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WORLD HEALTH ORGANIZATION
ORGANISATION MONDIALE DE LA SANTE

FOOD AND AGRICULTURE ORGANIZATION
ORGANISATION POUR L'ALIMENTATION ET L'AGRICULTURE

WHO/VBC/DS/88.67

ORIGINAL: ENGLISH

Distr.: LIMITED

DATA SHEET ON PESTICIDES

No. 67

THIOMETON

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CLASSIFICATION:

Primary use: Insecticide, acaricide

Secondary use: None

Chemical group: Organophosphorus compound

Date issued: March 1988

1.0 GENERAL INFORMATION

1.1 COMMON NAME: thiometon (BSI, E-ISO, F-ISO, F-ISO, JMAF), dithiomethon (France), M-81 (USSR), exceptions (Federal Republic of Germany, Portugal, Turkey).

1.1.1 Identity:

IUPAC: S-2-ethylthioethyl O,O-dimethyl phosphorodithioate

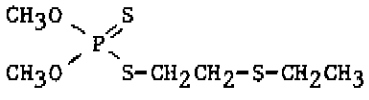
CAS: S-[2-(ethylthio)ethyl] O,O-dimethyl phosphorodithioate

CAS Reg. No.: 640-15-3

Molecular formula: $C_6H_{15}O_2PS_3$

Relative molecular mass: 246.3

Structural formula:



1.1.2 Synonyms: Dithiometon, Ekatin^R, Ekatin Aerosol, Ekatin^R, ULV, Ekatin WF ULV, Intrathion, Intration, Luxistelm, M-81.

1.2 SYNOPSIS: Thiometon is a systemic organophosphorus insecticide - acaricide with residual activity of up to three weeks. It is highly toxic to mammals by the oral route. Thiometon is rapidly metabolized in both animals and plants to the water-soluble sulfoxide and sulfone. Some of the metabolites of thiometon are more potent inhibitors of cholinesterases and are more toxic than thiometon itself.

1.3 SELECTED PROPERTIES

1.3.1 Physical characteristics: The pure product is a colourless oil with a characteristic odour; b.p. 110 °C at 13.3 Pa, d_4^{20} 1.209, n_4^{20} 1.5515.

1.3.2 Solubility: Thiometon is soluble in water at 200 mg/L (25 °C), and in most organic solvents, but only slightly soluble in light petroleum.

1.3.3 Stability: Low stability in the pure state, but stable in non-polar solvents. It is hydrolysed in aqueous solutions, both under alkaline or acid conditions.

1.3.4 Vapour pressure: 23 mPa at 20 °C.

1.4 AGRICULTURE, HORTICULTURE AND FORESTRY

1.4.1 Common formulations: Emulsifiable concentrates (250 g/L) and ULV (150 g/L). In emulsifiable concentrate formulations it is mixed with parathion, endosulfan, fenvalerate or quinalphos, and in ULV concentrate with parathion.

1.4.2 Susceptible pests: Thiometon is effective against sucking insects, mainly aphids, and mites on most crops. Others include psyllids, sawflies, jassids and thrips.

1.4.3 Use pattern: Used as a foliar spray on many crops and ornamentals. Applied at a 0.1% concentration rate when the plant is actively growing for maximum systemic effect. May also be used as a soil drench.

1.4.4 Unintended effects: Considered non-phytotoxic and of low toxicity to bees.

1.5 PUBLIC HEALTH PROGRAMMES: No recommended usage.

1.6 HOUSEHOLD USE: No recommended usage.

2.0 TOXICOLOGY AND RISKS

2.1 TOXICOLOGY - MAMMALS

2.1.1 Absorption route: Thiometon may be absorbed from the gastro-intestinal tract, through the intact skin or by inhalation of spray mist.

2.1.2 Mode of action: Thiometon is an organophosphorus insecticide which is not a strong cholinesterase inhibitor but when metabolized it converts to several potent cholinesterase inhibitors. Absorption is rapid and formulations may be more toxic than the pure compound.

