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   (2) Non Systemic fungicides [Sulphur, Copper, Heterocyclic Nitrogenous compounds (Captan, Captafol, Folpet) Quinone compounds, Miscellaneous fungicides, Organic Tin compound, Aromatic hydrocarbon].
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1. CLASSIFICATION OF FUNGICIDES

There are three bases of classifying the fungicides:

A. Mode of action against fungi
B. General use
C. Chemical nature

A. Classification based on mode of action:

i**. Protectants**: Chemicals that are applied before infection/disease is established.e.g. Sulphur, Captan, Thiram, Zineb, Mancozeb etc. These fungicides have two sub groups:

***a. Contact*:** The chemicals that target the fungus at rest either before or after presence on the host. Fungicides called eradicants are grouped in contact fungicides. In simple way, *Eradicants* are those fungicides that remove pathogens from an infection court. e.g., Copper, lime sulphur etc.

***b. Residual*:** Chemicals that are applied as a stationary layer on the host so as to stop the mobile fungus. E.g. Dithiocarbamate fungicides like Zineb, Maneb.

ii. Therapeutants: Chemicals that are applied after appearance of infection/disease to cure the disease by killing the pathogen. e.g. Oxathiins, benzimidazoles, Bordeaux mixture, antibiotics etc.

iii. Systemic: Chemicals that are absorbed by the treated plants and distributed or translocated to the different parts of the plant. The sites of action of these fungicides are different from the site of application. E.g. Oxathin, benzimidazoles, Metalaxyl, thiophanate, Antibiotics etc.

iv. Non-systemic: These fungicides that do not show systemic nature. They are mainly contact and residual and limited to the sprayed parts only. E.g. Sulphur, copper Quinone, heterocyclic nitrogenous group etc.

B. Classification based on General use:

i. Seed protectants: Captan, Thiram, Bavistin etc

ii. Soil protectants: Pre-planting: Chloroform, formaldehyde, vapam etc.
Post-planting: Captan, thiram, topsin etc.

iii. Foliage & blossom protectants: Dithane M-45, Bordeaux mixture, Bavistin, Blitox
iv. Fruit protectants: Captan, Difolatan, Dithane M-45, Topsin-M etc.
v. Tree wound dressing: Bordeaux pastes, Chaubattia paste etc.
vi. Eradicants; Copper, Lime sulphur etc.

A. Classification based on Chemical nature:

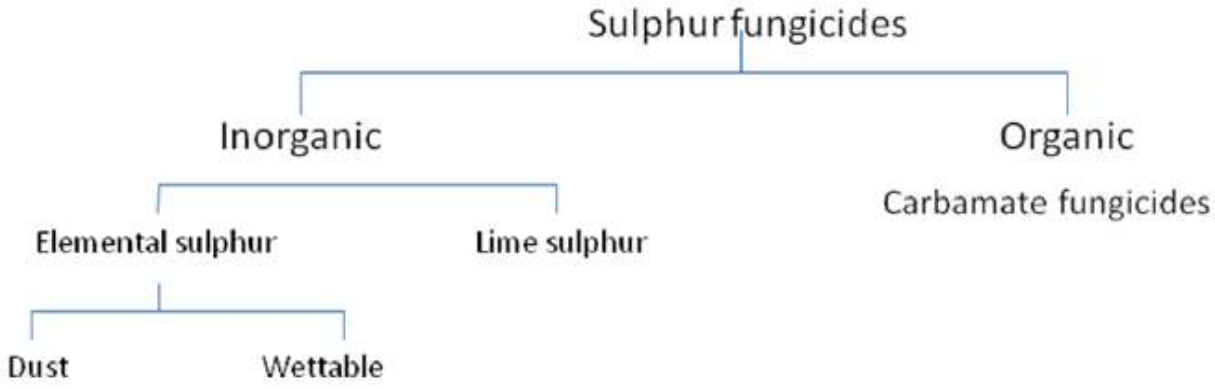
1. Sulphur fungicide
    Inorganic, e.g. powdered sulphur, wettable sulphur, lime sulphur etc.
    Organic, e.g. ferbam, ziram, thiram, zineb, maneb, nabam, vapam etc.
2. Copper fungicides, e.g. Bordeaux mixture, Burgandy mixture, copper oxychloride etc.
3. Mercural fungicides
    Inorganic, e.g. mercuric and mercurous chloride etc.
    Organic, e.g. phenyl mercury acetate, methoxy ethyl mercury chloride etc.
4. Heterocyclic nitrogenous compounds, e.g. captan, folpet etc.
5. Quinone compounds, e.g. chloranil, dichlone etc.
6. Oxathiin compounds, e.g. carboxin, oxycarboxin etc.
7. Benzimidazoles/Carbendazim group, e.g. benomyl, MBC etc.
8. Miscellaneous group, e.g. PCNB, dodine, antibiotics etc.

