

# VELSICOL<sup>®</sup>

## TECHNICAL PROBE<sup>®</sup>

**FOR MANUFACTURING  
HERBICIDES ONLY**

**ACTIVE INGREDIENTS:**

Methazole* .....	95%
Related Compounds .....	5%
TOTAL .....	100%

\*2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione.

**NET CONTENTS:**

E.P.A. Reg. No. 876-194-AA

E.P.A. Est. No. 36421-IL-1

### WARNING

**KEEP OUT OF REACH OF CHILDREN**

See Side Panel for Additional Precautions

*Manufactured For*  
**VELSICOL CHEMICAL CORPORATION**  
341 East Ohio Street  
Chicago, Illinois 60611

### WARNING

Harmful if swallowed, inhaled or absorbed through the skin or eyes. Do not get in eyes, on skin or on clothing. Avoid breathing dust mist. Keep out of the reach of children. Avoid contamination of feed and foodstuff.

In case of skin contact, wash immediately with soap and water. For eyes flush with plenty of water for at least 15 minutes and get medical attention.

Wear natural rubber gloves and protective clothing when handling. Wash hands, arms and face thoroughly with soap and water before eating or smoking. Wash all contaminated clothing with soap and hot water before reuse.

Do not contaminate water by cleaning of equipment or disposal of wastes.

### IMPORTANT

Do not store in direct contact with fertilizers, seeds, insecticides or fungicides.

### CONTAINER DISPOSAL

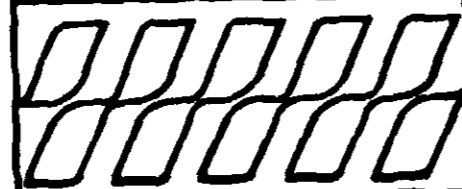
Do not reuse or burn empty containers. Dispose of empty containers by crushing and burying in a safe place away from water supplies.

### NOTICE

Because Velsicol Chemical Corporation has no control over storage, handling and conditions of use, which are of critical importance, Velsicol Chemical Corporation makes no representation or warranty either express or implied, for results or residues greater than any tolerance which may be established by appropriate governmental agencies, due to misuse, improper handling or storage of this material. Nor does Velsicol Chemical Corporation assume any responsibility for injury to persons, crops, animals, soil or property arising out of misuse, improper handling or storage of this material.

ACCEPTED.  
876-194  
3-24-75  
THE FEDERAL INSECTICIDE ACT  
E.P.A. REGISTRATION SUBJECT  
FOR THE NUMBERED UNITS  
TO ATTACHED LABELS

**BULLETIN**



**VELSICOL**  
AGRICULTURAL CHEMICALS

Bulletin No. 547-1  
March 1975

ACCEPTED

876-194

3-24-75

UNDER THE FEDERAL INSECTICIDE  
FUNGICIDE AND RODENTICIDE ACT  
FOR ECONOMIC POISON REG. NO. 876-194  
DATE 3-24-75  
BY COMMENTS

**PROBE®**

# FORMULATION MANUAL

ACCEPTED

MAR 24 1975

Under the Federal Insecticide,  
Fungicide, and Rodenticide Act  
as amended, for the  
registration under  
EPA Reg. No. 876-194

# PROBE® FORMULATION MANUAL

Bulletin 547-1

## NOTICE

Because Velsicol Chemical Corporation has no control over storage, handling and conditions of use, which are of critical importance, Velsicol Chemical Corporation makes no representation or warranty either express or implied, for results or residues greater than any tolerance which may be established by appropriate governmental agencies, due to misuse, improper handling or storage of this material. Nor does Velsicol Chemical Corporation assume any responsibility for injury to persons, crops, animals, soil or property arising out of misuse, improper handling or storage of this material.

Information provided herein is not intended to be a recommendation for the infringement of any patent.

**VELSICOL CHEMICAL CORPORATION**  
Quality Control and Technical Services Division  
341 East Ohio Street  
Chicago, Illinois 60611

## TABLE OF CONTENTS

	<u>Page</u>
I. Toxicology .....	1
II. Clean - Up Procedures for Methazole Spills .....	2
III. Disposal of Empty Containers .....	2
IV. Chemical and Physical Properties of Methazole .....	3
V. Probe Liquid Formulations .....	4
VI. Probe Dry Formulations .....	4
VII. Analytical Methods .....	7
VIII. Methazole Label Information .....	11

## I. TOXICOLOGY

### Acute Mammalian Toxicity

Acute toxicity of technical Probe to laboratory animals is shown below, followed by a tabulation of comparative figures for Probe herbicide formulations. Acute dermal LD<sub>50</sub>, acute inhalation LC<sub>50</sub>, primary skin irritation and eye irritation tests were performed according to the Federal Hazardous Substances Act (FHSA) or Title 49-Transportation, Chapter 1, Classification of Corrosive Hazards (DOT).

