

Pesticides Manufacturing

Industry Description and Practices

This document deals with the synthesis of the active ingredients used in pesticide formulations. The formulation of pesticides from the active ingredients is covered in a separate document.

The major chemical groups manufactured include:

- Carbamates and dithiocarbamates (carbofuran, carbaryl, ziram, and benthocarb)
- 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).

Special attention must be given to restricted substances. Production proposals for the following pesticides should be carefully evaluated: hexachlorobenzene, toxaphene, chlordane, aldrin, DDT, mirex, dieldrin, endrin, and heptachlor. (See the UN-ECE list of restricted substances and the international agreements on pesticides considered acceptable for manufacturing and use, for example, WHO 1996.)

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: chemical oxygen demand (COD), 13,000 milligrams per liter (mg/l), with a range of 0.4–73,000 mg/l; oil and grease, 800 mg/l, (with a range of 1–13,000 mg/l; total suspended solids, 2,800 mg/l, with a range of 4–43,000 mg/l. 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 replace highly toxic and persistent ingredients with degradable and less toxic ones. Recommended pollution prevention measures are as follows:

- 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 nonhalogenated and nonaromatic 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 makeup solutions for subsequent batches.
- Use dedicated dust collectors to recycle recovered materials.
- Vent equipment through a recovery system.
- Maintain losses from vacuum pumps (such as water ring and dry) at low levels.
- 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 that 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 that 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, GB 4.03, "Agricultural Pest Management" (World Bank 1993).

Target Pollution Loads

Implementation of cleaner production processes and pollution prevention measures can yield 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 EU reports give the pollution loads achieved for each type of pesticide and may be used as a reference.

Table 3, below, 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 to destroy toxic organics. Combustion devices should be operated at temperatures above 1,100° C with a flame residence time of at least 0.5 second to achieve acceptable destruction efficiency of toxics. However, temperatures of around 900° C are acceptable provided that at least 99.99% destruction/removal efficiency of toxics is achieved.

Liquid Effluents and Solid Wastes

Reverse osmosis or ultrafiltration 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 be feasible.

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

Emissions Guidelines

Emissions levels for the design and operation of each project must be established through the environmental assessment (EA) process on the basis of country legislation and the *Pollution Prevention and Abatement Handbook*, as applied to local conditions. The emissions levels selected must be justified in the EA and acceptable to the World Bank Group.

The guidelines given below present emissions levels normally acceptable to the World Bank

Group in making decisions regarding provision of World Bank Group assistance. Any deviations from these levels must be described in the World Bank Group project documentation. The emissions levels given here can be consistently achieved by well-designed, well-operated, and well-maintained pollution control systems.

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 emissions levels presented in Table 1 should be achieved.

Liquid Effluents

Table 2 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 data have been provided to assist in computing pollution reduction targets before the addition of pollution control measures.

The effluent levels presented in Table 3 should be achieved.

Bioassay testing should be performed to ensure that the toxicity of the effluent is acceptable (toxicity to fish = 2; toxicity to *Daphnia* = 8; toxicity to algae = 16; and toxicity to bacteria = 8).

Table 1. Emissions from Pesticides Manufacturing

(milligrams per normal cubic meter)

| Parameter | Maximum value |
|------------------------|---|
| PM | 20; 5 where very toxic compounds are present ^a |
| VOCs | 20 |
| Chlorine (or chloride) | 5 |

a. See the World Health Organization's list of extremely hazardous substances (WHO 1996).

Table 2. Load-Based Levels for Active Ingredients (AIs) in Effluents after Treatment in Pesticides Manufacture

(milligrams per kilogram active ingredient produced, or ppm of AI produced)

| Active ingredient | Daily maximum ^a | Monthly average ^b |
|--------------------------|----------------------------|------------------------------|
| Atrazine | 2.6 | 1.0 |
| Carbaryl ^c | | 0.73 |
| Carbofuran | 0.12 | 0.028 |
| 2,4-D ^{1c} | 0.12 | 0.034 |
| Diuron | 32 | 14 |
| Malathion | 0.24 | 0.095 |
| Parathion methyl | 0.77 | 0.34 |
| Trifluralin ^c | 0.32 | 0.11 |
| Ziram ^d | 5.7 | 1.9 |

a. Daily maximum not to be exceeded.

b. Monthly average not to be exceeded.

c. As total toluidine AIs, as trifluralin; after in-plant treatment before mixing with other wastewaters.

d. As total dithiocarbamates, as ziram.

Table 3. Effluents from Pesticides Manufacturing

(milligrams per liter, except for pH)

| Parameter | Maximum value |
|--------------------------|---------------|
| pH | 6–9 |
| BOD ^a | 30 |
| COD | 150 |
| AOX | 1 |
| TSS | 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 |

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

a. A BOD test is to be performed only in cases where the effluent does not contain any substance toxic to the microorganisms used in the test.

Solid Wastes

Contaminated solid wastes should be treated to achieve toxic organic levels of no more than 0.05 milligrams per kilogram.

Ambient Noise

Noise abatement measures should achieve either the levels given below or a maximum increase in background levels of 3 decibels (measured on the A scale) [dB(A)]. Measurements are to be taken at noise receptors located outside the project property boundary.

| Receptor | Maximum allowable log equivalent (hourly measurements), in dB(A) | |
|---|--|------------------------|
| | Day (07:00–22:00) | Night (22:00–07:00) |
| Residential, institutional, educational | 55 | 45 |
| Industrial, commercial | 70 | 70 |

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 in this document should be as described below.

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

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. The results should be reported to the responsible authorities and relevant parties, as required.

Key Issues

The key production and control practices that will

lead to compliance with emissions guidelines can be summarized as follows:

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

References and Sources

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