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

FAIR USE POLICY

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

19230

49p.

RESTRICTED

DP/ID/SER.A/1515
17 September 1991
ORIGINAL: ENGLISH

STRENGTHENING OF PESTICIDE DEVELOPMENT CENTRE

DP/IND/89/128

INDIA

Technical report: Controlled release formulations of pesticides findings and recommendations*

Prepared for the Government of India
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of L. Vollner, consultant in research and development controlled release pesticide formulations

Backstopping officer: B. Sugavanam,
Chemical Industries Branch

United Nations Industrial Development Organization
Vienna

---

* Mention of company names and commercial products does not imply the endorsement of the United Nations Industrial Development Organization (UNIDO). This document has not been edited.

V.91 28902

Table of contents

ABSTRACT

Title: Controlled Release Pesticide Formulations

Project No.: IND/89/128/11-64

Duration: 2 months, 27 January to March 1991

Objectives:

- To assist in developing new types of pesticide formulations, especially to introduce controlled release (slow release) formulations (CRF) into the laboratory of the Pesticide Development Centre (PDC), Udyog Vihar, Gurgaon-122 016, Haryana, India.

- To give lectures in the National Training Course, organized by PDC on Pesticide Formulation Technology, 4-15 March, 1991.

- To conduct a workshop on CRF for the Indian Pesticide and Pharmaceutical Industry, 18-19 March, 1991.

Expert introduced the following natural polymers for CRF:

Sodium Alginate (polysaccharide) of three different viscosity grades and cellulose derivatives such as hydroxy-ethyl-, hydroxy-propyl-, carboxy-methyl-, and ethyl-cellulose (some of them also of different viscosity grades). Furthermore, beta-cyclodextrin was supplied and some simple formulation experiments were carried out.

Outdoor evaporation experiments and release into water showed significant protection of lindane and diazinon in contrast to the EC formulation (Annex V).

I. INTRODUCTION

Controlled release formulations of pesticides are retarding repositories, which release their biologically active constituents into their environment over a defined period of time. In these formulations, the substances are chemically bound or physically incorporated in a polymer matrix by means of different techniques. The migration of the substances is, therefore, preceded by chemical reactions for bond cleavage or physical transport processes in and through polymers, which can be mathematically modelled. Whilst, in the meantime, there are quasi-standard methods for physical-chemical laboratory tests, biological activity tests are often performed in the field under conditions closely approximating actual applications. Several of these formulations have already achieved commercial status.

The prominent characteristics of these formulations are the reduction of the toxicity of the substances and of undesirable side effects on non-target organisms, as well as the prevention of premature disappearance of the active substances from the place of application as as result of degradation and transport processes under environmental con-
ditions.

The Pesticide Development Centre is developing and promoting safe, efficient and economic indigenous technologies for a new generation of pesticide formulations. Within these efforts, the centre decided to initiate work on CRF, and expert was invited for introduction of this new technology.

II. ACTIVITIES

A. Experimental Work

1. Formulation Laboratory

Together with the staff of the centre, expert carried out several CRF experiments using lindane and diazinon as model substances and alginate as formulating agent. Foliar applications and seed treataments were carried out. Films containing a.i. were used for release rate experiments.

2. Analytical Laboratory

Expert optimized capillary column conditions including injection port, detector (ECD) connection, flow rates of carrier, make up gas and splitter ratio, and carried our lindane residue analysis of plant leaves and of polymer films.

B. Theoretical Work

1. Review of CR Research

Expert reviewed the last three years' international reserach activities for PDC (and for other interested readers) in this field and listed addresses of authors for further contacts (Annex VI).

2 Training Programme on Pesticide Formulation Technology, 4-15March,1991

Expert chaired one session of the training course, conducted a short demonstration of CRF and held three lectures:

- Advances in Chemical Pest Control, 4 March, 1991
- Granular Formulations, 6 March, 1991
- Slow Release Formulations, 7 March, 1991

3. Project Proposal on CRF to the Government of Germany

For future supports in this field and for supplying training facilities at the experts's research centre in Germany to the staff of PDC and to other research institutes in India, expert has developed a project proposal together with the staff of PDC (Annex VII). Proposal might also appeal to other countries of RENPAP.

4. Workshop on CRF

Expert conducted as two days' workshop on March 18-19,1991, which was organized by PDC and CRF, dealing with the following main topics: -Systems for CRF - Kinetics of pesticides migration from the matrix - Laboratory approach for testing CRF- Outdoor tests - Artificial polymers - Natural polymers.

5. Further Activities

In connection with evaluating needs for CRF in India, expert held a lecture on Controlled Release Formulation at the Indian Agricultural Research Centre, Division of Agricultural Chemicals on 26 February, 1991.

III. RECOMMENDATIONS

A. Recommendations to PDC

1. Use of (water soluble)natural polymers for future experiments on CRF for the following reasons:

- non-toxicity to targets and environment
- biodegradability
  simple preparation
- cheap, if agricultural wastes (cellulose derivates) will be utilized in the future.

Expert delivered the following natural polymers for CRF: Sodium Alginate (polysaccharide) of three different viscosity grades and cellulose derivatives such as hydroxy-ethyl-,hydroxy-propyl, carboxy-methyl-, methyl-hydroxy-propyl- and ethyl-cellulose (some of them also of different viscosity grades).

Beta-cyclodextrin (CD), another promising natural polymer was also supplied. Since results show that by incorporating this material in the formulations, release rates of a.i. will be significantly slowed down, it is recommended to use this material in the future.

The "molecular encapsulation" using CD generally, results in further advantageous modifications of the properties of complex substances, including the following:

a) hydrophilicity is strongly reduced, i.e. wettabillity, rate of dissolution and extent of solubility is enhanced, which generally results in enhanced bioavailability.

b) volatile, liquid, and gaseous substances, or substances of intolerable odour can be converted into microcrystalline, stable, well formulable substances.

c) incompatible substances can be mixed when at least one of the reacting component is complexed.

d) the selectivity between herbivorous/non-herbivorous insecticides can be enhanced.

e) cyclodextrin complexes are per se micronized substances, they are easily dispergable, no elctric charging will occur.

f) long lasting effects (CR) can be ensured because the complex substances are only released on contact with water.

g) CD exerts a direct auxin-like effect on plants, therefore phytotoxic effects of pesticides can be reduced.

2. Basic requirements for developingCRF, is a properly and rapidly working analytical unit Since the analytical group seems to be overloaded with its own research work, strong efforts should be made to support the formulation laboratory with analytical facilities. A minimum requirement would be a gas chromatograph equipped with ECD and FID. For polar pesticides, a HPLC unit would be very useful.

3. Since one of the main objectives of the Centre is to avoid environmental problems, monitoring of pesticide emissions from larger scale experiments, as well as the monitoring of waste waters should be most seriously considered.

4. Expert has reviewed recommendations of former consultants and agrees on laboratory safety aspects, especially on the following:

-A.R. Woodford, 8 Dec.1987, page 19, No. 1 and 2
-S.Deri, 1 Dec.1987, page 9
-W.van Valkenburg, 9 July 1987, page 9, 18 January 1988, page 6, November/December 1988, page 7, No.14
-R.Teuber-Weckersdorf, 1 August 1988, page 2.

B. Recommendations to UNIDO

1. Training in CR technology and in evaluating the quality of formulations is needed (e.g. 2 x 3 months).

2. Review of analytical instrumentation and, if necessary, supply of instruments (as indicated in the recommendations to PDC).

3. Expert in capillary GC and GC/MS (2-3 weeks) or training in these techniques is needed (2 x 3 months).

IV. CONCLUSION

Working plan (Annex IV) could be followed quite well, in spite of heavy load on staff concerning the training programme and the visit of a UNIDO reviewing team at the same time. Some limitations also occured in getting rapid analytical data.

Formulations carried out showed slow release properties, especially on using alginates and the combination of alginate and cyclodextrin.

Simple preparations of alginate granules and seed coatings with different cellulose derivatives could achieved.

The controlled release concept could be promoted to a large group of pesticide formulating experts upon their visit to the centre.

