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

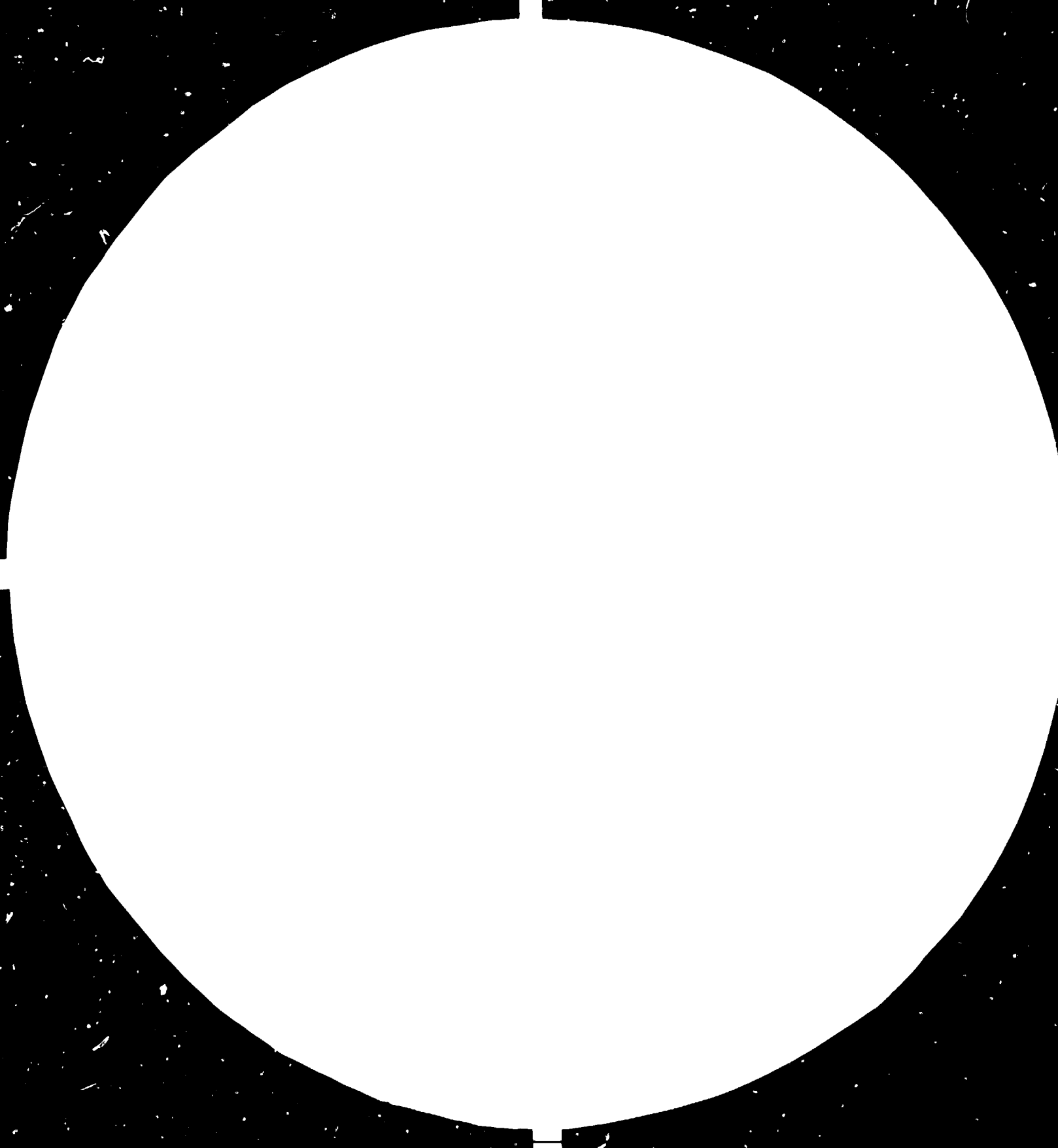
FAIR USE POLICY

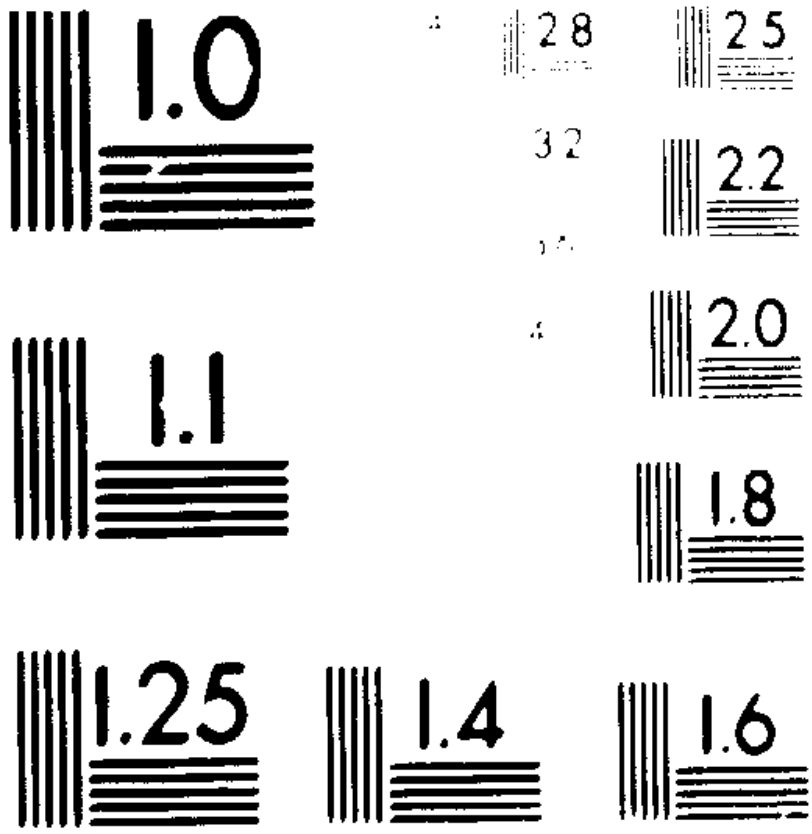
CONTACT

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





January 1984

RESTRICTED

ENGLISH

13214

India.

BIOSCIENCE AND ENGINEERING

DP/IND/80/003

INDIA

Technical Report*

Mission November 1983

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

Based on the work of Baruch S. Shasha
consultant on controlled release technology

United Nations Industrial Development Organization
Vienna

* This document has been reproduced without formal editing.

ABSTRACT

I reviewed program DP/IND/80/003 dealing with controlled release of pesticides. The main questions were whether the staff engaged in the program have access to tools needed, what progress was achieved so far and what one should expect in the forseeable future, and finally what improvements on operation can be suggested.

At the personnel level, in general the staff has done high quality research but I felt there are too many scientists assigned to the project. This observation became obvious when one considers the limitations in space and equipment. A director whose sole assignment is to coordinate and supervise the research at the local level is essential and can improve research output. At the know-how level there is a need to have access to the current patent literature. In this new field of controlled release most information can be found only within patents and not within the usual scientific books or journals. This point is very important because of the limited contact of the staff here with other laboratories outside India.

At the equipment level there is an urgent need for reliable mixing equipment that can handle enough material for large scale testings. I attribute, at least in part, results that cannot be reproduced due to poor mixing. After years of experience in this technology I found that proper mixing cannot be over-emphasized.

