Abstract: A method for delaying or preventing crystallization of materials susceptible to such crystallization by the use of a microencapsulation process is disclosed. The process provides for the use of microcapsules to slow or prevent the crystallization of formulations susceptible to such crystallization. In particular, the method includes a process for delaying or preventing crystallization through the use of encapsulated droplets of a solution of an active material which is substantially insoluble in aqueous conditions, where the encapsulating agent is a film formed from a modified urea-formaldehyde polymer.
METHOD FOR PREVENTING CRYSTALLIZATION

This invention includes a method for delaying or preventing crystallization of materials susceptible to such crystallization by the use of a microencapsulation process. In particular, this invention includes a method for delaying or preventing crystallization through the use of encapsulated droplets of a solution of an active material which is substantially insoluble in aqueous conditions, where the encapsulating agent is a film formed from a modified urea-formaldehyde polymer.

The use of membranes, coatings, and capsules for the controlled release of liquid materials is well known in the art of both agricultural and non-agricultural chemicals. In agriculture, controlled-release techniques have improved the efficiency of herbicides, insecticides, fungicides, bactericides, and fertilizers. Non-agricultural uses include encapsulated dyes, inks, pharmaceuticals, flavoring agents, and fragrances.

The most common forms of controlled-release materials are coated droplets or microcapsules, coated solids including both porous and non-porous particles, and coated aggregates of solid particles. In some instances, a water-soluble encapsulating film is desired, which releases the encapsulated material when the capsule is placed in contact with water. Other coatings are designed to release the entrapped material when the coating is ruptured by external force.

Still further coatings are porous in nature and release the entrapped material to the surrounding medium at a slow rate by diffusion through the pores. In addition to providing controlled release, such coatings also serve to facilitate the dispersion of water-immiscible liquids into water and water-containing media such as wet soil. Droplets encapsulated in this manner are particularly useful in agriculture, where water from irrigation, rain, and water sprays is frequently present. A variety of processes for producing such capsules is known.

A simple, inexpensive method for producing microcapsules of uniform and readily controlled size, which are suitable for use without further treatment, is disclosed in U.S. Patent No. 4,956,129 and U.S. Patent No. 5,332,584. The microcapsules
described in these patents are substantially water-insoluble liquid materials within a porous shell. The patents disclose the material's slow release rate of the encapsulated materials through the shell through diffusion.

Some materials, however, do not lend themselves to controlled release formulations, particularly materials having a tendency to crystallize in the aqueous phase. Thus, there exists a need in the art for a process to prevent crystallization of these materials by encapsulating solutions of materials having low melting points or low water-solubility, i.e., materials having a tendency to crystallize in the aqueous phase.

It has now been discovered that crystallization of a solution of an active ingredient material that has a low melting point or otherwise has a tendency to crystallize in the aqueous phase can be prevented or delayed using a microencapsulation process wherein the active material is encapsulated within a porous shell by a process which comprises:

(a) providing a saturated or supersaturated solution of the active ingredient (active solution) comprising said active solution and an etherified urea-formaldehyde prepolymer dissolved therein in which from about 50% to about 98% of the methylol groups of said prepolymer have been etherified with a C₄-C₁₀ alcohol;

(b) creating an emulsion of said active solution in a continuous phase aqueous solution comprising water and a surface-active agent, wherein said emulsion comprises discrete droplets of said active solution dispersed in said continuous phase aqueous solution, there being formed thereby an interface between the discrete droplets of active solution and the surrounding continuous phase aqueous solution; and

(c) causing in situ self-condensation and curing of said ureaformaldehyde prepolymer in the organic phase of said discrete droplets adjacent to said interface by simultaneously heating said emulsion to a temperature between about 20°C to about 100°C, and adding to said emulsion an acidifying agent and maintaining said emulsion at a pH of between about 0 to about 4 for a sufficient period of time to allow
substantial completion of in situ condensation of said resin prepolymer to convert the liquid droplets of said active solution to capsules consisting of solid permeable polymer shells enclosing said liquid material of active solution.

Microcapsules formed by this process provide stability against crystallization and are capable of effecting a slow rate of release of the encapsulated liquid active solution by diffusion through the shell to the surrounding medium. The present invention resides in the ability to prevent or delay crystallization of these materials by use of microcapsules formed by the process described above.

The present invention can be readily adapted to accommodate variations in the active materials used, the kind of product desired, and economic factors in general. As the following indicates, both essential and optional features of the process and the product thereof can be varied over a wide range.

A. Core Liquid

It is essential that the active material serving as the basis of the solution (i.e., the base solid) which forms the interior of the capsules (i.e., the core liquid) be of sufficiently small particle size. The particle size should be between 1 μm and 100 μm, preferably between 2 μm and 20 μm. The core liquid may consist of a solution of a single active base solid or one or more active solid base materials dissolved in an inert solvent. The core liquid solution may be saturated or supersaturated, but the solid base material is one that has a low melting point or low water solubility, i.e., the solid has a tendency to crystallize in the aqueous phase.

