

Pesticides Manufacturing

Industry Description and Practices

This document addresses the synthesis of the active ingredients used in pesticide formulations. The formulation of pesticides from these active ingredients is addressed in a separate guideline.

Major chemical groups manufactured include:

- Carbamates and dithiocarbamates (carbofuran, carbaryl, ziram, and benthio carb).
- Chlorophenoxy compounds (2,4-D, 2,4,5-T, and silvex).
- Organochlorines (dicofol and endosulfan).
- Organophosphorus compounds (malathion, dimethoate, phorate, and parathion methyl).
- Nitro compounds (trifluralin).
- Miscellaneous compounds such as biopesticides (for example, bacillus thuringiensis and pheromones), heterocycles (for example, atrazine), pyrethroids (for example, cypermethrin), and urea derivatives (for example, diuron).

Note: Refer to International Agreements on Pesticides considered acceptable for manufacturing and use. For example, see International Programme on Chemical Safety, The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification 1996-1997. Production proposals for the following should be carefully evaluated: Hexachlorobenzene; Toxaphene; Chlordane; Aldrin; DDT; Mirex; Dieldrin; Endrin; and Heptachlor (refer to UN-ECE list of restricted substances).

The principal manufacturing steps are: (a) preparation of process intermediates; (b) introduction of functional groups; (c) coupling and esterification; (d) separation processes (such as washing and stripping); and (e) purification of the final product. Each of these steps may generate air emissions, liquid effluents, and solid wastes.

Waste Characteristics

The principal air pollutants are volatile organic compounds (VOCs) and particulate matter (PM).

Liquid effluents resulting from equipment cleaning after batch operation contain toxic organics and pesticide residues. Cooling waters are normally recirculated. Wastewater concentrations are: 13,000 milligrams per liter (mg/L) (with a range of 0.4 to 73,000 mg/L) COD; 800 mg/L (with a range of 1 to 13,000 mg/l) oil and grease; and 2,800 mg/L with a range of 4 to 43,000 mg/L of total suspended solids.

Major solid wastes of concern include process and effluent treatment sludges, spent catalysts, and container residues. Approximately 200 kilograms (kg) of waste is generated per metric ton of active ingredient manufactured.

Pollution Prevention and Control

Every effort should be made to substitute highly toxic and persistent ingredients with degradable and less toxic ones. Recommended pollution prevention measures are to:

- Meter and control the quantities of active ingredients to minimize wastage.
 - Reuse by-products from the process as raw materials or as raw material substitutes in other processes.
 - Use automated filling to minimize spillage.
 - Use “closed” feed systems for batch reactors.
 - Use nitrogen blanketing where appropriate on pumps, storage tanks, and other equipment to minimize the release of toxic organics.
 - Give preference to non-halogenated and non-aromatic solvents where feasible.
 - Use high pressure hoses for equipment cleaning to reduce wastewater.
 - Use equipment washdown waters and other process waters (such as leakages from pump seals) as make-up solutions for subsequent batches.
 - Use dedicated dust collectors to recycle recovered materials.
 - Vent equipment through a recovery system.
 - Maintain losses to low levels from vacuum pumps (such as water ring and dry).
 - Return toxic materials packaging to the supplier for reuse or incinerate/destroy in an environmentally acceptable manner.
 - Minimize storage time of off-specification products through regular reprocessing.
 - Find productive uses for off-specification products to avoid disposal problems.
 - Minimize raw material and product inventory to avoid degradation and wastage which could lead to the formation of inactive but toxic isomers or by-products.
 - Label and store toxic and hazardous materials in secure banded areas.

A pesticide manufacturing plant should prepare a hazard assessment and operability study and also prepare and implement an Emergency Preparedness and Response Plan which takes into account neighboring land uses and the potential consequences of an emergency. Measures to avoid the release of harmful substances should be incorporated in the design operation, maintenance, and management of the plant.

Guidance on the selection and use of pesticides is provided in Guidelines and Best

Practice G 4.03 “Agricultural Pest Management” (World Bank, 1993).

Target Pollution Loads

Implementation of cleaner production processes and pollution prevention measures can provide both economic and environmental benefits.

Specific reduction targets for the different processes have not been determined. In the absence of specific pollution reduction targets, new plants should always achieve better than the industry averages quoted in the section on Waste Characteristics and should approach the load-based effluent levels. Certain publications such as the European Union reports present pollution loads achieved for each type of pesticide and may be used as a reference. The table in the Emissions Guidelines section presents the maximum load-based levels for active ingredients in the effluent after the addition of pollution control measures.

Treatment Technologies

Air Emissions

Stack gas scrubbing and/or carbon adsorption (for toxic organics) and baghouses (for particulate matter removal) are applicable and effective technologies for minimizing the release of significant pollutants to air. Combustion is used for the destruction of toxic organics. Combustion devices should be operated at temperatures above 1,100 degrees Celsius with a flame residence time of at least 0.5 second to achieve acceptable destruction efficiency of toxics. However, temperatures of around 900 degrees Celsius are acceptable provided at least 99.99 percent destruction/removal efficiency of toxics is achieved.

Liquid Effluents and Solid Wastes

Reverse osmosis or ultra-filtration is used to recover and concentrate active ingredients. Effluent treatment normally includes flocculation, coagulation, settling, carbon adsorption, detoxification of pesticides by oxidation (using ultraviolet systems or peroxide solutions), and biological treatment. Exhausted

carbon from absorption processes may be sent for regeneration or combustion. When the wastewater volumes are small and an onsite incinerator is appropriate, combustion of toxic wastewaters may also be feasible.

Contaminated solid wastes are generally incinerated and the flue gases are scrubbed.