2. NON-SYSTEMIC FUNGICIDES

1. Sulphur Fungicides

- Elemental sulphur use as a fungicide for a long time and even today it is one of the best for the control of powdery mildew diseases.
- In 1821, Robertson in England reported that sulphur is effective against peach mildew.

Sulphur fungicides can be classified as follows:



Inorganic sulphur

A. Elemental sulphur (ES):

- ES mechanically ground sulphurs have a tendency to form small aggregates which may be overcome by the addition of small amount of inert materials such as kaolin or lead aresenate.
- Occurs widely in nature both in free state and combination.
- Two elemental states are sulphides and sulphates.
- ES is imported to India for formulating fungicides.

Types of ES Fungicide: The ES Fungicide are available in two types of formulation

(i) Dusts/powder:

- "ground formulation" – mechanically ground and separated by air blast.
- Particle size is 74-47 microns. Eg. Sulfex, Cosan etc. Most common form available in India.
- Fungicidal efficiency depends on the fineness of its particle.

(ii) Wettable Sulphur:

- Any form of sulphur, such as ground formulation is made into WS by grinding with protective materials like casein, sulphyte lye and bentonite clay.
- In India, most commonly available in the form of 'micronised sulphur'. Eg. Sulrex.

- In recent years WS become more popular. They form uniform suspension in water use as spray.

B. Lime sulphur

- These were used prior to 1930s. They are effective against many fungi like powdery mildews, mites and leaf hoppers.
- LS is a mixture of calcium polysulphides and calcium thiosulphate.

- Different proportions of lime and sulphur are mixed in water to form LS. One common formula is:

Rock lime	20lbs
Sulphur	15 lbs
Water	50 gallons

Mechanism of action:

Mechanism of action of ES has been a subject of interest of many years, various were advanced and later refuted. One of the earliest theory,

i. Oxidised sulphur theory: SO2, SO3, Pentathionic acid: rejected due to role of pH of the solution in water. SO2, SO3, Pentathionic acid (oxidized derivatives of sulphur important in the reaction) no more toxic than could be accounted for by the hydrogen ion concentration of their solution in water.

ii. Hydrogen sulphide theory: rejected as H2S does no inhibit germination. Experiment indicated that formation of H_2S from ES was not detrimental to the germination of spores.

iii. Direct action theory: S acts as hydrogen acceptor in metabolic system and disturbs normal hydrogenation & dehydrogenation reaction of the cell.

i**v. Vapour phase activity:** S fungicides emits sufficient vapour to prevent growth of fungal spores.

v. Elemental sulphur interferes with energy production by intercepting electron of the substrate side of cytochrome C in the mitochondrial electron transport system. (Elemental sulphur possibly affects the electron transport in the respiratory system of sensitive fungi).

vi. The dialkyl dithiocarbamates are known to inhibit a multitude of enzymes; therefore, fungitoxicity probably involves concurrent pyruvate dehydrogenase reaction is particularly highly sensitive to dialkyl dithiocarbamates.

Disadvantages of Inorganic Sulphur fungicides:

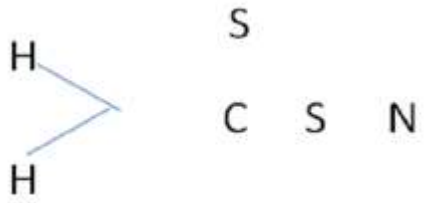
i. S sun scald in fruit crops like apple and also in cucurbits during warm climate.

ii. Blossoming period is sensitive to S injury. It inhibits pollen germination and leads to poor fruit set.

iii. High dose of lime-S reduces photosynthetic activity of the leaves.

