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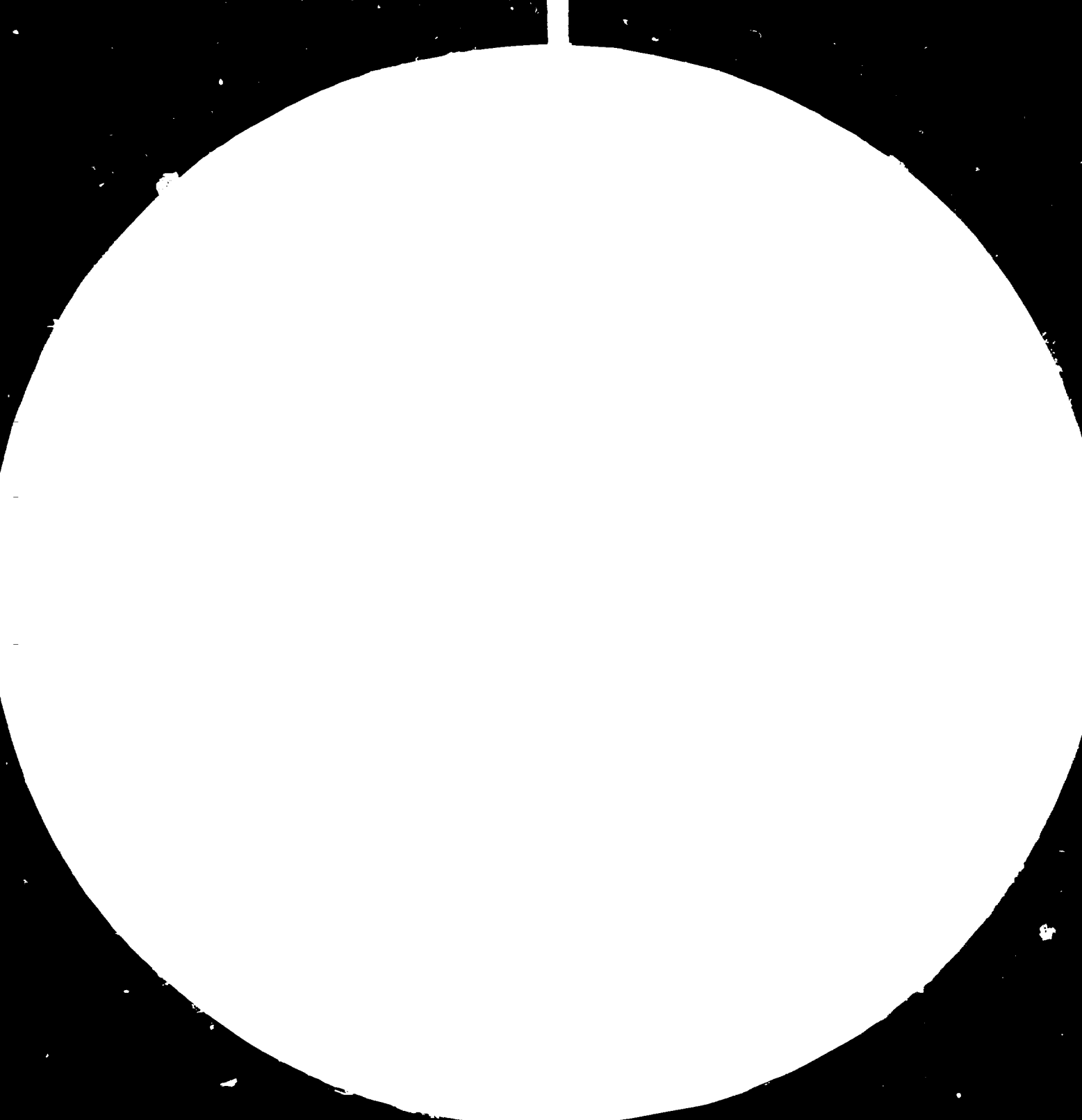

