Phosphoric Acid

Livestock

Identification of Petitioned Substance

Chemical Names: phosphoric acid; orthophosphoric acid (IUPAC name); H_3PO_4

Other Names: hydrogen phosphate; metaphosphoric acid; pyrophosphoric acid; white phosphoric acid; O-phosphoric acid; trihydroxidophosphorus; vococid; orthophosphate; sonac; wc-reiniger; orthophosphoramide

Trade Names:
HD CIP ACID™ (Aspen Veterinary Resources)
Acid Clean (Astro Products, Inc.)
Agrosan plus Acid Sanitizer (AgroChem)
FSD-34™ (Diversey)
Demand low foaming anionic acid sanitizer (Diversey)
Dividend anionic acid sanitizer (Diversey)
Hydri-San No. 468 (Hydrite)

CAS Numbers: 7664-38-2

Other Codes:
UNII-E4GA8884NN
E-number E338
EC/EINECS 231-633-2
EPA Pesticide Chemical Code 076001

Summary of Petitioned Use

Phosphoric acid is currently listed as an allowed substance in organic livestock production for use as a disinfectant, sanitizer, or cleaner for equipment.

> **§ 205.603 Synthetic substances allowed for use in organic livestock production.**
>
> In accordance with restrictions specified in this section the following synthetic substances may be used in organic livestock production:
>
> (a) As disinfectants, sanitizer, and medical treatments as applicable.
>
> (25) Phosphoric acid - allowed as an equipment cleaner, *Provided,* That, no direct contact with organically managed livestock or land occurs.

This limited scope technical report serves to support the sunset review of phosphoric acid in organic livestock production. The National Organic Standards Board (NOSB) Livestock Subcommittee has requested answers to two questions from the technical report template. These two questions serve as the focus of this limited report:

> **<u>Evaluation Question #11:</u> Describe all natural (non-synthetic) substances or products which may be used in place of a petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (ii)). Provide a list of allowed substances that may be used in place of the petitioned substance (7 U.S.C. § 6518 (m) (6)); and**
>
> **<u>Evaluation Question #12:</u> Describe any alternative practices that would make the use of the petitioned substance unnecessary (7 U.S.C. § 6518 (m) (6)).**

Characterization of Petitioned Substance

Mechanical removal of organic residues is an important first step in cleaning livestock facilities and equipment. Subsequent disinfecting of equipment and livestock facilities is an essential second step in disease prevention and control. In order for disinfectants to be effective, attached organic material and mineral scale need to be removed. Mineral scale can result when hard water is used in production settings. It is typically the combination of calcium and magnesium compounds that precipitate out of water and collect on surfaces. Water hardness will affect the likelihood and quantity of mineral scale deposition. High levels of calcium, magnesium, and alkalinity[1]are all components that increase the potential for scale formation (Sengupta, 2013).

In livestock facilities, phosphoric acid is used in both Clean-In-Place (CIP) and non-CIP systems[2] to remove encrusted surface matter and mineral scale found on metal equipment. The chemical reaction of the acid with minerals found in deposits makes them water soluble and thus easier to remove. For cleaning purposes, phosphoric acid is often combined with a surfactant, usually a detergent. An example is dodecylbenzene sulfonic acid (DDBSA) which is a component of the commercial product Hydri-san. It is also in StarSan, a steel and glass sanitizing product commonly used in the beverage industry.

Phosphoric acid is sometimes used to remove resistant biofilms, colonies of microorganisms that attach to a surface and are protected by a self-generated protective film of polysaccharide (Muhammad et al., 2020). Surfaces covered with mineral scale are particularly susceptible to biofilm attachment. It is important to note that when mineral scale is dislodged, the biofilm is also dislodged. Smooth surfaces are more difficult to colonize. Research indicates that biofilm bacteria are up to 1000-times more resistant to disinfectants than non-biofilm forming bacteria (Oliveira, 2014).

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Non-synthetic alternatives

No non-synthetic alternatives effective at removing encrusted surface matter and mineral scale were found. Previous USDA technical reports for phosphoric acid (USDA, 2003; USDA, 2021) suggested a review of scouring compounds and enzymatic cleaners as potential alternatives to phosphoric acid.

