Aqueous Potassium Silicate

Crops

Identification of Petitioned Substance

Chemical Names:
Potassium metasilicate
Dipotassium oxosilanediolate

Other Name:
Silicic Acid Potassium Salt
Soluble Potash Glass
Potassium silicate
Potassium water glass
Soluble potash water glass
Potassium silicate solution
Potassium polysilicate
Silicic acid, potassium salt

Trade Names:
Liquid Glass
Water Glass
AgSil
Kasil
Kasil 6
Pyramid 120
Caswell No. 701B
Sil-Matrix

CAS Number:
1312-76-1

Other Codes:
Pubchem: 66200
Chemspider: 59585
PS 7
HSDB 5798
EINECS 215-199-1
EPA Pesticide Chemical Code 072606
1312-76-1
11116-04-4
12698-85-0
EC number: 233-001-1

Summary of Petitioned Use

Following a petition and a supplemental petition, respectively in 2004 and 2006, the NOSB recommended the adoption of aqueous potassium silicate, for insect and mite protection and plant disease control in a November 30, 2007 vote (NOSB, 2007 a, b, c, d). A proposed rule was published on June 3, 2009 (Keeney, 2009). The final rule was published on December 13, 2010. Aqueous Potassium Silicate was added to the National List (Electronic Code of Federal Regulations, 2013) as follows:

> § 205.601: synthetic substances allowed for use in organic crop production, (e) as an insecticide (including acaricides or mite control) and (i) for plant disease control with a restriction that the silica used in the manufacture of potassium silicate must be sourced from naturally occurring sand.

As required by the Organic Foods Production Act, the National Organic Standards Board has the responsibility to review each substance on the National List within five years of its adoption to determine whether the substance should be renewed or removed from the National List. The NOSB has requested an updated technical evaluation report for aqueous potassium silicate to support their decision-making.

Characterization of Petitioned Substance

Composition of the Substance:

Aqueous Potassium Silicate is a synthetic material manufactured by combining natural mined sand and potassium carbonate in the presence of high heat to form water soluble glass beads. The glass is ground to a powder that is dissolved in water with heat and pressure. This product has many uses in several industries. In addition to its use in plant health and hydroponics, aqueous potassium silicate is used in electronics, monitors and screens, catalyst binders, welding rods, soaps and detergents, refractory cements, adhesive coatings, well drilling (Rawlyk and McDonald, 2001), and antifreeze (PQ Corporation, 2012). There is a very high demand for this product, thus the product is consistent and generally subjected to quality control prior to distribution and use. Aqueous potassium silicate should be distinguished from "slag." Slag is a byproduct of the metal ore smelting industry. Although, slag contains silicon dioxide, there is no process control over the presences of metal oxides, some of which may be considered toxic. Slag is used agriculturally as a source of aqueous silicate (Savant et al., 1999).

Source or Origin of the Substance:

Although not common, aqueous potassium silicate is present in some soils of volcanic origin (Takahashi et al., 2001, White et al., 1980). Mostly, soil is composed of aluminum silicate minerals and clays, e.g. kaolinite and halloysite. Synthetic potassium silicate is produced by direct fusion of silica and potassium carbonate. Raw materials used for the production of potassium silicate for organic use are naturally sourced quartz sand, potassium carbonate (potash, K_2CO_3), potassium hydroxide (KOH), water and fuels/energy, e.g. oil, gas, electricity. Filter aids (mostly from natural sources) are also used.

Properties of the Substance:

Potassium silicate is a colorless or yellowish, translucent solid appearing as glass-like pieces (Chemspider, 2013). The solid form may be processed to lumps, shattered pieces, or granular particles. In solution, potassium silicate is colorless. Due to their glass nature, solid amorphous silicates do not have discrete melting points but rather flow points. Aqueous silicate solutions have a melting point only slightly lower than that of water (Organization for Economic Cooperation and Development, 2004). Solid weight, index of refraction, density, melting point, and crystalline properties of potassium silicate vary with raw material stoichiometry. Aqueous potassium silicate solution used for organic agriculture is prepared from a product with 2.5:1 ratio of potassium carbonate to silicon dioxide. The specific gravity of this product is 1.39 g/cm^3 (20^{o}C). Aqueous potassium silicate is insoluble in alcohol, alkaline (pH 11.3-11.7) and hygroscopic. It decomposes in acid with the precipitation of silica. At low concentrations, aqueous potassium silicate is monomeric; however, as concentration increases aqueous potassium silicate becomes increasingly polymeric. In soils and clays, potassium and silicon occur in several forms, but are mostly associated with aluminum and oxygen in a coordinate polymeric form described as continuous tetrahedral sheets (mica-Illite) and three-dimensional tetrahedral frameworks (feldspars-orthoclase). Silicon in this form is not readily available for use by plants (Carey and Fulweiler, 2012).

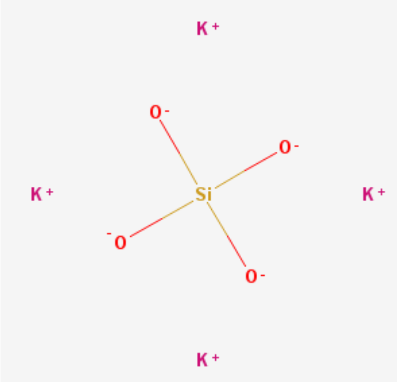


Fig 1. Structure of Potassium Silicate

Chemically, the basic structural units of potassium silicate are silicon-oxide tetramers (Figure 1). These are linked with each other via Si-O-Si bonds resulting in an infinite three-dimensional network. The negative charge of unshared oxygen atoms is balanced by potassium cations that are randomly spaced in the interstices. The extent to which balancing alkali ions are present in potassium silicate is defined by the molar ratio SiO_2/K_2O. The higher the molar ratio, the fewer potassium ions are present in the silica network and consequently determine the alkalinity of the molecule. In aqueous solution, potassium silicate is a mixture of monomeric tetrahedral ions, oligomeric linear or cyclic silicate ions and polysilicate ions (Brady et al., 1953). At environmental pH values, potassium silicate is poorly soluble as amorphous silica and monomeric silicic acid. Above a pH of 11 - 12 stable solutions of monomeric and polymeric silicate ions exist. Solubility rapidly decreases when the pH is lowered to 9.0, leading to increasing precipitation of amorphous silica. Below pH 9, only a small proportion is present as soluble monomeric silicate ions, the majority existing as insoluble amorphous silica gel (Fig. 2). Amorphous silicate glasses are only slightly attacked by water at ambient temperatures. They can be solubilized only at elevated temperature and pressure (ca. 150 °C and > 5 bar). Silicate powders obtained by water evaporation from silicate solutions are readily soluble in water.