Emission Guidelines

Emission levels for the design and operation of each project must be established through the Environmental Assessment (EA) process, based on country legislation and the *Pollution Prevention and Abatement Handbook* as applied to local conditions. The emission levels selected must be justified in the EA and acceptable to MIGA

The following guidelines present emission levels normally acceptable to the World Bank Group in making decisions regarding provision of World Bank Group assistance, including MIGA guarantees; any deviations from these levels must be described in the project documentation.

The guidelines are expressed as concentrations to facilitate monitoring. Dilution of air emissions or effluents to achieve these guidelines is unacceptable.

All of the maximum levels should be achieved for at least 95% of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours.

Air Emissions

The following emissions levels should be achieved:

Emissions from Pesticides Manufacturing

Parameter	Maximum value All values in milligrams per normal cubic meter (mg/Nm ³)
Particulate matter	20 and 5*
VOCs	20
Chlorine (or chloride)	5

* Where very toxic compounds are present (Refer to WHO's list of extremely hazardous substances).

Liquid Effluents

The following table presents the load-based levels for active ingredients in the effluent *after* pollution control measures have been applied. However, effluent discharges should be minimized to the extent feasible. These have been provided to assist in computing pollution reduction targets before the addition of pollution control measures:

Load-Based Levels for Active Ingredients in Effluents After Treatment

Active Ingredient (AI)	Daily Maximum ^a (mg/kg AI production) ^c	Monthly Average ^b (mg/kg AI production) ^c
Atrazine	2.6	1.0
Carbaryl ¹		0.73
Carbofuran	0.12	0.028
2,4-D ¹	0.12	0.034
Diuron	32	14
Malathion	0.24	0.095
Parathion	0.77	0.34
Methyl		
Trifluralin ^{1,2}	0.32	0.11
Ziram ³	5.7	1.9

^a Daily maximum not to be exceeded.

^b Monthly average not to be exceeded.

^c or parts per million parts (ppm) of AI produced.

¹ After in-plant treatment before mixing with other wastewaters.

² As total toluidine AIs, as Trifluralin.

³ As total dithiocarbamates, as Ziram.

The following effluent levels should be achieved:

Effluents from Pesticides Manufacturing

Parameter	Maximum value milligrams per liter (mg/L)
pH	6-9
BOD ₅ *	30
COD	150
AOX	1
Total suspended solids	10
Oil and grease	10

Phenol	0.5
Arsenic	0.1
Chromium (hexavalent)	0.1
Copper	0.5
Mercury	0.01
Active ingredient (each)	0.05

*BOD test is to be performed only in cases where the effluent does not contain any toxic to the micro-organisms used in the test.

Bioassay testing should be performed to ensure that toxicity of the effluent is acceptable (Toxicity to Fish, TF=2; Toxicity to Daphnia, TD=8; Toxicity to Algae, TA=16; and Toxicity to Bacteria, TB=8).

Note: Effluent requirements are for direct discharge to surface waters.

Solid Wastes

Contaminated solid wastes should be treated to achieve toxic organic levels of at least less than 0.05 mg/kg.

Ambient Noise

Noise abatement measures should achieve either the following levels or a maximum increase in background levels of 3 dB(A). Measurements are to be taken at noise receptors located outside the project property boundary.

Ambient Noise

Receptor	Maximum Allowable L_{eq} (hourly), in dB(A)	
	Daytime 07:00 - 22:00	Nighttime 22:00 - 07:00
Residential; institutional; educational	55	45
Industrial; commercial	70	70

The emission requirements given here can be consistently achieved by well-designed, well-operated and well-maintained pollution control systems.

Monitoring and Reporting

Frequent sampling may be required during start-up and upset conditions. Once a record of consistent performance has been established, sampling for the parameters listed above should be as detailed below.

Monitoring of air emissions should be on a continuous basis when the mass flow of toxic substances exceed 0.5 kg per hour. Otherwise, it can be on an annual basis. Liquid effluents should be monitored for active ingredients at least once every shift. The remaining parameters should be monitored at least on a daily basis.

Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Records of monitoring results should be kept in an acceptable format. These should be reported to the responsible authorities and relevant parties, as required, and provided to MIGA if requested.

Key Issues

The following box summarizes the key production and control practices that will lead to compliance with emissions guidelines:

- Substitute highly toxic and persistent ingredients with less toxic and degradable ones.
- Control loss and wastage of active ingredients.
- Return packaging for refilling.
- Use equipment washdown waters as make-up solutions for subsequent batches.
- Minimize wastage by inventory control and find uses for off-specification products.

Further Information

The following are suggested as sources of additional information (these sources are provided for guidance and are not intended to be comprehensive):

European Union. 199.. Best Available Technology Notes on Various Pesticides Manufacturing Processes.

Her Majesty's Inspectorate of Pollution. 1993. "Chief Inspector's Guidance to Inspectors", Environmental Protection Act 1990, Process Guidance Note IPR 4/B, Pesticide Processes.

Sittig, Marshall. "Pesticide Manufacturing and Toxic Materials Control Encyclopedia." Noyes Data Corporation.

United Nations Industrial Development Organization. 1992. *International Safety*

Guidelines for Pesticides Formulation in Developing Countries.

U.S. Environmental Protection Agency. 1988. *Pesticide Waste Control Technology.* Noyes Data Corporation.

World Bank Operational Manual. April 1993. "Agricultural Pest Management." Guidelines and Best Practice GB 4.03.

World Bank Environment Department. 1996. "Pollution Prevention and Abatement: Pesticides Manufacturing." Technical Background Document.

World Health Organization 1996. International Programme on Chemical Safety (IPCS), The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification 1996-1997.