

**Petition Submitted by BioStar Systems, LLC, Kansas City, MO.**

**Contact: Dr. William A. Torello**

Item A:

Petition for: **Synthetic Substance Allowed for the use in Organic Crop Production.**

Item B:

1. Substance Common Name:

Sulfuric Acid – Technical Grade

Other Names: Hydrogen Sulfate, Oil of Vitriol, Oleum.

Composition: H<sub>2</sub>SO<sub>4</sub>

2. Manufacturer's Name and Contact Information:

NorFalco LLC

6050 Oak Tree Blvd. Suite 190

Independence, OH 44131

USA

Phone: 216-642-7342

Fax: 216-642-9169

E-mail: [request@noranda.com](mailto:request@noranda.com)

3. Intended Use of Substance:

**Anaerobically Digested Poultry Manure: The use of sulfuric acid for stabilization of digested poultry manure to a pH under 4.5 but not below 3.5.**

The use of sulfuric acid is currently NOP approved as a processing and stabilization aid for organic liquid fish and some aquatic plant extract products (NOP 205.601(j)(7)). Sulfuric acid would be used in the same way with digested poultry manure to stabilize and ensure product viability and shelf life. Current usage of NOP approved citric acid cannot effectively reduce pH levels under 4.5. Without a reduction in pH to 4.5 or under, the product continues microbial activity anaerobically and aerobically to produce high levels of various gases causing unacceptably high pressures in shipping containers as well as changing the initial characteristics of the product by metabolizing biologically active compounds that give the product its high level of field efficacy. Reduction of pH to below 4.5 would also ensure against the possibility of microbial contamination by E. coli, Salmonella and fecal coliforms.

4. A List of Handling/Processing Procedures for Which the Substance will be used:

Anaerobically digesting poultry manure and litter is a three stage, contained process which involves hydrolysis, acetogenesis and methanogenesis carried out by groups of anaerobic bacteria to produce gaseous methane (biogas which is captured and transformed into usable “green” energy) and a liquid/solid slurry end product that is further processed into dry, solid granular and liquid organic fertilizer. The dry granular product is stable for packaging, transport and sale but the liquid material (which is the bulk of the end products) leaves the digester at pH levels ranging from 6.5 to 8.5 which will continue to metabolize at increasing rates during subsequent processing, packaging and transport. In short, at these pH levels, the liquid product is highly unstable.

Once out of the digester, the slurry is centrifuged to remove the bulk of solids for dry granular processing. The liquid remaining has significant levels of soluble and insoluble organic matter which is further processed by nano-filtration to remove large particles which would not pass through end user fertigation or drip irrigation systems. The residue left in the liquid after centrifugation and filtration is the substrate for continued microbial metabolism by resident and contaminate bacteria.

The method of handling and addition of sulfuric acid will be added by batch mode using only enough of the acid to lower the pH level under 4.5 but above 3.5 after which, the product can then be safely packaged, shipped and sold with the assurance of a reasonable shelf life. Amounts of sulfuric acid to be added will not exceed 1.0% of the total liquid volume of product and will be added manually to ensure excess acid is not used and optimum pH levels attained.

5. The source of the substance and a detailed description of its manufacturing or process procedures from basic component to the final product:

The production of sulfuric acid is by pollution control devices or scrubbers used during the smelting of various metal ores. Sulfur dioxide is captured by these scrubbers to reduce or eliminate the possibility of acid rain development. The sulfur dioxide gas which is captured is further concentrated and cleansed prior to the production of sulfuric acid.

The method of converting cleansed and concentrated sulfur dioxide to sulfuric acid is called the “contact process” and is a universally used procedure.

- A. Cleansing of sulfur dioxide gas.
- B. Wet sulfur dioxide gas is dried in a tower by direct contact with purified (93%) sulfuric acid then blown over catalyst beds and heat exchangers to cool the gas. The process causes sulfur dioxide to oxidize with oxygen in air resulting in sulfur trioxide.

