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Phase IV Review Reregistration Case #4086





UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D.C. 20460

JUN 1 1 1993

OFFICE OF PREVENTION, PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Sulfur Dioxide ("The Fruit Doctor")

Reregistration Case #4086

DP BARCODE D190758; EFGWB #93-0685

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The chemical "Sulfur Dioxide" is used as an indoor fumigant (warehouses, cold storage rooms, trucks, vans, boxcars and other transport vehicles). The fruit commodity for which this chemical product is used is grapes (post-harvest). It suppresses the grey mold disease caused by Botrytis cinerea.

The only environmental fate data requirement for "Sulfur Dioxide" as an indoor fumigant (food) is Hydrolysis (161-1). However, the chemistry of sulfur dioxide in aqueous media is well documented in the chemical literature. The Branch believes that there is sufficient information in the chemical literature to generate an environmental fate and transport assessment of "Sulfur Dioxide".

1. <u>IABEL RECOMMENDATIONS</u> ("The Fruit Doctor")

From the present label recommendations/supplement it is unclear to estimate the amount of sulfur dioxide that is required for a given amount of fruit enclosed in a given volume of storage/transportation site. The Branch believes that the registrant should improve its label to provide better guidance on proper usage of this highly toxic chemical.

2. CHEMICAL RELATIONSHIPS BETWEEN SULFUR DIOXIDE AND INORGANIC SULFITES

It is important to realize that "Sulfur Dioxide" and "Sulfites" are very closely related. Sulfur dioxide (a gas at normal temperature and pressure) is very soluble in aqueous media. Solutions of Sulfur Dioxide in water are acidic. The acidic nature of the solution is attributed to the hypothetical species "Sulfurous Acid". "Sulfurous Acid" has never been isolated but its anions "Sulfite" (SO₃²⁻) and "Hydrogen Sulfite" (HSO₃²⁻; also known as "bisulfite") exist and are present in solution. Sulfite salts do exist and are well known.

3. "THE FRUIT DOCTOR"

This "Sulfur Dioxide" product is sold in cylinders containing a mixture of liquified sulfur dioxide and gaseous sulfur dioxide under pressure.

4. OTHER USES OF SULFUR DIOXIDE

Sulfur Dioxide is used as a bleaching agent. Liquified Sulfur Dioxide is used as a solvent (non-aqueous) in many chemical reactions (Refer to Non-aqueous Solvent Systems, T.C. Waddington, ed., Academic Press, New York, 1965). Sulfur Dioxide is also used as a refrigerant. Sulfur dioxide (as a by-product of smelting operations and roasting of sulfide ores) is used in the manufacture of sulfuric acid. It is used in the manufacturing of sulfite salts and dithionites.

5. THE CHEMISTRY OF SULFUR DIOXIDE (Science Chapter)

See attachement.

THE CHEMISTRY OF SULFUR DIOXIDE

Two very important and distinct aspects of the chemistry of sulfur dioxide must be taken into consideration. One is its reactivity in the gaseous state; the other is its reactivity in aqueous media.

Under normal temperature and pressure (boiling point -10 C at ordinary pressure), sulfur dioxide (SO_2) is a colorless, toxic gas with a choking odor. The oxidation state of sulfur in sulfur dioxide is +IV. It oxidizes to sulfur trioxide (SO_3) when reacted with dioxygen in the presence of a catalytic agent.

The presence of sulfur dioxide gas in the atmosphere comes from natural and anthropogenic sources. Natural processes include geothermal activity (mostly volcanic activity). However, anthropogenic sources (mostly from industrial processes and man's domestic activities) cause serious environmental problems. The most notorious of these problems is "acid rain", which affect the urban population as well as contributing to the pollution of water bodies.

Gaseous SO_2 is readily soluble in water (3927 cm³ of SO_2 dissolve in 100 g of water at 20 C). The dissolution of SO_2 in water results in an acidic solution known as "sulfurous acid". "Sulfurous acid" has never been isolated, but spectroscopic studies suggest the presence of hydrated SO_2 molecules ($SO_2 \cdot nH_2O$), hydrogen sulfite (HSO_3) and sulfite (SO_3) anions and hydronium ions (H_3O^+). The predominance of these species depends on concentration, pH and temperature.

Sulfite salts have been isolated, some of them in crystalline form. Except for the sulfites of the alkali metals (sodium; potassium) and ammonium, most of the sulfite salts are rather insoluble in water.

Solutions containing sulfite and hydrogen sulfite anions behave as moderate reducing agents. Depending on the conditions of the reaction, the sulfite anion is oxidized to dithionate or sulfate. However, in the presence of strong reducing agents (for example, a sodium amalgam) sulfites can be reduced. Therefore, the subsequent chemistry of sulfites/hydrogen sulfites in aqueous media is determined by the pH and the redox conditions of the media.

Environmental Fate Assessment

The major concerns about this chemical (when used for pesticidal purposes) are related to accidental spills into water bodies and/or released of pressurized gas into the atmosphere. The extent of any potential damage would depend on the amount of gas released in relation to the size of the environmental compartment (water body; close/open space). It has been reported that many green plants could suffer severe stress at concentrations of sulfur dioxide as low as 1-2 ppm. Sulfur dioxide dissolved in aqueous media can be toxic to aquatic life.

References

Cotton, F.A. and Wilkinson, G. <u>Advanced Inorganic Chemistry</u>, Fifth Edition, 1988, John Wiley and Sons, New York.

Greenwood, N.N. and Earnshaw, A. <u>Chemistry of the Elements</u>, 1984, Pergamon Press, Oxford, UK.