Acute oral LD <sub>50</sub> (albino rats)	2501 mg/kg (male) 2501 mg/kg (female)
Acute dermal LD <sub>50</sub> (albino rabbits)	≅ 12,500 mg/kg (male) > 12,500 mg/kg (female)
Acute inhalation LC <sub>50</sub> (albino rats)	> 200 mg/l (4-hour exposure)
Primary skin irritation (albino rabbits)	Not a primary skin irritant nor does this material present a corrosive hazard to the skin.
Eye irritation (albino rabbits)	Group I - 5 minute wash: A marginal eye irritant. Group II - 24 hour wash: An eye irritant

### Comparative Toxicity of Formulations

	Technical Probe 95%	Probe 75WP
Acute oral LD <sub>50</sub> (mg/kg. albino rats)	2501 (M) 2501 (F)	2144 (M) 3620 (F)
Acute dermal LD <sub>50</sub> (50 mg/kg. - albino rabbits) FHSA: > 2000 mg/kg Not A Toxic Or Highly Toxic Substance	≅ 12,500 (M) > 12,500 (F)	> 2,000 (M) > 2,000 (F)
Acute inhalation LC <sub>50</sub> (albino rats) FHSA: > 200 mg/l Not A Toxic Or Highly Toxic Substance	> 200	> 200
Primary Skin Irritation (albino rabbits) DOT: Scale 1:10, < 5 Not A Primary Skin Irritant	< 5	< 5
Eye Irritation (albino rabbits) FHSA: Eye irritant requires eye protection during handling	Group I-5 minute wash: A marginal eye irritant Group II- 24 hour wash: An eye irritant	Group I-5 minute wash: An extremely irritating substance Group II- 24 hour wash: An extremely irritating and corrosive substance

### Special Studies

**Sensitization Study with Probe 75WP in Guinea Pigs:** The sensitization potential of Probe 75WP was evaluated using a procedure based on that of Buehler, E. V. Essentially no signs of irritation were noted during the serial applications or at challenge. Under the conditions of this test, Probe 75WP would not be considered a sensitizer.

### Handling Precautions

Avoid contact with eyes. Eye protection is necessary. In case of eye contact, flush with plenty of water for at least 15 minutes and get medical attention. In case of skin contact, wash immediately with soap and water. Avoid inhalation of vapors or dust. Wear natural rubber gloves and protective clothing when handling. Wash hands, arms and face thoroughly with soap and water before eating or smoking. Wash all contaminated clothing with soap and hot water before reuse.

## II. CLEAN-UP PROCEDURES FOR METHAZOLE SPILLS

Methazole is a pesticide and should be handled with respect. To protect against skin irritation, it is recommended that protective clothing be worn including complete coveralls, rubber boots, rubber gloves and a soft cap.

Spillages of dry materials should be swept up and placed in sturdy, leak-free containers. Traces of dust remaining after a thorough sweep-up should be scrubbed up with soap and water. The soap and water, brushes, mops and rags used should be combined with the sweepings. The containers should be sealed, appropriately labeled and transferred to an approved burial site.

Spilled liquid methazole formulations should be soaked up with any available absorbent such as sawdust, clay, vermiculite, sweeping compound or "Kitty Litter." The absorbent should be transferred to a sturdy, leak-free container. The contaminated area should be scrubbed with soap and water. The liquid washings should be soaked up with absorbent materials and combined with the original absorbent. Any brushes, rags, or mops used in the clean-up should be added to the absorbent. The collection container should be labeled, sealed and transferred to an approved burial site.

If the spillage is from a leaking container, the remaining liquid should be transferred to a properly labeled, leak-free container. The damaged container should be crushed and disposed of in an approved burial ground.

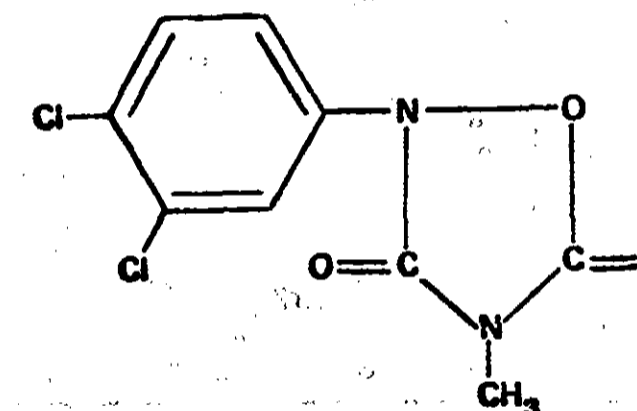
## III. DISPOSAL OF EMPTY CONTAINERS

Empty cardboard and paper containers should be compacted and transferred to an approved burial ground. Cans and drums should be securely closed and transferred to a professional drum reconditioner or punctured to prevent reuse and transferred to an approved burial site.