- C. Sulfur trioxide passes through absorption tower combining with water in 98% sulfuric acid to make additional sulfuric acid.

The total process is a pollution control measure which focuses on sulfur dioxide containment.

- 6. A summary of any available previous reviews by State or private certification programs or other organizations of the petitioned substance:

USDA/NOP: Both phosphoric and sulfuric acids are allowed for use as additives to liquid fish products (205.601(j)(7)). Sulfuric acid is used to adjust pH of the fish products to prevent further degradation and/or creating odorous gases. The amount of acid shall not exceed the minimum needed to lower the pH of the product to 3.5.

NOP interpretive letter: Per a February 6, 2004 letter from USDA-NOP to David Hiltz, with Acadian Seaplants Limited, regarding interpretation of current rules on use of phosphoric acid for pH adjustment in aquatic plant extract: "...Therefore, aquatic plant extracts, as long as manufactured consistent with the restrictions specified in section 205.601(j)(1), are allowed as synthetic substances for use in organic crop production, including the use of phosphoric acid to adjust the pH of the aquatic plant extracts".

Although phosphoric acid and sulfuric acid are not the same chemicals, they are grouped into the same regulatory text. They are used in the same manner for liquid fish products and for aquatic plant extracts.

We are submitting this petition for the same uses as those outlined for liquid fish and aquatic plant products. Poultry Litter/manure is also already approved by NOP.

- 7. Information regarding EPA, FDA and State Regulatory authority registrations including registration numbers:

EPA: Initial notification is required to have this substance on our site under the Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA) 40 CFR part 302. Release notification of the substance if spilled is regulated under Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA) 40 CFR part 372 and part 304. The sulfuric acid proposed for use does not contain any List 1, 2 or 3 inerts as per §6517c(1)(B)(ii);205.601(m)2. Manure itself is listed as an inert on EPA list 3. Sulfuric acid and water is on the EPA List 4 – Inerts of Minimal Concern.

FDA: Regulations pursuant to the FDA's food bioterrorism regulations apply to distribution, storage or use for food and food processing.

State(s): An initial written notification to the State Emergency Response Commission (SERC) and the Local Emergency Planning Commission (LEPC) are required within 60

days of having this substance on site. Any spillage of over 1000 lbs. must be reported immediately to the National Response Center (NRC), the SERC, and the LEPC. Both requirements will be met once sulfuric acid is brought on-site. Sulfuric acid was put on the State of California's Proposal 65 list effective March 14, 2003 which requires labeling of product if sold in the State of California.

8. The Chemical Abstract Service (CAS) number or other product numbers of the substance and labels of products that contain the petitioned substance – Sulfuric Acid.

Chemical Abstract Service (CAS) number: 7664-93-9

NIOSH Registry of Toxic Effects of Chemical Substances number: WS5600000

Department of Transportation (DOT) identification number: 1830 137

There are numerous product listings on the internet for liquid fish products (crop use) using phosphoric, sulfuric or citric acid for pH stabilization under current NOP rules. Two consolidated lists found were: Organic Materials Research Institute's (OMRI) brand name list, located at [http://www.omri.org/OMRI\\_datatable.htm](http://www.omri.org/OMRI_datatable.htm); and the Washington State department of Agriculture – 2004 Brand name materials list, located at <http://agr.wa.gov/FoodAnimal/Organic/MaterialsLists.htm>.

Labels of products that contain the substance: On the OMRI brand name list there are currently 23- "fish products, liquid – stabilized" listed as approved crop products. The Washington State department of Agriculture lists 16 "fish products" as a fertilizer & soil amendment on their brand name materials list.

Information about each product varied a great deal in detail. At individual vendors' sites (Rainyside.com – "How a fish becomes fertilizer") explains how "a small amount – less than 0.1% by weight- of phosphoric acid is used to drop the pH of the solubles to 4.5 or below. Without this acid addition, the enzymes in the fish would cause it to decay, create gases and to smell horrid-and, all the states realize this, and within certain guidelines is still considered 100% Natural Organic".

