phosphoric acid is released from the organic phase by contacting it with water or an aqueous solution of a base in one stage. The amount of water employed should be such that substantially all of the phosphoric acid passes into the aqueous phase from the organic. 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 depending upon the temperature employed; for example using water introduced at a temperature of 20°C an acid of H_3PO_4 content of 45% may be obtained. If desired, water at other than 20°C for example condensates obtained from a heat extractor

such as is used for vacuum concentrators may be employed. Typically temperatures in the range 20-40°C for the release step will be employed. 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. 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 the extract. It should be understood, however, that if a more dilute acid is desired more water may be employed. As mentioned above instead of employing simply water for the release, it is also possible to employ an aqueous solution of a base. Suitable bases include caustic soda and caustic potash, ammonium hydroxide, water soluble amines and basic phosphates such as those of the formula M_2HPO_4 where M is a suitable cation to render the material water soluble. The amount of base present is conventionally up to the amount required to neutralize all of the phosphoric acid in the extract to the dibasic form (e.g. MH_2PO_4) although smaller amounts may be employed if sufficient water is employed to extract the remaining H_3PO_4 values from the ketone extract.

In a preferred embodiment of the invention, there is provided a process wherein methyl isobutyl ketone contacts crude wet process acid of acidity (as hereinbefore defined) 74 to 79% in one stage at 25-50°C in a weight ratio of 1.2 to 1.4 : 1 to give an aqueous raffinate and an organic extract containing 28 to 40% by weight of H_3PO_4 , the extract is scrubbed with phosphoric acid with an impurity content sufficiently low to enable it to extract impurities from the extract, the scrub phosphoric acid containing an amount of H_3PO_4 of from 30-50% by weight of the amount of H_3PO_4 present in the extract, to give a scrubbed extract and used scrub liquor containing impurities which is fed to the first stage of the process in which the crude phosphoric acid is first contacted with the ketone, water then contacts the scrubbed extract in one stage at 20-40°C to give a ketone phase consisting essentially purified aqueous phosphoric acid, and the ketone phase is recycled to the first stage for contacting the crude phosphoric acid. Instead of the contact of scrubbed extract and water to make purified phosphoric acid, the scrubbed extract can be contacted with an aqueous solution of a base to give the ketone phase and an aqueous phase comprising a phosphate salt.

The final product obtained 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 fertilizer production. Alternatively, a less pure purified stream containing e.g. 95% of the initial H_3PO_4 content may be produced by using a high concentration of feed acid and little or no scrubbing.

The purified aqueous phosphoric acid made by the process of the invention may be further purified by raising its concentration and then crystallization as described and claimed in our Patent Application No. 44924/75. (Serial No. 1436115).

The process of the invention is illustrated by the following Example:

In the Example, the feed acid employed was of the following composition:

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

The extracting solvent was methyl isobutyl ketone.

The process is herein described with reference to the flow diagram of the accompanying drawing. 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:

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

WHAT WE CLAIM IS:—

1. A process for purifying wet process phosphoric acid from crude wet process acid of acidity (as hereinbefore 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.

2. A process according to claim 1 wherein said aqueous phase consists essentially of aqueous phosphoric acid.

3. A process according to claim 1 wherein said aqueous phase comprises a phosphate salt.

4. A process as claimed in any of claims 1-3 wherein the crude wet process acid has an acidity (as hereinbefore defined) of 65-85%.

5. A process as claimed in claim 4 wherein the crude wet process acid has an acidity (as hereinbefore defined) of from 70-85%.

6. A process as claimed in claim 5 wherein the crude acid has an acidity (as hereinbefore defined) of from 74-79%.

7. A process as claimed in any of claims 1 to 6 wherein the extraction of H_3PO_4 from the wet process acid into the methyl isobutyl ketone is carried out at from 25-50°C.

8. A process as claimed in claim 7 wherein the extraction is carried out at from 35-40°C.

9. A process as claimed in any of claims 1 to 8 wherein the methyl isobutyl ketone is contacted with the wet process phosphoric acid feed in an amount of from 0.5 to 2.0 : 1 by weight.

10. A process as claimed in claim 9 wherein the ketone is contacted with the wet process phosphoric acid feed in a ratio of from 1.0 to 1.5 : 1 by weight.

11. A process as claimed in any of the preceding claims wherein the H_3PO_4 content in the organic extract is from 28-40% by weight.

12. A process according to any of the claims 1 to 11 wherein the extract of the phosphoric acid in the ketone is subjected to a scrubbing operation before it is contacted with the water or aqueous base.

13. A process according to claim 12 wherein the scrubbing liquor after contact with the extract and containing impurities is fed to the first stage of the process in which the crude phosphoric acid is first contacted with the ketone in order to promote the formation of an aqueous raffinate.

14. A process according to either of claims 12 or 13 wherein the scrubbing liquor is phosphoric acid with an impurity content sufficiently low to enable it to extract impurities from the organic extract and is em-

relative to H_3PO_4 , and a less pure one containing phosphate not extracted into the organic phase which is suitable for use in fertilizer production. Alternatively, a less pure purified stream containing e.g. 95% of the initial H_3PO_4 content may be produced by using a high concentration of feed acid and little or no scrubbing.

The purified aqueous phosphoric acid made by the process of the invention may be further purified by raising its concentration and then crystallization as described and claimed in our Patent Application No. 44924/75. (Serial No. 1436115).

