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ENCAPSULATION OF PESTICIDES IN STARCH

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Weed, insect and pathogen pests of agricultural crops, forestry, horticultural plants and stored grain cause damage estimated at 20 billion dollars in the U. S. This is in spite of chemical control efforts consisting of applying approximately 1 billion pounds of active pesticidal ingredient to crops each year. Most of these pesticides are petroleum derived chemicals that have been accused of causing harm to the environment and to human health. Clearly, efforts to control pests in a socially conscious way can be improved. Only recently, have producers begun moving towards less dependence on chemical input by embracing agronomic practices such as integrated pest management, sustainable agriculture, and organic production. However, some of the pest control tools necessary to maintain a profitable operation within these systems are lacking.

There are several approaches to improving pest control products. First, new pesticides may be developed that have novel characteristics. This is a very expensive proposition, though, as costs may exceed $100 million from initial discovery to full registration by EPA. Another approach is to develop new and improved formulations of existing pest control products. Some of these new formulations involve the use of cornstarch as an encapsulating agent. Research over the past several years at the National Center for Agricultural Utilization Research, a USDA-Agricultural Research Service facility, has resulted in many types of starch formulations that have characteristics amenable to more judicious use of both chemical and biological pesticides. This discussion will review some of the advancements made in this area.

WHY STARCH?

Cornstarch is an extremely abundant commodity. Annually the U.S. corn crop contains about 250-300 billion pounds of starch. Although the corn wet millers process approximately 1 billion bushels of corn to produce about 32 billion pounds of starch, only about 4-5 billion pounds are used in non-food areas. The corn dry millers process about 200 million bushels

TABLE 1: Corn production and use (million bushels).

Year	Production	Processed (food, alcohol, other)	Export	Surplus
80/81	6,639	698	2,391	1,392
81/82	8,119	778	1,997	2,537
82/83	8,235	880	1,821	3,523
83/84	4,174	956	1,886	1,006
84/85	7,672	1,070	1,850	1,648
85/86	8,875	1,140	1,227	4,040
86/87	8,226	1,175	1,492	4,882
87/88	7,131	1,212	1,716	4,259
88/89	4,928	1,232	2,028	1,930
89/90[1]	7,525	1,271	2,369	1,345
90/91[2]	7,933	1,300	1,850	1,260

1. Preliminary
2. Projected
Source: USDA

to produce about 1 billion pounds of flour. Over the last eleven years, the corn carry-over surplus has averaged 2.5 billion bushels, exceeding 4 billion bushels in each of the years 1985-1987 (Table 1). Besides availability, starch is a very inexpensive (approximately 10 cents/pound) and easily modified polymer. Corn flour may also be used in place of starch to encapsulate pest control agents. While the protein in flour may inhibit certain encapsulation properties, it may offer additional advantages as well. Both flour and starch are 100% biodegradable, digestible by most leaf-feeding insects and may serve as excellent formulation materials.

ENCAPSULATION THEORY

Commercial non-encapsulated formulations of pesticides may lose activity quickly in the field due to leaching, volatility, microbial breakdown, adsorption to the soil, and other environmental factors. To compensate for these factors, pesticides are applied at a much higher rate than is needed to actually control the pest. This excess not only drives up the cost of application but may lead to environmental damage or toxicity to the crop or other non-target organisms. Encapsulation systems that are capable of reducing loss of activity should aid in the development of formulations containing less active agent with no loss of efficacy. Of course, not all pesticides need encapsulation to be effective. Generally, encapsulation increases the cost of the pesticide to the consumer. Therefore, the benefits of encapsulation in terms of economic and social costs must outweigh the cost of manufacture. Criteria that must be considered include: chemical and physical aspects of the active agent, e.g. volatility or corrosiveness; environmental stability due to sunlight, microbial degradation, etc.; human toxicity concerns;

toxicity to the crop or the environment; cost of the pesticide, i.e. can encapsulation reduce repeat applications (Shasha in press).

There are many types of encapsulation processes currently in use. One often thinks of a membrane-coated particle which contains all the active ingredient within. Starch encapsulation is not like this. Rather, the process of starch encapsulation results in a matrix with the active agent dispersed throughout and on the outside of the resulting mass. Due to the molecular structure of starch, the matrix will swell but not dissolve in water. This characteristic leads to sustained release of the active agent over time. The rate of release can be controlled by altering the starch or flour type, the encapsulation conditions, and by addition of other encapsulation ingredients. A zero-order release rate in which a consistent and constant amount of agent is released over time is desired. The amount should be in high enough concentration to kill the target pest but low enough to reduce environmental and health concerns (Fig 1). In addition to release of volatile or water soluble chemical pesticides, the starch matrices also serve as excellent baits for insects. These baits may contain chemical or biological insecticides and, due to the nature of the encapsulation procedure, the starch can extend the activity of agents that normally break down rapidly under environmental conditions.