2.1.3 Excretion products: Rats given 15 mg/kg b.w. of labelled thiometon orally, after 24 hours excreted 83% of the radioactivity in the urine and 5.5% in the faeces, with 4% remaining in the carcass after 96 hours. Maximum blood levels were attained after three hours. Primary metabolites were O-thiometon sulfoxide, O-thiometon sulfone and O,O-dimethylphosphoric acid in proportions of 26, 5 and 52% of the urinary excretion, respectively.

2.1.4 Toxicity, single dose

Oral LD_{50}:

Rat	225 mg/kg b.w. (pure)
Rat	190 mg/kg b.w. (technical thiometon)
Rat	100–120 mg/kg b.w. (as 25% EC formulation)
Guinea pig (M)	261 mg/kg b.w.
Rabbit (M)	95 mg/kg b.w.
Mouse (M)	66 mg/kg b.w.
Mouse (F)	62 mg/kg b.w.

Dermal LD_{50} (four hour exposure):

Rat (M)	>1 100 mg/kg b.w.

Intraperitoneal LD_{50}:

Rat (M)	45 mg/kg b.w.
Rat (F)	47 mg/kg b.w.

Intravenous LD_{50}:

Rat (M)	27.5 mg/kg b.w.
Rat (M)	35.5 mg/kg b.w.
Rabbit	22.0 mg/kg b.w.

Inhalation LC_{50} (one hour):

Rat (M,F)	>60 mg/L

Irritation:

Application of 0.5 ml 94.8% pure thiometon for 24 hours with occlusion to intact or abraded rabbit skin showed no evidence of irritative effects. Instillation of 0.1 ml 94.8% pure thiometon to rabbit eyes showed that thiometon had no irritant or corrosive effect.

2.1.5 Toxicity, repeated doses: Results of studies in rats given repeated doses of thiometon were inconsistent. Formulations may be significantly more toxic than the pure compound.

Oral: In a 12 month study in rats given thiometon from 0 to 18 mg/kg/day by gastric intubation, a level of $\geq$ 1 mg/kg/day caused a decrease in erythrocyte cholinesterase activity. At $\geq$ 2 mg/kg/day an additional decrease in plasma acholinesterase activity occurred. A slight reduction in weight gain occurred at 6 mg/kg/day which became more significant at the highest dose level. This effect was seen only in male rats. All histological findings were normal.

In another experiment rats given 4 to 7 doses of Intrathion (thiometon, supposedly impure) intragastrically at a dose level of 0.6 LD_{50} at three day intervals, showed clinical signs of poisoning after each dose. Some rats showed flaccid neuro-muscular paralysis after 10 to 19 days and on sacrifice showed significant decreases in the total phospholipid, sphingomyeline, phosphatidyl ethanolamine, phosphatidylserine and total and free cholesterol levels in lipid extracts of the spinal cords. Also seen were significant increases in phosphoinositides, polyglycerophosphatides, lecithin and esterified cholesterol levels.

In a 13 week study, male rats were given 5, 10, 15 or 20 mg/kg/day. All animals showed a mild to severe poisoning with all animals in dose groups $\geq$ 15 mg/kg/day dying. The survivors recovered after 10 weeks whilst still receiving thiometon and histological examination failed to reveal abnormal pathology at 13 weeks.

2.1.6 Dietary studies

Short term: In a four week study, groups of rats fed diets with thiometon at 0, 0.5, 2, or 5 ppm showed no effects upon plasma cholinesterase activity, growth and behaviour. A slight inhibitory effect on erythrocyte and brain cholinesterase activity was seen at the highest dose level of 5 ppm. No observed effect level (NOEL) was found to be 2 ppm.

In a 90 day study, groups of rats fed thiometon at 0, 5, 15 or 45 ppm showed mortality in the highest dose group after the fourth week. Plasma and erythrocyte cholinesterase activity was depressed in rats fed on a diet containing $\geq$ 15 ppm of thiometon and erythrocyte cholinesterase was only slightly inhibited in rats from the 5 ppm group. No histopathological changes were found.