A wide variety of active liquids can be encapsulated by the present process. The most useful liquids are those which do not react with either the prepolymer, the acid used in the self-condensation wall-forming step, or any of the other components in the system. Thus, any nonreactive liquid which will diffuse through the shell membrane is suitable. The liquid can be a single chemical compound or a mixture of two or more compounds. It can diffuse into water, soil, air, or any other surrounding medium. Preferably, the liquids suitable for encapsulation by the process of the present
invention should be solid at 30° C, have low solubility in water and at least moderate solubility in water-immiscible organic solvents.

Liquids suitable for encapsulation include chemical-biological agents such as herbicides, insecticides, fungicides, nematocides, bactericides, rodenticides, molluscides, acaricides, larvicides, animal, insect, and bird repellents, plant growth regulators, fertilizers, pheromones, sex lures and attractants, pharmaceuticals and flavor and odor compositions. The microcapsules of the present invention are particularly well adapted to pesticides, including thiocarbamates, dithiocarbamates, acetamides, anilides, sulfonamides, bisamides, triazines, organophosphorus compounds, natural fermentation products, and pyrethroids. The following are examples of such compounds. Details (e.g., structure, chemical name, commercial names, etc) of each of the pesticides with a common name can be found in the e-Pesticide Manual, version 3.1, 13th Edition, Ed. CDC Tomlin, British Crop Protection Council, 2004-05.

HERBICIDES
Beflubutamid, bromobutide, cafenstrole, diphenamid, fentrazamide, flupoxam, fomesafen, isocarbamid, isoxaben, pethoxamid, propyzamide, clomeprop, diflufenican, etobezanid, flufenacet, mefenacet, mefluidide, fetamifop, monalide, naproanilide, pentanochlor. picolinanof, benzoylprop, flumprop-M, alachlor, propachlor, propisochlor, thynylchlor, cloransulam, floransulam, perfluidone, asulam, oryzalin, chlorothiamid, chlorramben, pyriminobac-methyl, chlorlhal-methyl, aminopyralid, clopyralid, mesotrine, sulcotrine, benfuresate, ethofumesate, karbutilate, carbetamide, chlorpropham, desmedipham, phenisopham, phenmedipham, phenmedipham-ethyl, propam, butoxydim, cycloxydim, tepraloxydim, tralkoxydim, isoxaflutole, cinidon-ethyl, flumidenclor, flumioxazin, flumipropyn, benfluralin, butralin, dinitramine, ethalfluralin, fluchloralin, nitralin, oxyzalin, pendimethalin, prodiamine, profluralin, trifluralin, dinoseb, dinoterb, medinoterb acetate, aclonifen, bifenox, fluorodifen, fluoroglycofen-ethyl, fomesafen, lactofen, nitrofen, oxyfluorofen, dazomet, imazamethabenz-methyl, imazamox, imazapic, imazapyr, imazethapyr, bromoxynil, dichlofenil, dimefuron, methazole, oxadiargyl, oxadiazon, bromofenoxim, chomeprop, 2,4-D, MCPA, 2,4,5-T, ametryn and prometryn.
INSECTICIDES
Abamectin, emamectin, milbemycin oxime, azadirachtin, rotenone, bendiocarb, carbaryl, carbofuran, dimetilan, pirimicarb, alany carb, aldicarb, aldoxycarb, methomyl, thiodicarb, tliiofanox, aminocarb, butacarb, cloethocarb, dioxacarb, ethiofencarb, fenobucar, isoprocarb, methiocarb, metolcarb, mexacarbate, promecarb, propoxur, trimetacarb, XMC, xylylcarb, DNOC, sulfluramid, amidraz, chlordimeform, buprofezin, fenoxycarb, pyriproxyfen, thiocyclam, clothianidin, dinotefuran, imidacloprid, thiamethoxam, acetamiprid, thiacloprid, lindane, methoxychlor, pentachlorophenol, dioxabenzofos, fosmethilan, dimethoate, formothion, prothoate. azamethiphos, coumaphos, menazon, pyridaphenilhion, azinphos-ethyl, azinphos-methyl. dialifos, phosmet, pyrazophos, chloφ yrifos, chloφ yrifos-methyl, tebupirimfos, quinalphos, methidathion, bromophos, famp hur, fenchlorphos, jodfenphos, paration-methyl, temephos, trichlorfon, mearphon, cyanofenphos, EPN leptophos, fenamiphos, phostolan, acepate, isocarophos, methamidophos, indoxacarb, metoxadiazone, dialifos, phosmet, tetramethrin, Ωpronil, tebufenpyrad, tolenpyrad, acrinathrin, bifenthlor, cyfluthrin, gamma-cyhalothrin, lambda-cyhalothrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, theta-cypermethrin, zeta-cypermethrin, deltamethrin, fenfluthrin, fenopropathin, fenvalerate, esfenvalerate, permethrin, resmethrin, bioresmethrin, tefluthrin, tetramethrin, tralomethrin, transfluthrin, etofenprox, flufenprox, halfenprox, pyrimidifen, chlorfenapyr, spiromesifen, diafenthiuron, sulcofiiron sodium, hydramethylnon, isoprothiolane, malonoben, pyridaben, pyridalyl, triazamate, Rynaxypyr (DuPont).