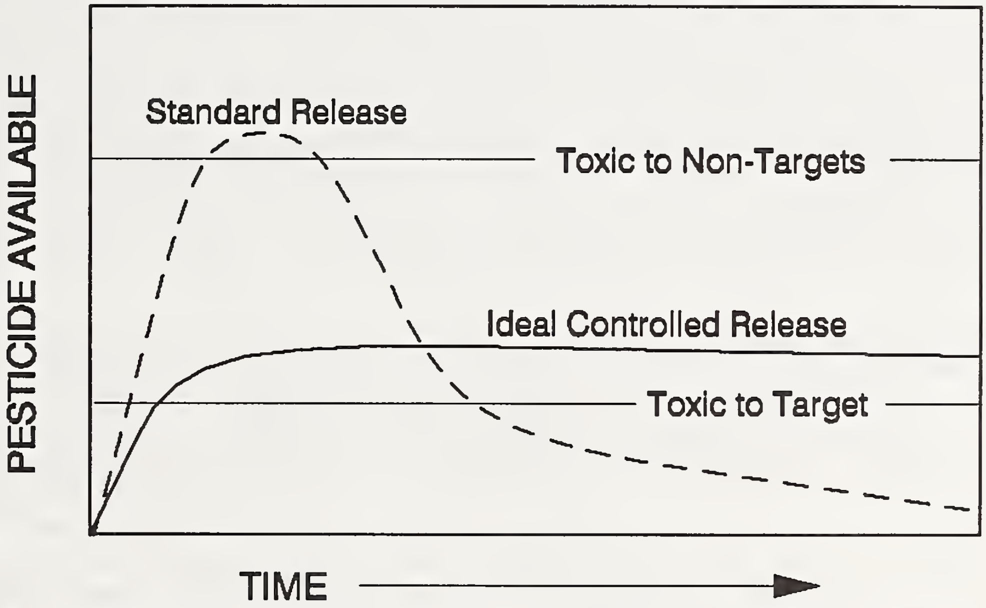

Figure 1. Theoretical fate of conventional and controlled release formulations of pesticides when applied to the same environment under the same conditions. Conventional formulations release most of their active ingredients immediately which may cause environmental damage through contamination of groundwater or damage to non-target organisms. Controlled release formulations, on the other hand, provide a sustained and usually lower rate of release over a longer period of time.

METHODS OF ENCAPSULATION

Starch may be used to make granular or sprayable formulations suitable for chemical or microbial pesticides (Table 2). While both sprayable and granular formulations can be used for soil and foliar applications, granular products are used mainly for soil application of pesticides whereas sprayables are used mainly for foliar application. Granular formulations have been of most interest while sprayable formulations have just recently been developed. Following is a description of the various types of formulations.

Table 2: Starch formulations of pesticides developed at NCAUR.

For Chemicals (All Granular)	For Microbials
Xanthide Process	Pregelatinized Granules
Borate Process	Pregelatinized Sprayable
Calcium Process	Adherent Granules
Cooked Starch	

Granular formulations made with chemical crosslinking agents. The first descriptions of using starch for entrapment of agricultural chemicals involved the use of chemicals such as sodium hydroxide or carbon disulfide to solubilize the starch. Herbicides could then be added and the solution crosslinked with a suitable agent such as xanthide, borate or calcium to yield a solid, single mass that could then be ground to produce granules of a desired size. The resulting granules contained herbicide distributed throughout the matrix. Field and greenhouse work revealed excellent efficacy, sustained released and reduced volatility of encapsulated herbicides. Although pilot-scale production was developed, these processes never received commercial interest, probably due to the harsh chemicals used (Schreiber et al. 1987).

Granular formulations made with cooked starch. Starch can also be solubilized by cooking at high temperature. When allowed to cool, branches of the starch molecule crosslink and, similarly become insoluble. Therefore, starch was cooked in a jet cooker at temperatures ranging from 90-143°C and then transferred to a mixer. While the starch paste was still hot, herbicide was added and mixed thoroughly. The paste was allowed to cool to a solid which was then ground to the desired particle size. Taken one step further, starch encapsulation can also be achieved in an extruder. Through the proper application of heat, water addition, and active agent addition, a product can be extruded in a continuous system such that the resulting product is a starch-encapsulated herbicide (Wing et al. 1991). Laboratory studies with these granules demonstrated reduced leaching of herbicides in columns compared to herbicides in commercial formulations. In 1990, multi hundred pound batches of three herbicides were prepared and tested in the field under a pilot project designed to evaluate the effectiveness of these starch formulations. Patent applications resulting from this work have received considerable interest from industry and licensing of the technology is being pursued.

