OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

20852

Pollution Prevention and Abatement Guidelines

for the

Pesticide Formulation Industry

This document is one of the chapters prepared for a forthcoming set of pollution guidelines jointly prepared by the World Bank, UNIDO and UNEP. The purpose is to give a succinct overview of the main issues affecting the subject industry sector, and of the best technologies and techniques available to avoid undue environmental impact. The regulatory framework within which the industry operates is briefly described by examples, and target discharge limitations that are economically achievable with currently available technology are suggested. The intended readership includes project personnel in investment and development institutions as well as anyone who wish to familiarize themselves with the key aspects of the industry concerned. The information is not sufficient by itself for detailed project design. For this more elaborate advice can be obtained from the references quoted or from other specialized sources of information. Comments on the draft should be submitted to Mr. Anil Somani, the World Bank, Environment Department, 1818 H Street N.W., Washington DC 20433, USA, fax. (202) 477-0968 with copy to UNIDO, Att. Mr. Ralph Luken, P.O. Box 300, A-1400 Vienna, Austria. Fax +43 1 23 07 449.

November 1993

Prepared by Keith S. Johnson, United Kingdom, for UNIDO, in the project US/GLO/91/202

TABLE OF CONTENTS

1 EXECUTIVE SUMMARY

The pesticide formulation industry generates relatively small quantities of wastes which can be toxic and polluting. Essentially a batch-orientated process operation using imported raw materials, potential areas of pollution can be effectively controlled.

Disposal of wastes involves an area of extreme environmental sensitivity, virtually reliant upon external resources for disposal. Scarce capacity in developing countries of high temperature incineration essential for the disposal of toxic wastes is an acknowledged constraint and in the medium term will cause, in some regions, problems of waste accumulation and storage.

Atmospheric emissions are low and easily controlled. Technology exists (B.A.T.) for the treatment of pesticide aqueous effluents to high standards of quality and is being adopted globally. Pesticide formulation sites, using currently available pollution control technology, with positive management should not constitute an environmental risk to the local community.

2 INTRODUCTION

It is important to recognize that the pesticide industry is divided into two distinct, and for the most part separate, areas of manufacturing operation and activity.

i. Pesticide production involving the chemical synthesis of active pesticide ingredients (a.i.).

ii. Formulation of synthesized active pesticides into products for registered use.

The environmental pollution aspects and control for the synthesis of pesticides is the subject of an associated but separate Guideline document. This Guideline document concerns environmental pollution control aspects associated with the <u>Pesticide Formulation</u> industry.

While some pesticide product formulation activity is directly linked with the synthesis plants, generally formulation units operate as separate and individually resourced manufacturing units. Large numbers of formulation units are distributed globally in both developed and developing countries, where possible in convenient proximity to areas of use. Plant sizes vary depending upon location and production type; but on the basis of seasonally-orientated manufacture output may be broadly categorized as follows:

Site Size	Output - tonnes per annum
Large	30,000 to 50,000
Medium	10,000 to 15,000
Small	',000 to 5,000.

LIST OF TABLES

APPENDICES

Active ingredients (a.i.) are imported, but economic use is made where practical and appropriate of high quality locally produced fillers, solvents and adjuvants necessary for product formulation.

It is essentially a batch-process orientated industry using, for the most part, simple techniques of grinding, mixing and blending, although more sophisticated technology is being introduced to produce, for example, more environmentally acceptable granular and encapsulated product types.

Pesticide formulation does not generate large volumes of waste for disposal. The main waste arisings include clean and contaminated package materials, plant residues, occasionally unwanted products and raw materials, and contaminated aqueous effluents from frequent plant cleaning and wash down. Air emissions at most are only lightly contaminated and are usually scrubbed and cleaned locally before discharge to the atmosphere.

Properly managed pesticide formulation plants during normal process operation do not constitute a serious pollution risk to the external environment. A potential risk of more serious proportions is however acknowledged in the event of an outbreak of fire from both the products of combustion and contaminated run-off from fire water.

This Guideline briefly reviews the various stages of pesticide formulation processes, identifies potentially polluting contaminants and waste arisings. Initiatives for waste recycling and re-use are explored and methods of treatment and safe disposal given for non-recoverable wastes. Examples of treatment technology for liquid effluents are given along with broad examples of discharge standards currently in use globally. A brief resume on essential aspects of health and safety monitoring in the factory workplace complementary to environmental control is also presented.