Progress was made mainly in the controlled release of Abate in mosquito larvicide formulations using monolithic matrices and in the controlled release of Carbofuran insecticide used extensively in rice paddies and encapsulated using the starch xanthide procedure. While testing is currently performed under field conditions for the monolithic system the testings for the controlled release formulation of Carbofuran is mostly under laboratory conditions. Both types showed significant improved persistency.

As for the foreseeable future (six months or less) one should expect large scale preparations and consistency of formulation of the insecticide Abate, distribution of the new formulation to qualified testing stations followed by analysis of data. A modified monolithic system using SBR latex for improved delivery and loading of active ingredient should be tried. As for the controlled release of Carbofuran, a large scale preparation and testing under field conditions should be expected in the near future. A modified encapsulation of the insecticide within the starch matrix should be made and tested. The improved techniques which were developed at the Northern Regional Research Center in Peoria, IL. was demonstrated to the staff at the National Chemical Laboratory in Pune.

INTRODUCTION

This project, Bioscience and Engineering DP/IND/80/003, was submitted by the Government of India. It was approved by UNDP in September 1981 to extend to August 1986 and deals with controlled release pesticide technologies.

Advantages of controlled release include less active agent and fewer applications, more effective control of the target organism, reduced toxicity to nontarget organisms, and reduced environmental pollution. Such systems are being developed and a few are being marketed boased on containment of the pesticide within either a polymer matrix or coating. Synthetic elastomers serve to control the release of antifouling agents in coatings for objects immersed in marine waters and for molluscicides. Insecticides incorporated in plastic strips provide slow release of the active agent over several weeks. An insecticide is now being sold in the form of microcapsules where a polyamide film surrounds the active agent.