FUNGICIDES
Cymoxanil, dodine, guazatine, iminoctadine, carpropanid, chloranformethan, cyilufenamid, diclocymet, ethaboxam, fenoxalin, furametpyr, mandipropanid, penthiopyrad, prochloraz, silthiofam, triforine, benalaxyl, benalaxyl-M, furalaxyl, metalaxyl, metal&xyl-M, boscalid, carboxin, fenhexamid, metsulfov&x, ofurace, oxadixyl, oxycarboxin, thifluzamide, tiadinil, benodanil, flutolanil, mebenil, fenfuram, methfuroxam, flusulfamide, trichlamide, zarilamid, zoxamide, furmecycloxx, dichlofluanid, tolylfuanid, cyazofamid, benthiavalicarb-isopropyl, iprovalicarb, awoxystrobin, dimoxystrobin, fluo xastrob, kresoxim-methyl, metominostrobin, orysastrob, picoxystrobin, pyraclostrobin, trifloxystrobin, biphenyln, chloroneb,
chlorothalonil, dicloran, hexachlorobenzene, pentachlorphenol, quintozene, tecnazene, benomyl, thiabendazole, thiabendazole-M, dichlorophen, diphenylamine, diethofencarb, climbazole, prochloraz, triflumizole, azaconazole, bromuconazole, cyproconazole, diclobutrazol, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, etaconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, fluconazole, furconazole-cis, hexaconazole, ipconazole, miconazole, myclobutanil, penconazole, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, uniconazole, uniconazole-P, famoxadone, fluopiclorid, chlozolinate, iprodione, myclozolin, procymidone, vinclozolin, captafol, captan, ditalimfos, folpet, binapacryl, dinobuton, DNOC, cyazofamid, fenamidone, glyodin, peflurazocate, dimethomoph, dodemorph, flumorph, pyrazophos, fentin acetate, chlozoline, drazoxolon, famoxadone, hymexazol, myclozolin, vinclozolin, furametpyr, fenarimol, bethioprd, fluazinam, cyprodinil, diflumetorim, ethirimol, fenamidone, pencycuron, famoxadone, hymexazol, myclozolin, vinclozolin, captafol, captan, ditalimfos, folpet, binapacryl, dinobuton, DNOC, cyazofamid, fenamidone, glyodin, peflurazocate, dimethomoph, dodemorph, flumorph, pyrazophos, fentin acetate, chlozoline, drazoxolon, famoxadone, hymexazol, myclozolin, vinclozolin, furametpyr, fenarimol, bethioprd, fluazinam, cyprodinil, diflumetorim, ethirimol, fenamidone, pencycuron, acibenzolar-methyl, nitrothal-isopropyl, phthalide, probenazole, pyroquilon, thicyofen, tricyclazole, a compound of formula A:

![A]

or an isomer or tautomer of such a compound (described in WO 03/074491, incorporated herein by reference), a compound of formula B:
or an isomer or tautomer of such a compound (registered as CAS-214706-53-3), or a compound of formula C:

![Chemical structure A]

or an isomer or tautomer of such a compound (described in EP-1-035-122 and registered under CAS-291771-99-8 and CAS-291771-83-0).

Of the many different types of core liquids useful in the present composition, pesticides are preferred, and certain classes of pesticides are particularly preferred. One such class is that ofazole fungicides. This class of compounds includes those disclosed in U.S. Patent No. 4,243,405, which is incorporated by reference in its entirety as if specifically set forth herein. Specific compounds within this class include azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, ipconazole, metconazole, myclobutanil, penconazole, prochloraz, propiconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, triticonazole, and uniconazole. Also included in the types of core liquids useful in the present invention include solutions of azoxystrobin, trifloxystrobin, fiuoxystrobin, metalaxyl-M, benalazyl, furalaxyl, tefluthrin, thiamethoxam, imidacloprid, clothianidin, thiacloprid, abamectin, lambda-cyhalothrin, aldicarb, fipronil, among others.
One can broaden the variety of crops on which certain pesticides, particularly herbicides, can be effectively used by including an antidote in the composition. The antidote helps to protect the crop from injury by the herbicide, without appreciable effect on the potency of the herbicide against the undesired weed species. The antidote thus renders the herbicide more selective in its action. Useful antidotes include acetamides such as N,N-diallyl-2,2-dichloroacetamide and N,N-diallyl-2-chloroacetamide, oxazolidines such as 2,2,5-trimethyl-N-dichloroacetyl oxazolidine and 2,2 spirocyclohexyl-N-dichloroacetyl oxazolidine, and 1,8-naphthalic anhydride. For maximum effect, the antidote is present in the composition in a non-phytotoxic, antidotally effective amount. By "non-phytotoxic" is meant an amount which causes at most minor injury to the crop. By "antidotally effective" is meant an amount which substantially decreases the extent of injury caused by the pesticide to the crop. The preferred weight ratio of pesticide to antidote is about 0.1:1 to about 30:1. The most preferred range for this ratio is about 3:1 to about 20:1.

