Abstract: The present disclosure is related to a low freezing temperature phosphoric acid composition. Phosphoric Acid (PA) has a typical concentration of 75, 80 and 85%. One of the drawbacks of phosphoric acid is that, as its concentration increases, its freezing temperature also increases. As a result, the main strength of acid used for various applications remains 75%/wt which freezes at -18°C; as it is easier to handle and store during cold season. A considerable amount of phosphoric acid is being transported and stored every year in large quantities, mainly at 75% or sometimes but more rarely, at 85%, requiring heating equipment to prevent solidification.
REDUCED FREEZING TEMPERATURE PHOSPHORIC ACID COMPOSITIONS AND METHODS

Cross-Reference To Related Applications

[001] This application claims priority under 35USC 119(e) to United States Provisional Application No. 62/146,473 filed April 13, 2015, incorporated herein in its entirety.

Field of the Invention

[002] The present disclosure relates to compositions and methods for phosphoric acid compositions having a reduced freezing temperature compared to neat phosphoric acid. The freezing of the phosphoric acid is reduced by combining the phosphoric acid with an additive that reduces the freezing of the phosphoric acid composition.

Background of the Invention

[003] Phosphoric Acid (PA) has a typical concentration of 75, 80 and 85%. One of the drawbacks of phosphoric acid is that, as its concentration increases, its freezing temperature also increases. As a result, the main strength of acid used for various applications remains 75%wt which freezes at -18°C; as it is easier to handle and store during cold season. A considerable amount of phosphoric acid is being transported and stored every year in large quantities, mainly at 75% or sometimes but more rarely, at 85%, requiring heating equipment to prevent solidification.

[004] In some heating processes, however, increased phosphoric acid temperature might not be desirable. This is expensive and "pumping" may be difficult, particularly when the phosphoric acid is provided in a plastic storage container.
which is not able to withstand the required higher temperature to allow the
phosphoric acid to be pumped.

[005] Typical phosphoric acid at 85% concentration freezes below 21.1°C or 70°F
which limit its usage during cooler season or requires permanent heating system to
avoid crystal formation; when crystal formation occurs, it causes delays in
manufacturing processes where it is used and ultimately has a significant cost
impact.

[006] As a standard procedure in the industry, when heating is not preferred and
when the process allows it, the recognized alternative is to use a lower strength of
phosphoric acid: i.e. 75% acid with a freezing point of -17°C, which still could
freeze during harsh winter condition and ultimately increase freight cost for users
as unnecessary water is being transported.

[007] Accordingly, it would be desirable to have a phosphoric acid composition
that provides the desired phosphoric acid concentration while having a lower
freezing that allows easy handling at lower temperatures than required by current
phosphoric acid products.

Summary of the Invention

[008] The present disclosure is directed to phosphoric acid compositions having a
reduced freezing temperature compared to neat phosphoric acid. The reduction in
freezing temperature is obtained by combining the phosphoric acid with an
additive that reduces the freezing temperature of the phosphoric acid composition.
The increase in the freezing temperature of the phosphoric acid, at a designated
concentration, is caused by a reduction of phosphoric acid solubility. Any additive
that can cause solvation and/or partial neutralization of the phosphoric acid without
the addition of water may be used, therefore increasing solubility of the crystals at
a lower temperature. The additive could be formed in situ by adding the related alcohol of the phosphoric acid ester.

In a first embodiment, the invention is directed to a low freezing temperature phosphoric acid composition including phosphoric acid having an acid concentration of between 50% and 95% wt. expressed as \( \text{H}_3\text{PO}_4 \) content and from about 0.01% by weight to about 10% by weight of an additive that reduces the freezing temperature of the phosphoric acid. The additive is selected from the group consisting of polyamines, amines, amidazoline, amidoamine, diester phosphate, triester phosphate, phosphonates, phosphinates, thiodiester phosphate, thiotriester phosphate, organic solvents, 2-ethyl hexyl phosphoric acid, tributylphosphate, dibutyl butyl phosphonate and combinations thereof, alkalin, alkalin earth phosphates salts such as sodium, potassium, magnesium phosphates for instance as well as metal phosphates such as transition metals phosphates.