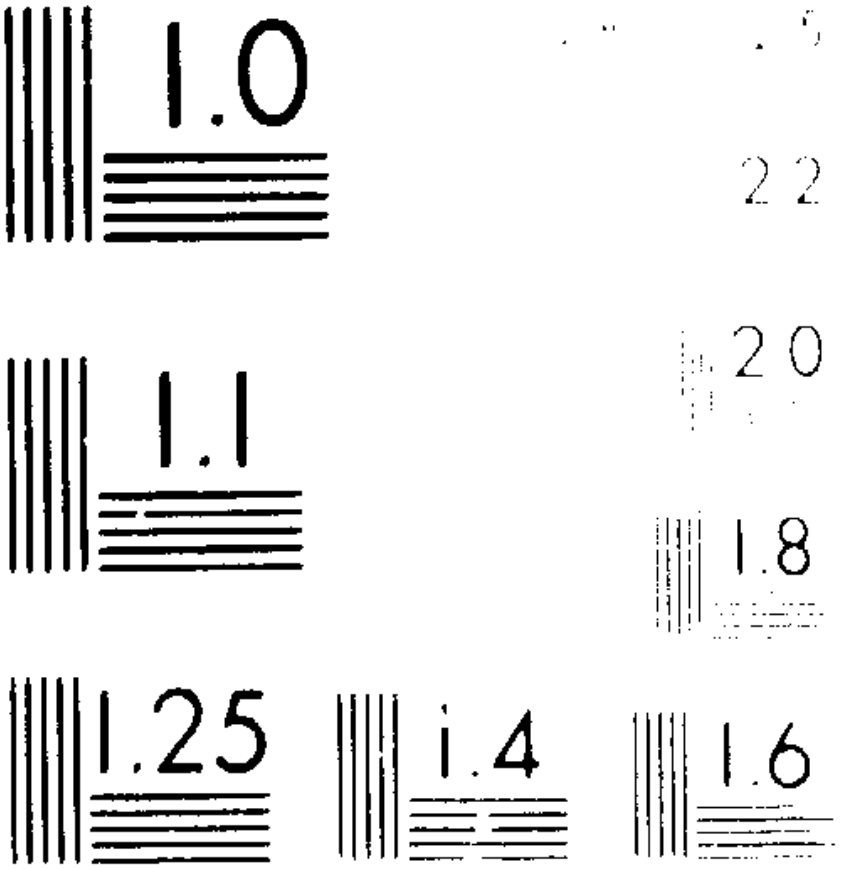
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DP/ID/SER.B/377
28 February 1983
English

BIOSCIENCE AND ENGINEERING

DP/IND/80/003

INDIA

Terminal report*

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 Dora K. Hayes,
expert on Controlled Release Project

United Nations Industrial Development Organization
Vienna

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Abbreviations

1. CP - Controlled Release
2. CTA - Chief Technical Advisor
3. DS ratio - Ratio of subtitution of the hydroxyl groups of the glucopyranosyl units of starch. A theoretical maximum DS is 3.0, since each glucopyranosyl unit has 3 hydroxyl groups.
4. ISI - Indian Standards Institution
5. NCL - National Chemical Laboratory
6. UNDP - United Nations Development Programme
7 UNIDO - United Nations Industrial Development Organization

ABSTRACT

The Controlled Release (CR) portion of the project, Bioscience and Engineering, DP/IND/80/003 India was reviewed from October 22 through October 29, 1982. The developmental objective of the project is to strengthen the expertise and research facilities available at the National Chemical laboratory (NCL) in biotechnology for the utilization of cellulosic resources and in the technology of controlled release pesticide formulation. The project has five objectives; the objective of this mission was to review the following objectives in detail: (No. 4) development of processes for production of controlled release pesticides by (a) micro-encapsulation and (b) a monolithic matrix; (No. 5(c)) training in research techniques in the relevant areas; (No. 6) training abroad of NCL scientists in relevant areas of specialization. Parts (a) and (b) of objective 5 are related to establishment of NCL as a center of excellence in technology of controlled release and are implicit in the examination of the concepts and substance of the project. The expert also visited scientists working on the biotechnology aspects to determine the potentials for interaction and cooperation among all scientists working on the project.

The timetable provided in the initial project document has been followed for the area reviewed in depth, that of Controlled Release (CR) of pesticides. The two major aspects of CR investigated were "Controlled Release Mosquito Larvicide" and "Microencapsulation". The important finding in the first aspect was that when a 2.5 cm square, 0.1-0.2 in thick, of a formulation of 5% abate in crosslinked natural latex was anchored about 10 cm below the surface of a 3 l jar containing 2.8 l of water, after 3 days the concentration of the pesticide was 0.5 ppm (100 times that required to kill larvae of the mosquito, Anopheles spp.). This was maintained for

9 months. Natural polymerized latex (rubber) possesses the environmentally desirable feature of being biodegradable.