In a 90 day study, beagle dogs fed thiometon at 0, 10, 20 or 40 ppm (equivalent to 0, 0.35, 0.65 and 1.40 mg/kg/day respectively) showed no effects on the amount of food consumed, growth, histopathology or behaviour. In the highest dose group, depression of plasma cholinesterase activity occurred towards the end of the study. Erythrocyte cholinesterase activity was affected in rats fed on a diet containing thiometon over 20 ppm. Brain cholinesterase activity remained normal in all dose groups. NOEL was 10 ppm.

Long term: A two year rat feeding study was initiated at doses of 0, 0.2, 1, 2 or 20 ppm. After six weeks the concentration was increased to 0, 1, 2.5, 6.25 or 300 ppm respectively. Shortly after increasing the dose levels, the rats fed on a diet containing 300 ppm lost weight and showed signs of acute poisoning and some deaths occurred. In the survivors the body weight remained low during the rest of the study due to decreased food and water consumption. In females of this group, haemoglobin, mean corpuscular volume and mean corpuscular haemoglobin levels were decreased as well as blood glucose, protein and cholesterol. Plasma, erythrocyte, and brain cholinesterases were strongly inhibited in both sexes at this dose level. Lower values for plasma and erythrocyte cholinesterase activities were occasionally observed in rats fed on a diet containing 6.25 ppm thiometon. In rats on a diet of 2.5 ppm erythrocyte cholinesterase activity was marginally reduced (<20%). Erythrocytes, leukocytes as well as amorphous uric acid crystals occurred in the urine at the highest dose level during the last half of the study. The urine also had a higher specific gravity. Relative organ weights were increased in the highest dose group save for the spleen which had a decrease in relative weight, and the liver which had a decreased relative weight in males only. No specific lesions were induced at any dose level. NOEL was 2.5 ppm.

Dietary administration of 6, 12 or 48 ppm thiometon to dogs for two years resulted in decreased cholinesterase activity in brain, plasma and erythrocytes at 48 ppm and in erythrocytes and plasma (marginal decrease) at 12 ppm. No changes in mortality or in histopathological, ophthalmological or behavioural parameters, nor dose-related changes in urinalysis, haematological or clinical chemistry parameters were observed. NOEL was 6 ppm.

2.1.7 Supplementary studies

Carcinogenicity: No tumours were found in the rat dietary studies described above, that could be related to administration of thiometon.

Mutagenicity: Thiometon was found to be mutagenic in metabolically non-activated systems in several strains each of Salmonella thyphimurium (his auxotrophs) G46, TA1530, TA1535, and Escherichia coli causing base substitutions. Thiometon did not demonstrate any mutagenic effect in two mouse micronucleus tests nor in an Ames Salmonella/microsome plate test.

Teratogenicity: Female rabbits treated with thiometon at 1 or 5 mg/kg/day from the sixth to the eighteenth day of pregnancy showed no evidence of teratogenic or embryotoxic effects.

Reproduction: A marginal effect on reproduction in rats was reported following dietary administration of 6.25 ppm for three generations. No adverse effects were noted at 1 or 2.5 ppm but at 6.25 ppm a lower lactation index, reduced viability, reduced pup weight and/or an increase in stillborn births were observed in some or all of the generations. There was no effect on gestation indices and no adverse histopathological or teratogenic effects.

Neurotoxicity: Flaccid neuromuscular paralysis was observed in rats 10-19 days after oral administration of 4-7 doses of Intrathion, each 0.6 of the LD_{50}, administered at three day intervals. These events were paralleled by biochemical changes in the spinal cord (Section 2.1.5). Examination of the spinal cord by light and electron microscopy revealed demyelination and nerve cell degeneration. In a special study in chickens, given thiometon intramuscularly at a dose of 35 mg/kg, and protected with atropine and pralidoxime, no signs of neurotoxicity were seen during an observation period of 29 days.

2.2 TOXICOLOGY - MAN

2.2.1 Absorption route: Thiometon may be absorbed from the gastrointestinal tract, through intact skin or from the lungs.