ORGANIC SULPHUR

- Carbamate fungicides form a very important group among fungicides. Most are foliage while some are used as soil and seed treatment.
- They are mostly Dithiocarbamates and very important group of fungicides.
- Fungicidal property of Carbamates was first reported by Tisdale in 1931 in the lab. Of E.I. DuPont company, the USA.
- But commercial production started a decade later. In 1934 patenting of dithiocarbamates by Tisadale and Williams, who patented Thiram.
- Commercially available all the carbamate fungicides are derivatives of Dithiocarbamic acid: this organic acid does not occur in the free state and was synthesized.
- The structural formula is



Dithiocarbamic acid

• Examples:

1. Thiram (TMTD, tetramethylthiuram disulphide or bis dimethylthiocarbamoyl disulphide):

- TMTD is a condensation product of dithiocarbamic acid. (two molecules in which the H atoms have been substituted by methyl groups).
- Thiram is being sold under a variety of other trade names such as Arasan, Tundas, Terson, Tulisan and so on.
- It is a leading seed treatment for wheat, rice, gram, peas, mustard, linseed sorgum and onion.
- Thiram is also used in the control of foliage diseases and act as an insecticides. Among the soil borne pathogens controlled by it are Pythium, Rhizoctonia, Fusarium and Protomyces.
- As a foliar spray, thiram was not as successful as its metallic compounds. For this reasons, several compounds have been developed which are as follows:

2. Ziram (Zn dimethyldithiocarbamate) *Its structural formula ,*
Trade names ; Ziram, zerlate
3. Ferbam (Ferric dimethyldithiocarbamate)
4. Nabam (Disodium ethylene ethylenebisdithiocarbamate)
5. Vapam (SMDC, sodium methyldithiocarbamate)
6. Zineb (Zn ethylene bisdithiocarbamate) *Its structural formula*

7. Maneb (Mn ethylene bisdithiocarbamate) *Its structural formula* Mancozeb (2% Zn + 78% Maneb)

All these fungicides are broad spectrum, less phytotoxic, used against foliar and seed-borne diseases of vegetables and cereals.

Copper fungicides

This is best known fungicide group. Prevost (1807) first used as fungicide for the control of bunt or smut disease of wheat. Then Bordeaux mixture was understood and discovered by Millardet (1882). Millardet observed that along the roadside at Medoc in Gironde, certain vines bore leaves while other had been defoliated by the disease. Millardet believed that the foliage on the same of the vines had persisted because of the dabbing of the leaves with verdigris or with a mixture of lime and copper sulphate.

A. Copper sulphate: Bordeaux mixture, Bordeaux paste, Burgundy mixture (Mason, 1887), Cheshunt compound (Bewley, 1921).
B. Copper oxychloride [$CuCl_2 3Cu(OH)_2$]: Blitox, Fytolan
C. Copper carbonate : Chaubattia paste
D. Cuprus oxide : Perenox

Composition of Bordeaux mixture: [1 gal=4.5459 lit; 1lb= 453.59 g]

Original :	4: 4: 50	or	5: 5: 50 (lb : lb : gallon)
1% :	4.5kg $CuSO_4$	or	1kg $CuSO_4$
	4.5kg unslaked lime		1kg unslaked lime
	450 L water		100 L water

Bordeaux Paste: It is normally prepared by adding 1 lb each of copper sulphate and lime in 1 gallon of water used for tree wound dressing to prevent fungal attack. Control stem bleeding disease of coconut [*Chalara paradoxa* (syn. *Thielaviopsis paradoxa*, *Ceratocystis paradoxa*)].

Burgundy mixture (Mason, 1887): It is a modification of Bordeaux mixture, is often used for tender foliage, since it is less phytotoxic. In this lime is substituted by sodium carbonate, and hence, is sometimes called 'soda Bordeaux'. It is mixture of $CuSO_4$ (10 lb) and Na_2Co_3 (12.2 lb) in 50 gallons of water. Burgundy mixture does not produce blemishes. Neither burgundy mixture nor other substitutes of Boredeaux mixture have been widely accepted.

Cheshunt compound (Bewley, 1921): 2 parts of copper sulphate and 11 parts of ammonium carbonate. 30 gms of this mixture dissolved in little hot water and solution made up to 9 lits with cold water. Chestnut compound is recommended for the control of 'damping off' diseases as a soil drench in nursery beds.

Chaubattia paste: Copper carbonate (800 gms) and red lead (800 gms) in 1 lit of lanolin or raw linseed oil. This paste was developed by Singh (1942, 43) at Govt. Fruit Res. Station Chaubattia in the Almora distt of U.P (now Uttarakhand) in India.

Fungicidal activity of Copper/BM:

 Cupric ion (Cu+++) get entered into the spores and mycelia and hinder/disrupt metabolic activity. It denatures proteins.

 Effective against leaf blight & fruit falls, rots associated with large number of diseases like apple scab, downy mildews.

 Has unique property, i.e. bactericidal activity against citrus canker.