Scouring compounds are also known as chemical abrasives. They are normally manufactured from inert or mildly alkaline materials and are typically combined with various soaps (Marriott et al., 2018). They are then used with brushes or metal sponges. Neutral scouring compounds can be combined with acid cleaners for removal of alkaline deposits and encrusted materials. Neutral scouring compounds are made from such items as volcanic ash, pumice, silica flours, and feldspar. They are used in manual scrubbing and scouring procedures. Slightly alkaline scouring compounds include borax and sodium bicarbonate. No published research could be found on the use of such compounds in animal facilities.

Enzymatic cleaners are now available on the market but are marketed in industries other than organic agriculture. Enzymes are proteins which catalyze chemical reactions. They break down soils and stains, and they are typically mild, noncorrosive, and safe to handle. The main industry using enzymes for cleaning is the clothing industry, where enzymes enhance biofilm removal (Stiefel et al., 2016).

It is now known that 40-80% of bacterial cells are able to form biofilms (Flemming and Wuertz, 2019). Biofilms are complex surface-attached communities of microorganisms. These communities can consist of single microbial species or a combination of species of bacteria, protozoa, archaea (single-celled, prokaryotic microorganisms that includes methanogens and those of harsh environments), algae, filamentous fungi, and yeast. They strongly attach to each other and to biotic or abiotic surfaces. Biofilms can result in disease outbreaks. For example, biofilm formation was found to make major mastitis-causing bacteria more resistant to the disinfectants typically used on commercial dairy-farms (Tremblay et al., 2014). Other problems caused by biofilms include food spoilage, pipe fouling, and ship hull fouling.

[1] Alkalinity refers to a water source's ability to neutralize acidity. Carbonate, bicarbonate, hydroxide, borate, silicate, and phosphate contribute to alkalinity (Sengupta, 2013).

[2] Clean-in-Place refers to cleaning the interior surfaces of pipes and equipment without dismantling them first. Non-CIP would involve at least some dismantling of the equipment before cleaning.

Non-synthetic alternatives to manage bacterial populations are currently under development. One solution is referred to as 'positive biofilms.' Positive biofilms involve using beneficial bacteria that are able to form biofilms that outcompete undesirable microorganisms (Guéneau et al., 2022). Such products would be applied to building surfaces to guide the microbial ecology of biofilms after cleaning and disinfection procedures. The positive biofilms limit the proliferation of undesirable microorganisms, such as *Salmonella* spp., *Escherichia coli*, *Enterococcus faecalis*, and *Enterococcus cocorum*, in building through nutritional and spatial competition. Most commercial 'positive biofilm' products are composed of species such as *Lactococcus* spp., *Lactobacillus* spp., or *Pediococcus* spp., often in combination with *Bacillus* spp. Large-scale evaluation of commercial products is still being conducted. *Bacillus subtilis* is an industrially important bacterium that forms rough biofilms at the air-liquid interface instead of on the surface of a solid phase in a liquid (Morikawa, 2006). This permits the control of infection caused by plant pathogens and the reduction of steel corrosion. It also allows for the exploration of novel compounds that could be used to control harmful biofilm formation.

Lu et al. (2019) reviewed several natural products as potential anti-biofilm agents, including anti-biofilm therapeutics undergoing clinical trials. There are anti-biofilm agents extracted from medicinal plants such as garlic; *Cocculus trilobus*; *Coptis chinensis*; cranberry polyphenols; *Herba patriniae*; *Ginkgo biloba*; phloretin, which is abundant in apples; citrus limonoids; and quercetin which exists in many fruits, vegetables, and grains. There are currently no commercial products available that are made from these substances.

New mixtures of products may prove beneficial as well. Rocha e Silva et al. (2020) described a product composed of a natural solvent (cottonseed oil), a plant-based surfactant agent (saponin), and two natural stabilizers (carboxymethylcellulose and glycerine). The authors reported that the formulation was stable, nontoxic, and highly efficient. It removed 100% of heavy oil from glass and metallic surfaces. Similar products could be developed for cleaning animal housing and equipment.

It is important to look at other industries which also depend on cleaning for potential solutions to problems encountered in cleaning and disinfecting livestock housing and equipment. For example, biocleaning has been developed for artifact restoration (Martino et al., 2020). The products used include sulfate-reducing bacteria (e.g., *Pseudomonas stutzeri*) and hydrolytic enzymes.