3 PESTICIDE FORMULATIONS AND PROCESSES

3.1 Formulation Objectives and Design

The main purpose of pesticide formulation is to produce a product which has optimum biological efficiency and is safe and convenient to use. The choice of formulation type is determined initially by the physico-chemical properties of the active ingredient and must also take into account long term storage life, safety and convenience to the user, and the need to avoid environmental problems.

A wide range of solid and liquid formulations has been available for many years (Ref. 1). The trend is now towards developing more environmentally-friendly formulations with improved safety and convenience to the manufacturer and user. A brief outline of the more important formulation types is given below (Ref. 2 and 3).

3.2 Formulation Types

Wettable Powders (WP)

These are simple mixtures of active ingredient, dispersing/wetting agents and fillers. The mixture is dry ground to give a fine powder which will re-disperse into water.

MIXING ----> DRY GRINDING -----> BLENDING

Soluble Concentrates (SL)

Where the active ingredient is sufficiently soluble in water, a concentrated solution is made by simple mixing.

Emulsion Concentrates (EC)

Where the active ingredient is sufficiently soluble in a non-aqueous solvent, a concentrated solution is made by simple mixing with the addition of an emulsifying agent, which produces a fine droplet emulsion on contact with water.

Oil-in-water Emulsions (EW)

The use of non-aqueous solvents may be avoided by making an emulsion of the oily active ingredient in water. This type of formulation requires careful choice of emulsifiers and stabilizers to prevent coalescence of the oil droplets.

PREMIX ----> COLLOIDAL HOMOGENIZER -----> ADDITION OF STABILIZERS

Suspension Concentrates (SC)

Highly concentrated dispersions of particles in the range 0.5 to 5 microns are made by wet milling with a dispersing agent, followed by the addition of anti-setting agents. The active ingredient must be very insoluble in water and must have a melting point higher than 60°C.

PREMIX --> AQUEOUS BEAD MILLING --> DE-AERATION --> ADDITION OF STABILIZERS

Suspoemulsions (SE)

This formulation type is becoming important for mixtures of solid and liquid active ingredients. Careful selection of the dispersing/emulsifier system is essential to prevent flocculation of the particles and droplets.

Water Dispersible Granules (WG)

Powders or suspensions can be converted into water dispersible granules by various processes, notably fluid bed or spray drying, wet agglomeration followed by drying, pan granulation or extrusion followed by drying. Each granulation technique has its advantages and disadvantages, and the correct choice is an important factor in the quality of the end product.

MIXING	-->	DRY GRINDING	-->	GRANU-LATION	-->	DRYING

Granules (GR)

Active ingredients are absorbed by or coated on to pre-formed granules for direct application to the soil or crop.

Controlled Release

Controlled release technology is receiving increasing attention in pesticide formulation. The active ingredient is coated with or physically trapped by polymers which slow down its rate of release. A specific example is microencapsulation (CS) where an aqueous emulsion of active ingredient droplets is encapsulated by a thin wall of polymer.

3.3 Environmental Factors in Formulation and Process Selection

More sophisticated formulations and process technology are being developed to meet the rapidly changing standards being set by safety, environmental and regulatory authorities. The relative properties of different formulation types are shown in Table 1.

Table 1. Relative Properties of Different Pesticide Formulations

	Best ----------> Worst
Ease of production	EC > WP > SC > WG
Safety and Hygiene	SC > WG > WP > EC
Packaging and Transportation Cost	WG > WP > FW > EC
Ease of Application	SC > EC > WG > WP
Disposal of Package	WG = WP > SC > EC
Physical Stability	WG > WP > EC > SC

EC: Emulsifiable Concentrate
WP: Wettable Powder
SC: Suspension Concentrate
WG: Water-Dispersible Granules

In order to overcome the hazards and inconvenience of handling dusty products, many manufacturers are switching from wettable powders to suspension concentrates or water dispersible granules. The use of non-aqueous solvents in emulsion concentrates can cause problems due to skin and eye irritation, solvent volatility and flammability. Because of this, there is increasing interest in water-in-oil emulsions and suspoemulsions. Where possible, water dispersible granules of liquid or low melting active ingredients are also being developed.

Controlled release techniques are being developed to give slow release of the active ingredient in the field and to minimize the toxic exposure risk during manufacture and application.

Seed treatment formulations as solutions or flowable suspensions can be a convenient and safe way of applying the active ingredient to the target in the case of fungicides and insecticides.

The increasing problem of pack rinsing and disposal in the field is causing manufacturers to formulate products as water dispersible granules wherever possible. In some cases, water-soluble packaging is being used to eliminate operator contact.