An important finding in the second aspect was that when 0.1 g of a matrix of hydrogen peroxide cross-linked starch xanthate (with one-tenth of the hydroxyl groups substituted (degree of substitution or DS - 0.3)), containing 25% carbofuran (a water soluble systemic insecticide)) was mixed with one liter of water under static conditions, 80% of the pesticide was released in 17 days. Without encapsulation, 80% of the pesticides was solubilized (lost) in 8 days. A desirable result would be extension of release time to 60 days. Other pesticide - starch xanthate combinations should also be considered.

NCL should undertake small and large-scale field studies of the efficacy of 5% abate - natural latex formulations against mosquito larvae in standing water such as municipal water supplies. Simultaneously and in close consultation with UNIDO expert, N. F. Cardarelli, NCL should proceed to develop prior to September 1984 the prototype of the latex squares and the processing procedures necessary for adoption by industry in India such as Hindustani Pesticides Ltd.

It was further recommended that both fundamental and empirical approaches be taken to determine in a systematic manner factors which would extend the release time of the starch-xanthate CR formulations.

INTRODUCTION

Project Background

The project, Bioscience and Engineering, DP/IND/80/003 was requested because earlier projects in NCL had suggested that production of microbial biomass product, saccharification of cellulose to glucose and production of CR pesticides were desirable for India and were capable of being brought to the pilot plant stage during the 5-year span of the project. In particular, reduction in the labour costs control of the larvae of mosquito genera (Anopheles) that are vectors for malaria and that breed in standing water used for minicipal water supplies and of control of the rice stem borer by using only one application per year or per crop cycle were given priority. Early interest in CR formulation for water hyacinth control has abated, due to interest in this aquatic plant as a source of biomass. The safety of personnel handling pesticide is enhanced by CR formulation.

Support for preliminary CR funding was obtained from NCL funds. Initial studies suggested that a CR formulation for release of abate over an extended time-span was possible and that a starch-xanthate matrix could be prepared. A CR formulation of 2,4-D on sawdust was prepared prior to 1981 to control parthenium, a weed which competes for grass-land. Pilot plant scale preparations of this product have shown promise in field tests.

Official Arrangements

The assistance was requested early in 1980; in June 1981 the project was revised and submitted as a project of the Government of India for obtaining technical assistance from the UNDP through UNIDO. It was approved by UNIDO and implemented in September 1981. The project will run through September 1981 to August 1986.

Contributions

The funds for CR equal about one-fourth of the $1,272,500 allocated by UNDP and the Rs.7,542,200 allocated by the government of India.

The original objectives of the project were:

1. Development of a fermentation process for the production of microbial biomass product from cellulose.
2. Development of a process for enzymatic hydrolysis of cellulose to glucose.
3. Development of a process for the conversion of glucose to ethanol based upon immobilized microbial whole cells.
4. Development of processes for the production of controlled release pesticides by microencapsulation and monolithic matrix binding.
5. Establishment of NCL as a centre for Research and Development in the areas of biotechnology of cellulose utilization and controlled release pesticide formulations, providing services and disseminating scientific and technical information, training in research techniques in the relevant areas, training abroad of NCL scientists in relevant areas of specialization.

These objectives have not been substantially revised, except that CR technology for control of water hyacinth has been given a lower priority, since this plant may have uses as a source of biomass. The emphasis on the starch xanthate and monolithic matrix has been increased and because of cost, work with polyamide, polyurea and polyvinyl alcohol matrices has been given a lower priority.

The objective of the present mission reported herein, consists of a review of the fourth objective and of the parts of the fifth objective dealing with the present status of the senior scientists and training programme of the personnel involved in the CR portion of the project and of the programme for visits to NCL by experts in CR at the suggestion of the CTA; brief discussions

were held with some key personnel involved in implementation of the first three objectives.

This report will cover the work from the initiation of the project, September 1981 to October 31, 1982.

Training

No training in CR was obtained using project funds during the first 13 months of the project; training and visits by experts have been planned for the next 3 years (see Annexure 1).

RECOMMENDATIONS

1a. Undertake small and large scale field studies on the effects of the 5% abate-latex formulation against mosquito larvae in bodies of standing water such as municipal water supplies; include in the tests measurements of the effects of sunlight. NCL may have instrumentation to determine radiance at the surface of the water and possibly at the level of the latex piece as well.

b. Simultaneously and in close consultation with UNIDO expert N. F. Cardarelli develop prior to September 1984 the proto-type of the latex rubber abate pieces.