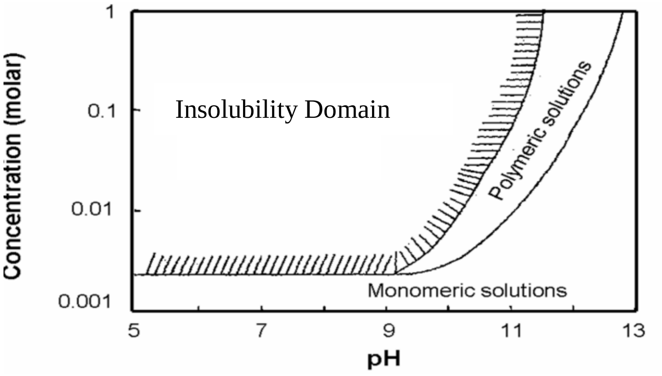


Figure 2. Soluble silicate speciation (Knight and Kinrade, 2001)

Specific Uses of the Substance:

There are two listings for aqueous potassium silicate on the National List scheduled to "sunset" (expire) on December 14, 2015. They are:

§ 205.601 Synthetic substances allowed for use in organic crop production.
  (e) As insecticides (including acaricides or mite control).
    (2) Aqueous potassium silicate (CAS #-1312-76-1)—the silica, used in the manufacture of potassium silicate, must be sourced from naturally occurring sand.
  (i) As plant disease control.
    (1) Aqueous potassium silicate (CAS #-1312-76-1)—the silica, used in the manufacture of potassium silicate, must be sourced from naturally occurring sand.

As required by the Organic Foods Production Act of 1990, the National Organic Standards Board is required to review each substance on the National List each five years to determine whether the substance should be renewed. Aqueous potassium silicate is used at a concentration range of 100-2000 mg/L to feed rice, wheat, barley, sugar cane, tomatoes, beans, curcurbits, strawberries, grapes, roses, turfgrass and ornamentals. It can be applied as a foliar spray directly to the leaves of plants (or as a nutrient solution to soil or hydroponic medium either prior to infection or infestation or during such an occurrence. Aqueous potassium silicate does not act directly on the disease-causing agents, e.g. fungal species or acarids, rather it is actively taken up by plants through roots, stems or leaves and serves to replenish plants' innate resistance through a number of mechanisms permitting enhanced activation of specific immune responses (Epstein, 1994; Datnoff, 2005).

Approved Legal Uses of the Substance:

EPA: Potassium silicate is listed in Title 40 (Protection of Environment), Part 180—tolerances and exemptions for pesticide chemical residues in food Subpart D—Exemptions From Tolerances, 180.1268: Potassium silicate is exempt from the requirement of a tolerance in or on all food commodities so long as the potassium silicate is not applied at rates exceeding 1% by weight in aqueous solution and when used in accordance with good agricultural practices.

Potassium silicate was registered by the US Environmental Protection Agency (EPA), Office of Pesticide Programs as a biopesticide, September 7, 2007 (PC Code 072606). The EPA noted the wide distribution of silicon in the earth's crust and concluded exposure to silicates was commonplace in activities involving contact with soil and natural water. Potassium silicate was approved as an active ingredient to be used as a fungicide, insecticide and miticide. Potassium silicate is used as a broad spectrum, preventative fungicide with optimum control obtained when used under a scheduled preventative spray program. Potassium silicate also provides suppression of mites, whiteflies, and other insects. It is approved for use on agricultural crops, fruits, nuts, vines, turf and ornamentals. The EPA accepted the data and information provided by PQ Corporation addressing the mammalian and non-target toxicology data requirements and concluded that they adequately satisfied data requirements to support the registration (Reilly et al., 2007). No additional data was needed to support registration. Potassium silicate is exempt from the requirement of a tolerance.

FDA: Silica and silica gel (a hydrated amorphous form of silica) are considered GRAS by FDA (21 CFR 182.90 and 21 CFR 182.1711). FDA provides that silicon is ubiquitous in the environment and further states that there is no evidence in the available information on aluminum calcium silicate, calcium silicate, magnesium silicate, potassium silicate, sodium silicate, sodium aluminosilicate, sodium calcium aluminosilicate, tricalcium silicate, silica aerogel, and talc that demonstrates or suggests reasonable grounds to suspect a hazard to the public when they are used at levels that are now current or that might reasonably be expected in the future.

Potassium silicate is listed under title 21—food and drugs, Part 178—indirect food additives: adjuvants, production aids and sanitizers, Subpart D—certain adjuvants and production aids as § 178.3297 colorants for polymers (d) Color additives and their lakes listed for direct use in foods, under the provisions of the color additive regulations in parts 73, 74, 81, and 82 of this chapter, may also be used as colorants for food-contact polymers. (e) List of substances: Aluminum and potassium silicate (mica).

USDA: Potassium silicate is listed under title 7—Agriculture, part 205—National Organic Program, subpart G—administrative, § 205.601—Synthetic substances allowed for use in organic crop production. The rule permits the use of potassium silicate for plant disease control and as an insecticide or miticides with the restriction that the silica, used in the manufacture of potassium silicate, must be sourced from naturally occurring sand.

Action of the Substance:

The application of aqueous potassium silicate has the potential to relieve biotic and abiotic environmental stress and soil nutrient depletion in plants. It is a source of dissolved silica (silicic acid). Dissolved silica is actively taken up by plants and concentrated in precipitated particulate form by a number of plant cells in a variety of morphological structures. Concentrations of precipitated particulate silica (opal) that retain genus- or species –specific morphological characteristics in higher plants are generally referred to as phytoliths (Guntzer et al., 2012). Although many species can thrive without much usable silica in the soil, plants use silica for phytoliths, if it is available. Phytolith formation is dependent upon the concentration of usable silica in the soil and on the particular plant species. Represented among phytoliths are plant components, some of which are only now being elucidated, that are intrinsically involved in plant defense against pests and pathogens (Fig. 3). Phytoliths are not evenly distributed in or among plant species. They also vary in size within and among plants. Recycled phytoliths return silicic acid to the soil solution. Because dissolved silica is added slowly to soil by weathering minerals containing aluminum silicate, usable silica removed from soil by growing plants is replaced mostly through litterfalls containing phytoliths. There is good evidence suggesting that silica resupply significantly depends on recycling phytoliths. It has been shown that naturally up to 85% of Si uptake in plants is derived from recycled phytoliths (Savant et al., 1996). Uptake of dissolved silica in plants by foliar application of aqueous potassium silicate is a highly effective way to provide usable silica for absorption by plants (Mecklenburg and Tukey, 1964; Bukovac et al., 1956). Thus, foliar application of aqueous potassium silicate to plants grown under silica depleted conditions that are under stress from disease or parasites is effective for restoring plant defenses and improving plant health (Menzies et al., 1992).