3.4 Primary Raw Materials

Pesticide active ingredients are synthesized from complex chemical processes to produce stable compounds which may be subsequently formulated into registered products for the consumer market. The active compounds are usually specifically produced for insecticide, fungicide and herbicide applications. Examples of compounds in current use are given in Table 2.

Table 2. Examples of Insecticides, Fungicides and Herbicides

COMPOUND	EXAMPLES
INSECTICIDES	
- Organo Phosphates	Dimethoate, Pirimiphos-methyl
- Carbamates	Carbaryl, Pirimicarb
- Organo-chlorines	Lindane, Heptachlor
- Pyrethroids	Permethrin, Cypermethrin
- Bio-rationals	Bacillus Thuringiensis, Pheromones
- Botanical	Avermactins, Derris Pyrethrins
FUNGICIDES	
- Dithio Carbamates	Manieb, Mancozeb
- Triazoles	Flutriafol, Propiconazole, Triamdimephorm
- MBC's	Benomyl, Carbendazim
- Morpholines	Fenpropimorph, Tridimorph
- Pyrimid[illegible]es	Ethirimol, Dimethirimol
- Phthalamides	Captan, Folpet
- Inorganics	Copper-based Fungicides, Sulphur
HERBICIDES	
- Triazines	Atrazine, Simazine
- Carbamates	Phenmedipham, Asulam
- Phenyl Ureas	Diuron, Chlortoluron
- Phenoxy Acids	2-4 D, MCPA
- Bipyridyls	Paraquat, Diquat
- Others	Glyphosate, Sulphonyl Ureas, Amida Xylenols, Imidazol Inones
RODENTICIDES	
- Coumarins	Brodifacoum, Difenacoum, Warfarin

Other raw material components include inert powder fillers, organic solvents, oils as diluents in combination with a range of surfactants to effect stable dispersions or suspensions when diluted with water or other solvent prior to application or use.

Water Usage

Water is frequently used as a diluent for specific formulation types, for example aqueous suspension concentrates and herbicides. Intermittent washdown of plant, pipelines and vessels also require considerable volumes of clean water. Small quantities of water are used for rinsing of safety and laboratory equipment. Normally mains supply is of adequate quality for these purposes.

Static reserves of stored water up to 200 m^3 capacity are now common place for fire fighting emergency situation. Depending upon plant size, total water usage ranges between 10 to 50 m^3 per day.

Energy Use

The pesticide formulation industry is essentially aligned to mixing and blending processes at ambient and intermediate temperature and reliant on a moderate electricity supply. Lesser use is made, depending on climatic conditions, of steam for heat exchange and space heating.

4 WASTE SOURCES AND CHARACTERIZATION

4.1 Atmospheric Emissions

Pesticide formulation process, for the most part, involves the mixing and blending of stable and non-reacting components which do not generate significant atmospheric emissions. Contaminated air streams are generated from air extraction equipment to remove dust and vapour contaminants from plant and vessels. These are normally vented to atmosphere via dedicated extraction/scrubbing equipment.

4.2 Liquid Effluent Waste Water

Aqueous effluents arise from plant washing, vessel cleaning, cleaning of safety and laboratory equipment, and spillages, all of which may contain significant concentrations of active pesticide adjuvants and diluents. An average production site will produce about 5 m^3 of effluent per day.

Contaminated run-off waters from roof tops and roadways, although dilute, may also contribute to the site liquid effluent loading. Volumes will vary with site size and climatic conditions. Normally contaminated waters are intercepted and stored for later treatment or reuse.

Dilute laboratory aqueous wastes are usually discharged to the site effluent system. Volumes are small and unlikely to exceed 100 litres per day.

Site sewage effluents, which may include shower and laundry water, are normally discharged via a separate system to on-site septic tanks or direct to public sewer.

4.3 Solid Wastes

Essentially three waste types are routinely produced. Quantities will vary depending upon size of plant and only broad estimates can be given for range of small to large operations.

Clean Wastes

Clean discarded package materials, cardboard, paper and plastic constitute a high volume, low density waste stream which is all recyclable. These wastes amount to 50 to 250 tons per annum.

Lightly Contaminated Wastes

Lightly contaminated bags and containers (plastic bottles, steel drums, etc) and floor sweepings constitute a high volume, low density waste stream requiring shredding and/or compaction and overpacking before disposal - usually to licensed landfill sites. These wastes amount to 50 to 250 tonnes per annum.

Hazardous and Toxic Wastes

Plant (raw material and product) residual wastes, extraction and scrubber medium residues, exhausted liquors and adsorbents are all toxic wastes; also off-specification, non recoverable raw materials and finished products, out-dated, unwanted products, effluent treatment sludges and laboratory wastes belong to this category.