 Also beneficial to some crops like grape vines and potatoes for better growth. Because Cu ions after entering into the host tissues act as micronutrients.

 BM can be injurious to apple & other plants in orchards. Hence, it should be used by high volume sprayer using larger quantity of water. BM can be phytotoxic to many plants in the cool weather. Because, during this time, stomata remain wide open which absorb more Cu salts.

Heterocyclic Nitrogenous Compounds

1. **Captan**: Trade name is Captaf. *Add structural formula*

 It is N-trichloromethyl-thio-4-cyclohexene-1,2- dicarboximide. Kittleson (1952) first prepared this compound and reported it fungicidal property. Hence called "Kittleson"s Killer".

 It is soluble in water, non-volatile and has pungent odour.

 Available in 50WP (spray) and TS WP (seed treatment)

 Low toxic to mammals and harmful to fish and aquatic animals. Low phytotoxic.

 It gives protective action up to 7-14 days.

 Applied as seed & soil treating (drenching) chemical. Foliar spray is also done selectively.

 Control damping-off diseases caused by *Pythium* spp.

 Acts by Co-carboxylase in the decarboxylation of pyruvates and also inhibits many oxidative enzymes.

2. Captafol: trade names are Foltaf, Difolatan

 N(1,1,2,2,-tetrachloroethyl thio-4-cyclohexene, 1,2-dicarboxymide).

 Introduced in 1961, USA. Available in 80%WP or 80% a.i. EC.

 Occasionally shows systemic nature.

 Action is due to –SCCl3 group which interfere SH-enzymes and oxidative process particularly activity of co-carboxylase.

3. Folpet: Trade name is Phaltan

 It is an analogue of Captan. Its amide structure is different from Captan that offers difference in their fungitoxic spectrum.

 N-(trichloromethylthio) phthalimide.

 It is more effective than Captan. Because, its amide is 100 times more toxic than the amide of captan.

Quinone Compounds

They are very good seed treating fungicides. Two fungicides of this group are:

1. Chloranil (TN Spergon) is 2,3,5,6-tetrachloro-1,4-benzoquinone.
2. Dichlone (TN Phygon) is 2,3-dichloro-1,4-naphthoquinone.

 Low mammalian toxicity, but becomes highly toxic if consumes orally.

 Chloranil is insoluble in water, partially soluble in chloroform, CCl4, CS2 and completely in ether.

 Chloranil decomposes at alkaline pH, but stable in acidic pH.

 In presence of sunlight and moisture, chloranil transforms into chloranilic acid, hence not useful against foliar diseases. Whereas Dichlone is stable and used as both spray and seed treatment.

 Both fungicides are compatible with commonly used seed treating fungicides.

 Actions: (i) Bind to SH and NH2 groups in the fungal cell
(ii) Disturbs Electron Transport Systems

Miscellaneous Fungicides

A. Halogenated nitrobenzene:

1. PCNB: Trade name is Brassicol. Now banned.

 Insoluble in water, but soluble in organic solvents.

 Used mostly against sclerotia forming fungi like *Rhizoctonia, Sclerotinia, Sclerotium* spp.

 Sometimes used in artificial medium to isolate *Fusarium* spp., as these fungi are insensitive to PCNB.

2. DCNA: Common name is Dichloran and TN is Botran.

 It is 2,6- dichloro-4-nitroaniline

 Low phytotoxic.

 Effective as spray against *Botrytis* infection and also post harvest fruit rot caused by *Rhizopus* and *Monilinia*.

B. Organic Tin compounds: Banned in India

 Inorganic tin compounds do not have fungicidal property while organic group does have.

 Majority have phtytotoxic property. Only triphenyl tin hydroxide (TPTH, TN is Duter) and triphenyl tin acetate, TN is Brestan) are useful fungicides.

 TPTA has insecticidal property for surface feeding insects. It was introduced in 1952 against potato late blight.

C. Aromatic hydrocarbon

Dinocap: TN are Karathane, Arathane, Crotothane, Mildex. *Add structural formula*

 It is 2,4-dinitro-6-octophenyl crotonate, developed in 1946.

 Insoluble in water, but soluble in organic solvents

 Incompatible with lime-sulphur and oil-based sprays.

 Available as 25WP and 48EC.

 Very effective against powdery mildews. Also it is a miticide.

 Karathane is better alternative of sulphur fungicides, as some crops like cucurbits and apple are S-sensitive.

 Has got very short residual life, hence residual action is poor.