

29. Fungicides - Classification - Inorganics - characteristics, preparation and use of sulfur and copper - Mode of action - Bordeaux mixture and copper oxychloride

Fungicides are chemicals that have the ability to reduce or prevent the damage caused by fungi in plants and their products. Fungicides are classified based on mode of action as protective, curative and eradicant fungicides.

Protective fungicides prevent fungal infection by sporicidal activity. These arrest the germination of spores or kill the fungal hyphae as they penetrate the leaf or prevent their penetration. **E.g. Sulphur**

Curative fungicides penetrate cuticle and kill young fungal mycelium growing in the epidermis and this prevents further development of fungal growth. E.g. **Organomercurials**.

Eradicant fungicides are agents that make control of fungus even after the symptoms become visible and that kill both newly developed spores and the mycelium. E.g. **Systemic fungicides**.

The early fungicides were inorganic materials like sulphur, lime sulphur, copper and mercury compounds.

Sulphur compounds

Elemental Sulphur is available in dust, wettable powder and colloidal forms. The efficiency of S dust increases with fineness of the particle size. A high proportion should pass through 200 – 300 mesh sieve. Colloidal sulphur is formulated with kaolin (diluent) with 40 per cent S and a particle size of $< 6 \mu$. Sulphur is a contact and protectant fungicide used to control powdery mildew in fruits, vegetables, flowers and tobacco. It is also effective against apple scab and rust of field crops. *Lime sulphur*: It is aqueous solution of calcium poly sulphides. It is prepared by sulphur solution in calcium hydroxide suspensions under pressure in the presence of air. Calcium penta sulphide and calcium tetra sulphide found in the mixture are the active materials of fungicidal value which on exposure to air release elemental S.

Mode of action: At first it was observed that S could not be the toxic agent. Sempio (1932) reported that the action was due to the production of various S derivatives. Another theory was that the fungal spores reduce S to H_2S which has shown to be toxic to the spores. However in 1953 this

theory was disproved as colloidal S was more effective than H₂S. Another hypothesis ascribed to various oxidation products such as SO₂, H₂SO₄ and thiosulphuric acid. Then no S derivative is responsible and came to Sempio and finally that S itself is fungi toxic.

Among the heavy metals only Cu and Hg have been widely used as fungicides although silver is most toxic metal cation. The relative toxicity is in the order of

Ag > Hg > Cu > Cd > Cr > Ni > Pb > Co > Zn > Fe > Ca

Copper compounds

Copper sulphate has been used since 18th century as seed treatment against cereal bunt later replaced by organomercurials. Cu ions in solution are toxic to all plant life. Selective fungicidal action can therefore be achieved by application of insoluble Cu compound on the foliage.

E.g. COC, Copper carbonate, Copper hydroxide, Bordeaux mixture etc.

Bordeaux mixture

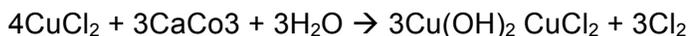
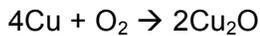
Millardet in 1882 discovered the Bordeaux mixture effective against powdery mildew. A mixture of copper sulphate and lime was initially applied as a paste and thus gained wide recognition as "Bovillie Bordelaise" (Bordeaux Mixture). As the initial mixture containing 8 kg of blue stone dissolved in 100 litres of water and 30 litres of lime suspension prepared with 15 kg lime was found to cause foliar injury. Various combinations were tried. Now a 4-4-50 mixture (copper sulphate in 1 b; lime in 1 b; water in gallons), is used but the concentration of the ingredients is varied depending on the purpose. However, the proportion of copper sulphate to lime usually remains constant. In India Bordeaux mixture is being made by preparing a solution of copper sulphate and quick lime (or hydrated lime) in finely ground form in separate containers and then mixing them simultaneously into a third container with copper sulphate like copper, wooden and earthen vessels. Wide variation in the composition of the resulting mixture will be observed due to chemical reactions between calcium hydroxide and copper sulphate in solution when the ratio between the components is changed. Bordeaux mixture named from the locality of its origin consists of Cu SO₄ (4.5 kg) and Ca (OH)₂ (5.5 kg) in 454 litres of water. It is prepared under a wide range of formulae. Once the mixture has been prepared it should be sprayed immediately on the crop since the toxicity decreases on standing. It is rather difficult to apply because the precipitate tends to block the nozzles. Jaggery or sugar is added to prevent crystallisation.

Mode of action is complex. The ai is probably not $\text{Cu}(\text{OH})_2$ but rather basic Cu SO_4 approximately to the formula $[\text{Cu SO}_4 \cdot 3 \text{ Cu}(\text{OH})_2]$. Bordeaux mixture is almost insoluble in water. So how is Cu mobilized in plants to kill the fungus? The exudates both from the surface of leaf and from the fungal spores can dissolve sufficient quantities of Cu from the dried deposits due to the presence of certain compounds like amino and hydroxy acids which can form chelates with copper.

B) Copper oxychloride

(Blue copper 50: Fytolan) Cupramar, Blimix 4%, Blitox 50%.

Copper oxychloride is one of the low soluble copper fungicides produced by the action of air on cupric chloride solution or scrap copper.



It is marketed in the form of wettable powder containing 50 and 90% copper oxychloride and dusts containing 4 to 12% metallic copper. The 50% formulation contains a diluent (Kaolin) and a surface active agent.

Burgandy mixture

This was introduced by Mason in 1887 by mixing copper sulphate (1 part) with sodium carbonate crystals (1 part) and is less effective than Bordeaux mixture.

Cheshnut compound

This is suggested by Bewley in 1921 consists of 2 parts of Cu SO_4 and 11 parts of $(\text{NH}_4)_2 \text{CO}_3$. The two compounds are well powdered thoroughly mixed and stored in air tight containers for 24 hours before use.

Chaubattia paste

This was developed at Government Fruit Research Station, Chaubattia, Almora district, UP. It is prepared by mixing copper carbonate (800 g) and red lead (800 g) in 1 litre of linolin or raw linseed oil. It is used as wound dressing agent on pruned parts.

Copper oxy chloride approximately $\text{Cu Cl}_2 \cdot 3 \text{ Cu}(\text{OH})_2$ is marketed as colloid and wettable powder. It is a protective fungicide used to control

potato blight, several leaf spots and effective against several diseases of horticultural crops.

***COPPER HYDROXIDE* Cu (OH)₂ IS A NEW FORMULATION INTRODUCED.**

Mode of action is the denature of proteins by free copper ions. Since enzymes are made up of proteins, the Cu inactivates the enzymes. The Cu kills the fungal spores by combining with the sulphohydril groups of certain enzymes.