Synthetic Alternatives

Earlier USDA technical reports (USDA 2003; 2021) on phosphoric acid have indicated that other strong acids have been used for cleaning operations but are not as effective or practical as phosphoric acid. These alternative acids included hydrochloric, hydrofluoric, sulfamic, sulfuric, and nitric acids. Acids have the ability to dislodge and dissolve mineral scale as long as the strength of the acid is high enough. When they dislodge the mineral scale, they also dislodge the biofilm and are thus important in its removal. Nitric and sulfuric acids are too corrosive to metal to be practical in livestock operations. Hydrochloric acid is used in descaling metals but is a health hazard because of toxic hydrogen chloride gas. Additionally, none of these acids besides phosphoric is currently permitted in organic livestock production. The previous technical reports concluded that phosphoric acid was more practical than these other alternative acids since it is the lowest in corrosiveness and is compatible with many surfactants.

Peracetic acid (CAS #-79-21-0) is permitted on the National List at § 205.603(a)(24) for sanitizing organic livestock facilities and processing equipment. The 2016 USDA technical report on peracetic acid (USDA, 2016) indicates that it is also effective in removing biofilms. Oxalic acid also effectively removes iron oxide rust without attacking the metal, but is currently only permitted in organic apiculture. Precautionary steps are also necessary with oxalic acid, since it reacts with hard-water constituents and forms a poisonous precipitate, calcium oxalate (Marriott et al., 2018).

Previous USDA technical reports for phosphoric acid used in organic processing/handling (USDA, 2003; USDA, 2021) suggested a review of colloids, sequestrants, and auxiliary compounds used in cleaners as potential alternatives to phosphoric acid. However, specific materials within each of these classes of products would need to be petitioned for addition to the National List and evaluated individually. Further, combinations of materials found to have multiple beneficial properties for cleaning and sanitizing (Shkromada et al. 2021) would also need to have any synthetic components assessed for compliance with the National List.

Electrolyzed oxidized water (EOW) is a relatively new material that can be used for disinfecting animal facilities (Hao et al., 2013a, b; Rahman and Murshed, 2019). EOW is on the National List under §205.603(a)(10)(iv), Chlorine Materials, Hypochlorous acid – generated from electrolyzed water. EOW is produced on-site by electrolysis of a 0.1% sodium chloride solution in an electrolysis chamber. The anode (positive electrode) and the cathode (negative electrode) of the chamber are separated by a diaphragm to form two separate compartments. The anode acidic EOW has a low pH (typically 2.3-3.0), a high oxidation-reduction potential (ORP) (>1000 mV), and contains relative concentrations of chlorine, hypochlorous acid, and hypochlorite (Fenner, 2005). The cathode alkaline EOW has a high pH and a low ORP. The physical properties and chemical composition of the EOW will vary depending on the concentration of sodium chloride, the amperage used, the electrolysis time, and the flow rate of the water (Fenner, 2005).

Anode EOW was shown to have strong anti-microbicidal activity against a broad variety of bacterial pathogens. There were, however, marked differences in the sensitivity of the different bacterial strains tested, with the gram-negative bacterium *Proteus mirabilis* and the gram-positive bacterium *Salmonella aureus* being more susceptible than the gram-negative *Pseudomonas aeruginosa* and gram-positive *Enterococcus faecium*. The latter species required more exposure time in order to be killed. EOW has also been shown to be effective on mycobacteria (e.g., *Mycobacterium avium*) as well as bacterial endospores. It is also reported to have fungicidal activity and can inactivate bacterial and fungal toxins (Fenner, 2005).

<u>Evaluation Question #12:</u> Describe any alternative practices that would make the use of the petitioned substance unnecessary (7 U.S.C. § 6518 (m) (6)).

Cleaning and disinfecting (C&D) are essential elements in disease prevention and control on any animal production or processing facility. In fact, Schmidt (1997) discusses the properties of the types of contaminants that can be found on surfaces (fat-based, protein-based, etc.) and how these properties, together with the properties of the different types of surfaces, will affect the C&D procedures. This would include choice of cleaning agents. However, C&D is much easier when there is no encrusted material or mineral scale to remove. Preventing such occurrences, therefore, would be important in reducing or eliminating the need for phosphoric acid as a cleaning tool.