Total volumes of these waste types is generally smaller and less frequently generated than clean or lightly contaminated wastes. Excluding liquid aqueous effluents probably less than 100 tonnes per annum total wastes for largest sites. Scope for further reduction in quantity also exists in many cases incorporating process changes and modifications to enable point source recycling of uncontaminated process/product residues.

These waste types are all potentially toxic and hazardous requiring secure containment, full identification and safe storage pending authorised disposal, preferably by high temperature incineration.

4.4 Fugitive Emissions - Upset Conditions

Pesticide formulation process activities are conducted in fully contained and bunded work areas. Loss of materials due to leakage, valve failure or spillage etc. are intercepted and prevented from reaching the external environment.

Large quantities of liquid and solid wastes can arise in the event of an emergency situation of fire or flood. Contingency plans for the containment and on-site storage of these wastes pending safe disposal are a vital element of a site environmental protection plan.

4.5 Environmental Impacts

Many compounds processed in pesticide formulation are, depending upon type, potentially toxic and hazardous to animal, fish and plant life. Extreme measures are essential to ensure that all process emissions and residues are, by means of interception and containment, prevented from contaminating the environment.

Air

Contaminated air streams are normally scrubbed or filtered, resulting in only small localized emissions of dust or vapour. Nuisance situations can arise from chemical odours, but these can be controlled by activated carbon adsorption.

Water

Potential pollution risks to water courses and groundwater exist and must be controlled. Outdoor areas for raw material storage should be roofed to avoid contamination of rainwater.

Pesticides are highly toxic to fish, animal and plant life. Contamination to surface, ground water and potable supplies could have disastrous effects. A real hazard could arise in fire situations which can generate large volumes of contaminated water with run-off risks to the external environment.

Land

Acknowledging that pesticides are designed for controlled and dilute application in the field, high concentrations of products arising from spillage, irresponsible dumping will have sterilizing effects and cause leaching problems over a long period of time.

5 POLLUTION PREVENTION AND CONTROL

It is important to identify that pesticide formulation plants function and operate with imported raw material active ingredients, adjuvants and diluents. This section of the industry is not faced with the production of complex waste by-products likely to arise in the associated industry of chemical synthesis of active pesticide compounds.

Relatively simple operational changes and implementation of routine procedures into the manufacturing process can achieve significant reductions in waste arisings with benefits of recovered valuable raw material and ultimately overall reductions in disposal costs.

5.1 Management Implications

Site management should have a clearly defined policy for waste minimisation with established objectives against which performance may be measured. Staff training and commitment to the achievement of objectives are essential to the success of the operation. Each plant should be accountable for all the processing/recycling or disposal of wastes produced.

Individual batch components (active ingredients, adjuvants and diluents) must be quantified to establish theoretical versus actual yields, a mass balance calculated and sources of deficiency investigated. Waste recycling should form an integral part of the manufacturing process. Disposal costs should be identified with the plant unit which produces the waste as an added incentive for minimisation. Recycled/recovered materials should be recorded to demonstrate overall benefits.

5.2 Examples of Waste Recycling/Re-use

Package Waste

Clean package materials, arising outside the manufacturing areas and away from contamination risk, comprising plastic, paper and cardboard, should be segregated for off-site recycling. Usually a small financial return is available which off-sets labour costs.

Contaminated Packages - Containers

Scope for recovery of these waste types is limited. Contaminated polythene containers cannot be cleaned and fully detoxified and must be compacted or shredded for disposal (Ref. 4). Small metal containers up to 25 litre capacity should be washed, crushed and recycled as scrap metal. Standard 200 litre metal drums, commonly used in the industry, following rinsing have two recovery outlets:

i. Non-toxic (solvent, surfactant) drums, may be disposed of via contractors for secondary use, with the exception of the food industry.

ii. Toxic containers used for pesticide active ingredients (raw material or finished product) must not be re-used outside of the industry. Rinsed, detoxified and crushed, the drums are suitable for scrap metal recovery. In some situations, raw material drums may be returned to the supplier for use of the same raw material.

Process Residues

- Where appropriate all drums should be rinsed to remove residues with the common solvent and washings consigned to the batch process.

- Pipelines, vessels should be drained and residues along with concentrated washings returned to the process as make-up for subsequent batches.

- Dedicated dust extractors (manually or automatically operated) should be used to recycle uncontaminated residues at source.