## IV. CHEMICAL AND PHYSICAL PROPERTIES OF METHAZOLE

### A. NOMENCLATURE AND FORMULAS

- 1) Chemical Name: 2 - (3, 4 - Dichlorophenyl) - 4 - methyl - 1, 2, 4 - oxadiazolidine - 3, 5 - dione
- 2) Common Names:
  - a) Methazole (ANSI, WSSA)
  - b) Bioxone
  - c) VCS 438 ( Velsicol Code Number )
- 3) Trademark Name: PROBE®
- 4) Molecular Formula: C<sub>9</sub>H<sub>6</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>3</sub>
- 5) Structural Formula:



- 6) Molecular Weight: 261.05

### B. PHYSICAL PROPERTIES

- 1) Appearance of Technical: off white to tan crystalline solid; odorless when pure.
- 2) Melting Point: 123-124° C.
- 3) Apparent Density: 1.24
- 4) Boiling Point: Decomposes before boiling
- 5) Decomposition Temperature: Not available
- 6) Vapor Pressure: Less than 10<sup>-6</sup> mm Hg.
- 7) Flammability: Non - Flammable
- 8) Stability: Methazole formulations have excellent long term stability. Technical material in water will decompose on exposure to sunlight. Degrades at higher temperatures. Do not heat tech or solutions above 150° F.

#### IV. CHEMICAL AND PHYSICAL PROPERTIES OF METHAZOLE (continued)

##### 9) Solubility:

	<u>W/V %</u>
Water	1.5 ppm
Methanol	0.65 %
Xylene	5.5 %
Acetone	9 %
Methyl Ethyl Ketone	11 %
Cyclohexanone	18 %
Methylene Chloride	19 %
Dimethyl Formamide	27 %

#### V. PROBE LIQUID FORMULATIONS

Because of the limited solubility of methazole in the commonly used agricultural solvents, no emulsifiable concentrate has been developed. Velsicol has done some work with Flowable concentrates (a suspension of finely divided solid particles in a liquid carrier), but these formulations are still in the developmental stages.

#### VI. PROBE DRY FORMULATIONS

##### A. WETTABLE POWDERS

###### 1) Carriers

PROBE 75WP is formulated by dry blending with surfactants and HiSil® 233 and then milling. HiSil® 233 is a synthetic, hydrated silica of extremely fine particle size. PROBE® wettable powders made on HiSil® exhibit excellent long term stability, good flow properties, and good wetting and suspensibility.

If other carriers are substituted, the formulation should be checked for long term stability as some materials can catalytically degrade methazole.

###### 2) Wetting and Dispersing Agents

The selection of proper surfactants is essential to the preparation of fast dispersing and stable wettable powder suspensions. Wetting agents lower the surface tension of the water to permit rapid wetting of the powder. Dispersing agents overcome the attractive forces between particles and prevent agglomeration.

With the proper mixture of wetting and suspending agents, it is possible to make methazole wettable powders which have excellent wetting and suspending properties. Within the United States, materials should be chosen which are exempt from requirement of tolerance by the EPA.

The combination of Aerosol O. S. and Polyfon F used in our present PROBE® 75WP (See Section VI D) provides excellent wetting and suspending properties even after one year's storage at 122° F. (50° C). There are undoubtedly other combinations which would be equally efficacious.

We have found from our experiences that it is best to add the surfactants to the preblend and then grind all the ingredients together. In some instances this order of addition and grinding may have to be changed.

##### 3) Equipment

###### a) Blender

A large ribbon blender is recommended to dry blend the raw materials. It is necessary that the blender provides a good mixing action, because it is essential that a homogeneous mixture is obtained prior to the milling step. Since all the ingredients are dry powders, a spray manifold is not required. The blender should be totally enclosed in order to prevent excessive quantities of dust being blown into the air.

###### b) Milling Equipment

Several years of formulation experience indicate that excellent PROBE® 75 Wettable Powders can be produced by passing the material first through a hammer mill with a relatively coarse screen and then through an air mill. Because of its ability to produce extremely fine particles, an air mill is recommended for Probe wettable powders. An acceptable Probe wettable powder can be produced with a hammer mill, but this product will not have as fine a particle size, nor as good a suspensibility, as the air milled product.