At present, there are no digested poultry manure products in the marketplace and, as such, there are no labels to reference. We represent the first company to anaerobically digest poultry manure countrywide.

9. The substance's physical properties and chemical mode of action including:
  - A. Chemical interactions with other substances, especially substances in organic production:

Sulfuric acid used with poultry manures and litter will allow biologically derived nitrogen

compounds to remain in solution versus being volatilized during the filtration process. The pH of excreted manures tends to be alkaline (7.8 – 8.3 s.u.) because of the use of limestone (calcium source for bone mass) in the animal feed, and because of the natural generation of uric acids and ammonium in the urine and feces of the animal. This is caused via the animals' digestion of proteins into simpler nitrogen compounds.

By adding a small amount of sulfuric acid to lower the pH to not less than 4.5, the biological breakdown of the uric acids and ammonium into more volatile forms of nitrogen (ammonia) and organic (carbon based) compounds (fatty acids) are slowed which would otherwise release odorous compounds. This reduction in pH in the liquid poultry manure product would stabilize the product for subsequent packaging, transportation and sales by totally inhibiting microbial activity and significantly increasing shelf life.

#### (b) Toxicity and environmental persistence of sulfuric acid:

Once sulfuric acid is added to the poultry manure, the acid portion of the substance is neutralized by the manure and its oxidized form sulfate ( $\text{SO}_4^{2-}$ ) is left. The added sulfur (S), although negligible, is considered beneficial to the crop. Sulfur, in its oxidized form sulfate ( $\text{SO}_4^{2-}$ ), is an essential nutrient in the formation of chlorophyll and the amino acids within the plant. The residual oxidized form of sulfate ( $\text{SO}_4^{2-}$ ) in the manure takes on forms and functions within crops to be considered a nutrient as opposed to being a contaminant.

#### 1. Forms:

- Plants absorb mostly  $\text{SO}_4^{2-}$ ; small quantities of  $\text{SO}_2$  can be absorbed by plant leaves.
- Plant S ranges between 0.1 and 0.5% S and varies with plant type:

#### 2. Functions:

- S-containing amino acids cystine, cysteine, and methionine, essential components of protein, comprise 90% of plant S.
- S deficient plants produce less protein and accumulate nonprotein N as  $\text{NH}_2$  and  $\text{NO}_3^-$  leaf  $\text{NO}_3^-$  accumulates under S deficiency reducing food quality.
- Adequate S improves crop quality by narrowing N/S ratio to 9:1 to 12:1 needed for effective use of N by rumen microorganisms.

- S is needed for synthesis of chlorophyll and coenzyme A, this being important for oxidation and synthesis of fatty acids and amino acids.

- S is a component of ferredoxins, an Fe-S protein in chloroplasts. Ferredoxin is important in NO<sub>2</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> reduction and N<sub>2</sub> assimilation by root nodule bacteria.

- S is responsible for the characteristic taste and smell of mustard and onion plants.

Toxicity and environmental persistence of any other material within the sulfuric acid, such as residual metals, is tightly controlled during the second phase of the production process of sulfuric acid. Technical grade product will be used in the manure product to insure any residual metals will meet the technical specifications enclosed with this application and to otherwise not jeopardize any state or federal limits for metals in soil amendments.

(c) Environmental impacts from its use or manufacture.

Sulfuric acid is a pollution control byproduct of the metal smelting industry. If not turned into a product this byproduct would ultimately form acid rain in our atmosphere. Consumer use (industrial, agricultural, commercial) of sulfuric acid truly benefits the environment by allowing the metal industry to produce a high quality product instead of a large volume waste.

(d) Effects on human health.