- Off-specification finished products should be regularly re-processed and prolonged storage of these avoided.

- Unwanted raw materials and finished products where possible should be disposed of by special arrangement to selected customers at reduced price or gratis, thus avoiding high costs of storage and waste disposal.

5.3 New Technology and Process Changes

Increasing use is being made of membrane technology (reverse osmosis and ultra-filtration). Dilute aqueous washings containing valuable active ingredient can be effectively concentrated by de-watering and re-used, thus avoiding loss of product to the drain and difficult effluents for subsequent treatment.

All new and refurbished plants should, at the design stages, critically review all areas of potential waste arisings and provision made for these to be reduced. These measures include: bulk handling systems (reduction of contaminated containers); in-line rinsing and recovery of wash waters; and automated filling of products for cleaner handling and minimising spillage risk.

5.4 Housekeeping

Good housekeeping practices must be strictly implemented at all plant levels to minimize safety and hygiene exposure risk and to avoid the creation of contaminated wastes from spillage which cannot be recycled and increases problems of waste disposal. Cleaning wastes from equipment and plant areas may be reduced by use of low volume high efficiency cleaning systems such as: high pressure hoses or add-on spray nozzles; low volume floor scrubbing machine; squeezes to push residues to where they can be collected; etc..

5.5 Hazardous Materials Handling, Management and Disposal

Most pesticides are potentially hazardous and dangerous and require strict controls in handling and use. Detailed handling and safety procedures are essential and must be supervised by a manager or responsible person.

Waste storage and disposal involves an area of extreme environmental sensitivity and strict legal controls. Despite measures for recycling, varying quantities of non-recoverable wastes will inevitably emerge for disposal.

Waste should be segregated at source into categories i.e., clean, lightly-contaminated, and toxic, and separately stored to await disposal. Clean and lightly-contaminated wastes should be compacted or shredded and baled to reduce volume. All discarded containers should be punctured or crushed to prevent secondary use.

All toxic wastes must be securely contained, usually within steel 200 litre open-top drums and fully labelled with contents description. Drummed wastes should be stored in a secure, bunded area to await disposal.

Waste Disposal

Strict legal controls cover the disposal of waste materials, requiring authorisation from the waste disposal authority into licensed disposal facilities.

Clean - (non-recoverable) and Lightly Contaminated Wastes

Provided the wastes are over-packed to prevent contact risk to operators, these waste types are normally accepted into licensed landfill sites for co-disposal with refuse.

Toxic Wastes

These wastes, comprising product residues, sub-standard raw materials and products, sludges, etc, present difficulties for disposal.

Low concentration wastes containing organic residues and less than 1% pesticide may be acceptable for disposal, into secure licensed landfill co-disposal sites, depending upon license conditions and inherent toxicity of the pesticide.

Virtually all concentrated pesticide wastes and particularly those containing organochlorine compounds, now require destruction by high temperature incineration at 1100-1200°C with at least 2 seconds residence time. Stack gas scrubbing facilities may be required.

While high temperature incineration is available and increasing in developed countries, in many areas in developing countries little capacity is available. Currently, circumstances leave no alternative but waste storage to await the development of suitable disposal outlets. Meanwhile, limited incineration capacity, depending on location may be secured for example, through:

- Installation of small package high temperature incinerators (Ref. 5);
- Shared capacity from larger multi-national companies possessing in-house facilities (Ref. 5);
- Use of cement kilns (Ref. 5, 6 and 17); and
- National schemes or initiatives for exportation of wastes to developed countries for incineration.

5.6 Treatment Technology

Pesticide formulation plants produce relatively small volumes of aqueous effluent ranging from:

- 1 m^3 per day for small plants
- 5 m^3 per day for medium-size plants
- 20 - 50 m^3 per day for large plants.

On average, a discharge of 5 m^3 per day is likely to be the norm. The effluent is highly toxic and polluting to both water courses and groundwater: full containment and treatment prior to disposal is essential. Current treatment technologies include:

- evaporation ponds.
- partial chemical treatment followed by evaporation ponds or discharge to sewer.

Chemical/Physical Treatment B.A.T.

Treatment technology developed over the past ten years is now available to fully treat and de-toxify pesticide aqueous effluents. Chemical flocculation pre-treatment is used to remove virtually all suspended matter including the bulk of pesticide as a small volume of settled sludge which is subsequently disposed of as solid toxic waste.