2. Develop quality control criteria for the abate latex formulation.

2a. Continue in a systematic fashion to prepare large number of starch-xathate formulations containing carbofuran and to evaluate release rates of these formulations suggested variables are: DS ratio, double encapsulation, particle size, oxidizing agent, (other alkali metal hydroxide), type of starch, addition of latex, possible "other" crosslinking agents.

The goal of this work is to decrease the rate at which carbofuran is released from starch-xathate so that this pesticide formulation can be applied only once to a given rice crop.

b. Evaluate release rates of carbofuran from starch-xanthate formulations

in water, in soil and in actual small paddy fields out-of-doors.

3. Determine structure and properties of the starch-xanthate preparations. This should include scanning electron microscope studies of the surfaces of various formulations (and possibly electron microscopy of thin sections), light microscopy. Develop information on relevant physico-chemical parameters (kinetics etc.) to be correlated insofar as possible with empirical data obtained in the laboratory and in the field.

4. Develop a bioassay system for the starch xanthate pesticide formulations.

5. Reexamine available additives to starch-xanthate which will decrease the release rate of the active ingredients (Bentonite was tested, but did not decrease the release rate).

6. Evaluate other pesticides in slow release formulations using starch-xanthate as the matrix. These might include abate and some other pesticides.

7. Expedite the visit of R. B. Mitra to world experts, facilitate attendance and presentation of paper by senior scientists at scientific meetings such as the Controlled Release Symposium in July at San Francisco, California, USA, initiate training abroad for scientists and encourage visits by senior scientists and trainees to other CR facilities when abroad (see annexure 1).

8. Hold group discussions as often as possible including representatives from the divisions involved in the research. Especially useful will be exchanges among the various disciplines at an early stage, so that the problems of each can be appreciated by the others.

9. Contact the experts in the interim between visits if these experts are willing to assist by furnishing information and advice to scientists involved in the project; furnish summaries and progress reports in advance of review visits to these individuals if the mechanisms utilized to do so are consistent with UNIDO policy.

REPORT ON PROGRESS

I. PRESENT STATUS OF THE PROJECT

Investigations carried out in attainment of goals 4 and 5 (see p. 5) were discussed individually with members of the Polymer Science and Organic Synthesis Divisions. A meeting was held with members of these groups plus representatives of the Physical Chemistry and Chemical Engineering Divisions (see Annexure 2) and the discussions are summarized in Annexure 3).

II. PROGRESS ON CONTROLLED RELEASE MOSQUITO LARVICIDE (LATEX-ABATE FORMULATION

Latex (60% centrifuged) obtained from rubber estates from Kerala was analyzed for total solids content and alkalinity per ISI specifications* and deammoniation experiments were carried out.

Master batches of natural rubber latex containing 5, 8 and 10% of abate (200 g batch) were prepared as a starting material. Using the 5% formulation 12 formulations were processed using the conventional chemicals** plus carbon black and vulcanized at 120°C and 2500 lb pressure for 15 min. Sheets were approximately 0.1-0.2 in thick. From these 12 samples 8 were tested for release rate of abate in water.

The results of the assays to date are summarized in Table 1 (Fig. 1, to be supplied). Samples prepared with 8 and 10% abate were not tested further, since the abate separated from the formulation during mastication/milling.

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* India Standard Methods of Test for Natural Rubber Latex. Part 1. Dry rubber content, total solids, coagulum content, viscosity sludge content, density, total alkalinity KOH number, mechanical stability, volatile fatty acid number, pH, total nitrogen, total copper, total iron, total manganese and total ash. IS: 3708 (Part I) - 1966, Indian Standards Institution, Manak Bhavan, 9 Bahadur Shah Zafar Marg, New Delhi 1, India.

** % Latex - 167 corresponds to 100 parts DRC, Abate - 5, Carbon black

In a second series of experiments the twelve 5% abate-latex formulations were prepared in sheets approximately 0.1-0.2" thick without vulcanization. From these 12 samples two batches were assayed for release rate in water.

Eight samples were selected from the 16 vulcanized and unvulcanized samples for bioassay.

During April-June 1982 six additional samples were selected for bioassay.

The bioassay was conducted by placing squares of the 5% abate formulation, 2.5 X 2.5 X 0.15 in, in 31 jars containing tap water. Weight of the formulation per jar was calculated so that if all the abate was released the concentration would be 1 ppm.

All of the chemical evaluations and bioassays that were underway will be terminated by November 5, except those with formulation 8.

Coir pith (coconut husk) was added to the latex-abate formulation and labelled 53100 (100 parts of coir pith to 100 parts of latex) and the release rate is being determined. To date, from formulation 8, 0.312 ppm has been released in a consistent manner over a 36 week span and is going on still.