In addition to the review article which contains more than 50 publications, many other papers on CRF were supplied by expert.

V. LITERATURE

1) A.F. Kydonieus, Controlled Relase Technologies, Methods, Theory and Applications, CRC Press, N.Y. (1978)

2) K.-H. Koenig, Fortschritte im chemischen Pflanzenschutz, Chemie in unserer Zeit, 24. Nr. 5 and Nr. 6 (1990), VCH Verlagsgesellschaft, D-6940 Weinheim

3) J. Szeitli, Cyclodextrins in Pesticides, Starch/Stärke 37, Nr. 11 (1985), VCH Verlagsgesellschaft, D-6940 Weinheim

4) M- Bahadir and G. Pfister, Controlled Release of Pesticides, Chemistry of Plant Protection 6, Springer-Verlag Berlin-Heidelberg (1990)

5) L. Vollner, Pesticide Formulation with Natural Polymers, 7th Symposium, IUPAC, Hamburg, FRG 1990

6) Aqualon, Technical Publications, Aqualon GmbH, Paul-Thomas-Straße 58, 4000 Duesseldorf 13, FRG

7) U.K. Srivastava, N.T. Patel, Pesticides Industry in India, Indian Institute of Management, Ahmedab, India (1990)

8) The Hindu, Survey od Indian Agriculture, 1990, National Press, Madras, India

9) B.S. Parmar, P.Dureja, Minimizing Environmental Hazards of Agrochemicals, Society of Pesticides Science , India, Division of Agricultural Chemicals, IARI, New Delhi, India (1990)

10) W.Van Valkenburg, Pesticide Formulations, Marcel Dekker, Inc., New York (1973)

Annex I

Persons Contacted

UNDP	M. Islam	Country Dir. UNIDO
	S. Pal	Assistant Programme Officer
RENPAP	S.P. Dhua	Regional Coordinator
HIL	D.R. Sharma	Deputy Gen. Manager
	R.S. Mathur	National Project Director
PDC	K. Dhari	Nat. Project Coordinator
	P.K. Ramdas	Head Formulation Lab.
	S. Kumar	Dy. Product Manager
	S.Y. Pandey	Head Analytical Lab.
	N.R. Bhateswar	Head Biology Lab.
IARI	P.N. Tiwari	Dir. Nuclear Res. Lab.
	B.S. Parmar	Head Agr. Chemicals Lab.
	S.K. Mukejee	Ex. Head Agr. Chem. Lab.

UNDP = United Nations Development Programme
RENPAP = Regional Network on Pesticides in Asia and the Pacific
HIL = Hindustan Insecticides Limited
PDC = Pesticides Development Center
IARI = Indian Agricultural Research Institute

Annex II

Pesticides Selected for Future Work

1. Phorate

2. Carbofuran

3. Diazinon

4. Pyrethroids

5. Lindane

UNIDO

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

JOB DESCRIPTION

IND/89/128/: 11-64

Post title	Expert in Controlled Release Formulations of Pesticides
Duration	2 m/m
Date required	Jan/Feb 1991
Duty station	Pesticide Development Centre (PDC) Udyog Vihar, Gurgaon-122 016, Haryana, India. Expert will stay in New Delhi and commute to PDC.
Purpose of project	To develop controlled release pesticidal formulations for local needs.
Duties	The consultant will be required to advise and assist the technical personnel at the Pesticide Development centre on the laboratory development and scaling up of micro-encapsulation and other techniques for controlled release formulations of pesticides. He will formulate guidelines for the choice of suitable type of controlled release formulations, selection of formulation ingredients etc. most suited to the region. The consultant is also required to deliver lectures/ conduct a short course on various controlled release techniques which can be adopted by the industry, to the invited pesticide industry personnels.

..../

Qualifications

The candidate should be a chemist/ chemical technologist with adequate experience on the development of micro-encapsulation and other types of CR formulations. He should also have adequate industrial experience prferably in the scaling up of the CR techniques developed in the laboratory to pilot plant/ semi commercial plant level.

Language

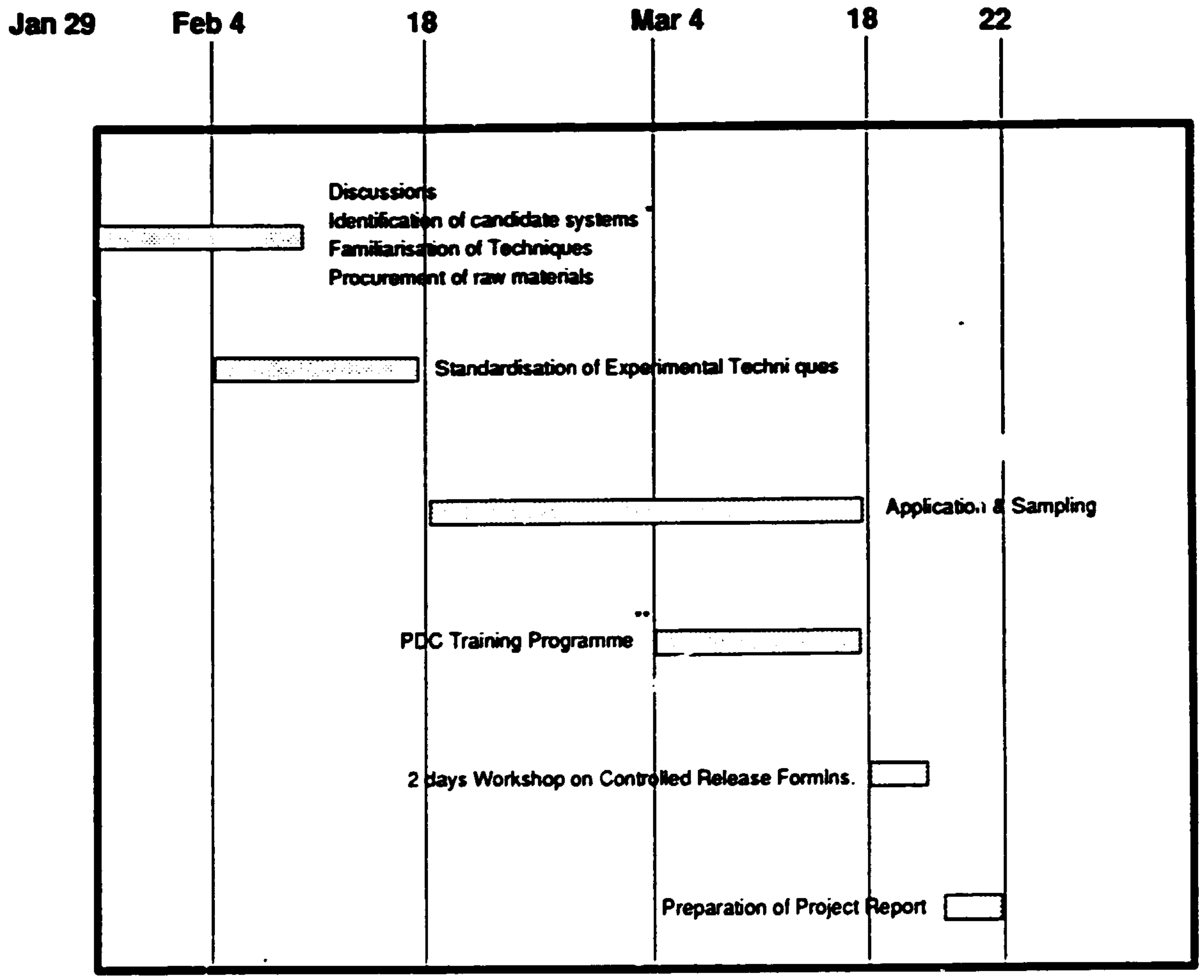
English

Background information

It is an institution building project of Government of India sponsored by UNDP/UNIDO aimed to augment, the capabilities of Pesticide Development Centre located in Gurgaon, Haryana, India close to Indira Gandhi International Airport, New Delhi to assist the pesticide industry sector in India by developing and promoting safer efficient and economic indigenous technologies for new generation pesticide formulations and utilising indigenously available microbial and botanical products integrated with the development of relevant modern application technologies.