The various batches of technical methazole produced to date in several different manufacturing facilities have all been high melting, friable, free flowing powders. This is a product which readily lends itself to milling, and a high quality, high concentration wettable powder can be produced with relative ease.

###### c) After Blender

The use of a ribbon blender or other suitable blender is recommended after the mill to reblend the formulation after milling.

###### d) Bagging Equipment

A bagging line suitable for handling light weight powders is necessary. It is desirable to have some means of de-aerating the product before packaging, especially if the product is air milled.

##### 4) Formulation Procedure

The blender is charged with the full quantity of methazole, carrier, and surfactants. The ingredients are blended until a homogeneous mixture is obtained.

The material is passed through first a hammer mill and then an air mill. In most systems there is a ribbon blender between the hammer mill and the air mill. After passing through the air mill, the particle size should be fine enough that 99% will pass through a 200 mesh

sieve (74 microns). Particle size distribution curves for typical batches of air milled Probe 75 WP have shown that the majority of the particles fall in the two to five micron range. If the PROBE wettable powder is hammer milled only, the particle size and suspensibility will not be as good as the air milled material.

After milling, the material is reblended and packaged. Because of the low bulk density of air milled material, de-aeration is desirable.

## B. DUSTS

Dusts are generally made by first preparing a dust concentrate of 25% to 75% and then letting this concentrate down with an inert diluent such as talc. The dust concentrate is made in the same way a wettable powder is made, only the wetting and suspending agents are left out. PROBE wettable powder can also be used as a dust concentrate. It is essential that the dust concentrate be well blended with the diluent to assure a homogeneous mixture. There are numerous materials that may be used as diluents for the dust base, however, long term storage studies are recommended to make sure the diluent does not promote the chemical degradation of methazole.

## C. GRANULES

### 1) Carriers

PROBE 5% granules may be successfully formulated on montmorillonite clay. Cyclohexanone is used as a solvent for spray impregnation of the granules. It has been found that some clays promote the catalytic degradation of methazole so long term stability studies should be run on any carrier selected for methazole granules.

A 24/48 mesh granule is compatible with most application equipment and is suitable for most uses. The 24/48 mesh granule is the most common size range for most agricultural products formulated in the United States and is readily available from different clay producers. For these reasons, the 24/48 mesh size is recommended for PROBE formulations. However, larger or smaller granules may be better for some uses. High quality granules with a minimum of fines should be used.

### 2) Equipment

An enclosed tumbler blender with a built-in spray manifold is recommended. Ribbon blenders can be used but the attrition of the blades produces excess fines.

### 3) Formulation Procedure

PROBE technical can be dissolved in a suitable solvent and spray impregnated directly onto the granules. Adequate safety precautions should be employed when using flammable solvents.

In the manufacture of PROBE 5% granules the technical methazole is dissolved in hot cyclohexanone (100° F. to 110° F.). Do not let the solution temperature exceed 120° F. or degradation of the methazole may occur. The spray lines, the blender and the granules should also be warm enough to prevent formulation of crystals.

The spray time should be long enough to assure complete coverage of the granules and the granules should be after-blended for a few minutes to assure that a homogeneous mixture is obtained. Excessive blending should be avoided as this tends to produce fines. In a typical tumbler blender, a combined spray and blend time of 6 to 12 minutes is adequate.

The granules may be packaged immediately after impregnation.

## D. TYPICAL DRY FORMULATIONS

### 1) PROBE 75% Wettable Powder

Ingredients	Wt/Wt %
Methazole Technical (95%)	80.5
HiSil 223*	15.0
Polyfon F**	3.0
Aerosol O. S.***	1.5
	<b>100.0 %</b>

\* a product of PPG Industries

\*\* a product of Westvaco-Polychemicals

\*\*\* a product of American Cyanamid

### 2) PROBE 5% GRANULAR

Ingredients	Wt/Wt %
Methazole Technical (95%)	5.26
Cyclohexanone	10.00
Montmorillonite granules 24/48 mesh	84.74
	<b>100.00%</b>

## VII. ANALYTICAL METHODS

### I. ANALYSIS OF TECHNICAL PROBE

#### APPLICABILITY

This method is used for a quantitative determination of methazole [2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione] in Technical Probe.

#### PRINCIPLE

The method is based on analysis by infrared spectroscopy utilizing the band at 755 cm<sup>-1</sup> (13.25 microns) for the analysis of methazole.

#### REAGENTS AND APPARATUS

1. Infrared spectrophotometer;
2. NaCl cells, 0.5 mm matched;
3. Volumetric flasks, 10 ml;
4. Acetone, spectrograde;
5. Methazole, reference analytical grade.