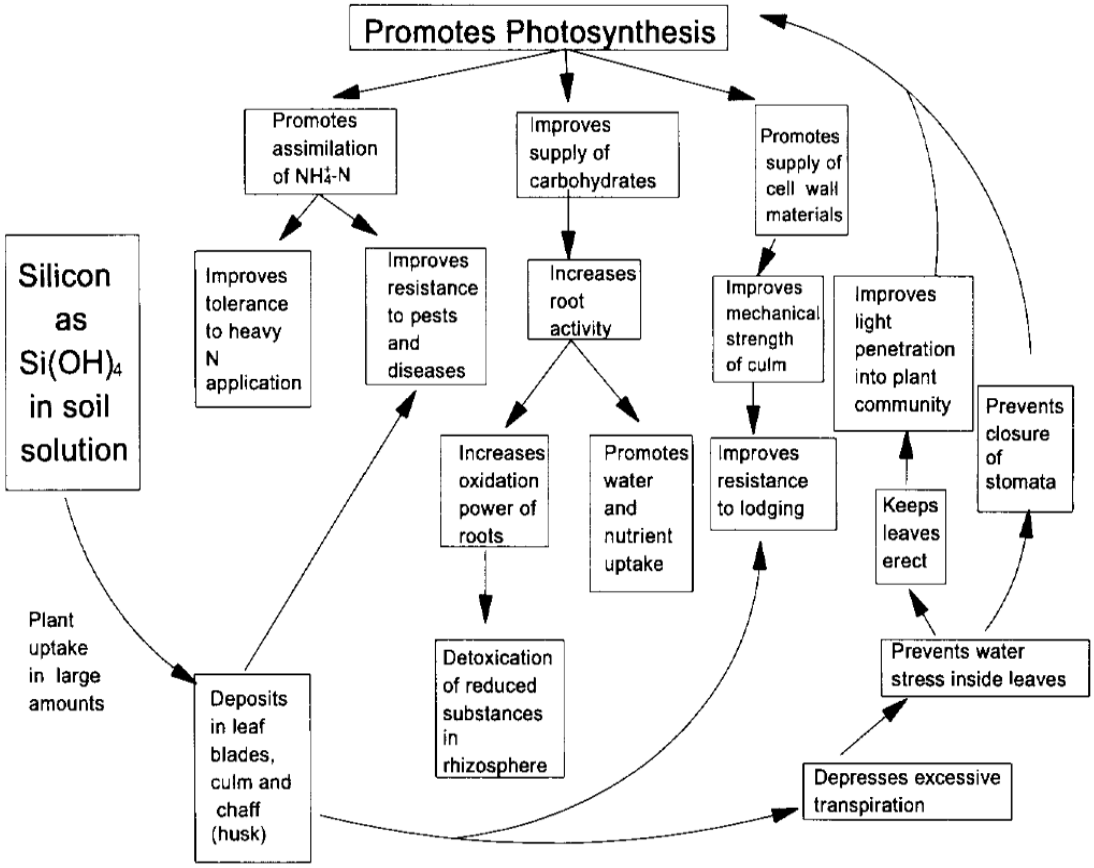


Fig. 3. Beneficial effects of soluble silicate in plants (Takahashi, 1995; Takahashi et al., 1990)

Combinations of the Substance:

Aqueous potassium silicate is on the National List for use as a treatment of plant disease and an insecticide. It is commonly used alone or in combination with other substances that are on the National List such as sesame oil, mineral oil, potassium bicarbonate, elemental sulfur, neem, paraffinic oil, garlic oil, hydrogen peroxide, peroxyacetic acetic in treating mildews, fungi, aphids and mites in a number of crops. Aqueous potassium silicate may also be used in combination with other sources of silica to ensure and augment plant health prior to and after infection or infestation.

Status

Historic Use:

Silicon is one of the most abundant elements in the earth's crust. Although, silicon is very common geologically, it is rarely found free in the environment. Silicon is not a component of rain, nor is it present in the air at a significant concentration. Silicon containing minerals (silica) in soil are subject to some weathering over time. This process is slow and influenced by environmental factors such as temperature and pH (Fig 4). Silica released into solution can combine with other chemicals to form clay, but may leach into streams and rivers that flow to the oceans. Soluble silica is also absorbed by plants. Because plants actively take up silica as mono-silicate, the ability of plants to absorb silicon from soil and the amount of silicon that can be taken up by plants depends on the concentration of silicic acid in the soil solution rather than on the total silicon concentration of the soil.

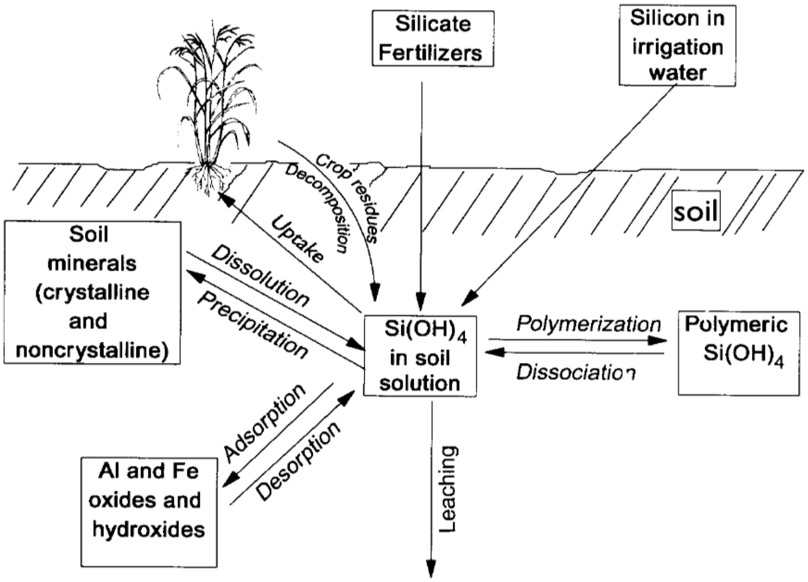


Figure 4. Main Transformations/processes influencing silicon concentration in soil solution (Savant et al., 1996)

Silica accumulation by plants varies by species from excluders that have below a 0.5% silica level to accumulators that concentrate over 1% and up to as much as 10% of silica by weight. Seven out of ten of the most produced crops are accumulators. In natural ecosystems, the phytoliths are left to recycle. In crop cultivation, because phytoliths may be exported, the concentration of available silica as phytoliths is depleted since a fraction of the amorphous silica does not return to the soil. Continuous, silica depletion can result in greater incidence of disease and infestation since plants lacking silicon cannot respond effectively to biotic stress (Gunzer et al., 2012). Thus, aqueous potassium silicate has been used as a soil amendment or as a foliar spray to restore silicon and the ability of plants to prime their innate immune defenses.

Organic Foods Production Act, USDA Final Rule:

Aqueous Potassium Silicate was added to the National List on December 14, 2010 (75 FR 77521) as follows:

> § 205.601 Synthetic substances allowed for use in organic crop production.
> (e) (2) Aqueous potassium silicate (CAS #—1312–76–1)—The silica, used in the manufacture of potassium silicate, must be sourced from naturally occurring sand.
> (i) (1) Aqueous potassium silicate (CAS #—1312–76–1)—The silica, used in the manufacture of potassium silicate, must be sourced from naturally occurring sand.