Working Plan

Workplan of Dr. Lajos Vollner - UNIDO Expert to PDC
Jan 29 - Mar 22, 1991

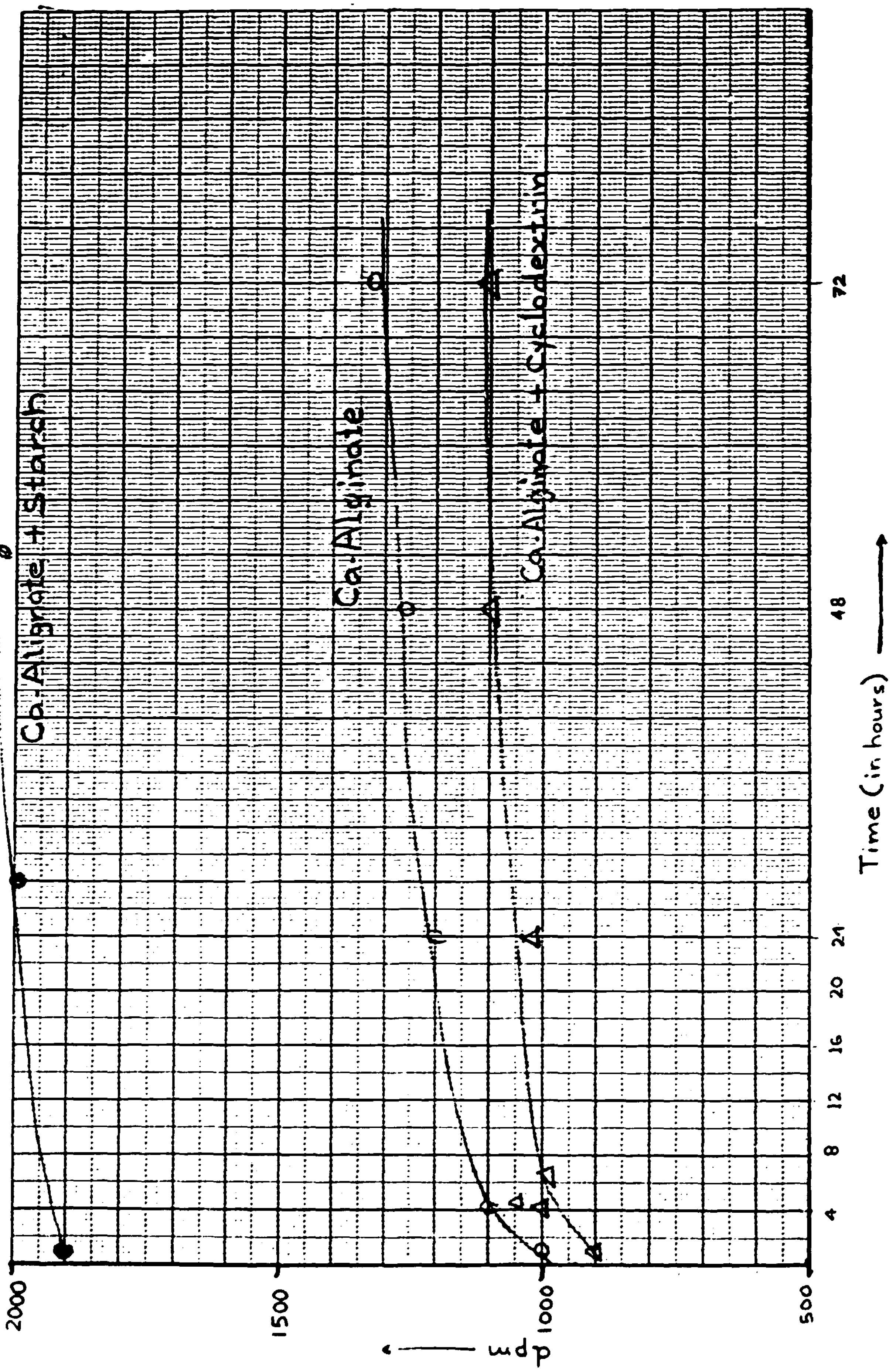


* Lindane, Phorate & Diazinon prefferred

** Lectures prefferred
i) Controlled Release Formulations
ii) Granular Formulations
iii) Advances in Pesticide formulations

Annex V

DIAZINON RELEASE RATES



Controlled Release Pesticide Formulations

A review of the last three years' research activities

by

L. Vollner

National Centre for Environmental Sciences, GSF,
Ingolstaedter Landstraße 1, 8042 Neuherberg, Germany

This review was prepared in connection with a UNDP/UNIDO scientific and technical mission to India, January/March 1991, and in connection with a IAEA TC Mission to Indonesia, April 1991.

The review does not necessarily include all papers published around the world during the last three years, but considers all the proceedings of the Controlled Release Society, Inc. from 1988, 1989, 1990, as well as the Seventh International Congress of Pesticide Chemistry of IUPAC, Hamburg 1990. Since these two groups are acting significantly in controlled release sciences and in pesticide formulations respectively, the survey can be considered as a relevant collection (54 references) of ideas and data on this topic.

Since many of the abstracts do not deal with details of experiments, and since the aim of this report was not to render protocols for controlled release preparations, a list of authors' addresses is given to the interested reader for further consultations. On the other hand, formulating agents are mentioned in almost every case. They will be listed in a table in addition to the text to allow rapid consideration for possible formulation work.

The review does also include publications on flavours and pheromones for possible combination with pesticides.

Abbreviations as occure in the text:

a.i.	Active Ingredient
CR	Controlled Release
CRF	Controlled Release Formulation(s)
EC	Emulsifiable Concentrate
EVA	Ethylen Vinyl Acetate
MC	Micro Capsule(s)
ME	Micro Encapsulation(s)
PVC	Poly Vinyl Chlorine
WP	Wettable Powder

Novel antifouling CR-systems were examined by Peppas and Romanos, 1988 (1). For the release of molluscicides, formulations have been prepared from acrylic suspensions and emulsions containing 50-60 % solids.This material is applied as a thin coating for CR by a composite phenomenon of diffusion/swelling and dissolution on ships's bulls. A CR-period of 3-6 months is to be expexted.

Levy et al., 1988, 1989 and 1990 (2,3,4,) absorbed Abate (O,O,O',O'-tetramethyl O,O'-thiodi-p-phenylene bis-phosphorothioate and other larvicides) on crosslinked polyacrylamide granules (Culigel), in order to control mosquitos.
The preparation was done by submerging the polymer granules in an aqueous solution of the larvicide. Bioassays have indicated that the a.i. can be slow-released according to a first-order kinetics. An effective period of 4-6 months could be reached with this formulation, containing approximately 22% a.i.

Seng and Fong, 1988 (5) used latex for coating of fertilizers. Using prevulcanized latex concentrates (vulcanised with sulphur, zinc diethyl dithiocarbamate and zinc oxide) in a fluidized bed film coating driver, the authors could extend the release time of urea up to 15 weeks instead of one day of the nonformulated material.

Organosilicon compounds have been used by Zsifkovits and Gruening, 1988 (6) to encapsulate pesticides.
The ME process stars mixing the a.i. with the formulating agent followed by adding this mixture to the external water phase under emulsifying conditions. The crosslinking reaction is supported by a catalyst (e.g. Lewis acid), and proceeds at room or slightly elevated temperature. After 3 to 72 hours, the dispersion will be stabilized by adding a protective colloid. Results showed an extended active period of a synthetic pyrethroid up to 21 days, in contrast to 10 days (WP) or 1 day(EC).

Tsujy et al., 1988 (7) used polyurea for ME of fenitrothion. The formulation was sprayed on cotton plants and the toxicity against tobacco cutworms was examined. All the used new formulations (different capsule diameters and wall thickness) showed longer residual effect than the EC formulation.