Clarified, filtered effluent is passed through beds of activated carbon to adsorb soluble organic matter including residual pesticides. Exhausted carbons depending upon location and resources are either sent to a contractor for regeneration or, disposed of as solid toxic waste. High quality non-toxic effluents virtually free of pesticide (sub ppb levels) are consistently produced (Ref. 7 and 8). Full details of the treatment currently representing Best Available Technology (B.A.T.) and examples of treated effluent quality are given in Appendix I. Small package treatment plants capable of treating between 1 to 10 m^3 per day are now commercially available at moderate cost and have already been adopted and installed in a number of developed and developing countries world wide (Ref. 9).

Alternative Treatment Technologies and Disposal Operations

Currently chemical treatment (e.g. hydrolysis) / biological treatment / membrane filtration / carbon adsorption represents the Best Available Technology for pesticide effluent treatment. Emerging technology involving ozone and ultra violet/peroxide oxidation as a tertiary treatment could produce ultra pure final effluent suitable for re-use in manufacture of pesticide formulations.

Capital and O&M Costs

Safety, Health and Environmental (SHE)

Controls in the pesticide formulation industry are stringent and demanding. Control and containment measures cover a wide area ranging over flame-proof electrical installations, fully-contained and air extracted/scrubbed production plant, effluent treatment and waste processing equipment. Estimates to comply with 1992 S.H.E standards are in the region of 30% of the capital cost for a new plant (Ref. 13).

Pollution Control Equipment

A list of capital and operation and maintenance costs for essential equipment for environmental protection and control is given in Table 3.

Table 3 Capital and O&M Costs for Pollution Control Equipment

Item	Capital costs (US$)	Operation and Maintenance costs (% of total production costs)
Overall costs for new plant[a]	30%[c]	5 - 10
Overall costs for old plant[b]		10-15
Package effluent plants		
- 1 m^3 batch capacity	13,000	
- 5 m^3 batch capacity	75,000	
Air Cleaning		5-10 % for a suitable mix of equipment, see above
- Bag-house filters	10,000	
- Wet Scrubber units	30,000	
Waste Handling Equipment		
- Waste shredder	30,000	
- Waste compactor	15,000	
- Drum crusher	14,000	

[a]With in-built pollution control systems, including waste reduction recycling facilities.
[b]By virtue of increased necessity for additional S.H.E monitoring surveillance, operator protection and in particular a higher proportion of off-site waste disposal.
[c]of the capital cost for a new plant (Ref. 13)

6 OCCUPATIONAL HEALTH AND SAFETY ISSUES

Pesticides for most plants are highly toxic and require stringent measures of hygiene and safety controls at all stages of the formulation process. Toxic exposure risks can arise from physical contact, and airborne contaminants in the form of dust, fume and vapour.

Plant atmospheres should be regularly sampled and monitored for compliance with appropriate threshold limit valves (TLV) (Ref.10) or in the absence of these, in-house hygiene standards.

All unit processes, so far is reasonably practical should be enclosed with use of fully extracted charging hoppers and filling hoods. Additional protection must be given to operators, depending on the nature of the task, in the use of protective clothing. This should include, gloves, overalls, boots, helmets, eye shields, dust masks and breathing equipment. Eye wash bottles and showers should be strategically placed throughout the plant.

Medical facilities and surveillance are an essential requirement. There should be a medical centre or clinic on-site with trained first aid person or nurse in attendance and the services of a visiting physician.

7 GLOBAL OVERVIEW OF DISCHARGE REQUIREMENTS

A number of well established guidelines have emerged from developed countries regulating the discharge quality requirements of pesticides to the receiving aqueous environments.

Problems do, however, continue to persist in developing countries where discharge standards are sparse or non-existent. Attempts to adopt the standards of more developed countries are frequently frustrated by a lack of technological resources for both effluent treatment and equally important analytical equipment and methodology to monitor for residual quantities of pesticides contaminants. This problem must be acknowledged when considering pesticide projects in developing countries with regard to:

i) The range of active ingredients to be used
ii) The possible need for full containment and recycling of plant aqueous residues rather than disposal as effluent.
iii) At the extreme, the complete withdrawal of a pesticide from the manufacturing range, which cannot be controlled to specific discharge standards.

This particularly applies to pesticide compounds listed in the so-called E.C. Black list and U.K. red lists. (Ref. 11 & 12). The ultimate objective of these lists is to severely restrict or ban completely a range of pesticides from all discharges to the aqueous environment.

8 TARGET/PREFERRED GUIDELINES

8.1 Pesticide Waste Waters

Effluents produced from the formulation of pesticide products are toxic and polluting and must be fully detoxified by treatment before discharge to the aqueous environment. Volumes of effluents generated are for the most part low and for a medium size plant unlikely to exceed 5 to 10 m^3 per day.