In another embodiment, the invention is directed to a method to prepare low freezing temperature phosphoric acid composition including the steps of combining a phosphoric acid having an acid concentration of between 50% and 95% by weight expressed as \( \text{H}_3\text{PO}_4 \) content and from about 0.01% by weight to about 10% by weight of an additive that reduces the freezing temperature of the phosphoric acid.

**Brief Description of the Drawings**

FIG. 1 illustrates a comparison of the freezing temperatures of typical 75% acid, typical 85% and the phosphoric acid composition of the present invention.

**Detailed Description of the Invention**

The present invention is directed to compositions and methods of a phosphoric acid composition which provides reduced freezing compared to neat
phosphoric acid, and in addition, provides improved storage, handling and reduces freight cost.

[0013] The phosphoric acid composition of the present invention will not freeze during extreme cold temperature, allowing manufacturing operations to continue in contrast to competitive composition in the art. In addition, this will also provide decreased freight cost over time as heat is not required in transport or use. Moreover, the absence of heat required and the reduced freight has a positive impact in terms of carbon footprint and related environmental issues. The increase in the freezing temperature of the phosphoric acid, at its concentration, is caused by a reduction of phosphoric acid solubility versus temperature. Any additive that can cause solvation and/or partial neutralization of the phosphoric acid without the addition of water may be used therefore increasing solubility of the crystals at a lower temperature.

[0014] In a first embodiment, the invention is directed to a low freezing temperature phosphoric acid composition including phosphoric acid having an acid concentration of between 50% and 95% by weight expressed as H₃P0₄ content and from about 0.01% by weight to about 10% by weight of an additive that reduces the freezing temperature of the phosphoric acid, wherein the additive is selected from the group consisting of polyamines, amines, amidazoline, amidoamine, diester phosphate, triester phosphate, phosphonates, phosphinates, thiophosphate, thiophosphate, thiotriester phosphate, organic solvents, 2-ethyl hexyl phosphoric acid, tributylphosphate, dibutyl butyl phosphonate, alkalin, alkalin earth phosphates salts such as sodium, potassium, magnesium phosphates for instance as well as metal phosphates such as transition metals phosphates and combinations thereof, alkalin, alkalin earth phosphates salts such as sodium, potassium, magnesium
phosphates for instance as well as metal phosphates such as transition metals phosphates.

[0015] In a particular example of the present invention, the phosphoric acid composition (referred to as LT-85%) is an 85% phosphoric acid with a freezing temperature below -19°C (4°F).

[0016] Additional components such as surfactants or salts can also be included without departing from the spirit of the invention. The phosphoric acid may be produced by a variety of methods, and may have the purity required for a typical application.

[0017] The reduced freezing phosphoric acid of the present invention may be used for any purpose for which neat phosphoric acid may be used. In addition the reduced freezing phosphoric acid can be added to asphalt to produce improved asphalt for road pavements.

[0018] Appreciating the concept of the present invention, one skilled in the art would recognize multiple applications where the phosphoric acid compositions of the present invention could be used in addition to asphalt, including but not limited to water treatment, food application, fertilizer, detergency and metal finishing.

[0019] In another embodiment, the invention is directed to a method to prepare low freezing temperature phosphoric acid composition including the steps of combining a phosphoric acid having an acid concentration of between 50% and 95% by weight expressed as H₃PO₄ content and from about 0.01% by weight to about 10% by weight of an additive that reduces the freezing temperature of the phosphoric acid.
In a particular embodiment, the method achieves the same effect by creating the additive in situ by adding, for instance, the alcohol related to the phosphoric acid ester to be used as the additive. As a non-limiting example of this concept using triethylphosphoric acid ester as an additive, the ester is made typically by reacting phosphoric acid and the related alcohol; which would be ethanol in this situation. Therefore, adding the ethanol directly into the phosphoric acid, the ester is formed in situ; triethylphosphoric acid ester.

The additive used to reduce the freezing of the phosphoric acid is present in a concentration sufficient to reduce the freezing of the phosphoric acid to the desired value. Examples of additives that may be used to reduce the freezing of phosphoric acid include polyamines, amines, amidazoline, amidoamine, diester phosphate, triester phosphate, phosphonate, phosphinate, thiodiester phosphate, thiotriester phosphate, phosphonate, phosphinate, organic solvents, alkalin, alkalin earth phosphates salts such as sodium, potassium, magnesium phosphates for instance as well as metal phosphates such as transition metals phosphates or combinations thereof. Further, additional potential additives are provided in Table I.