2.2.2 Dangerous doses: No published information available.

2.2.3 Observations on occupationally exposed workers: Twelve female agricultural workers exposed to Intrathion showed changes in catalase, cytochrome oxidase and ceruloplasmin levels. Some of these changes persisted for six months post-exposure. These parameters are generally not examined for in cases of organophosphorus poisoning and their interpretation is difficult. Reduced blood cholinesterase activity has been reported in workers during thiometon manufacture but there were no signs of illness.

2.2.4 Observations on exposure of the general public: No published information available.

2.2.5 Observations on volunteers: No published information available.

2.2.6 Reported mishaps: A 63 year old female ingested the equivalent to a full glass of a 50% thiometon (Ekatin 50%) formulation. The victim experienced painful abdominal cramps, diarrhoea, a weak and rapid pulse and cold extremities. The victim vomited many times and was generally sleepy, weak with extensive fasciculations visible on

the trunk and limbs. Tendon reflexes were elicitable and quadriceps muscle reflexes lively. Plantar was of the flexor type. Neuromuscular synapse insufficiency tests were normal but the victim had low blood acetylcholinesterase activity. The dose was apparently non-fatal.

2.3 TOXICITY TO NON-MAMMALIAN SPECIES

2.3.1 Fish LC_{50}:

Rainbow trout	8.0 mg/L (96 hr)
Carp	13.2 mg/L (96 hr)

2.3.2 Birds: No published information available.

2.3.3 Other species: Thiometon was observed to be slightly toxic to Daphnia magna, green algae, earthworms and bees.

3.0 REGULATORY AUTHORITIES: RECOMMENDATIONS ON REGULATION OF COMPOUND

3.1 RECOMMENDED RESTRICTIONS ON AVAILABILITY

(For definition of categories see the Introduction to Data Sheets).

Liquid formulations of 600 g/L and over, Category 2
Other liquid formulations, Category 3
Solid formulations of 250 g/kg and over, Category 3
Other solid formulations, Category 4

3.2 TRANSPORTATION AND STORAGE

All formulations: Thiometon should be transported and stored in clearly labelled impermeable containers, away from containers of food and drink. Storage should be under lock and key, secure from access by children and other unauthorized persons.

3.3 HANDLING

All formulations: Full protective clothing (see section 4.3) should be used by those handling the compound. Adequate washing facilities should be available at all times during the handling and should be close to site of handling. Eating, drinking and smoking should be prohibited during handling and before washing after handling.

3.4 DISPOSAL AND/OR DECONTAMINATION OF CONTAINERS

All formulations: Containers must be firstly decontaminated and then crushed and buried below topsoil. Care must be taken to avoid subsequent contamination of water sources. Decontamination of containers in order to use them for other purposes should not be permitted.

3.5 SELECTION, TRAINING AND MEDICAL SUPERVISION OF WORKERS

All formulations: Pre-employment medical examination of workers is necessary. Workers suffering from active hepatic or renal disease should be excluded from contact with thiometon. A pre-employment and periodic blood cholinesterase test for workers is desirable. Special account should be taken of the workers' mental ability to comprehend and follow instructions. Training of workers in techniques to avoid contact is essential.

3.6 ADDITIONAL REGULATIONS RECOMMENDED IF DISTRIBUTED BY AIRCRAFT

All formulations: Pilot and loaders should have special training in application methods and in recognition of the early symptoms of poisoning. Protective clothing (Section 4.3) must be worn. Flagmen, if used, should wear overalls, an impermeable broad brimmed hat, impermeable boots and gloves, and a respirator, and be located well away from the dropping zone.

3.7 LABELLING

Formulations in Category 2, Minimum Cautionary Statement

"DANGER - POISON"
(SKULL AND CROSS-BONES INSIGNIA)

Thiometon is a highly toxic organophosphorus compound which inhibits cholinesterases. Contact with the skin, inhalation of dust or spray, or swallowing may be fatal. Wear protective gloves, clean protective clothing, and a respirator of the organic-vapour type when handling this material. Wash immediately after handling. Ensure that containers are stored under lock and key. Empty containers must be decontaminated and disposed of in such a way so as to prevent all possibility of accidental contact with them. Keep the material out of reach of children and well away from foodstuffs, animal feed and their containers. In case of contact, immediately remove contaminated clothing and wash the skin thoroughly with soap and water; for eyes, flush with water for 15 minutes.