Because of the diverse properties of hundreds of biologically active chemicals for which controlled release would be beneficial and because the environments into which the formulations would be placed vary so widely, considerable research is needed to optimize the numerous controlled release systems. Obviously, for the systems to be accepted on a broad scale, they must be both technically and economically feasible.

This is the third "review by expert" on this project dealing with controlled release of pesticides. The first review

was by Dr. Dora K. Hayes, USDA, Beltsville, MD 20705, USA dated 15 December 1982 and the second by Dr. Nate F. Cardarelli, University of Akron, Akron, CH, USA dated 23 February 1983. Among Dr. Hayes recommendations were: to conduct field studies of Abate-latex formulations, develop quality control criteria for these formulations, establish parameters of encapsulation of Carbofuran using starch xanthate formulations to determine release rates of active ingredient and evaluate other pesticides using starch xanthate as a matrix. Among Dr. Cardarelli's recommendations were: to move up the completion date for the Temephos(Abate)-natural rubber project to June 1985 and the Carbofuran project to December 1985, reformulate natural rubber latex with increased Temephos content, provide necessary equipment to the formulations group and entomology group and provide additional training to personnel. The purpose of my mission was to review pest research accomplishments relating to controlled release technologies at the National Chemical Laboratory (NCL), suggest analytical methods to evaluate new formulations, discuss with NCL scientific personnel current trends in this field, make recommendations on future lines of research, equipment needs, and training of personnel.

I. Report on Controlled Release of Carbofuran and Fenitrothion Systems.

by.Dr. R. Rajagopalan

Carbofuran is a broad spectrum systemic insecticide, very effective against the common rice pests like the leaf hopper and the stem borers. It is at present applied as 3% granule (commercially available) two to three times at the rate of 15 to 20 kg per hectare during rice cultivation lasting about 3 to 4 months.

It was decided to develop a controlled release Carbofuran system which will have considerably less handling hazards and which will be effective for the whole season with a single application.

Two polymeric matrices were initially chosen for encapsulating Carbofuran, viz. starch and polyvinyl alcohol (PVAl).

The encapsulation by polyvinyl alcohol was standardized using Carbofuran extracted from the 50% formulation. Using such purified Carbofuran, the encapsulation was carried out by dispersing it in polyvinyl alcohol solution followed by addition of sodium sulfate solution with stirring to precipitate the PVAl and deposit Carbofuran particles. The PVAl coating was then hardened by heating it with Vanadyl Sulfate in acid medium.

Encapsulation in starch matrix was carried out by first converting starch to its xanthate with CS_2 and NaOH

followed by dispersing the active ingredient (Carbofuran) and cross linking with H_2O_2 or HNO_2 in acid medium.

The release characteristics of these systems were determined initially in static water with occasional stirring and following the amount of Carbofuran released spectrophotometrically.

The variation of the release characteristics were studied with respect to the degree of substitution of the xanthate, the percentage of Carbofuran incorporated, and the type of oxidizing agent used.

In the case of the polyvinyl alcohol system, the main variable was the percentage of Carbofuran in the encapsulated product.

From the release characteristics, it was observed that the PVAl system had a much higher release lasting for about 3 to 4 days only. With the starch system, however, a product having a fairly uniform release for about 20 days could be obtained at a Carbofuran content of 25%.

At this stage, the PVAl system was abandoned because of this much faster release rate. In addition, the encapsulation technique did not work if technical Carbofuran was used (instead of pure Carbofuran) as the polyvinyl alcohol precipitated and coagulated soon after its addition.

The objective of this programme was to develop a controlled release system which will last for 6 to 8

weeks so that a single application will take care of the plant for the whole season. Hence attempts were made to reduce the release rate by using additions to Carbofuran such as rubber latex, polystyrene, and vegetable oil. All these additives could reduce the release rate to some extent and the vegetable oil gave the best results leading to a product lasting for about 60 days. Laboratory trials on release studies in flooded soil showed release properties lasting for about 35 to 40 days. This product seems to meet all the requirements based on our release studies in the laboratory. It is now planned to grow rice plants in small plots and test the efficacy of this product against the rice pests.

Since at 25% Carbofuran content the conventional dose is only about 2 kg/ hectare, there will be practical difficulty in broadcasting such a small amount over a wide area. Hence work was undertaken to granulate this formulation with inert materials like bentonite, china clay, etc. to arrive at a concentration of 3 to 5%. From these studies, a china clay granulated product could be made satisfying the requirements.

Future Study: The Carbofuran-starch xanthate formulation is being subjected to field trials in small laboratory plots at present. Depending upon the results, suitable modifications will be made if necessary. Scaling up of the encapsulation process will be taken up as soon as the Sigma-blade mixer is obtained.