The utility of many pesticides can also be broadened by the inclusion of synergists in the pesticide composition. Synergists are compounds which have little or no pesticidal activity of their own, but when combined with a pesticide produce a combination with a potency significantly greater than the additive sum of the potencies of the compounds applied individually. Useful synergists include 5- 1-[2-(2-ethoxyethoxy)ethoxy]ethoxy]-1,3-benzodioxole (sesamex), 1,4-di-(1,3-benzodioxol-5-yl)tetrahydrofuro [3,4-c] furan (sesamin), 1-methyl-2-(3,4-methylenedioxyphenyl)oclyl sulfoxide (sulfoxide), and 5-[2-(2-butoxyethoxy)ethoxymethyl-6propyl]-1,3-benzodioxole (piperonyl butoxide). When included, synergists are present in effective amounts, i.e., at any pesticide to-synergist ratio at which a synergistic effect is observed. This ratio varies widely from one combination to the next.

B. Prepolymer

Prepolymers suitable to the present invention are partially etherified urea-formaldehyde prepolymers with a high solubility in the organic phase and a low solubility in water. In its non-etherified form, the prepolymer contains a large number
of methylol groups, -CH₂OH, in its molecular structure. Etherification is the replacement of the hydroxyl hydrogens with alkyl groups, and is achieved by condensation of the prepolymer with an alcohol. When the alkyl groups comprise four carbon atoms or more and they have replaced more than about 50% of the hydroxyl hydrogen atoms on the prepolymer molecule, the prepolymer becomes soluble in the organic phase. Complete etherification is to be avoided, however, since hydroxyl groups are needed for the in situ self-condensation polymerization which occurs in the wall-forming step. Therefore, the prepolymer useful in the present invention are those in which from about 50% to about 98% of the hydroxyl hydrogen atoms have been replaced by alkyl groups of 4 to 10 carbon atoms each. In preferred practice, about 70% to about 90% of the groups have been etherified with a C₅C₆ alcohol. Both straight-chain and branched-chain alcohols are useful in the present invention, and all carbon atom ranges quoted herein are to be inclusive of their upper and lower limits.

Etherified urea-formaldehyde prepolymer are commercially available as solutions in alcohol or in a mixture of alcohol and xylene. The alcohol used as the solvent is normally identical to that used as the etherifying agent. Those in most common use are n-butanol and iso-butanol. The degree of etherification (butylation) in these commercial products ranges between 70% and 90%, and the solution contains from 50% to 85% by weight of prepolymer. Minor amounts of free formaldehyde are also frequently present. These solutions are typically sold as cross-linking agents for alkyd resins and used primarily for the formulation of coating and finishing products such as paints and lacquers.

Urea-formaldehyde prepolymer which have not been etherified are also available commercially, either in aqueous solutions or as water dissolvable solids, for use as adhesives. These can be etherified by condensation with the desired alcohol in a weakly acidic alcohol solution. The water of condensation is distilled off as an azeotrope with the alcohol until the desired degree of condensation (etherification) has been reached.

Urea-formaldehyde prepolymer themselves can be prepared by known techniques, notably the base-catalyzed reaction between urea and formaldehyde in water at a
weight ratio of 0.6 to 1.3 parts formaldehyde to one part urea by weight (1.2:1 to 2.6:1 on a molar basis), at a pH of 7.5 to 11.0 and a temperature of 50°C to 90°C. Etherification is then accomplished as described in the preceding paragraph.

The degree of etherification can be monitored by the quantity of water driven off during the distillation. Although the degree of etherification can be varied over a wide range to accommodate the needs of the reaction system, the rate of polymerization in the subsequent wall-forming step decreases as the degree of etherification increases. Too high a degree of etherification, therefore, tends to inhibit the progress of the wall formation. However, the water solubility of the prepolymer also decreases with increasing degree of etherification. Since low water solubility is a desirable feature of the prepolymer, it is best to avoid too low a degree of etherification. Thus, the suitable and preferred ranges are those stated above.

The organic solution comprising the core liquid and the etherilled prepolymer is most conveniently formed when the latter is predissolved in a solvent, as it is when commercially sold for the coatings and finishings industry. In the absence of such a solvent, there is a high degree of hydrogen bonding between the hydroxyl groups, and the prepolymer is a waxy solid which is difficult to dissolve in the capsule core liquid. Polar organic solvents are particularly useful for preventing the hydrogen bonding and dissolving the prepolymer; examples include alcohols, ketones, esters, and aromatics. When etherifying agents of high chain length are used, aliphatics and other non-polar solvents can also be used. The most useful solvents are the same alcohols used as the etherifying agents, the solution being taken directly from the reaction mixture of the etherification process.