If poisoning occurs, call a physician. Atropine and pralidoxime are accepted antidotes, repeated doses may be necessary. Artificial respiration also may be needed.

Formulations in Categories 3 and 4, Minimum Cautionary Statement

"WARNING - POISON"
(SKULL AND CROSS-BONES INSIGNIA)

(for test of statement see above).

3.8 RESIDUES IN FOOD

Maximum residue levels

Maximum residue levels have been recommended by the Joint FAO/WHO Joint Meeting on Pesticide Residues. Acceptable daily intake for man has been estimated to be 0-0.003 mg/kg body weight.

4.0 PREVENTION OF POISONING IN MAN AND EMERGENCY AID

4.1 PRECAUTIONS IN USE

4.1.1 General: Thiometon, an organophosphorus pesticide is highly toxic to mammals. Besides the oral route, it may be absorbed through the intact skin and by inhalation of dust or spray mist. Repeated exposure may have a cumulative inhibitory effect on cholinesterases. Most formulations should be handled by trained personnel wearing protective clothing.

4.1.2 Manufacture and formulations: For T.L.V. no information available.

Closed systems and forced ventilation are required to minimize the exposure of workers to the chemical.

4.1.3 Mixers and applicators: When opening the container and when mixing, protective impermeable boots, clean overalls, gloves and a respirator of the organic-vapour type should be worn. Mixing, if not mechanical, should always be carried out with a paddle of appropriate length. When spraying tall crops or during aerial application, a respirator should be worn, as well as an impermeable hat, protective clothing, boots and gloves. The applicator should avoid working in spray mist and avoid contact with the mouth.

Particular care is needed when equipment is being washed after use. All protective clothing should be washed immediately after use, including the insides of gloves. Splashes must be washed immediately from the skin, or eyes, with large quantities of water. Before eating, drinking or smoking, hands and exposed skin, should be washed.

4.1.4 Other associated workers (including flagmen in aerial operations): Persons exposed to thiometon and associated with its application should wear protective clothing and observe the precautions described above in 4.1.3 under "Mixers and applicators".

4.1.5 Other populations likely to be affected: With good agricultural practices, subject to 4.2 below, other persons should not be exposed to hazardous amounts of thiometon.

4.2 ENTRY OF PERSONS INTO TREATED AREA

Unprotected persons should be kept out of tall crops for four days and out of other crops for 24 hours.

4.3 DECONTAMINATION OF SPILLAGE AND CONTAINERS

Residues in containers should be emptied in a diluted form into a deep pit, and empty containers should be burned or buried, taking care to avoid contamination of water sources. Re-use of empty containers is prohibited (section 3.4). Spillage of thiometon and its formulations should be removed by washing with 5% sodium hydroxide solution and then rinsing with large quantities of water.

4.4 EMERGENCY AID

4.4.1 Early symptoms of poisoning: Early symptoms of poisoning may include excessive sweating, headache, weakness, giddiness, nausea, vomiting, hypersalivation, stomach pains, blurred vision, slurred speech and muscle twitching. Later there may be convulsions and coma in cases of severe poisoning.

4.4.2 Treatment before person is seen by a physician, if these symptoms appear following exposure: The person should stop work immediately, remove contaminated clothing and wash the affected skin with water and soap, and flush the area with large quantities of water. If swallowed, and if the person is conscious, vomiting should be induced. In the event of collapse, artificial resuscitation should be given, bearing in mind that if mouth-to-mouth resuscitation is used, vomit may contain dangerous amounts of thiometon.