II. Controlled Release Fenitrothion System.

Fenitrothion is an effective pesticide for mosquitoes. The aim of the programme is to develop sprayable dispersions of controlled release microcapsules of fenitrothion to be used as a long lasting coating on the water and roofs for protection against mosquitoes especially in slums.

Microencapsulation of fenitrothion by interfacial polycondensation in polymeric and polyamide matrices is being investigated. The monomeric materials used were the diacid chloride like sebacoyl chloride and ethylene diamine, toluene diisocyanate and polyamines and polyisocyanates as crosslinking agents. The interfacial polycondensation technique has been studied and microcapsules in the range of 1 to 30 microns diameter have been obtained.

Future work: The development of a controlled release system for fenitrothion is to be further studied with regard to its release characteristics found on degree of crosslinking, capsule diameter, and wall thickness. The methodology of the study of the release properties is to be worked out.

III. Work is to be initiated on developing controlled release systems for some more pesticides. Initially a lypophilic organophosphorus soil pesticide (phorate) will be taken up for encapsulation in a starch matrix.

Controlled Release Mosquito Larvicide Formulations in a Monolithic Matrix

by Dr. D. Raghunath, Project Leader

A 60% natural rubber latex and Abate/Temephos (larvicide) were selected for developing suitable formulations for the release of Abate in a slow and steady rate over a period of 6-8 months in static water.

In order to achieve a technically feasible product, formulations containing 5 to 14 parts of Abate in the rubber matrix were studied for their processing characteristics, release rates of the active ingredient, and longevity.

In the formulations, in addition to 60% natural rubber and Abate, commercially available emulsifying agents, plasticizers and porosigens, viz. $CaCO_3$, were made use of. Out of the 33 formulations, 28 formulations were subjected to bioassay studies in the laboratory and two of the formulations were found to be promising. The formulation containing 14% Abate, $CaCO_3$ and a plasticizer appeared to have longer longevity, was selected for bioassay studies in small experimental ponds in the natural surroundings. The results so far are encouraging and the experiments are being continued.

60% natural rubber latex and Abate (larvicide) were selected for developing suitable formulations for the release of Abate in a slow and steady rate over a period of 6-8 months in static water.

In order to arrive at a technically feasible product 33 formulations were tried; out of these 5 formulations would not be processed in the conventional method and hence discarded; the 28 formulations containing 5-14 parts of Abate in the matrix were developed and bioassayed for its efficacy.

As a starting material, a masterbatch containing 5, 10 and 14 parts of Abate in 60% N.R. latex was prepared in the conventional manner. The product thus obtained was subjected to further processing common in the rubber industry. The formulations, conditions and the observations are as follows:

Experiments	Conditions	Results (Bioassay)
1) 5 formulations	Natural rubber base Compression moulding with conventional compounding ingredients	In most of the samples the release of the toxicant was too fast.
	Casting method	No release over 2 weeks
2) 2 formulations	Pretreated, unvulcanized	Toxicant release over a period of 36 weeks
3) 7 formulations	Natural rubber with fillers, compounded and vulcanized	Discontinuous release

Experiments	Conditions	Results (Bioassay)
4) 4 formulations	Compounded by the addition of vulcanizing dispersions and oven cured	Although results were encouraging, there were processing difficulties.
5) 5 formulations	Compounded with the addition of porosigens/plasticizer	Compounding difficulties
6) 1 formulation	Plastics as base material	No toxicant release
7) 3 formulations	Increase of Abate in the matrix and change of the plasticizer	Results (bioassay) are encouraging and is in progress
8) 1 formulation	With commercially available Abate concentrate: Cast sheet	Very fast release

Remarks

Out of the formulations tried the two formulations at Sr. No. 2, had a longevity of 38 weeks and toxicant concentration (0.05 - 1 ppm, average 0.44) was evaluated in open air and sunlight in 40 l. aquaria containing aquatic plants. The dispensers were placed in floating as well as submerged forms. As the sample appeared to be promising, one of them was selected for simulated field trials in trenches of 10 ft. x 2 ft. x 1 foot. However, after two weeks it was observed (by bioassay method) that the release of the toxicant had slowed down, probably due to the deposit of silt. In order to improve the product and reduce the cost, attempts are being made to develop 5-6 newer formulations.

In view of this, the field trials in and around Poona have been postphoned.

Difficulties:- Abate (Temephos) an imported larvicide used in these formulations is not available for further work; unless a sizeable quantity is made available, the time schedule cannot be adhered to.