No studies have been conducted to date out-of-doors but the following test of out-of-doors efficacy has been set up and will be initiated during the week of November 1, 1982.

Eight 50 l aquaria will be placed in a well drained sunny garden spot and filled with about 45 l water. The tanks will initially contain the following:

1. Tap water + formulation 8* (abate/latex)

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* Formulation 8: Latex -

Abate - 5 g/100

2. Tap water + 53100**

3. Sand, gravel, vegetation, fish + formulation 8

4. Sand, gravel, vegetation, fish + 53100

5. Tap water + abate - 5 ppm

6. Sand, gravel, vegetation, fish + formulation 8

7. Tap water + abate - 1 ppm

8. Biomass + abate - 1 ppm.

Latex will be anchored 2 in below the surface.

Actual field trials on stagnant water in Mula-Mutha, a reservoir for the Pune water supply and in septic tanks will be deferred until adequate data from the open air aquaria has been obtained.

Advice will be obtained on statistical validation of the test plan and test data from all trials. This is particularly important in the large scale trials, since excessive replications of these tests due to poor planning are costly and time consuming.

N. F. Cardarelli, who is due to visit NCL during November 1982, will be consulted on aspects of development to the pilot plant stage, such as feasibility, cost calculations, money-saving techniques, machinery required, public relations, scale-up problems, etc.

III. ENCAPSULATION

A. General

Controlled release formulations for insect control can have the advantages of increased safety for the user, reduced manpower costs since fewer application are required and sometimes reduced exposure of the environment to initial and/or total amounts of pesticide since the CR formulation makes possible use

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**53100 = Latex 167, Abate 5 and Coir Pith 100.

of lesser quantity of insecticide than if the product is not so treated. Several controlled release formulations have been examined since the project was initiated. These have included fenitrothion in polyurea capsules, and in polyamide capsules and carbofuran in polyvinyl alcohol matrices and a starch-xanthate matrix. The carbofuran in the starch-xanthate matrix is probably the most economical formulation since starch is readily available in India at relatively low cost. Emphasis in October 1982 was therefore on this CR formulation.

During the first year of the project polymer chemists, organic chemists, and entomologists made the primary contributions. However in September 1982, plans were made for increasing the involvement of chemical engineers and physical chemists in order to facilitate the transitions from the bench to the pre-pilot plant stage.

Problems have been encountered in these studies in obtaining "pure" carbofuran and sufficient quantities of dursban.

B. Starch-xathate-carbofuran formulation

Initial work on starch-xanthate-carbofuran matrices was carried out on a bench scale (10-15 g pesticide context) and release rates of these formulations was determined in distilled water spectrophotometrically. In these initial studies the DS ratio was 0.3 and the carbofuran was present at a concentration of 25-70% dry weight of formulation. Subsequently the preparation was scaled up to 100 g active ingredient.

In brief, the preparation method (according to B. Shasha) consists of mixing a starch solution (15% sludge in water of a local Indian starch) with sodium hydroxide (1.0 N) and carbon disulfide (0.43 M CS_2 per mole of starch (since 70% pf CS_2 reacts with starch, the actual moles reacted is 0.3)). The material is cooled in an ice water bath, then brought to room temperature

over 2 hr. The mixture is neutralized to pH 8, the carbofuran is added with agitation and the pH is brought to 5.0-6.0 with acetic acid. Then hydrogen peroxide (preferred because gas does not cause holes in the matrix) or sodium nitrite is added to produce disulfide cross-linking to a solid gel. The material is washed, dried, and ground to 5-30 mesh size in a mortar and pestle. In glassware maximum batch size is 50 g.

In order to scale-up the preparation and provide adequate agitation the 2 liter Waring Blender (which chills and heats) could be used. This equipment has not yet arrived. Also much needed is a 20-25 liter Sigma Blade Mixer.

Release rate studies have been conducted in water and in aqueous soil preparations in the laboratory at a concentration of .1 g (70% AI) formulation/ liter distilled water or with 1 g formulation (25% AI) per Kg soil. The soil is mixed with the formulation in a large column equipped with a stopcock and distilled water is added to a height of 1 in above the soil. The water is drained and replaced daily; alternatively static samples are prepared in which an individual preparation is required for each day so that no disturbance occurs until sampling time.

Using these techniques, with a carbofuran concentration of 25% based on dry weight, 80% of the carbofuran was released over 17 days.