El-Leithy et al., 1988 (8) used PE and EVA to incorporate niclosamide for control of schistosomiasis snails. PE was mixed with the a.i., transferred into glass mould and thermally cured at 130-140 °C. EVA (10% solution in methylene chloride) was vortexed with the a.i. and after a short time quickly poured to glass mould. Left for 24 hours in a refrigerator and then vacuum dried at room temperature. Release rates during 5 days have been studied, but no comparison was reported to the commercially formulated material.

Jamil et al., 1988 (9) reported on field experiments of an EVA carbofuran formulation, which was developed by Bahadir et al. 1987 (10). The authors found an extended period of efficacy compared to the commercial GR formulation.

Herbig et al., 1988 (11) developed a CR diazinon eartag for cattle, supplying the a.i. at a constant rate for several months (more than 4 months). The formulating agent of the membrane based eartags has not been described in detail. Efficacy studies have shown that horn flies can be controlled by applying one eartag per animal, and the cattle were observed to have less than 90% flies than did untreated control cattle.

Bohm et al., 1988 (12) reported on the development of encapsulation of microbial insecticides, like Bacillus thuringiensis. All of the (not in detail) described ingredients used in the preparations are non-toxic to birds and animals. The MC are inherently self sticking and dissolve at a pH 7.5. They resist rain, are easy to produce and are cost effective.

Schreiber et al., 1988 (13), Trimnell and Shasha, 1989 (14) and Franklin et al., 1989 (14a) encapsulated atrazine and other herbizides in starch to provide CR of these materials. The encapsulated atrazine e.g. at the level of 5% was released in 20 days up to 43%, while the commercial suspension provided immediate availability of the a.i. to the water phase at 75-80%. Slower release was found when atrazin was used as the technical powder rather than as a solution or liquid suspension.

Tocker, 1988 (15) reported on self-microencapsulating pesticide compositions using methomyl and oxamyl as a.i.. The polymethyl methacrylate (Elvacite 2008, Du Pont) based preparations represent a versatile, simple, potentially low-cost concept for CRF. A solution of 0.4 technical methomyl, 8.0 g Elvacite in cyclohexanone, 1 g xylene and 1.0 g xylene and 1.0 g Tween was added to 200 ml of gently stirred water, producing a suspension of microspheres (sizes about 15 micron).The release rate in 24 hours was 55% of methomyl and 65% of oxamyl.

CR of essential oils for perfumes and food flavours were studied by Keneipp et al., 1988 (16), using polymeric microparticles of the copolymer of HEMA with MAA.
The preparation of the CR-system was done in a simple way: approximately 2 g of the polymeric material were placed in a vial and approximately 10% (w/w) perfume or food flavour was added. After 24 hours of absorption, CR studies were performed in an incubator at 37 °C using a pH 7 buffered aqueous solutions. A release period of more than 12 hours could be reached, which is significantly longer than release rates using commercial formulations of these volatile compounds.

Starch was used for CR encapsulation of flavours by Wienen et al., 1989 (17). Different kinds of starch were suspended in water at the level of 5,7,10 or 12 % (w/w) in a 100 ml teflon digestion bomb, and heated by microwave at 720 W. After cooling to 40 °C, 10 % linalool was added to the pastes. Pastes were dried overnight at 40 °C to form films, washed with hexane to remove unbound flavour and extracted with hot ethanol to effect flavour release for analysis. Release rates were not mentioned.

Belcher and Crainich announced in 1989 (18) ME of organophosphates, carbamates and pyrothroids. No details of formulating agents and no release rates of. a.i. have been reported.

Slight improvement of antifeedents activity could be reached by Wilkins et al., 1989 (19), using latex based CRF of polythyleneglycol and polyvinylacetate. Cypermethrin was incorporated in addition to cadaverine and neem oil in the formulations. The formulations were applied as a spray to rice plants, and brown plant hopper was used as a testing insect.

Herbig et al., 1989 (20), reported on the preparation of porous beads for CRF of agrochemicals. The beads are prepared by a phase-inversion process that involves dissolving a polymer (cellulose acetate, polyurethane, polysulfone, PVC or polyvynilidene fluoride) in a solvent or solvent mixture and then spraying this into a precipitation bath (containing a polymer nonsolvent that is miscible with the polymer solvent). In the precipitation bath, nonsolvent replaces solvent in the polymer-containing droplets, precipitating the polymer to porous beads. These beads constitute a reservoir-type delivery system between 75 to 90 % (w/w) of a.i. Diazinon and some pheromones were absorbed and tested.

Haslbeck et al., 1989 (21) investigated antifouling coatings (paints) of gelatin/gum arabic capsules incorporating tributyltin chloride (TBTCI) and cross-linked it with glutar-aldehyde and quinone. Furthermore simazine and benzoic acid were incorporated into urea formaldehyde and acrilic polymer capsules.
After two months exposure, the prints with CR capsules of TBTCI (6 and 10% w/w) were significantly less fouled than paints of the controls.

A long term CR-trifluralin field test was carried out by Burton et al., 1989 (22) at about 13 °C and the results were found to successful to control root growth. A daily release rate of approximately 13 micro g could be assessed during the 7 years period. No details of formulating agents are described in the abstract.

Fenitrothion MC was developed by Kawada et al., 1989 (23) in order to improve residual efficacy of this pesticide against cockroaches. Polyurethane was used as the wall material, incorporating 20% a.i..
The new formulation showed higher residual effect than the reference commercial formulation after a test period of 8 weeks.

Wing, 1989 (24) found that the use of starch matrix is effective for encapsulating herbicides like alachlor. Rate of a.i. release can be controlled by the type of starch used, and by the particle size of the product.
Results show a great reduction in leaching in contrast to the commercial formulations.

Potter et al., 1989 (25), reported on the use of protein based microparticles (Nurture) to enhance and prolong the insecticidal activity of synergized pyrethrins. A formulation containing 1% (w/w) a.i. was prepared from a commercial concentrate. The concentrate also contained synergists and petroleum distillate, resulting in formula concentrations of 20% piperonyl butoxine, 3.3 % octyl bicycloheptane dicarboximide and 4.8% petroleum distillate. The resultant product was a fine, free-flowing powder with a particle size of 1 to 10 microns.
The new formulation extended the temporal efficacy of pyrethrins significantly (up to thirteen months) against cockroaches.

Hussain et al., 1989 (26), tested CRF in combination with UV absorbing compounds, to prevent rapid degradation of deltamethrin by sun-light.
Results showed that among the materials tested 2,4-dihydroxy-benzophenone provides the best UV protection. Long chain aliphatic alcohols, paraffins, silicon oils and plant oils were used as carriers for a.i. and protective agent.

Cyclodextrins (CD) can be used /Szejtli, 1989 and 1990 (27) and 1985 (28); Gottneid and Friedman, 1989 (29)/ for complexing pesticides. The advantages of this methods include UV-stabilization, reduction of volatility and bad smell, enhancement of wettability, solubility and biovailability. The CD complexation furthermore may also result in a retarded release of a.i.. The hydroxyl groups on the CD ring are available for reactions in the same way as are the OH-groups on carbohydrates. Cross-linking reagents have been used to form CD polymers.

Schacht et al., 1989 (30) used EVA-type reservoirs of the fungicide metalaxyl for application in hydrocultures.
The a.i. was placed in a polymer envelope and the cumulative release rate into a nutrient solution was studied.
The results show that the release rate was proportional to the surface area and to the film thickness of the envelope used. By changing the solution, results showed an extended active period of the fungicide up to more than 10 days in contrast of 1 day to the commercial formulation.

Hargrove and Francis reported 1989 (31) on a CR plant nutrient membrane-system of a copolymer (dicyclopentadien) and a vegetable oil (linseed, soya, etc.). This mixture is applied to a tumbling bed of fertilizer granules at elevated temperatures (65-95 °C). This formulation has been commercially available for a long time (since 1971) in the U.S.A.

Murphy et al., 1990 (32) used d,l-polylactic acid with different plasticizers, like triethylcitrate (TEC), triacetin, dibutyl sebacate or dibutyl phthalate for CRF of urea.
The aqueous pseudolatex was prepared by emulsifying an organic polymer solution into an optimmized aqueous surfactant solution. This despersion was then plasticized with one of the mentioned materials, and applied to urea granules at a minimum film forming temperature. The optimal plasticizing agent for extending release was 10% (w/w) TEC.