Work Programme:-

1. Modifications in the present formulations and scaling up to 1 Kg. batch.
2. Use of synthetic polymers as matrix in place of natural rubber.

RECOMMENDATIONS

MAJOR:

I. Manpower Reorganization as described in the "Abstract".

II. Better Access to Literature.

Most of the new knowledge in the field of controlled release of pesticides is available only through patent literature. Most all of these patents are in English language and issued in the United States. I recommend that the library at NCL subscribe to the Official Gazette of the United States Patent and Trademark Office, which is published weekly and contains mainly three sections: a) General and Mechanical, b) Chemical, and c) Electrical, all of which can be of interest. Subscription information can be obtained from the Superintendant of Documents, Government Printing Office, Washington, D.C., 20402, U.S.A. The following is a list of recent U.S. patents dealing with encapsulated pesticides:

Jaffe, Microencapsulation Process, U.S. 4,272,398 (June 9, 1981

Himel and Cardarelli, In-Flight Encapsulation of Particles, U.S. 4,286,020 (August 25, 1981)

Himel and Cardarelli, In-Flight Encapsulation of Particles, U.S. 4,353,962 (October 12, 1982)

Scher, Encapsulation Process and Capsules Produced Thereby, U.S. 4,285,720 (August 25, 1981)

Kydonieus, Process for Controlling Cockroaches and other Crawling Insects, U.S. 4,320,113 (March 16, 1982)

Lim and Moss, Encapsulation of Labile Biological Material, U.S. 4,324,683 (April 13, 1982)

Mazzola, Encapsulated Bleaches and Methods for their Preparation, U.S. 4,327,151 (April 27, 1982)

Orth, Jr., Slow-Release Nitrogen Fertilizer Employing Waste Proteinaceous Animal Food and Method of Making and Use, U.S. 4,328,024 (May 4, 1982)

Young and Prussin, Adherent Controlled Release Pesticides, U.S. 4,352,833 (October 5, 1982)

Hoshi and Matsukawa, Process for the production of Microcapsules, U.S. 4,353,809 (October 12, 1982)

Senyei and Widder, Method of Incorporating Water-Soluble Heat-Sensitive Therapeutic Agents in Albumin Microspheres, U.S. 4,357,259 (November 2, 1982)

Allan and Ko, Method for Preparing a Controlled Release Composition, U.S. 4,388,352 (June 14, 1983)

Ishida, et al., Process for Manufacturing Regenerated Cellulose Hollow Fiber. U.S. 4,388,256 (June 14, 1983)

Tocker, Controlled Release Granules, U.S. 4,399,122 (August 16, 1983

Connick, Jr., Controlled Release of Bioactive Materials using Alginate Gel Beads, U.S. 4,401,456 (August 30, 1983)

Cardarelli, Controlled Release of Herbicide Compounds utilizing a Thermoplastic Matrix, U.S. 4,405,360 (September 20, 1983)

Lowery, et al., Microporous Hollow Fiber and Process and Apparatus for Preparing such Fiber, U.S. 4,405,688 (September 20, 1983)

The cost of a patent copy is one dollar and can be ordered from the Commissioner of Patents and Trademarks, Washington, D.C., 20231, U.S.A. Be sure to include the patent number.

At the NCL library I found only one reference handbook dealing with pesticides. The following are recommended:

a) Pesticide Manual, 5 th Edition (1977), edited by H. Martin and C.R. Worthing and issued by the British Crop Protection Council.

b) Herbicide Handbook, 4 th Edition or later. This book can be purchased from Weed Science Society of America, 309 West Clark Street, Champaign, Illinois, 61820, U.S.A.

c) Farm Chemical Handbook, Meister Publishing Co., 37841 Euclid Ave., Willoughby, Ohio, 44094, U.S.A.

III. Large scale mixing equipment is lacking. A Double Planetary Mixer with 2 gal. capacity is recommended. Literature was sent recently to Dr. R. Rajagopalan at NCL, Pune.

IV. Quick and reliable quality control tests of granular encapsulated products within starch matrices is needed. An article dealing with this subject was sent to NCL and a copy is enclosed herewith. Although bioassay of formulations are essential, screening tests that can save valuable time are important.

V. Advanced training in current trends and new techniques dealing with encapsulation is needed. The location should preferably be the U.S. in a government or academic institution for a period of not less than 3 months. I also recommend the solicitation of top scientists in the field to spend a sabbatical year at NCL, Pune.

MINOR:

I. Try to entrap larvicides within SBR latexes to improve loading, reproducibility, and efficacy. Many types of SBR latexes are available commercially.