5.0 FOR MEDICAL AND LABORATORY PERSONNEL

5.1 MEDICAL DIAGNOSIS AND TREATMENT IN CASES OF POISONING

5.1.1 General information: Thiometon is an organophosphorus pesticide, highly toxic to mammals. It is readily absorbed from the gastrointestinal tract, through the intact skin, and by inhalation of dust or spray mist. It is converted *in vivo* to the oxygen analogues of thiometon which are more potent inhibitors of cholinesterases.

5.1.2 Symptoms and signs: Initial symptoms and signs of poisoning may include excessive sweating, headache, weakness, giddiness, nausea, hypersalivation, vomiting, stomach pains, blurred vision, slurred speech and muscle twitching. More advanced signs of poisoning may be convulsions coma, loss of reflexes and loss of sphincter control.

5.1.3 Laboratory: The most important finding is reduction of activity of blood cholinesterases. Urinary levels of organic phosphorus containing metabolites may also be used as a measure of exposure. Neither method is specific for thiometon.

5.1.4 Treatment: If the pesticide has been ingested, unless the patient is vomiting, rapid gastric lavage should be performed using 5% sodium bicarbonate. Care must be taken to avoid pulmonary complications from solvents following ingestion of emulsifiable concentrate formulations. For skin contact, the skin should be washed with water and soap. If the compound has entered the eyes, they should be washed with copious volumes of water or isotonic saline. Care must be taken by the victims attendants to avoid their own intoxication from contaminated clothing, skin or body fluids.

Persons without signs of respiratory insufficiency but with manifest peripheral symptoms should be treated with 2-4 mg of atropine sulfate by intravenous injection followed by 250 mg toxogonin (adult dose) or 1 000 mg pralidoxime chloride (adult dose), by slow intravenous injection. The additional therapy with pralidoxime (or toxogonin) is likely to be successful if administered within 24 hours of the onset of intoxication. However, it may continue to be effective in the following days and treatment should continue until no further benefit to clinical or biochemical parameters is observed. More atropine may be given as needed. Persons with severe intoxication, with respiratory difficulties, cyanosis, convul-

sions or unconsciousness should immediately be given oxygen and atropine sulfate followed by pralidoxime chloride. In such severe cases 4-6 mg of atropine sulfate should be given initially followed by repeated doses of 2 mg at 5-10 minute intervals. Diazepam may be given to control convulsions. The patient's condition should be carefully observed as a guide to further administration of atropine. Symptoms will reappear if tissue concentrations of thiometon or its metabolites remain high when the effect of atropine wears off. Rales in the lung bases, myosis, nausea, bradycardia, salivation or convulsions indicate inadequate atropinization. Overdosage with atropine (pulse rate over 140, dry mouth, flushed face) is rarely serious, but underdosage may be fatal. The airways should be kept free and artificial resuscitation should be applied if required, preferably by mechanical means. If necessary intubation should be performed. Application of morphine, aminophylline, phenothiazines, and reserpine is contraindicated. The patient should not be allowed to return to work until blood cholinesterase activity is over 80% of pre-exposure levels.

5.1.5 Prognosis: If the acute toxic episode is survived and if needed adequate artificial resuscitation has been given, the chances of complete recovery are good. However, in very severe cases, particularly if artificial resuscitation has been inadequate, prolonged anoxia may give rise to permanent brain damage.

5.1.6 References of previously reported cases: No published information available, other than case cited in section 2.2.6.

5.2 SURVEILLANCE TESTS

Test	Normal level*	Action level*	Symptomatic level*
Plasma cholinesterase	100%	50%	variable
Whole blood or erythrocyte cholinesterase	100%	70%	usually 40%

5.3 LABORATORY METHODS

5.3.1 Detection and assay of compound: Urinary metabolites may also be determined in order to give an indication of exposure. Thin-layer, gas and liquid chromatography methods have been used to analyze thiometon in technical products and in its formulations. Analysis of residues in plant and animal tissues have been described by gas chromatography and flame photometry methods.

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5.3.2 Other tests in case of poisoning: Activities of cholinesterases in the blood, provide the most useful aid for diagnosis of poisoning, but are not specific for thiometon intoxication.

*Expressed as percentage of pre-exposure activity.

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