Side chain crystalline polymers were successsfully used by Stewart et al., 1990 (33), to demonstrate temperature sensitive CR devices.
Delivery systems were prepared by bulk co-polymerization of n-alkyl-meth-acrylates and multifunctional meth-acrylates in the presence of liquid or solid a.i.. Up to 40% diazinon (w/w) e.g. gave excellent release kinetics. Release rate changes of up to two orders of magnitude may be obtained over relatively small temperature changes.

Ramdas and Khetan, 1990 (34), developed a self-spreading formulation for the control of surface feeding/inhabiting aquatic pests. The formulation contains a stabilized suspension of a micronized pesticide in a non toxic oil phase, containing optimized amounts of lypophilic surfactants, dispersed in aliphatic alcohol. The droplets of the formulation, on contact with water, spread spontaneously and break down into evenly distributed micro globules. These globules, consisting of the encapsulated pesticide, remain floating and dispersed on the water surface.

The possible use of succinoglycan for water-based agrochemical formulations was reported 1990 by den Ottelander (35). This material is in many respects similar to xanthan, but has greater structuring power than xanthan. Suspension concentrates and water external emulsions were studied but no release rate data has been reported yet.

Mulqueen and Spicer, 1990 (36) reported on the use of polydimethyl siloxane for seed treatment, incorporating pesticides. But no more details could be found in that abstract.

Lubosch, 1990 (37) developed a CR seed treatment method using hydroxymethyl-propyl-cellulose and polyvinylalcohol. Carbofuran was used a.i.
Author could reduce the total amount of a.i. upto 25%, using this formulation method. The period of protection was up to 6 weeks.

Ohtsubo et al., 1990 (38) encapsulated fenitrothion with polyurethane and studied the relationship between the physical factors such as mass median diameter and wall thickness, and the stability of the MC by breaking tests. But no CR rates experiments were carried out so far.

Chiba et al., 1990 (39) could reach good CR results by modifying solid pesticide technicals.In the study, water soluble kasugamycin, acephate and water insoluble probenazol were used as core powders. As fine powders, hydrophobic titanium dioxide treated with dimethyldichlorosilane were used.

Vollner, 1990 (40) reported on CR formulations using natural polymers like polisaccharides, starch or derivates of cellulose. A number of chlorinated insecticides, carbamates and several herbicides were used for the laboratory, greenhouse and field experiments. Using alginate formulations for less water soluble pesticides and hydroxyethyl cellulose for highly water soluble pesticides, release rates could be slowed down significantly.

Brown et al., 1990 (41) developed a ME method for fungicide seed treatment and for foliar insecticides using an interfacial polymerization process. Formulating agents were toluenediisocyanate and polymethylene polyphenylisocyanate with diamines to form polyurea.
Zero order release was obtained for the a.i. from the MC with rates between o.5. to 1.0 micro g/l compared to 35 micro g/l forthe commercial formulation.

ME of pesticides by in-situ interfacial condensation polymerization was reported by Scher, 1990 (42), using isocyanate monomers. Formulations of three ICI herbicides (Eradicane, Vernolate and Flurochloridon) and two different formulations of the insecticide Fonofos have been developed and are now commercially available.

Szente, 1990 (43) reported on the use of cyclodextrin for molecular encapsulation of acephate, malathion, DDVP. The vapor pressure of a.i. could be decreased significantly even at elevated temperatures. The losses upon heat stress of the complex was found only up to 8-12%, while the corresponding commercial formulation lost 70-80% of a.i..

Kawada et al (44), reported on the development of d-Cyphenotrin ME for cockroach control. Field experiments showed an extended active period of 2 months against insects. The formulating agent is not mentioned in details.

CR pheromone formulations have been reported by Cork et al., 1989 (45).
PVC was used as a formulating agent using 40% of vinyl chloride/vinyl acetate emulsion copolymers with a 1:1 mixture of the plasticizers Cerechlor (ICI) and di-(2 ethyl)-phthalate. To this 1% pheromone and an equivalent of antioxydants, and an UV screener were added. The mixture was homogenized and degassed on a rotary evaporator for one hour. The pre-polymer was then shaped into sheets by sandwiching between two glass plates and curing at 150 °C for 15 minutes.
Release rate studies showed a long (up tp 50 days) extended active period of aldehyd and conjugated dien type a.i. The formulation is now commercially available.

Zhenya et al., 1989 (46) reported on the development of a monolithic CRF of the sex pheromone of Ostrinia furnacalis, cis, trans-12-tetradecenyl acetate, incorporated in a copolymer matrix of acrylic acid-itaconic acid-vinyl acetate. In the preparation process, the crosslinker is added at room temperature to avoid volatilization of the a.i.. The release rate is regulated by changing the crosslinker (fluoraluminosilicate) contents, the agent loading levels, and by adding some suitable additives.

Jones, 1989 (47) found a water soluble acrylic resin formulation highly suitable for the CR of the pheremone 1,7-dioxaspiro(5,5) undecane. The release rate characteristics of the polymer resin can be varied through modifications of a number of parameters including particle size, ratio of a.i. to polymer, copolymer ratios and choice of monomers, molecular weight and degree of branching.

Brown and Howell, 1989 (48), used polyethylen dispensers for CR studies of codling moth pheromones /E8,E10-dodecaien-1-01(E8,E10-1-OH), dodecan-1-01(12-OH) and tetradean-1-01(14-OH)/. Release rates could be significantly extended in contrast to several other types of dispensers such as MC, holow fibers, etc..

Emara et al., 1990 (49), reported on the use of natural rubber formulations of the molluscicides niclosamid (ethanolamine salt). The release of a.i. from the elastomeric matrix was found to start following zero order kinetics and ends up according to a diffusion controlled mechanism.

Leonhart et al., 1989 (50) and 1990 (51), reported on the use of CR dispensers for detection of gypsy moth populations with its pheromone. Nine commercial dispensers (including PVC pellets, rubber septums, etc.) were used for the preparation of formulations, but only one (USDA-1) design gave good results of field application. The material has not been described yet.

Weatherstone described 1990 (52), CRF of pheromones in general, listing trilaminates, hollow fibers, MC, lowables and ropes, and formulating parameters.

Staten et al.. 1989 (53), reported on the improvement of CR pheromone formulations for pink bollworm detection, using membrane lure systems.

Weiss and Hasting, 1989 (54), reported on the use of CR dispensers for the mating disruption of the grape berry moth. The pheromones (9-dodecenyl acetate and 11-tetradecenyl acetate) were entrapped into a semisolid thermoset polymer matrix. Authors did not discribe the formulation agents yet.

References:

1. Peppas N.A. and Romanos P.V., Environmental cracking of long-term antifouling controlled release systems, Proceed. Inter. Symp. Control Bioact. Mater. (PISCBM), 15,(1988), Controlled Release Society,Inc. (CRSI)

2. Levy R., Nichlos M.A. and Miller T.W., Control of immature mosquitoes with a single-, joint-, or multi-action polymer-base insecticide delivery system, PISCBM, 15, (1988), CRSI (see No 1).

3. Levy R., Nichlos J.A., Hornby J.A. and Miller T.W., Controlled release of mosquito larvicides and pupicides from a crosslinked polyacrylamide CULIGEL SP superabsorbent polymer matrix, PISCBM 16, (1989), CRSI.

4. Levy R., Nichlos M.A. and Miller T.W., Controlled release of ABATE 4-E from CULIGEL crosslinked polyacrylamide granules to control semipermanent-and permanent- water mosquitoes, PISCBM, 17, (1990), CRSI

5. Seng Y.C. and Fong S.F.,Studies on the use of natural rubber latex for coating of fertilisers, PISCBM, 15, (1988), CRSI.

6. Zsifkovits W. and Gruning B., Studies on microencapsulated pesticides made by encapsulation with organosilicon compounds, PISCRBM, 15, (1988), CRSI.