II. Analyze formulations by elemental analysis such as Chlorine and Sulfur. Details of procedures were sent recently to Dr. Rajagopalan.

III. Use only unmodified starch for encapsulation of Carbofuran.

IV. Newer encapsulation techniques as demonstrated to NCL staff during my visit should be tried.

V. Effects upon entrapment of larvicides and insecticides of ionic and non-ionic emulsifiers should be examined.

VI. Preliminary encapsulation studies of living bacteria such as Bacillus thuringensis should be conducted. This type of organism was shown to be a potent pathogen against mosquitoes but can survive for only a very short time in the open.

6-19-73

METHODS FOR TESTING AND FACTORS AFFECTING RATE OF RELEASE OF ENCAPSULATED PRODUCTS PREPARED VIA STARCH XANTHATE[1/]

Baruch S. Shasha

Northern Regional Research Center
Federal Research
Science and Education Administration
U.S. Department of Agriculture
Peoria, Illinois 61604

A simple and economical way to entrap water-insoluble compounds, including pesticides, within a starch matrix was reported.[1,2] The procedure consists of dispersing the active agent in an aqueous starch xanthate solution and subsequently crosslinking the starch xanthate either oxidatively, or with multivalent metal ions, or with difunctional reagents such as epichlorohydrin. Cereal flours, which contain about 10% protein along with starch, also can be xanthated and used as an encapsulating matrix. Upon crosslinking, which is effected within a few seconds under ambient conditions, the entire mass becomes gell-like and, on continued mixing for an additional few seconds, becomes a particulate solid that can be dried to low moisture content with only minimal or no loss of entrapped chemical.

[1/] Presented at the 5th International Symposium on Controlled Release of Bioactive Materials, National Bureau of Standards, Gaithersburg, Maryland, August 14-16, 1978.

Starch is one of the most abundant biopolymers. It consists of glucopyranose units of α-D-(1→4) linkages and hydrolyzes completely to yield D-glucose. Because of the abundance of free hydroxyls, starch is easily derivatized. Degree of derivatization or substitution (D.S.) is defined as the number of substituents per glucose unit. Thus, theoretically a D.S. of 3 is possible. For the purpose of encapsulation, starch is derivatized through xanthation to yield a D.S. of 0.1-0.3 followed by crosslinking to yield starch xanthide. The chemistry and technology of xanthates,

$$\text{Starch-OH} + CS_2 + \text{NaOH} \longrightarrow \text{Starch-O}\overset{\overset{S}{\|}}{C}\text{SNa}$$

$$\xrightarrow{H^+,\ [O]} \text{Starch-O}\overset{\overset{S}{\|}}{C}\text{S}\overset{\overset{S}{\|}}{C}\text{O-Starch}$$

especially cellulose xanthate, is well documented.[3] In recent years, crosslinked starch xanthate has been shown to have potential as a paper additive,[4] for reinforcement of rubber,[5] for making of powdered rubber,[6] and for removing heavy metals from aqueous solutions.[7]

FACTORS AFFECTING RATE OF RELEASE[a]

Shelf life of the starch-encapsulated pesticides is good, and there is no appreciable loss on storage during at least 1 year. When placed in open containers for several weeks, loss of volatile agent is negligible.

---

[a] Mention of a pesticide in this paper does not constitute a recommendation for use by the U.S. Department of Agriculture nor does it imply registration under FIFRA as amended.

However, when products are wetted or immersed in water, active agent is then released from the matrix. A simple laboratory screening test (wet test) was devised for comparing release properties of thiocarbamate-containing products to assist in selection of formulations for subsequent bioassay. Other factors that affect the rate of release are the characteristics of the entrapped chemical; for example, in an aqueous medium, the higher the solubility in water of the active agent, the faster it will diffuse out of the starch matrix. Thus, the herbicide S-ethyl dipropylthiocarbamate (EPTC) will be released faster than the herbicide S-ethyl diisobutylthiocarbamate (butylate). (Water solubility of EPTC at 20° is 370 ppm and of butylate at 22° is 45 ppm.)

The use of polymeric materials in controlled release application systems almost always involves consideration of the solubility and diffusivity of the active agent in the polymer matrix.[8] The literature deals extensively with the solution, diffusion, and permeation of low-molecular-weight gases, vapors, liquids, and ions in polymer films.[9-14]

The characteristics of the polymeric xanthate matrix used for the encapsulation also play an important role in the rate of release. It is found,[2] for example, that under moist conditions an acid-modified flour matrix releases active agent faster than an acid-modified flour-starch mixture and that this mixture releases faster than starch alone.