Table I
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<th>Trade Name</th>
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<td>LUMISORB PSE 20 GMS-K</td>
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<td>LUMISORB 5S K</td>
<td>Sorbitan Triacetate</td>
<td>2.1</td>
<td>Ameliorating agent; volume and texture improvement of slower-set fluids in cakes, mousses, and mousses in sorbettes. Emulsifier in coffee whiteners, stabilizers and seasonings, improver, emulsifier, and stabilizers in frozen desserts and ice cream; improves stability and texture in icings and fillings; emulsifier and improves extensibility in puff foods; improves cream and texture in whipped toppings.</td>
<td>178.3402</td>
<td>Kosher for Pareve, Halal</td>
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<td>LUMULSE 40-O K</td>
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<td>573.800, 573.820</td>
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<td>184.1595, 184.1523</td>
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<tr>
<td>LUMULSE GMO-300 K</td>
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<td>Emulsifier for use in preparation of meal milk replacement fluids, providing aid in the production of animal feeds using molasses.</td>
<td>184.1595, 184.1523</td>
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<td>LUMULSE GMS K</td>
<td>Mono- and Diglycerides</td>
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<td>Emulsifier for use in preparation of meal milk replacement fluids, providing aid in the production of animal feeds using molasses.</td>
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<td>HODAG CB-6 KP</td>
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<td>Sugar and Beer Processing. Acidic or beer sugar stabilization and improves purity, increases efficiency of natural materials, and overhauls problems relating to hard-to-handle particulate.</td>
<td>172.2854, 176.210</td>
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<td>36%tive silicone emulsion</td>
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<td>Sugar and Beer Processing. Acidic or beer sugar stabilization and improves purity, increases efficiency of natural materials, and overhauls problems relating to hard-to-handle particulate.</td>
<td>172.2854, 176.210</td>
<td>Kosher for Pareve</td>
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As discussed, surfactants used in asphalt emulsions, such as Evotherm® and Cecabase™, may be used to produce the reduced freezing phosphoric acid. In one embodiment, the additive is present in concentrations between 0.01% by weight to 10% by weight. In other embodiments, the additive is present in concentrations between 0.02% by weight to 5% by weight. The additive may be added to achieve a concentration of 0.1% by weight in the phosphoric acid.

The following example of an embodiment of the invention demonstrates that the types of additives described above can reduce the freezing of phosphoric acid at temperatures as low as 30 degree Celsius to levels where the phosphoric acid can be easily handled and pumped without heating. These examples are not intended to limit the full scope of the invention in any manner.

Example 1

In this example, triethylphosphate was added phosphoric acid having a concentration of 85% wt. expressed as $\text{H}_3\text{PO}_4$ content to achieve a concentration of 0.3% by weight of (85%LT). The freezing of neat phosphoric acid (i.e. phosphoric acid 85% wt.) was monitored at temperatures ranging from -19C, fridge compartment set at ~2C. and compared over a period of 6 month to the freezing of the Typical 75% acid and Typical 85% acid. Whereas the 85%LT and 75% acid remained liquid, the 85% neat acid started exhibiting crystals. The results are shown in FIG. 1.
What is claimed is:

1. A low freezing temperature phosphoric acid composition comprising phosphoric acid having an acid concentration of between 50% and 95% wt expressed as H₃PO₄ content and from about 0.01% by weight to about 10% by weight of an additive that reduces the freezing temperature of the phosphoric acid, wherein the additive is selected from the group consisting of polyamines, amines, amidazoline, amidoamine, diester phosphate, triester phosphate, phosphonates, phosphinates, thiodiester phosphate, thiotriester phosphate, organic solvents, 2-ethyl hexyl phosphoric acid, tributylphosphate, dibutyl butyl phosphonate, alkalin, alkalin earth phosphates salts such as sodium, potassium, magnesium phosphates for instance as well as metal phosphates such as transition metals phosphates and combinations thereof, alkalin, alkalin earth phosphates salts such as sodium, potassium, magnesium phosphates for instance as well as metal phosphates such as transition metals phosphates.