Like any acid, sulfuric acid can be harmful to humans if it comes in contact with skin during handling. This is detailed in the report titled "criteria for a recommended standard... Occupational Exposure to Sulfuric Acid" compiled by these organizations:

- U.S. Department of Health, Education, and Welfare
- Public Health Service
- Center for Disease Control
- National Institute for Occupational Safety and Health

10. Safety information about the substance including a Material Safety Data Sheet (MSDS) and a comprehensive substance report from the National Institute of Environmental Health (NIEH) Studies.

MSDS and technical specification is included from the manufacturer.

The MSDS and above referenced study are being submitted instead of the substance

report from the NIEH, which could not be found.

11. Research information about the petitioned substance which includes comprehensive substance research reviews and research bibliographies, including reviews and bibliographies which present contrasting positions to those presented by the petitioner in supporting the substance's inclusion on the National list.

One contrasting position to adding sulfuric acid to the National list is an August 1, 2003 petition to the NOSB from Harmon Systems International, LLC. Harmon Systems International petition advocates the inclusion of sulfurous acid to the National list processed via one of their generators instead of "...sulfuric acid, which requires a synthetic and unnatural process to produce..."

Much of the information regarding other approved products' use of an acid to adjust pH remains very general, or does not exist, either via their respective websites, or by calling the informational numbers. Under current NOP rules each of these products could and may already use some sulfuric, phosphoric or citric acid.

Our petition does not attempt to gloss over the details of the sulfuric acid manufacturing process or say that the substance is not harmful when used incorrectly. We do however, recognize that sulfuric acid is a value-added product of pollution prevention, and when the substance is used in accordance to current NOP guidelines either in liquid fish products or in anaerobically digested poultry manures, we believe it promotes soil and plant health and allows for the safe and minimally odorous transport to organic crops around the country.

Sulfuric acid, as stated earlier in the application, is a product of pollution control. This fact alone is of enormous environmental benefit because of the sheer volume of sulfuric acid produced annually in North America. Sulfuric acid production topped 39,500 tons in 1985 and continues to be one of the most widely used production chemicals year after year.

12. This synthetic substance is necessary for the production and handling of anaerobically digested poultry manure and litter because:

Sulfuric acid was shown to be the most effective acid to minimize ammonia emissions and odors. In our trial process, we tried various methods to control odor, including enzymatic microbiological inhibitors, carbon dioxide and peracetic acid. We have also contemplated the use of other strong mineral acids like nitric and hydrochloric acid; but these acids are cost prohibitive, do not provide the added benefit to crops that sulfur would, will not be organically certified, and do not provide the additional pollution control benefits from recycling by-product chemicals. Furthermore, sulfuric acid effectively inhibits unwanted microbial activity in our liquid product when pH levels are under 4.5.

Other organic materials that could potentially lower the pH of would include citric acid or acetic acid. Because citric acid and acetic acids are considered weaker acids than sulfuric acid, much larger amounts of these acids would be needed to lower the pH of the final product. This would increase costs of producing the final product, resulting in higher costs to be passed to the end-customer. Furthermore, the amount of citric or acetic acid necessary to move pH levels down past 4.5 leave an unacceptable amount of citric acid residue in the final product (over 20%). Also, in view of the new certification laws currently being enacted in California (our prime market), we strongly believe that we would need to move pH levels down to 4.0 or below to ensure inhibition of microbial growth.

We believe sulfuric acid is the best choice for this product since it is a very strong mineral acid requiring comparatively low volumes and for the following reasons:

- It is a by-product of pollution control so the manufacture of the material has a positive environmental benefit.
- Any residual sulfur in the end product provides a positive nutritional benefit to the crop as described in question nine of this application.
- It is already used in other products listed for use in organic crop production like liquid fish products and aquatic plant hydrolysates.

Alternative methods such as wind row composting or static aerated piles defeats the purpose of utilizing the new technology of “in-vessel” anaerobic digestion which accomplishes normal composting in days rather than months and allows for the recycling of large volumes of manure in short periods of time.

13. A Commercial Confidential Information Statement which describes the specific required information contained in the petition that is considered to be Confidential Business Information (CBI).

We are not claiming any CBI at this time.