7. Tsuji K., Tsuda S., Ohtsubo T. and Takeda H. Microencapsulation of pesticide-particle design and biological characteristic, PISCRBM,15, (1988), CRSI,292-293.

8. El-leithy E., Kassam M., Akbarieh M. and Tavashi R., Controlled release formulations of niclosamide as molluscicide for focal control of Schistosomiasis snails, PISCRBM, 15, (1988), CRSI, 346-347.

9. Jamil F.F., Quershi M.J., Haq A., Bashir N. and Naqvi S.H.M. Effectiveness of the controlled-release cabofuran formulation for pest control in cotton using isotope techniques under pot and field conditions, PISCRBM, 17, (1990), 59-60.

11. Herbig S.M., Smith K.L., Banfield M.G. and Ackers S., Diazinon-releasing membrane-based cattle eartags, PISCRBM, 15, (1988), 228-229.

12. Bohm H., Friend D. and Tompkins G., Encapsulted microbial insecticides with enhanced environmental protection, PISCRBM, 15, (1988) CRSI, 230.

13. Schreiber M.M., Wing R.E., Shasha B.S. and White M.D., Bioactivity of controlled release formulating of herbicides in starch encapsulated granules, PISCRBM, 15, (1988), CRSI, 223-224.

14. Trimnell D. and Shasha B.S., Controlled release formulations of atrazine for potential reduction of groundwater pollution, PISCRBM, 16, (1989), 275.

14a. Hall F.R., Reed J.P. and Trimnell D., Preemergence applications of herbicides encapsulated in starch for overcoming accelerated thiocarbamate degradation, PISCRBM, 16, (1989), 424-425.

15. Tocker S. , Self-microencapsulating pesticide compositions, PISCRBM, 15, (1988), 50-51.

16. Keneipp L.A., Korowin K.A., Brannon M.L. and Peppas N.A., Delivery of selected principal essential oils used in flavoring,PISCRBM, 15, (1988), CRSI, 89-90.

17. Wienen W.J., Tenbarge F.L. and Friedman R.B., Encapsulation and controlled release of flavors by corn starches, PISCRBM, 16, (1989), 283.

18. Belcher W.R. and Crainich V.A., Novel delivery systems for insect control, PISCRBM, 16, (1989), CRSI, 285.

19. Wilkins R.M., Wechakit D. and Okello-Ekochu E., Controlled release of insect antifeedants, PISCRBM, 16, (1989), CRSI, 267-268.

20. Herbig S.M., Smith K.L. and Banfield M.G., Porous beads for controlled release of agrichemicals, PISCRBM, 16, (1989), CRSI, 261-262.

21. Haslbeck E.G., Loeb G.I. and Mihm J.W., Microencapsulation of biocides for use in antifouling coatings, PISCRBM, 16, (1989), CRSI, 273-274.

22. Burton F.G., Cataldo D.A., Voris P.V., Skiens W.E., Griggs R.D., Decker O.D., Adriano D.C. and Murphy C.E., Field validation and performance specifications of a long-term controlled-release herbicide delivery system for multiple-year control of root growth, PISCRBM, 16, (1989), CRSI, 277-278.

23. Kawada H., Tsuda S., Ohtsubo T., Shinjo G. and Tsuji K., Fenitrothion microcapsule for cockroach control, PISCRBM, 16, (1989), CRSI, 441-442.

24. Wing R.E., Cornstarch encapsulated herbicides show potential to reduce groundwater contamination , PISCRBM, 16, (1989), CRSI, 430-431.

25. Potter R.C., Gupta K.L., Reierson D.A. and Rust M.K., Extended efficacy for synergized pyrethrins via a novel delivery system, PISCRDM, 16, (1989), 271-272.

26. Hussain M., Perschke H. and Kutscher R., An internationally coordinated research programme on the study of controlled-release pesticides using nuclear techniques, PISCRDM, 16, (1989), 269-270.

27. Szejtli JL., Formulation of insecticides with cyclodextrins, 7th Symposium IUPAC, Hamburg, FRG,(1990)

28. Szejtli J., Cyclodextrins in Pesticides, Starch/ Starke 37, (1985),11, 382-386.

29. Gottneid D.J. and Freidman R.B., Cycloedextrin-containing polymers as agents for controlled release, PISCRBM, 16, (1989), 422-423.

30. Schacht E., Steurbaut W. and De Smet G., A simple pesticide dosage form for application in hydroculture, PISCRBM, 16, (1989), CRSI, 265-266.

31. Hargrove G.L. and Francis J.A., Controlled release of plant nutrients via osmotic pump : A commercial reality, PISCRBM, 16, (1989), CRSI, 28,-29.

32. Murphy M.A., O'Donnell P.B., Coffin M.D., Fineg J. and McGinity J.W., Applications of biodegradable aqueous latex dispersions to controlled release fertilizers technology, PISCRBM, 17, (1990), 144-145.

33. Stewart R.F., Greene C.L. and Bhaskar R.K., Temperature activated controlled release of biologically active agents by side chain crystalline polymer materials, PISCRBM, 17, (1990),CRSI, 172-173.

34. Ramdas P.K. and Khetan S.K., A self-spreading formulation for the control of surface feeding / inhabiting aquatic pests, 7th ymposium IUPAC Proceeding, (1990), 59.

35. den Ottelander D., Succinoglycan: A new structuring agent for water-based agrochemical formulations, 7th Symposium IUPAC Proceeding, 1990, 69.

36. Mulqueen P.J. and Spicer A.R., New seed coating technology, 7th Sumposium IUPAC Proceeding, (1990), 90.

37. Lubosch J., A slow release system for seed-treatment composed of a network from hydrogen bonds, 7th Symposium IUPAC Proceeding, (1990), 94.

38. Ohtsubo T., Tsuda S. and Tsuji K., Theoretical study on physical factors of fenitrothion microcapsules influencing the physical strength, 7th Symposium IUPAC Proceeding, (1990), 86.

39. Chiba K., Yonemura S. and Noguchi T., Surface modification of pesticide technicals by dry blending method and its applications to controlled release formulations, 7th Symposium IUPAC Proceeding, (1990), 87.

40. Vollner L., Agrochemical formulations for improved efficacy and reduced environmental impacts : Slow release formulations with natural polymers, 7th Symposium IUPAC, Hambur, FRG, (1990), 80.

41. Brown D.J., Bird N.R. and Marrs G.J., Bioefficacy improvement by the microencapsulation of an exploratory fungicide and insecticide, 7th Symposium IUPAC Proceeding, (1990), 81.

42. Scher H.B., Microencapsulation of pesticides by in-situ interfacial conensation polymerization: Biological and application properties, 7th Symposium IUPAC Proceeding, (1990), 82.

43. Szente L., Formulation of insecticides with cyclodextrins, 7th SymposiumIUPAC, Hamburg, FRG,(1990)

44. Kawada H., Ohtsubo T., Shinjo G., Tsudo S., Abe Y. and Tsuji K., d-Cyphenothrin microapsule for cockroach control, 7th SymposiumIUPAC Proceeding, (1990), 93.

45. Cork A, Hall D.R., Mullings J.L. and Jones O.T., A new PVC resin formulation for controlled release of insect pheromones, PISCRBM, 16, (1989), CRSI,9-10.

46. Zhenya Z., Yeging K., Ruiyi Z. and Deren Z., Controlled release of sex pheromone from acrylic copolymer matrix, PISCRBM, 16, (1989), CRSI, 432-433.

47. Jones O. T., The development of a controlled release formulation of the olive fly (Dacus oleae) pheromone which is suitable for lureand kill treatments, PISCRBM, 16, (1989), CRSI, 241-242.

48. Brown D.F. and Howell J.F., Field performance of a new type of pheromone dispenser for disruption of mating of codling moths inapples orchards, PISCRBM, 16, (1989), CRSI, 243-244.

49. Emara L.H., Yehia A.A., Sidky M., Abdelbary A., Kassem M., Tawashi R., Controlled release ethanolamzine salt from elastomeric matrices, PISCRBM, 17, (1990), CRSI, 263-264.