International

Canada - Canadian General Standards Board Permitted Substances List – Aqueous Potassium Silicate is not on the Canadian Permitted Substance List (CAN/CGSB-32.an1-2006). Alternatively, bound silica containing substances, bentonite, biotite, clay, feldspar, granite dust, greensand, mica, sand, zeolite, diatomaceous earth, and kaolin clay are listed as substances that may be used for organic crop production in Canada.

CODEX Alimentarius Commission, Guidelines for the Production, Processing, Labelling and Marketing of Organically Produced Foods (GL 32-1999)

In its section on substances for use in soil, fertilizing, and conditioning, the Codex Alimentarius Commission, "Guidelines for the production, processing, labeling, and marketing of organically produced foods," lists several bound silicon containing mineral substances such as clay, bentonite, perlite and zeolite. It also lists mineral powders (stone meal, silicates), diatomaceous earth, silicates, clay (bentonite) and sodium silicate in its section on substances for plant pest and disease control. Potassium silicate is not specifically listed.

European Economic Community (EEC) Council Regulation, EC No. 834/2007 and 889/2008

Commission Regulation (EC) No 889/2008 annex I lists several bound silicon containing soil amendments including stone meals and clays, but includes basic slag, a substance containing usable silica. Quartz sand is listed in annex II for use as a pesticide. Potassium silicate is not specifically listed.

Japan Agricultural Standard (JAS) for Organic Production

Notification No. 1605, Japanese Agricultural Standard for Organic Plants from the Japan Ministry of Agriculture, Forestry and Fisheries (October 27, 2005) provides for bound silicon containing soil amendments in its attached table 1. These include stone meal, bentonite, calcined diatomaceous earth. In addition this document lists basic slag and slag silicate fertilizer, both of which may be sources of silica that is available to plants. For treatment of plant disease, diatomaceous earth is listed.

International Federation of Organic Agriculture Movements (IFOAM)

IFOAM does not specifically mention the use of potassium silicate. However, basic slag and clay (e.g. bentonite, perlite, vermiculite and zeolite) are included in the IFOAM Indicative List of Substances for Organic Production and Processing in the section describing fertilizers and soil conditioners, and clay (e.g. bentonite, perlite, vermiculite and zeolite), diatomaceous earth, silicates (e.g. sodium silicates, quartz) are listed in the section describing crop protectants and growth regulations (IFOAM, 2007).

Evaluation Questions for Substances to be used in Organic Crop or Livestock Production

Evaluation Question #1: Indicate which category in OFPA that the substance falls under: (A) Does the substance contain an active ingredient in any of the following categories: copper and sulfur compounds, toxins derived from bacteria; pheromones, soaps, horticultural oils, fish emulsions, treated seed, vitamins and minerals; livestock parasiticides and medicines and production aids including netting, tree wraps and seals, insect traps, sticky barriers, row covers, and equipment cleansers? (B) Is the substance a synthetic inert ingredient that is not classified by the EPA as inerts of toxicological concern (i.e., EPA List 4 inerts) (7 U.S.C. § 6517(c)(1)(B)(ii))? Is the synthetic substance an inert ingredient which is not on EPA List 4, but is exempt from a requirement of a tolerance, per 40 CFR part 180?

Aqueous potassium silicate is a synthetic, manufactured by a process that chemically changes substances extracted from naturally occurring mineral sources. It is also mineral by character and can be grouped in the "vitamin and mineral" category provided by 7 U.S.C. 6517. All data requirements have been fulfilled and/or waived by the Biopesticides and Pollution Prevention Division of the Environmental Protection Agency for the approved unconditional registration of products that contain potassium silicate as their sole active ingredient. An exemption from the requirement of a tolerance for the pesticide ingredient, potassium silicate was granted so long as potassium silicate is not applied at rates greater than 1.0% by weight in aqueous solutions.

Evaluation Question #2: Describe the most prevalent processes used to manufacture or formulate the petitioned substance. Further, describe any chemical change that may occur during manufacture or formulation of the petitioned substance when this substance is extracted from naturally occurring plant, animal, or mineral sources (7 U.S.C. § 6502 (21)).

Potassium silicate glass (lump) is manufactured (Fig. 5) by the direct fusion of precisely measured portions of pure silica sand (SiO_2) and potash (K_2CO_3) in oil, gas or electrically fired furnaces at temperatures above 1000 °C according to the following reaction:

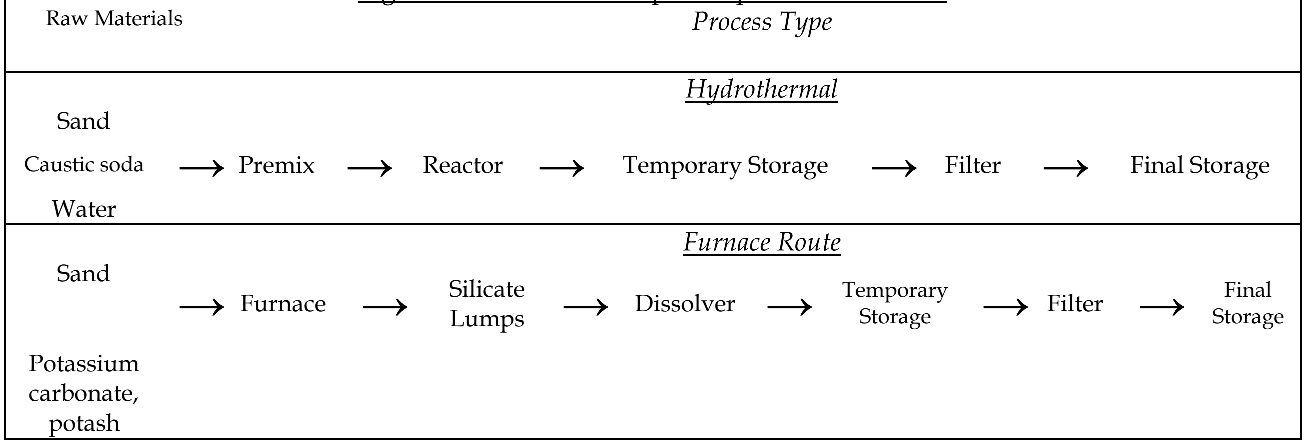
$$K_2CO_3 + x\ SiO_2 \rightarrow K_2O\ .\ x\ SiO_2 + CO_2$$

Aqueous potassium silicate ("waterglass") may be produced (Fig. 5) either by dissolving potassium silicate lumps in water at elevated temperatures (and partly at elevated pressure), or for certain qualities by hydrothermally dissolving silica sand in potassium hydroxide solution according to the equation:

$$2KOH + x\ SiO_2 \rightarrow K_2O\ .\ x\ SiO_2 + H_2O$$

Depending upon manufacturer's specifications, solutions are subsequently filtered to remove residual turbidity and adjusted to yield products to a particular specification. Amorphous potassium silicate powders are produced by drying aqueous solutions in spray or drum dryers. These products are further treated to modify powder properties, e.g. particle size, bulk density. Crystalline potassium silicate powders with a specific composition containing different amounts of water of crystallization can be produced by various routes. The products are separated, sieved, and processed as required.