The ability of materials to encrust a surface depends on the surface tension of those materials (Marriott et al., 2018). The type of material used will also affect the type of C&D chemicals that can be used. Marriott et al. (2018) characterized the various surfaces with regard to their suitability.

- Black metals are prone to rust so are often tinned or galvanized. Neutral detergents are recommended for cleaning such surfaces.
- Tin surfaces are easily corroded by strong alkaline and acid cleaners.
- Cement should be dense, acid resistant, and non-dusting. Acid brick may be used in place of concrete.
- Glass should be smooth and impervious and should be cleaned with moderately alkaline or neutral detergents.
- Rubber should be nonporous, non-spongy, and not affected by alkaline detergents. All rubber surfaces can be impacted by organic solvents and strong acids.
- Stainless steel is generally resistant to corrosion. It has a smooth surface and is impervious.

Microbial populations may form biofilms as a protective response to environmental stresses such as UV radiation, desiccation, limited nutrients, high pressure, and antimicrobial agents. The events leading to biofilm formation are complex but are believed to start with reversible attachment. Both inert and biological surfaces can be used for the initial bacterial attachment. The physicochemical properties of the surface will determine how quickly biofilms develop. These properties include surface roughness, hydrophobicity, surface charge, and presence of conditioning films. The choice of surfaces in animal housing, therefore, can affect biofilm formation. Remodeling the surface or coating the surface with substances that do not encourage bacterial adhesion are strategies that could be implemented to impede the establishment of bacterial biofilms (Flemming and Wuertz, 2019).

The chemical properties of the water used in cleaning operations should be considered. Hard water with varying amounts of calcium, magnesium, and other alkali metals interferes with the effectiveness of cleaning products. Hard water also contributes to the formation of precipitates. Such precipitates allow for the accumulation of debris and microorganisms, making effective C&D difficult. If a farm has hard water, it may be more economical to use a water softener to mitigate the problem of precipitates, rather than relying on more C&D (Marriott et al. 2018).

The removal of encrusted material from a surface can be done through mechanical action of high-pressure water, steam, air, and scrubbing. It can also be done through the use of surfactants that reduce surface tension of the cleaning medium and allow more close contact with the material.

The Federal Pasteurized Milk Ordinance (PMO) requires milking operations to employ effective C&D procedures for product-contact surfaces of multi-use containers, utensils and equipment used in the transportation, processing, condensing, drying packaging, handling and storage of milk or milk products before each use (or at regular intervals for certain systems) (FDA, 2019). While the PMO does not mandate specific materials for disinfection, it does reference food-contact surface sanitizing materials with tolerance exemptions at 21 CFR 180.940. In addition to chemical sanitization, other approved methods include the use of steam or hot water. Some methods maybe be recommended for certain applications over others. For example, caustic solutions of sodium hydroxide, another material permitted on the National List at §205. 605(b), are recommended for soaker-type bottle washers, to be followed by clean water rinse or chemical treatment to prevent recontamination (FDA, 2019).

Cleaning procedures in other industries may inform new and different means of preventing encrusted material and mineral scale in livestock operations. The fouling of ship hulls is a significant obstacle to efficient ship operation. Copper-based antifouling coatings have been used, however, bans are being considered because of copper leaching into the water (Chambers et al., 2006). Holm et al. (2003) looked at non-toxic alternatives to the toxic antifouling paints being used on ship hulls. One alternative was silicone coatings. The authors then developed a portable rotating brush device that can be used to clean hulls without damaging the coating. No published research looking at the use of this material in animal agriculture facilities was found in the literature reviewed for this report. However, this alternative may be worth investigating for the treatment of animal housing and equipment to minimize attachment of organic material and mineral scale, and increase ease of cleaning.

Report Authorship

The following individuals were involved in research, data collection, writing, editing, and/or final approval of this report:

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All individuals are in compliance with Federal Acquisition Regulations (FAR) Subpart 3.11—Preventing Personal Conflicts of Interest for Contractor Employees Performing Acquisition Functions.

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