It has been suggested[2] that either the protein component in the flour or the lower molecular weight of the starch component of the flour contributes to a faster release of butylate. Also, the recovery of the encapsulated agent is higher with starch than with acid-modified flour-starch mixture and poorest with acid-modified flour alone.

Addition of small amounts of latex such as SBR 1502 to the xanthate retarded significantly the rate of release of 1,2-dibromo-3-chloropropane (DBCP). Addition of predissolved polymers such as polystyrene in benzene seems to have the same effect. On the other hand, the rate of release of butylate or of EPTC was not changed significantly by the addition of latex SBR 1502 nor by the addition of polystyrene.

When made with xanthates having a D.S. of 0.3 and with H_2O_2 as an oxidant, products release the active agent more slowly than do those made with the same D.S. but with $NaNO_2$ as an oxidant. The reason seems to be that with $NaNO_2$, during the neutralization step, NO_2 gas is produced and partly entrapped within the starch matrix. Upon drying, the end product has many cracks that facilitate the release of active ingredient. With H_2O_2, on the other hand, the product has a smooth and continuous surface.

The technique of double encapsulation provides a slower rate of release with certain pesticides than does single encapsulation, especially in cases where a single encapsulation does not entrap all of the active

agent and some of it is adsorbed loosely to the surface of the starch matrix. The double encapsulation technique involves the addition of another layer of xanthate to the crosslinked xanthate containing the active agent. After mixing, the second layer is crosslinked as before.

Finally, the mesh sizes of the end product also seem to influence rate of release. Preliminary data show that EPTC and DBCP with granular sizes of mesh 30 or higher have a rate of release faster than product with granular size of mesh lower than 30.

METHODS FOR TESTING ENCAPSULATED PRODUCTS

While bicassay tests are the ultimate tests for encapsulated products, they are time-consuming and unavailable in most laboratories. Thus, quick and indicative ways were sought to screen large number of samples for their comparative rate of release. The tests fall mainly into two broad categories: (1) those which examine the rate of breakdown of starch by enzymatic means and hence the release of active ingredient, and (2) those which examine the rate of diffusion of active ingredient from the starch matrix.

The rate of breakdown is related to the degree of crosslinking of starch by the disulfide bonds. It was examined by measuring the swelling of the encapsulated product in water and by measuring the amount of free

glucose released under standard conditions upon treatment of the encapsulated product with diazyme (an amylase type enzyme that hydrolyses starch to free glucose). A good correlation was found between swelling and diazyme tests and they are complementary to each other.

If the encapsulated agent is a solid with low solubility in common solvents, then the product is examined through a magnifying lens with 30-50 times magnification to observe whether loose particles of the agent are present unencapsulated.

A second test, which is more meaningful and easy to carry out, involves immersion of the product in a diluted aqueous iodine solution for 1-2 min. Since only the starch part will stain with iodine, the observation of the immersed sample through the lens will reveal the entrapment's quality.

If the encapsulated agent is a solid or is a liquid soluble in common organic solvents, then, besides the iodine test, a portion of the product (about 10 g, containing 15% encapsulated agent) is suspended in the appropriate organic solvent (50 ml) for 1 hr. The portion of the agent extracted reflects the part that is not encapsulated or that is close to the surface of the encapsulated granule.

If the encapsulated agent is a volatile liquid, a portion of the product is exposed to an air current (well-ventilated hood will suffice) and the remaining product is analyzed periodically. Another simple test, the "wet test," consists of placing several 1-g portions of the

duct in 2 ml of water. The water is allowed to evaporate, and after hr another 2 ml of water is added and again allowed to evaporate. dition of water and evaporation is repeated a total of 4 times, and dried product is analyzed after each wetting-drying cycle for loss encapsulated agent.

HODS OF ENCAPSULATION

rch Xanthate

For the purpose of encapsulation, corn starch (162 g dry basis) is rried in water (1 liter) and mixed with carbon disulfide (40 ml), llowed by sodium hydroxide (40 g) dissolved in water (350 ml). ation occurs immediately. The mixing is continued until a homogeneous ture is obtained. In about 1 hr, the xanthate is ready to be used. product has a D.S. of 0.3 and is useful for encapsulation for up to days when kept at 5°C. Nevertheless, to minimize the formation of products, it is advisable to prepare a fresh batch as needed. For the paration of starch xanthate with a D.S. of 0.2, the above recipe is llowed except that the amounts of carbon disulfide and sodium hydroxide halved.