Figure 5 Production of aqueous potassium silicate



Evaluation Question #3: **Discuss whether the petitioned substance is formulated or manufactured by a chemical process, or created by naturally occurring biological processes (7 U.S.C. § 6502 (21)).**

Silicon is found in soil chemically combined with oxygen, aluminum and the alkali metallic elements. Quartz or silica (silicon dioxide, or SiO_2) is the most common constituent of sand found in inland continental and non-tropical coastal settings. Quartz sand is chemically inert, resistant to weathering and only sparingly soluble in water at neutral pH. After quartz, feldspar is the second most common mineral on earth. Like quartz, feldspar contains silicon that is unavailable to plants. Because it is more subject to weathering than quartz, feldspar is more abundant in soils and clays throughout the world. Kaolin clay is a good example of a weathered feldspar soil component. Kaolin is relatively stable and has the chemical formula $Al_2Si_2O_5(OH)_4$. Weathering leaches out bioavailable magnesium, sodium, calcium, iron, and potassium from feldspar, but leaves silicon behind in the clay minerals. Although there is abundant silicon in soils, silicon from quartz or feldspar is not abundantly bioavailable. Potassium carbonate is purified potash. Potash is a potassium containing substance derived from minerals or plants. For example, potash can be ash left from burning wood, but is found in many minerals such as feldspar. Mineral sources of potash are geographically widespread and potash mining is a well-established industrial sector. Potassium hydroxide is also a member of the potash family of compounds. It is strongly basic and has a wide variety of industrial applications. Potassium carbonate and potassium hydroxide are both available in a number of purity grades, including food grade, and US Pharmacopeia approved products.

Some soils, for example volcanic soils from Northern California contain kaolin-like clay that is rich in bioavailable potassium and silicon (White et al., 1980). This material is called Halloysite. It is likely to contain volcanic derived potassium silicate glass that has weathered to produce leached bioavailable silicic acid and potassium. It is important to note that this soil is generally rare and highly subject to leaching of silicon.

The process of fusing quartz sand with potassium carbonate or potash with heat to form glass produces a synthetic product containing bioavailable silicon, silicic acid, a weak acidic form of silica. Silicic acid is generally thought to be the form of silicon that is taken up by plants from the soil as a nutrient.

<u>Evaluation Question #4:</u> Describe the persistence or concentration of the petitioned substance and/or its by-products in the environment (7 U.S.C. § 6518 (m) (2))

Aqueous potassium silicate is registered with the US Environmental Protection Agency (Reilly et al., 2007) as a pesticide. Its environmental impact was reviewed by the Organization for Economic Cooperation and Development (2004). When dissolved in water, the active ingredient potassium silicate dissociates into potassium cations, hydroxide anions, and mono- and polysilicic acids. Potassium silicate does not contain any volatile organic compounds and will not degrade to any hazardous or environmentally persistent breakdown products. Dissolved soluble silica from commercial sources will be indistinguishable from dissolved soluble silica from natural sources and any soluble silica input into aquatic or terrestrial environments will be insignificant in relation to the high flux of the natural silica cycle. It is estimated that silica is introduced into the environment via weathering at a rate of approximately 2000 kg/square km/year and natural waters may contain 3.8-363 ppm soluble silica depending on the geological materials with which the waters are in equilibrium. The primary hazard to non-target organisms results from the alkaline pH of the active ingredient, potassium silicate, a soluble silicate compound. The end-use product is approximately pH 11.1, but it is unbuffered. Therefore, when applied to terrestrial and aquatic environments, commercial potassium silicate formulations will have little effect on pH due to the high buffering capacity of the natural environments. As inorganic substances, soluble silicates are not amenable to photo- or biodegradation. However, risk is minimal due to low toxicity, use pattern, and application methods. In natural waters, most dissolved silica results from the weathering of silicate minerals. Silica is continuously removed from water by biochemical processes: diatoms, radiolarians, silicoflagellates, and certain sponges serve as a sink for silica by incorporating it into their shells and skeletons as amorphous biogenic silica, frequently referred to as opal ($SiO_2 \cdot nH_2O$). Commercial soluble silicates rapidly degrade to molecular forms that are indistinguishable from natural dissolved silica. When used as a pesticide, potassium silicate residues are low relative to naturally present concentrations and other uses in the environment. Minimal potential for additional exposure exists to insects, fish and other non-target wildlife as a result of potassium silicate use as a pesticide. No efficacy data were required, EPA because no public health uses are involved.

<u>Evaluation Question #5:</u> Describe the toxicity and mode of action of the substance and of its breakdown products and any contaminants. Describe the persistence and areas of concentration in the environment of the substance and its breakdown products (7 U.S.C. § 6518 (m) (2)).

Aqueous potassium silicate is registered with the US Environmental Protection Agency (EPA—Reilly et al., 2007) as a pesticide and its environmental impact was reviewed by the Organization for Economic Cooperation and Development (2004). The EPA cited the Human Environmental Risk Assessment on Ingredients of European Household Cleaning Products (HERA, 2005), and the NOSB, Technical Advisory Panel Report, 2003, conclusions that the use of potassium silicate was unlikely to result in any adverse effect to the environment or non-target organisms when used as an pesticide and treatment for plant disease. The EPA also cited findings by the US Food and Drug Administration that the strong chemical similarity between sodium and potassium silicate makes it possible to use risk assessment data for either of them interchangeably. When applied as a foliar spray, any potential environmental/ecological effects produced by potassium silicate were expected to be negligible and no exposure to birds or aquatic organisms was expected. Acute toxicity testing in fish, invertebrates, and algae indicate a low order of toxicity with effect concentrations between 210 and 1700 mg/l. No long-term tests are available for fish, invertebrates or algae. As a result of the low molar ratio, sodium metasilicate and its hydrates (MR 1.0) exhibit a higher alkalinity than the silicates of higher molar ratio. With the assumption that the primary hazard of soluble silicates is their alkalinity, it is expected that sodium metasilicate generally exhibits a higher toxicity than silicates of molar ratios 3 - 4. This is confirmed by toxicity data available for fish. Concerning invertebrate and algal toxicity, studies are available only for silicates of molar ratios 3-4 or of unknown ratio. Soluble silicates are currently of low priority for further work because of their low hazard profile.

<u>Evaluation Question #6:</u> Describe any environmental contamination that could result from the petitioned substance's manufacture, use, misuse, or disposal (7 U.S.C. § 6518 (m) (3)).