The concentration of the prepolymer in the organic phase is not critical to the practice of the invention, but can vary over a wide range depending on the desired capsule wall strength and the desired quantity of core liquid in the finished capsule. It will be most convenient, however, to use an organic phase with a prepolymer concentration of from about 1% to about 70% on a weight basis, preferably from about 5% to about 50%.
C. Optional Additives

Optional additives include solvents, polymerization catalysts, and wall-modifying agents.

Solvents provide a means for controlling the wall-forming reaction. As explained in Section E below, the reaction occurs when protons come in contact with the urea-formaldehyde prepolymer. The organic phase must be sufficiently hydrophilic to attract protons to the interface from the bulk of the aqueous phase, yet sufficiently hydrophobic to prevent large amounts of protons from crossing the interface and causing polymerization to occur throughout the bulk of the droplet. An appropriately selected solvent added to the organic phase can correct the character of the organic phase to achieve these results. Clearly, the need for a solvent and the type of solvent needed—hydrophobic or hydrophilic—depends on the nature of the liquid core material. Aliphatic and alicyclic solvents are examples of hydrophobic solvents, and alcohols and ketones are examples of hydrophilic solvents. The amount of solvent can be varied as needed to achieve the desired results.

Catalysts capable of enhancing the wall-forming reaction can be placed in either the aqueous or organic phase. Catalysts are generally used when the core material is too hydrophobic, since they serve to attract protons toward the organic phase. Any water-soluble catalyst which has a high affinity for the organic phase and is capable of carrying a proton can be used. Carboxylic and sulfonic acids are particularly useful. Examples include orthochlorobenzoic acid, 2-phenyl-2,2-dichloroacetic acid, benzoic acid, salicylic acid, p-toluenesulfonic acid and dodecylbenzene sulfonic acid. The same catalytic effect can be accomplished by dissolving salts of these acids in the aqueous or organic phase and then acidifying the aqueous phase. The acid form is produced by ion exchange.

Wall-modifying agents serve to modify the character of the wall by varying its permeability to the core material. Suitable wall-modifying agents contain a substantial number of hydroxy or mercapto groups capable of reacting with the methylol groups on the prepolymer. The wall modifier can be used in the organic solution to add
multiple linkages to the methylol groups to increase the degree of cross-linking, or to exhaust active sites on the prepolymer to decrease the degree of cross-linking. Thus, depending on the kind of modifier used and the ratio of modifier to prepolymer, the permeability of the wall (and consequently the release rate of the core liquid) can be either increased or decreased. Castor oil is one example of such an agent. The preferred cross-linking wall-modifying agent is pentaerythritol tetrakis (mercaptopropionate) sold under the tradename MERCAPTATE Q-43 ESTER, by Cincinnati Milacron Chemicals. Other poly-functional mercaptan esters of a similar nature can be used.

D. Emulsion Formation

Once the organic solution is formed, an emulsion is formed by dispersing the organic solution in an aqueous solution comprising water and a surface-active agent. The relative quantities of organic and aqueous phase are not critical to the practice of the invention, and can vary over a wide range, limited mostly by convenience and ease of handling. In practical usage, the organic phase will comprise a maximum of about 55% by volume of the total emulsion and will comprise discrete droplets of organic solution dispersed in the aqueous solution.

The surface-active agent can be any of the wide variety of compounds known to be useful for lowering the surface tension of a fluid interface. Nonionic and anionic types are both useful. Examples of nonionic agents are long chain alkyl and mercaptan polyethoxy alcohols, alkylaryl polyethoxy alcohols, alkylaryl polyether alcohols, alkyl polyether alcohols, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene ethers, and polyethylene glycol esters with fatty or rosin acids. Examples of anionic agents are the calcium, amine, alkanolamine, and alkali salts of alkyl and alkylaryl sulfonates; vegetable sulfonates; and ethoxylated and propoxylated mono- and diethers of phosphoric acid. Blends of surface-active agents are also useful. Preferred surface-active agents are polyethelene glycol ethers of linear alcohols and alkali salts of alkyl and alkylaryl sulfonates.

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The quantity of surface-active agent is not critical to the invention, and can vary over a wide range. For convenience, the agent generally comprises from about 0.1% to about 5.0% by weight of the aqueous phase. The agent can be added before or after the emulsion is formed.

In some systems, emulsion stability can be enhanced by adding a protective colloid to the aqueous phase. A protective colloid stabilizes a dispersed system against aggregation, flocculation, and coalescence. Many materials are known to function as protective colloids and are available commercially, including polyvinyl alcohols, alginates, alpha- and gamma protein, casein, methyl cellulose, carboxymethyl cellulose, gelatin, glues, natural gums, polyacids, and starch. The colloid can be added to the aqueous phase prior to the formation of the emulsion, or to the emulsion itself after it has been formed. Although the colloid is an optional additive, its inclusion in the present system is preferred. Polyvinyl alcohol protective colloids are particularly preferred.