50. Leonhardt B.A., Schwalbe C.P., Mastro V.C., Paszek E.C. and DeVillbis E.D., Controlled-release formulations for dispensing the pheromone of the Gyspy Moth, PISCRBM, 16, (1989), CRSI, 249-250.

51. Leonhardt B.A., Mastro V.C., DeVillbis E.D., Paszek E.C., Harte E.M. and Schwalbe C.P., Comparison of commercial controlled-release dispensers for detection of Gyspi Moth population with its pheromone, PISCRBM, 17, (1990), CRSI, 146-147.

52. Weatherston I., Controlled-release formulations of pheromones, PISCRBM, 17, (1990), CRSI, 55-56.

53. Staten R.T., Flint H.M., Miller E., Weddle D. and Yamamoto A., Changing stratedies and technology for Pink Bollworm detection and control systems with pheromone, PISCRBM, 16, (1989), CRSI, 247-248.

54. Weiss L.L. and Hastings J.B., Biological and chemical analyses of polymer entrapped pheromones for the mating disruption of the Grape Berry Moth, PISCRBM, 16, (1989), CRSI, 244-246.

Address List of Authors

1. School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, U.S.A.

2. Lee County Mosquito Control District, Post Office Box 06005, Fort Myers, Florida 33906.

3. As above

4. As above

5. Rubber Research Institute of Malaysia, P.O.Box 10150, 50208 Kuala Lumpur, Malaysia.

6.F. Joh. Kwia Gesellschaft m.b.H., A-2100 Leobendorf, Austria.

7.Pesticides Research Laboratory, Takarazuka Research Centre, Sumitomo Chemical Co. Ltd., Konohanaku, Osaka 554 Japan.

8. National Research Center, Cairo, Egypt and faculty of Pharmacy, University of Montreal, Canada.

9. Nuclear Institute for Agricultural & Biology, P.O.Box 128,Faislabad, Pakistan.

10. As above

11.Bend Research, Inc. Bend, Oregon 97701.

12. Lim Technology Laboratories, Inc. Richmond,VA 23219, USDA, Beltsville, MD 20705, USA.

13. USDA-ARS, Department of Botany and Plant Pathology, Purdue University, West Lafayette, IN 47907.

14. Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agricultural, Peoria, Illinois 61604

14 a. Laboratory for Pest Control Application Technology, The Ohio State University, Wooster, OH 44691.

15. E.I.duPont de NeMours & Co., Inc., Agricultural Products Department, Expertimental Station, Wilmington, DE 19898.

16. School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907, USA.

17. American Maize-Products Company, Hammond, IN 46320-1094.

18.CDS Inc., Dayton, OH, USA, 45459.

19. Department of Agricultural and Environmental Science, Newcastle University, Newcastle upon Tyne NE1 7RU, U.K..

20. Bend Research, Inc., Bend, Oregon 97701.

21. David Taylor Research Center, Code 2841, Annapolis, MD 21402.

22. Battelle, 505 King Avenue, Columbus, OH 43201.

23. Agricultural Science Research Laboratory, Takarazuka Research Center, Sumitomo Chemical Co. Ltd., Takarazuka, Hyogo 665, Japan.

24. Northern Regional Research Center, Agricultural Research Service-USDA, Peoria, IL 61604.

25. Basic Bio Systems, Inc., 2837 Ft.Missoula Rd., Missoula, MT 59801.

26. Agrochemicals Unit, FAO/IAEA Programme, International Atomic Energy Agency,A-2444 Seibersdorf, Austria.

28. Biochem. Res. Laboratory of Chinoin Pharm.-Chem. Works, Endrodi S.u. 38/40, S-1026 Budapost ,Hungary.

29.American Maize-Products Co., Hammond, IN 46320-1094, U.S.A..

30. Laboratory of Organic Chemistry, State University of Ghent, Belgium.

31. Sierra Chemical Company, Milpitas, CA 95035.

32. College of Pharmacy, University of Texas at Austin, TX 78712, USA

33. Landec Labs, Inc. Menlo Park, CA, USA

34. Pesticide Development Centre, Udyog Vihar, Gurgaon-122 016, India

35. International Bio-Synthetics B.V., Komvest 43, 8000 Brugge, Belgium

36. Dow Chemical Company Limited, Letcombe Regis, Wantage, Oxfordshire, OX12 9JT, England

37. Bayer AG, D-4019 Monheim, Germany

38. Agricult. Science Res. Laboratory, Takarazuka Res. Center, Sumitomo Chemical Co., Ltd., Taketsukasa Takarukaza 65, Japan

39. Central Res. Lab., Hokko Chemical Industry Co., Ltd., 2165 Toda, Atsugi, Kanagawa 243, Japan

40. Forschungszentrum fuer Gesundheit und Umwelt, GSF, Muenchen, Ingolstaedter Landstrasse 1, D-8042 Neuherberg, Germany

41. ICI Agrochemicals, Jealotts Hill Res. Stat., Bracknell, Berks. RG12 6EY, U.K.

42. ICI Agricultural Products, Western Research Center, 1200 South 47th Street, Richmond, CA 94804, USA.

43. CYCLOLAB, Cyclodextrin Research and Development Laboratory, Budapest, Endrodi S. 38/40, Hungary.

44. Agricultural Science Research Laboratory, Takarazuka Research Center, Sumitomo Chemical Co.Ltd., Takarazuka, Hyogo 665, Japan.

45. ODNRI, Central Avenue, Chatham Maritime, Chatham, Kent ME4 4TE, England.

46. East China University of Chemical Technology, Shanghai, P.R.China.

47. Biological Control Systems Ltd., Treforest Industrial Estate, Pontypridd, Mid Glamorgan, CF37 5SU, UK.

48. U.S. Department of Agricultural, Agricultural Research Service, Yakima, Washington 98902, U.S.A..

49. National Research Centre, Dokki, Cairo, Egypt.

50. Agricultural Research Service, US Department of Agriculture, BARC-West, Beltsville, Maryland 20705.

51. U.S. Dept.of Agriculture, Agricultural Research Service, Beltsville, Maryland 20705.

52. Technology Services Group, 1625K Street, N.W. Washigton D.C. 20006, U.S.A..

53. USDA-APHIS, Phoenix, Arizona 85040.

54. AgriSense, Fresno, CA 9372 USA.

March 1991

Project Proposal to the Government of Germany

1.1

Title:

Development of New Pesticide Formulations (Controlled Release)

1.2

Objectives

- To develop and adapt new formulation techniques, especilly for tropical and sub-tropical applications
- To transfer laboratory and small scale technology to pilot-plant scale technology and to field applications,

1.3

Location of activities:

Pesticides Development Centre (PDC), Udyong Vihar, Gurgaon-122 016, India, in cooperation with the

Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi-110 012, India

and

Forschungszentrum fuer Gesundheit und Umwelt (GSF), Muenchen, 8042 Neuherberg, Germany

1.4

Duration:

3 to 5 years

The first 2 years will be a pilot phase with reviewing of progress by a steering committee, participating of three representatieves of both countiries at the end of the second year. 3rd and up to 5th years will be used for finalization of work.

1.5

Beginning:

Middle of 1991

1.6

Budget:

First year in TDM (thousand US $) :

	PDC		GSF	
Personnel costs				
scientists	40		90	
assisstants	-		45	
engineers	20		-	
Supply	30		10	
Training	25		-	
Literature	4		2	
Travel	15		15	
Sub- Total	134	(90)	162	(108)
Total TDM	**296**	**(198)**		

5 years in TDM :

1991/92	*92/93*	*93/94*	*94/95*	*95/96*
296	296	241	241	241

Total: **1,315 (876)**

1.7

Benefits:

- minimizing industrial toxicants in the environment and other non-biodegradable additives
- utilizing natural polymers (e.g. agricultural wastes)
- enhance of biological activity of compounds applied
- extention of international efforts in environmental protection

2.1

Background information:

2.1.1: General

One of the major deficiences in current pesticide technology is that pest control may be very temporary even with the best pesticides available. Pesticides may often be applied in excessive amounts to maintain the necessary levels of activity during the time period for which pest control is most urgently needed.