These xanthates contain 12-14% solids. Higher solids content (up 20%) can be made, but the gel thus produced is too thick to handle ily. Significant reduction in viscosity occurs upon mixing the thate in a high-speed Waring Blendor for 10-20 seconds. For certain

formulations, one might use acid-modified starch or acid-modified flour (both are commercially available). The xanthates here are much less viscous, and a solids content of 50% or higher can be easily achieved.

Other polyols can also be used for encapsulation via xanthation. Polymers such as cellulose and polyvinyl alcohol are easily xanthated, although one might not apply the same recipe as with starch.

Encapsulation of Liquids Such as Butylate

(a) Using H_2O_2 as oxidant, starch xanthate at D.S. of 0.3 (200 g) is cooled to 5°C and mixed thoroughly with butylate (6.7 E, 10 g) followed by the addition of glacial acetic acid (8 ml)-H_2O_2 30% (5.5 ml). After being mixed and allowed to stand for 15 min, the mixture is filtered and pressed under a rubber dam to remove most of the water. The product is ground with a Waring Blendor and dried in a hood to yield 38 g of granular material containing 16.4% butylate.

(b) Using $NaNO_2$ as oxidant, starch xanthate at D.S. of 0.17 (120 g) is mixed with 50% $NaNO_2$ solution (3.5 ml), followed by butylate (6.7 E, 10 g) and glacial acetic acid (10 ml). The product is isolated and dried as above to yield 25 g product containing 22.4% butylate.

These procedures to encapsulate butylate are easily adaptable to encapsulate low-melting products and compounds with a high degree of solubility in organic solvents.

Encapsulation of Solids Such as Coumaphos

For encapsulation of this type of material, finest powder (air milled or alike in mesh size) should be used.

Starch xanthate at D.S. of 0.3 (1200 g) is cooled to 5°C and mixed in a Waring Blendor with 20 g Coumaphos (technical grade). Acidification and crosslinking are performed with addition of glacial acetic acid (45 ml) and H_2O_2 30% (25 ml). The product is isolated and dried as above to yield 193 g of encapsulated Coumaphos containing 10.4% active ingredient.

REFERENCES

1. Shasha, B. S., Doane, W. M., and Russell, C. R., Starch encapsulated pesticides for slow release, J. Polym. Sci., 14, 417, 1976.
2. Doane, W. M., Shasha, B. S., and Russell, C. R., Encapsulation of pesticides within a starch matrix, in Controlled Release Pesticides, Scher, H. B., Ed., Am. Chem. Soc., Washington, D.C., 1977, chap. 7.
3. Rao, S. R., Xanthates and Related Compounds, Marcel Dekker, Inc., New York, 1971, p. 395.
4. Hamerstrand, E., Carr, M., Hofreiter, B., and Russell, C. R., Starch xanthide in pilot paper machine trials, Staerke, 28, 240, 1976.
5. Buchanan, R. A., Seckinger, H. L., Kwolek, W. F., Doane, W. M., and Russell, C. R., Controlling particle size and structure of starch xanthide in elastomer masterbatches, J. Elast. Plast., 8, 82, 1976.
6. Abbott, T. P., James, C., Doane, W. M., and Russell, C. R., Injection molding of conventional formulations based on starch-encased powdered rubber, J. Elast. Plast., 7, 114, 1975.
7. Wing, R. E., Doane, W. M., and Russell, C. R., Insoluble starch xanthate: Use in heavy metal removal, J. Appl. Polym. Sci., 19, 847, 1975.
8. Rogers, C. E., Structural and chemical factors controlling the permeability of organic molecules through a polymer matrix, in Controlled Release Pesticides, Scher, H. B., Ed., Am. Chem. Soc., Washington, D.C., 1977, chap. 2.

9. Crank, J. and Parks, G. S., Eds., Diffusion in Polymers, Academic Press, New York, 1968.

10. Rogers, C. G., Solubility and diffusivity, in Physics and Chemistry of the Organic Solid State, Vol. II, Fox, C., Labes, M., and Weissberger, A., Eds., Wiley-Interscience, New York, 1965, chap. 6.

11. Machin, D. and Rogers, C. E., Free volume theories for penetrant diffusion in polymers, Polym. Prepr., 11, 142, 1970.

12. Hopfenberg, H. B., Ed., Permeability of Plastic Films and Coatings to Gases, Vapors, and Liquids, Vol. 6 of Polymer Science and Technology, Plenum Press, New York, 1974.

13. Crank, J., The mathematics of diffusion, 2nd ed., Clarendon Press, Oxford, 1975.

14. Flynn, G. L., Yalkowsky, S. H., and Roseman, T. J., Mass transport phenomena and models. Theoretical concepts, J. Pharm. Sci., 63, 479, 1974.