In order to decrease the release rate double encapsulation, fillers, higher DS ratios, small changes in formulation composition or preparation techniques, various fillers and other cross-linking agents will be evaluated in turn. In addition possible technique for determining initial properties which relate to subsequent release rates will be evaluated. This will include some light and electron microscopy. In cooperation with physical chemists and chemical engineers, fundamental and practical characteristics important in determining release rate will be determined. A bioassay for efficacy on paddy

under actual use conditions will be developed.

C. Microencapsulation of fenitrothion in polyurea and polyamide matrices and preparation of carbofuran in polyvinyl alcohol.

These preparations are being studied in at the bench level and details of formulations and preparations will be considered in depth at the next review. The efficacy of these preparations has not been extensively assayed, either in distilled water or under simulated field conditions. The cost of the materials is greater than that for starch-xanthate-carbofuran formulations. Other advantages may be found which will lead to adoption of these formulations for agricultural use. The strategy for research on these materials is one of capability development rather than process development so that when needed, the foundations will be laid.

Annexure 1

PLANNED TRAVEL TRAINING AND VISITS BY EXPERTS IN CONTROLLED RELEASE, 1982-1984

Training

2 mo	R. N. Sharma, Entomologist Beltsville, Md., Fargo, ND, MRRL, USDA	1983
2 mo	Harish Narian	1984
3 mo	N. Amarnath, Beltsville, Akron, Oh, (Jaffe, Cardarelli)	1983
2 mo	P. G. Shukla	1983
2 mo	Mrs. P. P. Pawar	1984
2 mo	Dr. M. G. Kulkarni	1983

MEETING ATTENDANCE TRAINING

N. Rajagopalan
Controlled Release Symposium - July 1983
San Francisco, Calif., USA

D. Ragunath
Controlled Release Symposium - July 1983
San Francisco, Calif., USA

VISITS BY EXPERTS - 1983-84

1.	Baruch Shasha Starch-xanthate-pesticide CR	March 1983
2.	Howard Jaffe Poly-lactic/glycolic/caprolactone/ pesticide CR (soil, implants)	October 1983
3.	Danny Lewis	Between Oct-Dec 1983
4.	D. K. Hayes	January 1984
5.	N. F. Cardarelli or Alternate	Jan/Feb 1984
6.	Baruch Shasha	late 1984

Annexure 2

Scientists working on the Controlled Release Mosquito Larvicide Project

- 8-5-35456 from Polymer Science Division

D. Raghunath (Project Leader and Scientist E)

N. Amarnath (Scientist A)

Miss D. Bhatnagar (Graduate trainee who left in June 1982)

Microencapsulation Project 8-5-3456

1. N. Rajagopalan (Project Leader) (Scientist C)
2. Dr. Harishnarayan (Scientist A)
3. Mr. C. Bhaskar (SSA)
4. Mr. P. G. Shukla (SLA)

(Dr. N. D. Ghatge, Scientist F) 10% time

(Dr. R. M. Joshi, Scientist + E-1) 10% time

Collaboration with

1. Dr. R. A. Mashelkar, Head Chemical Engineering Division
2. Dr. M. G. Kulkarni, Polymer Engineering
3. Dr. A. P. B. Sinha, Head, Physical Chemistry Division
4. Dr. R. N. Sharma (Entomology) Organic Chemistry Division

Annexure 3

SUMMARY OF THE MEETING - OCTOBER 26, 1982

In attendance

1. Dr. M. G. Kulkarni, Scientist, Polymer Engr. Group
2. Dr. R. A. Mashelkar, Head, Chem. Engr. Dept. (Polymer Engineering)
3. Dr. A. P. B. Singh, Head, Physical Chemistry Division
4. Dr. R. B. Mitra, Organic Chemistry
5. Mr. N. Rajagopalan, Polymer Chemistry
6. Dr. R. N. Sharma, Entomology
7. Mr. D. Raghunath, Polymer Chemistry
8. Dr. Harish Narain, Polymer Chemistry
9. Dr. L. K. Doraiswamy, Director, NCL
10. Dr. D. K. Hayes, USDA, Beltsville, Md.

At this meeting the work carried out on CR at NCL was critiqued by attendees. Dr. Doraiswamy emphasized the opportunities for cooperation among the four divisions represented. During the next year this cooperation will be encouraged and increased over that during the first project year.

Figure 1 - Will be supplied when sent to D. K. Hayes

Figure 2 - Will be supplied when sent to D. K. Hayes