National and international pollution control legislation (Ref. 11 and 12) is progressively imposing severe restrictions on all pesticide substances in effluents requiring the virtual elimination of these before discharge to the external environment. Currently (1992) there are no official discharge standards available for pesticide formulation plants (Ref. 16). Discharge limits for formulation sites are normally derived in consultation with the local controlling water authority.

In deciding discharge limits due account will be taken of local disposal sources, for example water course soakaway or sewer, and also the treatment scope of the Best Available Technology (BAT). An example of effluent quality currently obtainable by BAT and the likely basis for the derivation of specific discharge limits is shown in Table 4. For the purpose of monitoring and control, particularly in developing countries, it would be convenient and appropriate to adopt discharge standards based upon limiting concentrations of specific parameters, including pesticides, per unit volume of treated effluent discharged.

Table 4 Effluent Quality Obtainable by Chemical Treatment and Physical Adsorption

Specification/Parameter	Effluent Quality Untreated (mg/l)	Chemical treatment (mg/l)	Final - activated adsorption treatment (mg/l)
Biological oxygen demand[a]	-	-	-
Chemical Oxygen Demand (COD)	Up to 5000	1500	200
Total Organic Carbon (TOC)	Up to 2000	1000	100
Total Suspended Solids (TSS)	Up to 1000	100	50
pH	?	8-10[b]	6-8[c]
Pesticides[d]			
- Organo-Chlorines	Up to 1000	Less than 100	Less than 0.1
- Organo-Nitrogen	Up to 1000	Less than 100	Less than 0.1
- Pyrethroids	Up to 1000	Less than 100	Less than 0.1
- Phenoxy Compounds	Up to 1000	Less than 100	Less than 0.1

[a]Biological Oxygen Demand (BOD) is not a reliable parameter as some effluent components may be non-biodegradable.
[b]Process is alkaline at this stage.
[c]pH adjusted in final effluent before discharge
[d]Broad examples; there are in excess of 500 pesticide compounds in existence. Each group at least will require separate treatment evaluation to assess pesticide removal efficiency

9 MONITORING PARAMETERS

9.1 Atmosphere

Normally in-house air cleaning scrubbing and absorption techniques ensure that only minimal levels of pesticides are likely to escape to atmosphere. Random air sampling in the proximity of discharge vents on the boundary of the site may be necessary to establish the efficiency of air-cleaning equipment used.

9.2 Effluents/Water

Effluent/water discharges from pesticide plants are legally controlled by "consents" or permits issued by the appropriate controlling water authority. These impose a range of quality parameters on the discharge, usually including a limiting volume or concentration depending on the place of disposal (water course, soakaway or sewage). For pesticide formulation plants the control parameters will be stringent and likely to include:

i) Chemical Oxygen Demand (COD) or
Total Organic Carbon (TOC)
ii) Total Suspended Solid (TSS)
iii) pH
iv) Pesticide Residues -single component and total

10 REFERENCES

1. Valkenburg, W. van., Pesticide Formulations, Marcel Dekker Inc, New York, USA, 1973.

2. Advances in Pesticide Formulation Technology, ACS Symposium Series 254, Washington DC USA, 1983.

3. Trends in the Formulation of Pesticides - An Overview, Seaman, D., Pesticide Science, 1990, 29, 437-449.

4. Waste Compaction, Crushing and Shredding, Rodan Engineering Ltd, Unit 5, Millbrook Business Park, Crowborough, East Sussex, UK.

5. Disposal of Unwanted Pesticide Stocks, Guidance on the Selection of Practical Options, International Group of National Associations of Manufacturers of Agrochemicals (GIFAP), Brussels, Belgium.

6. Pesticide Disposal In A Cement Kiln, Pakistan, Huden, G.H., Agency for International Development, Washington DC, USA.

7. Carbo-Flo Water Effluent Treatment, Technical Brief, ICI Agrochemicals, Fernhurst, Haslemere, Surrey, UK.

8. Purification of Process Water Contaminated By Agrochemical Pesticides, Using the Carbo-Flo Process, Report 187, 1992, Agricultural Research Department, The Winand Staring Centre: Institute of Agricultural Engineering, Wageningen, Netherlands.

9. Sentinel/Carbo-Flo Water Effluent Treatment for Agrochemicals Industry, E Allman & Co Ltd, Birdham Road, Chichester, West Sussex, UK.

10. Threshold Limit Valves and Biological Exposure Indices (revised annually). American Conference of Governmental Industrial Hygienists (ACGIOH).