Losses to the environment and from environmental actions prevent most of the pesticide from reaching its biochemical site of action in target species.

New formulations technology can be highly effective in increasing pesticidal effectiveness. A few of the parameters of pesticide efficiency that can be improved with better formulations include volatility, water solubility, photodecomposition, and poor penetration into target species. This field is in its infancy, and research on formulation needs to be greatly expanded, especially in controlled release (CR) technology.

2.1.2 : Pesticied Development Centre, (PDC), Udyog Vihar, Gurgaon

The Pesticide Development Centre (PDC) is the country project of India, supported by UN Development Programme (UNDP) and exicuted by UNIDO to deal with the aspects related to R+D in pesticide formulations to promote the newer and safer formulations and also in using locally available raw materials. In addition, the centre looks into the development of bio- and botanical pesticies with the view of reducing high amounts of industrial pesticides, thus protecting the environment from undesired side effects.

The centre also serves as the Technical Coordinator Unit in Pesticide Formulation Technology and Quality Control for the UNIDO supported Regional Network on Pesticides for Asia and the Pacific (RENPAP).

The centre developed, since it became fully operational in 1985 the following newer types of formulations:

- a suspension concentrate of carboxin
- water dispersible granules of isoproturon
- a concentrate emulsion of butachlor
- a microemulsion of butachlor
- controlled release granucls of basalin
- a self-spreading oil formulation of *Bacillus sphaericus* and benzene hexachloride.

The formulation laboratory of the centre is well equipped, having following main instruments:

- Fluidised Bed Granulation System, Aeromatic
- Erweka All Purpose Equipment with Pelletizer and Coating Pan, Erweka Apparatebau GmbH
- Climatic Chamber, Heraeus
- Spray Drier, Bucchi
- Spinnig Drop Tensiometer, Kruess

- Extruded Type Granulator, Fauji-Paaudal
- Laser Based Particle Size Analyzer, Malvern
- Powder Characteristics Tester, Hosokawa
- Colloid Mill, Schuett
- Fluid Energy Mill
- Digital Viscometer, Brookfield
- Dynomill, Willy A. Backhofen

The Pilot Plant of the centre is equipped as well as the formulation laboratory having about 25 units for larger quantities of preparations.

The center has experimental fields of about 20 ha.

2.1.3 : The governmental, research centre ***Forschungszentrum fuer Gesundheit und Umwelt (GSF), Muenchen***, (former name: Gesellschaft fuer Strahlen und Umweltforschung, Muenchen) Germany within its widespread efforts to protect humans and the environment from negative effects of industrial chemicals, has broad know how in pesticides behaviour in the enviroment, in analytical chemical techniques, and within the scope described, especially in conrolled release pesticide formulation research.

To extend experimental facilities for both sides and to bring together research and their results for utilization in the field of applied environmental protection, this project represents a relevant contribution from both sides.

3.1

Implementation:

After aproval of the project, a detailled working plan will be developed by the steering committee.

After selection of problem areas and pesticides, the GSF laboratory in Germany carries out experiments adapting published formulation methods and developing new formulations. Simulated environmental tests and small scal field experiments will follow.

The best promising formulation will be selected for pilot plant experiments and transfered to PDC.

The GSF laboratory will also assisst in analytical chemical procedures for examinig field samples like grains, vegetables, soil, ground water etc..

PDC will prepare new formulations on his own and take over the recommended methods for experimental field tests. Based on the promising results, PDC will transfer the method to the pilot plant unit and will organize large scale field experiments in India.

After succesful examination, the formulation will be transfered (patented) to the pesticide formulating industry.

The cooperation will be supported by exchange of scientists and by annual review meetings. The GSF laboratory offers trainig facilities in this field to 1-2 fellows of PDC per year.

3.2

Possible application areas and chemicals:

Rice paddy	:	carbofuran, phorate
Cotton field	:	diazinon
Suspression of termites	:	lindane
Mosquito eradication	:	lindane, pyrethroids

Possible combination of insecticides with attractants and pheromones and sreening for natural pesticides will be included in the research work.

L.Vollner/P.K.Ramdas

GRANULAR FORMULATIONS

L. Vollner, UNIDO, Vienna

The prime purpose of formulation is the dilution of pesticide down to a level at which it will be toxic to the pest, but will not cause damage to desirable plants, fish, birds, animals, and natural habitats.

The forms which the products take upon delution include dust concentrates, wettable powders, water soluble powders and liquids, emulsifiable concentrates, flowable emulsion, flowable suspension concentrates and granular products.

Factors for the selection of the types of formulation

1. Purpose of application (insecticide?, herbicide?, fungicide?, etc.) , kind of application

2. Pest involved

3. Properties of chemical

4. Weather conditions

5. Availaibility of equipment

6. Environment/Economy

Granular Formulations (GR) meet many requirements,and devlopments of new proaucts have increased significantly during the last two decades.

Advantages of GR:

1. simple and safe handling during processing and application

2. practically no dusting during processing and application

3. no drifting during application

4. easy to transport and good storage properties

5. reduced volume due to high bulk density

6. possible combination with fertilizers

7. good flow and dosing properties

Some applications areas:

1. use as emergence soil herbicides

2. use against soil pests

3. treatment of water

4. use in forestry

5. application by air plane

6. possible long time effects (controlled release)

Characteristics of GR:

In case of GR, the pesticide diluting agent is an inert solid material, which is called "carrier". This inert material should not have any pesticidal activity and of course should not have any degradating influence to the a.i.

Inert materials can be divided into three general categories:

inorganic materials	botanicals	synthetics
clays	maize cab	inorganic
carbonates	nut shells	organic
sulfates		
oxides etc.		

A granular inert has a limited size range of 8 to 80 mesh.

For any given granular material at least 90% by weight of the product must be within the designated mesh range (e.g. 16/30), and the remaining 10% may be distributed on either end of the designated mesh range.

There are many factors which may influence the properties, and thereby the quality of inerts (carriers):

1. sorptive capacity

2. flowability

3. size distribution

4. bulk density

5. number of particles per unit weight

6. water disintegrability

7. dry hardness

8. dustiness

The concentrations of a.i. in these products range from 2 to 20% (40%), with the most common concentration within 5 to 20%.

Choice of concentration depends on many factors including

1. the nature of pest to be controlled

2. rate of application necessary to give control

3. ability of equipment for accurate appliance of GR

4. environmental safety/economics of competitive products

Methods of preparation:

The most common method of producing granular pesticidal products is direct impregnation. In the last 20 years efforts have been made by pesticide manufacturers to develop more effective, but less toxic pesticides. Many of these new chemicals have, however, different physical and chemical properties that do not allow the use of the direct impregnation method. Efforts have therefore been made to develop new formulation techniques, some of which have become commercial. Some of these methods are listed below:

1. Direct impregnation

2. Suspension impregnation

3. Sticking techniques

4. Post drying techniques

5. Vacuum evaporation

6. Melt-on technique

7. Extrusion technique

8. Agglomeration technique

Conclusion

To increase the effectiveness of pesticides and to minimize environmental pollutions problems, newer formulations and application techniques are being introduced.

Granular or encapsulated formulations are necessary for highly toxic chemicals like phorate, alicarb etc.

In case of encapsulated formulations attempts should be made to use biodegradable polymer matrix, in order to minimize additional contamination.

In India, work on introducing such specialized formulations has to be accelerated with the sole objective of environmental safety and better pest control.

References:

1) W.Van Valkenburg
Pesticide Formulations, Marcel Dekker Inc., New York, 1973

2) U.K. Srivastava, N.T. Patel
Pesticides Industry in India, Indian Institute of Management, Ahmedabad, 1990

UNIDO COMMENTS

The report gives a summary of the work carried out in the Pesticide Development Centre on Controlled Release Formulation Technology. This technology has already been well tested for its success but less commercialized because the industries are not putting enough resources into the development work and also in getting the products registered. The Pesticide Development Centre is in an unique position to develop such environmental friendly technology in India and also in the Asia region. The author has already given some future projects to be handled by the centre and this should be taken up by the project authorities in collaboration with the Ministry of Agriculture.