Additional compounds which serve as protective colloids are the salts of lignin sulfonate, such as the sodium, potassium, magnesium, calcium or ammonium salts. Among commercial lignin sulfonates are TREAX®, LTS, LTK and LTM, respectively, the potassium, magnesium and sodium salts of lignosulfonate (50% aqueous solutions), Scott Paper Co., Forest Chemical Products; MARASPERSE CR® and Marasperse CBOS-3®, sodium lignosulfonate, American Can Co.; Polyfon 0®, Polyfon T®, Reax 88B®, Reax 85B®, sodium salts of lignin sulfonate and Reax C-21®, calcium salt of lignin sulfonate, Westvaco Polychemicals; Orzan S and Orzan A, the sodium and ammonium salts of lignosulfonate, ITT Rayonier, Inc.

The actual quantity of colloid is not critical and any amount which is effective in enhancing the stability of the emulsion can be used. It is most convenient to use between about 0.1% and about 5.0% colloid by weight in terms of the aqueous phase.

The droplet size in the emulsion is not critical to the invention. For greatest utility of the final product, the droplet size will fall in the range of about 0.5 microns to about 4000 microns in diameter. The preferred range for most pesticidal applications is from...
about 1 micron to about 100 microns in diameter. The emulsion is prepared by the use of any conventional high shear stirring device. Once the desired droplet size is attained, mild agitation is generally sufficient to prevent droplet growth throughout the balance of the process.

E. Wall Formation

Once the dispersion and desired droplet size are attained, the system is acidified to a pH of between about 0 and about 4.0, preferably between about 1.0 and about 3.0. This causes the etherified urea-formaldehyde prepolymer to polymerize by self-condensing in situ and from a shell completely enclosing each droplet. Acidification can be accomplished by any suitable means, including adding any acid which is water-soluble, including formic acid, citric acid, hydrochloric acid, sulfuric acid, phosphoric acid, and the like. Acidification can also be achieved by the use of acidic dispersants or surface-active agents, provided that such components are added to the system after the emulsion has been formed.

As the polymer wall becomes more rigid, contact between the active groups on the prepolymer becomes increasingly more difficult. Thus, the in situ self-condensation polymerization reaction is self-terminating and is generally allowed to run to completion. The reaction can be arrested before completion, however, by raising the pH. In this manner, the wall tightness, rigidity, and permeability can be controlled. This can also be accomplished in most cases by a wall modifier as described above.

The rate of the in situ self-condensation polymerization reaction increases with both acidity and temperature depending upon the pH. The reaction can therefore be conducted anywhere within the range of about 20°C to about 100°C, preferably between about 40°C and about 70°C. The reaction will generally be complete within a few hours, although with high acidity and high temperature, the reaction can be completed within minutes.

Once the capsules are formed, they can be stored and used as an aqueous dispersion, or filtered and recovered as dried capsules. In either form, the capsules are useful and
effective in the slow release of the core liquid. Dispersions are preferably stabilized by dispersants dissolved in the continuous phase. Since most dispersants are more effective in neutral or basic solutions, it is preferable to raise the pH of the dispersion once the wall has been formed. This is accomplished by any water-soluble base. Any conventional dispersant can be used. Typical dispersants include lignin sulfonates, polymeric alkynaphthalene sulfonates, sodium naphthalene sulfonate, polymethylene bis-naphthalene sulfonate, and sodium N-methyl N-(long chain acid) taurates.

A unique feature of the process of the invention is that the solid permeable polymer shells enclosing the organic phase droplets are formed by means of condensation of the urea-formaldehyde prepolymer in the organic phase adjacent to the interface formed between the organic phase droplets and the aqueous phase solution. This is a consequence of the urea-formaldehyde prepolymer being dissolved in the organic phase.

The advantages of forming the polymer shells on the organic side of the interface are several. The first is that the process itself is more easily controlled than the prior art processes, which involve wall-forming condensation in the aqueous phase. When the condensation takes place in the aqueous phase, the wall-forming polymer can deposit upon the walls of the container in which the emulsion is present, on the agitator or any other structure which may be present, in addition to depositing on the droplets. In contrast, the wall-forming polymer that condenses on the organic side of the interface does not deposit on any of the container walls or other structures.

Additionally, when the condensation takes place in the aqueous phase, as in the prior art, a reduced amount of dispersed organic phase must be used inasmuch as if a higher dispersed organic phase content is utilized, the dispersion gets too thick and gels, thus effectively preventing formation of the microcapsules. Condensation on the organic side of the interface thus allows higher dispersed organic phase loading to be obtained because a gel is not formed in the aqueous phase.

In the examples set forth herein, in which the organic phase contains a pesticide, a higher loading of organic phase results in a more concentrated pesticide formulation.
This enables substantial cost savings to be achieved in manufacturing, packaging and transportation.

The following examples are offered as illustrative of both the process and product of the present invention, and are intended neither to define nor limit the invention in any manner.