Granular formulations made with pregelatinized starch. Although chemicals make up the vast majority of pesticides sold, biological pesticides are beginning to increase in importance. Concerns about groundwater pollution, non-target toxicity, and human health have prompted many companies to begin developing microbial pesticides. These pesticides, most notably Bacillus thuringiensis (Bt), an insecticide, are generally effective against a small range of pests and are generally non-toxic to other organisms. While the above encapsulation methods work well with chemical pesticides, microbials will not tolerate either harsh chemical treatments or elevated temperatures. However, it is still possible to use starch as an encapsulating agent. Commercially available products called pregelatinized starch (or flour) work very well with microbial insecticides. These starches are prepared by subjecting cornstarch or flour to high heat in the presence of water. Water removal results in a dry powder that, upon mixing with realtively small amounts of cold water, becomes highly dispersed, almost solubilized. After a short time, the starch molecules crosslink, finishing the gelling reaction. Of course, active agents can be added to the water before addition of the starch. The resulting mass then, contains active agent entrapped throughout the starch matrix. With this process, living agents survive well and the starch will protect the agent after application in field conditions. The versatility and simplicity of this process allows for incorporation of many kinds of compounds. Field studies have demonstrated that sunlight screens that absorb damaging ultraviolet wavelengths extend activity of UV sensitive compounds or organisms when incorporated during the starch formulation process. For example, Bt when incorporated into starch granules without any additive, lost all activity within four days. If Congo red was added to the formulation, however, Bt activity remained for up to 12 days when exposed to direct sunlight (Dunkle and Shasha 1988). Feeding stimulants, attractants, or repellents that affect insect behavior have also been used in the starch formulation such that the insect is easier to control with less active ingredient. When the commercial feeding stimulant COAX was added to the formulation, the amount of Bt could be reduced by three fourths the recommended rate with excellent control of European corn borer larvae in the field (McGuire et al. 1990).

Currently, several companies have expressed an interest in this technology and licensing activities are taking place. Technology utilizing the extruder as well as simply using pregelatinized starches and flours have gained the attention of industry who, we anticipate, will commercialize these novel formulations.

Sprayable formulations. Although granular formulations are extremely efficient methods of distributing pesticides, they only make up about 10% of the pesticide market. The remainder of the market is composed primarily of sprayable formulations. By adding pregelatinized starch in low concentrations to spray tanks, the resulting solution is sprayable. Then, as the starch crosslinks after spraying, a film is formed encapsulating the pesticide directly on the leaf or soil surface. This film can last from 1 to 21 days under greenhouse conditions depending on the type of pregelatinized starch used and on the types of other compounds that are also added. For example, if sugar is added to the starch prior to mixing with water, the sugar not only helps disperse the starch but it also imparts a sticking characteristic to the film. Formulations of Bt containing the sugar-starch combination applied to cotton leaves in the greenhouse imparted protection for more than seven days longer than formulations lacking the sugar and starch. Additionally, the sugar-starch combination appears to inhibit washoff by rainfall. The alkali conditions on the cotton leaf surface are apparently detrimental to survival of Bt. The presence of the sugar-starch solution, however, appears to inhibit breakdown of the insecticidal activity, probably due to the excellent buffering capacity of the starch (McGuire and Shasha 1990).

This technology has also received industry interest as the patent is exclusively licensed to a company. Again, we hope to see the technology commercialized in the near future.

Adherent granules. A very recent development in our laboratories has led to the discovery of granules that, when applied to wet surfaces will adhere to those surfaces. Upon drying, the granules remain stuck and resist washoff due to simulated rainfall in the greenhouse. There are many potential uses for this type of formulation where increased residual activity and decreased amounts of pesticide are desired. While this work must be considered preliminary, it demonstrates the versatility of starch and flour in terms of their usefulness in agricultural formulations of pesticides.

POTENTIAL ECONOMICS OF STARCH ENCAPSULATION

Because none of the starch encapsulation technology has reached the marketplace, we can only speculate as to how much starch will actually be used. However, one billion pounds of active ingredient probably represents 10-20 billion pounds of formulated product. Easy calculations can then be made to determine, based on market percentages, how much starch may be used. It is up to industry to determine how economical and effective the starch encapsulation process will be with their various products and applications.

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