11. E.C. Directive 76/464. Black List Substances - Dangerous to the Aquatic Environment.

12. U.K. Red List (Provisional) - Substances - Dangerous to the Aquatic Environment.

13. Personal Communication. K.S. Johnson UNIDO Consultant with ICI Agro-Chemicals Plc. Safety and Stewardship Department, September 1992.

14. Guides to Pollution Prevention. EPA/625/7-90/004 - The Pesticide Formulation Industry. United States Environmental Protection Agency, Washington D.C, U.S.A.

15. Development Document for Best Available Technology, and New Source Performance for the Pesticide Chemical Industry (Proposed). EPA/821-R-92.005,

April 1992- United States Environmental Protection Agency, Washington D.C, U.S.A.

16. Personal Communication. K.S. Johnson, Consultant to UNIDO with Dr. G.M. Jett, United States Environmental Protection Agency, Washington D.C., September 1992.

17. Integrated International Safety Guidelines for Pesticide Formulation in Developing Countries, United Nations Industrial Development Organization, Vienna. 1992.

APPENDIX I

Treatment of Aqueous Effluent from the Manufacture of Agrochemical Products

1. Introduction

Pesticides in general have a low solubility in water and are usually manufactured in the form of wettable powders, suspension concentrates or miscible liquids.

The breakdown in stability by chemical treatment of mixed effluents causes the flocculation and settlement of a high proportion of the pesticide ingredient in the form of a dense sludge. Soluble organic substances including pesticide residues are removed by adsorption onto activated carbon. This process offers a convenient method of detoxifying aqueous plant effluents arising from the formulation of pesticides.

2. Treatment Process

It is necessary to collect plant effluents in a common sump. This offers storage capacity, and means of buffering the changes in composition of effluent which can frequently occur.

The flocculation process is normally conducted on a batch treatment system using a conical-based cylindrical vessel. This allows the settlement of sludge residues in the cone, and a means of decanting the upper supernatant clarified effluent.

Optimum conditions for flocculation/clarification of effluent are pH 10-12. The addition of iron salts and lime (calcium hydroxide) to aqueous pesticide effluent normally induces rapid flocculation of all suspended solids.

The inclusion of a small amount of polyelectrolyte will serve to accelerate the coagulation of flocculants and subsequent settlement.

The addition of an adsorbent clay and possibly powdered activated carbon can be beneficial in the removal of trace residual pesticide if this is deemed to be necessary.

Ideally a vessel 5 - 10 m^3 capacity with mechanical agitation is suitable for collection and treatment.

To maintain a consistent standard of high quality finish effluent, a second stage of activated carbon adsorption should be considered. This should comprise of at least 2 x 1 tonne beds of activated carbon operating in series flow.

High activated carbon granules (14/44 mesh), surface area less than 1000 m^2/g should be used.

Coal- or wood-based carbon granules will give the best adsorption performance. Coconut shell carbons, by virtue of their relatively small pore sizes, are generally unsuitable for pesticide effluent treatment.

Flow rates of clarified sand-filtered effluent should be regulated through the beds to allow a minimum of one hour contact residence time.

Final effluents are normally clear, virtually colourless and non-toxic.

Disposal with consent of controlling authority can be directed to a sewer, soakaway, or in hot climates possibly to an evaporation pond. Direct discharge of effluent to a water course is not recommended.

Sludges from the process can be dried in shallow drying beds and subsequently disposed of to a designated waste disposal site.

TREATMENT PERFORMANCE

The performance of the above described treatment process is summarized in the table below.

Product	Effluent Initial Loading µg/l (ppb)	Residue in Treated water µg/l (ppb)	Reduction %	Limit of Detection	Source
atrazine	5,100,000	4.0	>99.9	0.4	USA
atrazine	240,000	N.D	>99.9	0.06	Netherlands
alachlor	795,000	<4.8	>99.9	0.4	USA
bentazon	480,000	N.D	>99.9	0.075	Netherlands
permethrin	237,500	N.D	>99.9	0.4	USA
cypermethrin	50,000	N.D	>99.9	0.02-0.04	UK
pirimicarb	225,000	N.D	>99.9	0.02-0.04	UK
carbaryl	225,000	N.D	>99.9	0.02-0.04	UK
dicamba	35,000	N.D	>99.9	0.02-0.04	UK
2,4-D	200,000	N.D	>99.9	0.02-0.04	UK
paraquat	200,000	N.D	>99.9	0.02-0.04	UK

N.D= not detectable