EXAMPLE 1

An aqueous solution was prepared containing 309.6g water, 4.0g of an alkylnaphthalene sulfonate, sodium salt (CAS# 79103-93-8), and 11.2g of a naphthalene sulfonic acid polymer with formaldehyde, sodium salt (CAS# 50-00-0). The pH was then lowered to <2.0 with concentrated sulfuric acid.

A saturated organic solution was prepared by mixing 320g of a mixture of the RS/SR and RR/SS diastereomeric pairs of the fungicide propiconazole and 80g of 2-methylnaphthalene and raising the temperature to 50°C. This was then cooled to 30°C and 52g of Cymel U-1050-10 Resin (a 60% n-butanol solution of a partially butylated urea-formaldehyde prepolymer in which the degree of butylation of 70-90%) was added.

The organic solution was slowly added, with agitation, to the aqueous solution. The agitation rate was increased to get an average particle size of the emulsion droplets to between 2 µm and 20 µm. The mixture was then heated to 55°C for three hours under gentle agitation. Heating was discontinued and the pH raised to 9 with ammonium hydroxide.

EXAMPLE 2

An aqueous solution was prepared containing 309.6g water, 4.0g of an alkylnaphthalene sulfonate, sodium salt (CAS# 79103-93-8), and 11.2g of a naphthalene sulfonic acid polymer with formaldehyde, sodium salt (CAS# 50-00-0). The pH was then lowered to <2.0 with concentrated sulfuric acid.
A saturated organic solution was prepared by mixing 160g of the fungicide myclobutanil and 240g of 2-methylnaphthalene and raising the temperature to 50°C. This was then cooled to 30°C and 52g of Cymel U-1050-10 Resin (a 60% n-butanol solution of a partially butylated urea-formaldehyde prepolymer in which the degree of butylation of 70-90%) was added.

The organic solution was slowly added, with agitation, to the aqueous solution. The agitation rate was increased to get an average particle size of the emulsion droplets to between 2 µm and 20 µm. The mixture was then heated to 55°C for three hours under gentle agitation. Heating was discontinued and the pH raised to 9 with ammonium hydroxide.

As various changes could be made in the above methods without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.
We Claim:

1. A process for delaying or preventing the crystallization of a material having the tendency to crystallize in the aqueous phase which comprises

(a) providing an active solution comprising said material having a tendency to crystallize in the aqueous phase and an etherified urea-formaldehyde prepolymer dissolved therein in which from about 50% to about 98% of the methylol groups of said prepolymer have been etherified with a C₄-C₁₀ alcohol;

(b) creating an emulsion of said active solution in an continuous phase aqueous solution comprising water and a surface-active agent, wherein said emulsion comprises discrete droplets of said active solution dispersed in said continuous phase aqueous solution, there being formed thereby an interface between the discrete droplets of active solution and the surrounding continuous phase aqueous solution; and

(c) causing in situ self-condensation and curing of said urea-formaldehyde prepolymers in the organic phase of said discrete droplets adjacent to said interface by simultaneously heating said emulsion to a temperature between about 20°C to about 100°C, and adding to said emulsion an acidifying agent and maintaining said emulsion at a pH of between about 0 to about 4 for a sufficient period of time to allow substantial completion of in situ condensation of said resin prepolymers to convert the liquid droplets of said active solution to capsules consisting of solid permeable polymer shells enclosing said material.

2. A process according to claim 1 in which from about 70% to about 90% of the methylol groups of the prepolymer of step (a) have been etherified.

3. A process according to any one of claims 1-2 in which the alcohol with which the methylol groups of the prepolymer of step (a) have been etherified is a C₄-C₆ alcohol.
4. A process according to any one of claims 1-3 in which the alcohol with which the methylol groups of the prepolymer of step (a) have been etherified is n-butanol or isobutanol.

5. A process according to any one of claims 1-4 in which from about 70% to about 90% of the methylol groups of the prepolymer of step (a) have been etherified and the alcohol with which said methylol groups have been etherified is n-butanol.

6. A process according to any one of claims 1-5 in which, prior to the formation of the active solution of step (a), the prepolymer of step (a) is dissolved in an alcohol which is identical to that with which the prepolymer has been etherified.

7. A process according to any one of claims 1-6 in which the surface active agent of step (b) is selected from the group consisting alkali salts of alkyland alkylaryl sulfonates.

8. A process according to any one of claims 1-7 in which the aqueous solution of step (b) further comprises a protective colloid.

9. A process according to any one of claims 1-8 in which the aqueous solution of step (b) further comprises from about 0.1% to about 5.0% by weight of a polyvinyl alcohol protective colloid.

10. A process according to any one of claims 1-9 in which the prepolymer of step (a) comprises from about 1% to about 70% of the active solution on a weight basis.

11. A process according to claim any one of claims 1-9 in which the prepolymer of step (a) comprises from about 5% to about 50% of the organic solution on a weight basis.