Potassium silicate and its raw materials, particularly potash or potassium carbonate, are likely to have undergone heating in a kiln or refractory as part of their processing. The product itself, potassium silicate is a glass that requires heating to over 1000°C. In most cases, the source of energy is natural gas. However; coal fired or electric furnaces may also be used. Eleven potassium silicate manufacturers and distributers were listed on the Thomas.net manufacturing website. Of all of the manufacturers in the US, only the PQ Corporation was reporting greenhouse gas emissions. Data for 2011 emissions of CO_2 for PQ Corporation are provided in Table 1. Total CO_2 emissions from these six facilities is less than 0.002% of CO_2 emissions from all reporting facilities listed by the EPA in 2011.

Table 1. 2011 Greenhouse Gas Emissions from Large Facilities

Facility ▲	City	State	Total 2011 Reported Emissions (metric tons CO_2)	Sectors
PQ Corporation - Augusta, GA	Augusta	GA	16,290	Chemicals
PQ Corporation - Chester Plant	Chester	PA	24,999	Chemicals
PQ Corporation - Gurnee, IL	Gurnee	IL	17,147	Chemicals
PQ Corporation - Jeffersonville, IN	Clarksville	IN	14,618	Chemicals
PQ Corporation - Kansas City, KS	Kansas City	KS	13,127	Chemicals
PQ Corporation - St. Louis, MO	Saint Louis	MO	16,929	Chemicals

Because silica is insoluble at low pH, the discharge of improperly treated wastewater containing silicates into sewers can damage sewage treatment equipment and prevent proper sewage treatment.

<u>Evaluation Question #7:</u> Describe any known chemical interactions between the petitioned substance and other substances used in organic crop or livestock production or handling. Describe any environmental or human health effects from these chemical interactions (7 U.S.C. § 6518 (m) (1)).

At the recommended concentration for the potassium silicate foliar spray, reactivity with other substances used in organic crop or livestock production or handling is not expected. Potassium silicate is stable under all conditions of use and storage. Significant (unintended) exposure of the terrestrial environment as a side effect of applications does not occur. Silicates are naturally found in soils. Potassium silicate gels and generates heat when mixed with acid and may react with ammonium salts resulting in the evolution of ammonia gas. Flammable hydrogen gas may be produced on contact with aluminum, tin, lead, and zinc. Compatibility with these substances should be considered when used concomitantly with aqueous potassium silicate.

<u>Evaluation Question #8:</u> Describe any effects of the petitioned substance on biological or chemical interactions in the agro-ecosystem, including physiological effects on soil organisms (including the salt index and solubility of the soil), crops, and livestock (7 U.S.C. § 6518 (m) (5)).

Silicon (Si) is absorbed by plants through roots and stoma as monosilicic acid. There is evidence that it is both actively and passively transported throughout the plant, and deposited in the form of opal

(Richmond and Sussman, 2003). There are many articles and reviews supporting positive and beneficial effects of soluble silicates on bolstering abiotic and biotic stress (Rodriguez et al., 2001; Liang et al., 2007; Epstein, 1999). For example, rice leaves, stems, and culms of plants grown in the presence of bioavailable silicon show an erect growth. Silicon increases rice resistance to lodging and drought, and dry matter accumulation in cucumber and rice. Silicon can positively affect the activity of some enzymes involved in the photosynthesis of rice and turfgrass as well as reduce rice leaf senescence. Silicon can lower the electrolyte leakage of rice leaves, promoting greater photosynthetic activity in plants grown under water deficit or heat stress. Silicon increases the oxidation power of rice roots, decreases injury caused by climate stress such as typhoons and cool summer damage in rice, alleviates frost damage in sugarcane and other plants, and favors supercooling of palm leaves. Silicon reduces the availability of elements such as manganese (Mn), iron (Fe), and aluminum (Al) to roots of plants such as rice and sugarcane and increases rice and barley resistance to salt stress. Moreover, the most significant effect of silicon to plants, besides improving their fitness in nature and increasing plant productivity, is the suppression of insect feeding and plant diseases.

Treatment with potassium silicate may not be appropriate when crops are used for feeding or as forage for livestock since its addition hardens some plants, making them both more difficult to chew and digest. Furthermore, monosilicic acid naturally strengthens the phyto-skeleton, thus the addition of potassium silicate as a foliar nutrient may result in the production of less tender fruits and vegetables or forage for grazing animals (Mayland and Shewmaker, 2001). Potassium silicate is not effective for every insect infestation or plant disease (Redmund and Potter, 2005). As a foliar spray, potassium silicate is not expected to alter soil chemistry by its application. However, soils depleted in silicic acid from leaching, or crop choice that produce desirable characteristics for organic production, may not provide sufficient protection against specific infestations or disease. The addition of potassium silicate via a foliar spray can safely augment plant defenses transiently to prevent crop damage, although in some case the addition of silicates may alter plant characteristics (Menzies, 1992; Hinsark et al., 1953). Silica supplementation can result in elongation and thickening of stems, delayed antithesis and flower deformation in some species depending on the level of accumulation of silica by the plant species, the type of silica supplement used and the method by which it was applied. In addition to morphological changes, changes in micronutrient in plants may occur as a result of silica supplementation (Kamenidou et al., 2008; Mattson and Roland, 2010).

Consistent with its role in protecting plants from microbial disease, silica in certain grasses has been found to reduce microbial digestion by ruminate gut flora. These grasses without the addition of silica appear to be good fodder for grazers; however, with higher silica concentrations these grasses become less digestible. The same does not appear to be true for non-accumulators such as legumes which show little reduction in digestibility with added silica (van Soest and Jones, 1968). Herein, continued leaching of silica from soil may improve digestibility, while increasing vulnerability to microbial infection.

<u>Evaluation Question #9:</u> Discuss and summarize findings on whether the use of the petitioned substance may be harmful to the environment (7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i)).

The Environmental Protection Administration (EPA) has published a tolerance exemption for potassium silicate with the caveat that it not be applied at rates exceeding 1% by weight in aqueous solution. Potassium and silica are naturally present in excess of what would be applied to the environment as potassium silicate. Avian dietary studies obtained from public literature by EPA, indicate no apparent toxicity resulting from short-term, sub-chronic consumption of dietary silicon and conclude that potassium silicate will not adversely affect birds. Studies from the Organization for Economic Cooperation (OECD) and the EPA indicate soluble silicates were practically non-toxic to fish and that toxicity resulted from the effects of high pH at a range of pH 7.2-10.1, rather than from any direct effects of the test substance. Because most natural aquatic ecosystems fall within the range of pH 6-9 and due to the high buffering capacity of these ecosystems, effects on pH by applied potassium silicate is highly unlikely. The presence of soluble silicates in water has been demonstrated to be beneficial to fish by reducing the bioavailability (and toxicity) of soluble aluminum in fish-bearing waters.