2. A low freezing temperature phosphoric acid composition comprising phosphoric acid having an acid concentration of between 50% and 95% wt expressed as H₃PO₄ content and from 0.02% by weight to 0.2% by weight of an additive that reduces the freezing temperature of the phosphoric acid, wherein the additive is selected from the group consisting of polyamines, amines, amidazoline, amidoamine, diester phosphate, triester phosphate, phosphonates, phosphinates, thiodiester phosphate, thiotriester phosphate, organic solvents, 2-ethyl hexyl phosphoric acid, tributylphosphate, dibutyl butyl phosphonate, alkalin, alkalin earth phosphates salts such as sodium, potassium, magnesium phosphates for instance as well as metal phosphates.
such as transition metals phosphates and combinations thereof and combinations thereof, alkalin, alkalin earth phosphates salts such as sodium, potassium, magnesium phosphates for instance as well as metal phosphates such as transition metals phosphates.

3. A method to prepare low freezing temperature phosphoric acid composition comprising the steps of:

   (i) combining a phosphoric acid having an acid concentration of between 50% and 95% wt expressed as $\text{H}_3\text{PO}_4$ content and from about 0.01% by weight to about 10% by weight of an additive that reduces the freezing temperature of the phosphoric acid.

4. The method of claim 3, wherein the additive is selected from the group consisting of polyamines, amines, amidazoline, amidoamine, diester phosphate, triester phosphate, phosphonates, phosphinates, thiodiester phosphate, thiotriester phosphate, organic solvents, 2-ethyl hexyl phosphoric acid, tributylphosphate, dibutyl butyl phosphonate, alkalin, alkalin earth phosphates salts such as sodium, potassium, magnesium phosphates for instance as well as metal phosphates such as transition metals phosphates and combinations thereof, alkalin, alkalin earth phosphates salts such as sodium, potassium, magnesium phosphates for instance as well as metal phosphates such as transition metals phosphates.

5. A method to increase the freezing temperature of a solution containing phosphoric acid at a defined concentration consisting of the steps of:
(i) combining phosphoric acid crystals at a defined concentration with an additive the will increase solubility of the crystals at a lower temperature.

6. The method of claim 6, wherein the additive causes solvation of the phosphoric acid crystals.

7. The method of claim 6 or 7, wherein the additive causes partial neutralization of the phosphoric acid crystals.

8. The method of claim 6 wherein the additive is selected from the group consisting of polyamines, amines, amidazoline, amidoamine, diester phosphate, triester phosphate, phosphonates, phosphinates, thiodiester phosphate, thiotriester phosphate, organic solvents, 2-ethyl hexyl phosphoric acid, tributylphosphate, dibutyl butyl phosphonate, alkalin, alkalin earth phosphates salts such as sodium, potassium, magnesium phosphates for instance as well as metal phosphates such as transition metals phosphates and combinations thereof, alkalin, alkalin earth phosphates salts such as sodium, potassium, magnesium phosphates for instance as well as metal phosphates such as transition metals phosphates.

9. The method of claim 3 or 5, wherein the additive is formed in situ by adding the related alcohol of the phosphoric acid ester.
INTERNATIONAL SEARCH REPORT

International application No. PCT/US2016/026904

A. CLASSIFICATION OF SUBJECT MATTER

<table>
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<td>(2016.01)</td>
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC - 252/70; 252/71; 252/73; 252/74; IPC(8) - C01B 25/18; C09K 3/18; C09K 5/20 (2016.01); CPC - C01B 25/18; C09K 3/18; C09K 5/20 (2016.05) (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where applicable, search terms used)

Orbit, Google Patents, Google Scholar, Google

Search terms used: phosphoric acid, H3PO4, reduc+, low+, prevent", depress", freeze+, melt+, temp+, ester

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<td>X</td>
<td>US 5,219,675 A (KAMIDE et al) 15 June 1993 (15.06.1993) entire document</td>
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<td>Y</td>
<td>US 2,273,781 A (HOCHWALT) 17 February 1942 (17.02.1942) entire document</td>
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Further documents are listed in the continuation of Box C.

See patent family annex.

Date of the actual completion of the international search 06 June 2016

Date of mailing of the international search report 11 JUL 2016

Name and mailing address of the ISA/

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, VA 22313-1450

Facsimile No. 571-273-8300

Form PCT/ISA/210 (second sheet) (January 2015)