The process of the invention is illustrated by the following Example:

In the Example, the feed acid employed was of the following composition:

Specific gravity	1.66
H_3PO_4	77.4%
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Fe	0.23%
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The extracting solvent was methyl isobutyl ketone.

The process is herein described with reference to the flow diagram of the accompanying drawing. 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 $25^\circ C$. 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:

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

WHAT WE CLAIM IS:-

1. A process for purifying wet process phosphoric acid from crude wet process acid of acidity (as hereinbefore 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.

2. A process according to claim 1 wherein said aqueous phase consists essentially of aqueous phosphoric acid.

3. A process according to claim 1 wherein said aqueous phase comprises a phosphate salt.

4. A process as claimed in any of claims 1-3 wherein the crude wet process acid has an acidity (as hereinbefore defined) of 65-85%.

5. A process as claimed in claim 4 wherein the crude wet process acid has an acidity (as hereinbefore defined) of from 70-85%.

6. A process as claimed in claim 5 wherein the crude acid has an acidity (as hereinbefore defined) of from 74-79%.

7. A process as claimed in any of claims 1 to 6 wherein the extraction of H_3PO_4 from the wet process acid into the methyl isobutyl ketone is carried out at from $25-50^\circ C$.

8. A process as claimed in claim 7 wherein the extraction is carried out at from $35-40^\circ C$.

9. A process as claimed in any of claims 1 to 8 wherein the methyl isobutyl ketone is contacted with the wet process phosphoric acid feed in an amount of from 0.5 to 2.0 : 1 by weight.

10. A process as claimed in claim 9 wherein the ketone is contacted with the wet process phosphoric acid feed in a ratio of from 1.0 to 1.5 : 1 by weight.

11. A process as claimed in any of the preceding claims wherein the H_3PO_4 content in the organic extract is from 28-40% by weight.

12. A process according to any of the claims 1 to 11 wherein the extract of the phosphoric acid in the ketone is subjected to a scrubbing operation before it is contacted with the water or aqueous base.

13. A process according to claim 12 wherein the scrubbing liquor after contact with the extract and containing impurities is fed to the first stage of the process in which the crude phosphoric acid is first contacted with the ketone in order to promote the formation of an aqueous raffinate.

14. A process according to either of claims 12 or 13 wherein the scrubbing liquor is phosphoric acid with an impurity content sufficiently low to enable it to extract impurities from the organic extract and is em-



played in an amount of H_3PO_4 of from 30-50% by weight of the amount of H_3PO_4 present in the organic extract.

15. A process according to any one of the preceding claims wherein the extract and water or aqueous base are contacted at 20-40°C.

16. A process according to claim 2 or any of claims 4 to 15 when appendant thereto wherein water contacts the extract in a weight ratio of 0.2 to 0.4 : 1 by weight of extract.

17. A process according to claim 12 or 14 wherein the methyl isobutyl ketone contacts crude wet process acid of acidity (as herein before defined) 70-85% in an amount of 0.5 to 2.0 : 1 by weight to give an organic extract and an aqueous raffinate, the organic extract is scrubbed and the contacted with water to give the ketone phase and an aqueous phase consisting essentially of purified aqueous phosphoric acid.

18. A process as claimed in claim 17 wherein the crude acid has an acidity (as herein before defined) of from 74-79%.

19. A process as claimed in claim 17 or 18 wherein the extraction of H_3PO_4 from the wet process acid into the methyl isobutyl ketone is carried out at from 25-50°C.

20. A process as claimed in any one of claims 17-19 wherein the ketone is contacted with the wet process phosphoric acid feed in a ratio of from 1.0 to 1.5 : 1 by weight.

21. A process as claimed in claim 20 wherein the ketone is contacted with the acid in a ratio of from 1.2 to 1.4 : 1 by weight.

22. A process as claimed in claim 1 wherein methyl isobutyl ketone contacts crude wet process acid of acidity (as herein before defined) 74 to 79% in one stage at 25-50°C in a weight ratio of 1.2 to 1.4 : 1 to give an aqueous raffinate and an organic extract containing 28 to

40% by weight of H_3PO_4 , the extract is scrubbed with phosphoric acid with an impurity content sufficiently low to enable it to extract impurities from the extract, the scrub phosphoric acid containing an amount of H_3PO_4 of from 30-50% by weight of the amount of H_3PO_4 present in the extract, to give a scrubbed extract and used scrub liquor containing impurities, which is fed to the first stage of the process in which the crude phosphoric acid is first contacted with the ketone, water then contacts the scrubbed extract in one stage at 20-40°C to give a ketone phase containing less than 3% of the H_3PO_4 present in the extract, and an aqueous phase consisting essentially of purified aqueous phosphoric acid, and the ketone phase is recycled to the first stage for contacting the crude phosphoric acid.

23. A modification of the process as claimed in claim 22 wherein the scrubbed extract is contacted with an aqueous solution of a base to give the ketone phase and an aqueous phase comprising a phosphate salt.

24. A process for preparing purified phosphoric acid substantially as herein before described in the Example.

25. A purified phosphoric acid obtained by a process as claimed in any one of claims 1, 2, 4-22 and 24.

26. An aqueous phase comprising a purified phosphate salt obtained by a process as claimed in any one of claims 1, 3, 4-15 and 23.

27. A purified phosphoric acid obtained by a process as claimed in any one of claims 17-21 and 24.

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