Soluble silicates are used in aquatic ecosystems by diatoms, radiolarians, silico-flagellates, and certain sponges (Wallace et al., 2012). Potassium silicate is not toxic for terrestrial or aquatic plants, although solutions at high pH may influence short biomass accumulation under experimental conditions. Potassium silicate is not toxic to honeybees at the concentration administered for the foliar spray (Reilly et al., 2007). Potassium silicate dissociates into potassium cations, hydroxide anions, and mono- and poly-silicic acids in water. It does not contain any volatile organic compounds and will not degrade to any hazardous or environmentally persistent breakdown products. Potassium is a common basic cation found in the environment. It is an essential element in human and plant nutrition. In plants, potassium has an important role in enzyme activation and the maintenance of cellular osmotic balance; as in plants, potassium is necessary in animals for maintaining osmotic equilibrium as well as participating in life-supporting activities such as nerve impulses, heartbeat, and enzyme activation. Potassium is a common soil plant nutrient and fertilizer (as K_2O). Potassium comprises approximately 2.59% of the Earth's crust by weight. The primary source of naturally occurring soluble potassium is from the weathering of potassium containing minerals, e.g. alkali feldspars. Mobility of potassium in the soil is dependent upon the clay content, the type of clay (vermiculite, illite, montmorillonite, or kaolinite), and to a lesser extent, pH. Potassium content is higher in high clay content soil and is greater with 2:1 clays (e.g. montmorillonite) than in 1:1 clays, e.g. kaolinite. Silicon is ubiquitous in the environment, comprises approximately 32% of the soil by weight and is present as dissolved silica, amorphous silica in the solid phase, and silica bound to organic matter. Silica and silica gel (a hydrated amorphous form of silica) are considered GRAS by FDA (21 CFR 182.90 and 21 CFR 182.1711). Worldwide production of soluble silicates (sodium silicate, disodium metasilicate, and potassium silicate) is approximately 3-4 million metric tons per year. Soluble silicate exposure (from commercial sources) to aquatic and terrestrial environments occurs via uses in detergents, pulp and paper effluent, water/wastewater treatment, soil stabilization, and as fertilizer.

<u>Evaluation Question #10:</u> Describe and summarize any reported effects upon human health from use of the petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (i), 7 U.S.C. § 6517 (c) (2) (A) (i)) and 7 U.S.C. § 6518 (m) (4)).

Silicon dioxide and various silicates are part of the normal human diet. Silicon compounds consumed as added food ingredients contribute only a minor proportion of the total dietary silicon intake. The water-soluble silicates are also of low acute toxicity. No significant tissue accumulation, pathology, or toxicity has been reported from the ingestion of very slightly soluble GRAS silicon compounds. There is no evidence in the available information on potassium silicate that demonstrates or suggests reasonable grounds to suspect a hazard to the public when used as a foliar spray at the levels suggested for plant defense from pests and disease (HERA, 2005).

FDA has determined that sodium silicate and potassium silicate can be used interchangeably. Sodium silicate has been determined to be GRAS (Generally Recognized as Safe) by FDA (21 CFR 182.90 and 21 CFR 182.1711) for limited use in canned potable water as a corrosion inhibiting agent. The overall toxicological risk from human exposure to potassium silicate is negligible. Although, treatment of crops may result in run-off to surface and ground water, silica and potassium are ubiquitous and cannot be distinguished from natural sources. Potassium silicate is ubiquitous in the environment so there is routinely exposure to it without toxic effects. Human exposure to potassium silicate is expected in residential, school and day care areas, as everyone is daily exposed to potassium silicate in dust, dirt, soil, etc., but the additional amount of potassium silicate found in foodstuff as a result of the use of this product is expected to be minuscule compared to these other sources. The risk from the consumption of residues is not expected for the general population, including infants and children. Because no toxicological endpoints were determined, risk from the consumption of potassium silicate residues is not expected for populations in residential, school and day care settings, including infants and children. Agricultural use of potassium silicate is subject to the Worker Protection Standards (WPS), requiring Personal Protective Equipment (PPE) a long-sleeved shirt, long pants, socks, shoes and gloves, plus a 4 hour Restricted Entry Interval (REI). FDA has concluded that potassium silicate represents no hazard to the public (Select Committee on GRAS Substances (SCOGS) Opinion: Potassium silicate, 1979). Aggregate exposure to potassium silicate by field workers and applicators may occur via oral, dermal and inhalation routes. These risks are measured via the acute toxicity studies submitted to support registration. As the oral toxicity study for potassium silicate showed no toxicity at the maximum dose tested (2,000 mg/kg), the risks anticipated from oral exposure are considered minimal. Because the inhalation toxicity studies for potassium silicate showed no toxicity either (Toxicity Category IV), the risks anticipated for this route of exposure are also considered minimal. Results of the acute dermal toxicity study indicated moderate to low toxicity at the maximum dose tested, although dermal irritation was observed, however at normal concentrations the anticipated risks from dermal exposure are also considered to be of low consequence. Therefore, the risks from aggregate exposure via oral, dermal and inhalation exposure are a compilation of three low risk exposure scenarios and are considered negligible (OECD, 2004). A determination has been made by FDA and EPA that no unreasonable adverse effects to the U.S. population in general, and to infants and children in particular, will result from the use of potassium silicate when label instructions are followed (Reilly et al., 2007).

Evaluation Question #11: 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)).

This National List specification for this substance is limited to foliar application of aqueous potassium silicate. There is no known natural substance producing the same short term effect on plant health as aqueous potassium silicate in a foliar spray. However, other forms of silica and application methods for these substances are available as approved supplements for the soil that can provide the same protection over a longer term against plant disease.

In “Humus and the Farmer”, Friend Sykes provides that the “well-being of mankind is interdependent with that of the animal, the plant and the living soil” and a fertile soil is one rich in humus (Sykes, 1949). Humus maintains silica in soil. Its components, compost and manure are rich sources of plant derived silica. Silica in compost is maintained by phytolith recycling. Silica in manure is increased as a result of the effect silica has on plant tissue digestion of specific forage grass species. Thus, maintenance and addition of humus through careful recycling of compost and manure will maintain silica in the soil.

Several silica rich organic sources that may be used for compost are rice (*Oryza sativa*) hulls, sugarcane (*Sacharum spp.)* bagasse and high organic muck from an estuarine environment such as the Florida everglades (Gascho, 2001).

The beneficial effects of aqueous potassium silicate administered as a foliar spray have been shown for a number pathogens and pests on a range of plants. The mechanisms for plant disease resistance vary for the plant species and the pest or disease. A number of biopesticides also produce similar results in protecting plants from disease and pests. Biopesticides are pesticides derived from such natural materials as animals, plants, bacteria, and certain minerals. For example, canola oil and baking soda have pesticidal applications and are considered biopesticides. Biopesticides are usually inherently less toxic than conventional pesticides. Biopesticides generally affect only the target pest and closely related organisms, in contrast to broad spectrum, conventional pesticides that may affect organisms as different as birds, insects, and mammals. Four hundred biopesticides were registered with EPA in 2013. For organic crops there are three major classes of biopesticides:

1. Microbial pesticides consist of a microorganism (e.g., a bacterium, fungus, virus or protozoan) as the active ingredient. Microbial pesticides can control many different kinds of pests, although each separate active ingredient is relatively specific for its target pest[s]. For example, there are fungi that control certain weeds, and other fungi that kill specific insects.
2. The most widely used microbial pesticides are subspecies and strains of Bacillus thuringiensis, or Bt. Each strain of this bacterium produces a different mix of proteins, and specifically kills one or a few related species of insect larvae. While some Bt's control moth larvae found on plants, other Bt's are specific for larvae of flies and mosquitoes. The target insect species are determined by

whether the particular Bt produces a protein that can bind to a larval gut receptor, thereby causing the insect larvae to starve.

3. Biochemical pesticides are naturally occurring substances that control pests by non-toxic mechanisms.

Several companies produce aqueous potassium silicate (McGrath and Shishkoff, 1999) for organic use. In addition, EPA has approved a number of biopesticides, also approved for organic use that are effective for similar purposes as aqueous potassium silicate, e.g., a treatment for powdery mildew, aphids, and mites. Aqueous potassium silicate is representative of a group of substances that have been shown to be effective variably depending upon soil conditions, climate, crop, and variety. The mode of action for many, if not of the alternatives to potassium silicate effective against plant disease and insect damage is as a predator, pathogen, repellent or poison of plant pathogens and pests. In contrast, potassium silicate plays an active role in disease resistance by strengthening and stimulating plant immunity. The action of applying potassium silicate in a foliar spray serves to induce natural phytoalexins, chitinases and strengthen stroma and cell walls. Potassium silicate works to naturally build the plant's immunity to disease and insect attack (Bockhaven et al., 2013, Epstein, 2009; Ahuja et al., 2012; Hayasaki et al., 2008; Rodriguez et al., 2004).

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

Potassium silicate acts to strengthen plants in their defense from diseases and pests. The beneficial effect of potassium silicate was shown for the following fungi: powdery mildew (*Blumeria graminis*), septoria (*Phaeosphaeria nodorum* and *Mycosphaerella graminicola*), and eyespot (*Oculimacula yallundae*). Potassium silicate has a demonstrate effect on stalk rot (*Leptosphaeria salvinii*), rice blast (*Magnaporthe grisea*), fusarium wilt (*Fusarium*), tan spot (*Cochliobolus miyabeanus*), melting seedlings (*Thanatephorus cucumeris*), and leaf spots (*Monographella albescens*) in rice. Although, this may be the result of precipitation of amorphous silica in plants which acts as a mechanical barrier, potassium silicate can also protect plants by other processes that boost their defense mechanisms, including the accumulation of lignin, phenolic compounds, and phytoalexins. Potassium silicate has been shown to trigger rapid and extensive deployment of the natural defenses of the plant either indirectly by sequestering cations or directly by increasing some protein activity. Potassium silicate also limits damage caused by insects and acarids that are harmful to crops, such as aphids, mites, insect borers (*Chilo suppresalis*), yellow borers (*Scirpophaga incertulas*), rice chlorops (*Chlorops oryzae*), rice leafhopper (*Nephotettix bipunctatus cinticeps*), brown leafhoppers (*Nilaparvata lugens*), weavers spider mites (*Tetranychus spp.*), or mites (Seaman et al., 2013, a,b,c,d,e,f,g,h).

Alternatives to the use of potassium silicate variety are diverse in mechanism particularly because they address aspects of general organic practice, rather than provide a means to strengthen the plant. For example, variety selection is important for the horticultural characteristics and pest resistance profile. Soilscape is critical, i.e., well-structured, adequately drained and aerated soil that supplies the requisite amount and balance of nutrients. Use of sterile practice when handling seed and plants so as not to cross contaminate is important for containing disease. A spring planting of may become infected before a main season crop and thus can be used as an indicator.

Crop rotation is an important management practice for pathogens that overwinter in crop debris. Rotating between crop families helps to prevent many diseases. This may not always be effective for pathogens with a wider host range or those that do not overwinter. Rotation with a grain crop, preferably a sod that will be in place for one or more seasons, deprives disease-causing organisms of their host, and improves soil structure promoting vigorous plant growth. Soluble silica in the landscape tends towards leaching out, redistribution or accumulation depending upon the climate and vegetation. Water abundance and movement determine silica distribution in the absence of vegetation (Sommer et al., 2006). Because crop plants are distributed among silicon accumulators and non-accumulators maintaining a balance of between silica accumulators and non-accumulators should be sought, where particular attention is paid to composting the accumulators in order to retain silica (Ma et al., 2001).

Airflow and leaf_drying is good, since plant diseases are often favored by long periods of leaf wetness. Promoting faster leaf drying, placing rows with the prevailing wind, or increasing row or plant spacing, can slow disease development. Fields surrounded by trees or brush, tend to hold moisture after precipitation. These should be avoided if possible. Mulching and ground cover choices are important. Scouting fields weekly is a key to early detection and evaluating control measures. The earlier a disease is detected, the more likely it can be suppressed with organic fungicides. When available, scouting protocols should be followed for both diseases and pests. Accurate identification of disease problems, especially recognizing whether they are caused by a bacterium or fungus, is essential for choosing an effective control strategy. Anticipate which diseases are likely to be problems that could affect yield and be ready to take control action as soon as symptoms are seen (Caldwell et al., 2013; Carrol et al., 2013a,b).

Silicon is brought to the earth's surface through tectonic and volcanic action and redistributes to the oceans via water contained in runoffs, streams and rivers. The dynamics of this distribution in nature are poorly understood: particularly in soils and between soils and plants. It is apparent that there will be a tendency for soluble silica unincorporated in plant material to leach out of its soil at a higher rate than redistribution of silicon from soil or clay. Furthermore, intensive farming without recycling silicon accumulators will further deplete the soil. Friend Sykes in "Humus and the farmer", describes the careless work of the county of Kincardine, County War Agricultural Committee in attempting to reclaim farmland located in the high moorlands (>1,100 ft elevation) of Northern Scotland and his humus based solution for their blunder to restore fertility to this land without artificial fertilizer. In the eight year plan, a four inch layer of topsoil is carefully managed with the addition of lime and slag; planting of an assortment of grasses, broadleaf forages and oats, including both silicon accumulators and non-accumulators; and grazing the land on and off with sheep. The land required regular replenishment with lime but no more. The slag was necessary only in the beginning and to save time (Sykes, 1949). It is apparent that leaching at high elevation has removed nutrients from the soil of this farm and its humus. The initial ingredients to restoring fertility are lime and slag, a substance rich in soluble silica. As silica is returned to the soil in the form of slag other nutrients including phosphates become balanced.

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