12. A process according to claim any one of claims 1-9 in which the protective colloid of step (b) is a polyvinyl alcohol and comprises from about 0.1% to about 5.0% by weight of the aqueous phase.
13. A process according to claim any one of claims 1-9 in which the droplets of the dispersion formed in step (b) are from about 0.5 microns to about 4000 microns in diameter.

14. A process according to any one of claims 1-9 in which the droplets of the dispersion formed in step (b) are from about 1 micron to about 100 microns in diameter.

15. A process according to any one of claims 1-9 in which the in situ self-condensation in step (c) is done at a pH of between about 1.0 and about 3.0.

16. A process according to any one of claims 1-9 in which the in situ self-condensation in step (c) is done at a pH of between about 1.0 and about 3.0 and at a temperature between about 40°C and about 70°C.

17. A process according to any one of claims 1-16 wherein said active solution contains a wall-modifying agent which serves to modify the character of the wall by varying its permeability to the core material.

18. A process according to any one of claims 1-17 wherein said wall-modifying agent is pentaerythritol tetrakis (mercaptopropionate).

19. A process according to any one of claims 1-18, wherein said solid permeable polymer shells enclosing said material provide a slow rate of release of said material through said shells.

20. The process according to any one of claims 1-19, wherein said material comprises a compound selected from Beflubutamid, Bromobutide, Cafenstrole, Diphenamid, Fentrazamide, Flupoxam, Fomesafen, Isocarbamid, Isoxaben, Pethoxamid, Propyzamide, Clomeprop, Diflufenican, Etobenzanid, Fluacenacet, Mefenacet, Mefluidide, Fetamifop, Monalide, Naproanilide, Pentanochlor, Picolinafen, Benzoylprop, Flamprop-M, Alachlor, Propachlor, Propisochlor, Thencylchlor,
Cloransulam, Floransulam, Perfluidone, Asulam, Oryzalin, Chlorthiamid,
Chloramben, Pyriminobac-Methyl, Chlorthal-Methyl, Aminopyralid, Clopyralid,
Mesotrione, Sulcotrione, Benfuresate, Ethofumesate, Karbutilate, Carbetamide,
Chlorpropham, Desmedipham, Phenisophaein, Phenmedipham-Ethyl, Propham, Butroxydim,
Cycloxydim, Tepraloxydim, Tralkoxydim, Isoxaflutole, Cinidon-Ethyl, Flumiclorac,
Flumioxazin, Flumipropyn, Benfluralin, Butralin, Dinitramine, Ethalfuralin, Fluchloralin, Nitalin,
Oryzalin, Pendimethalin, Prodiaime, Profuralin, Trifluralin, Dinoseb, Dinoterb, Medinoterb Acetate,
Aclonifen, Bifenox, Fluorodifen, Fluoroglycofen-Ethyl, Fomesafen, Lactofen,
Nitrofen, Oxyfluorfen, Dazomet, Imazamethabenz-Methyl, Imazamox, Imazapic,
Imazapyr, Imazethapyr, Bromoxynil, Dichlobenil, Dimefuron, Methazole, Oxadiargyl,
Oxadiazon, Bromofenoxim, Chomeprop, 2,4-D, MCPA, 2,4,5-T, Abamectin,
Emamectin, Milbemectin, Milbemycin Oxime, Azadirachtin, Rotenone, Bendiocarb,
Carbaiy1, Carbofuran, Dimetilan, Pirimicarb, Alanyacarb, Aldicarb, Aldoxyacarb,
Methonyl, Thiodicarb, Thiol'anox, Aminocarb, Butacarb, Clothocarb, Dioxacarb,
Ethiofencarb, Fenobucarb, Isopropycarb, Methiocarb, Metolcarb, Mexacarbate,
Promecarb, Propoxur, Rynaxypyr, Trimethacarb, XMC, Xylylcarb, DNOC,
Sulfuramid, Amitraz, Chlordimeform, Buprofezin, Fenoxyacarb, Pyriproxyfen,
Thiocyclam, Clothianidin, Dinotefuran, Imidaclorpid, Thiamethoxam, Acetamiprid,
Thiacloprid, Lindane, Methoxychlor, Pentachlorophenol, Dioxabenzofos, Fosmethilan,
Dimethoate, Formothion, Prothoate, Azamethiphos, Coumaphos, Menazon,
Pyridaphenthion, Azinphos-Ethyl, Azinphos-Methyl, Dialifos, Phosmet, Pyrazophos,
Chlorpyrifos, Chlorpyrifos-Methyl, Tebupirimf’us, Quinalphos, Melhidalhion,
Bromophos, Famphur, Fenchlorphos, Jodfenphos, Parathion-Methyl, Temephos,
Trichlorfon, Mecarpon, Cyanofenoxim, EPN Leptothos, Fenamiphos, Phosfolan,
Acephate, Isocarbophos, Methamidophos, Indoxacar, Metoxadiazone, Dialifos,
Phosmet, Tetramethrin, Fipronil, Tebufenpyrad, Tolfenpyrad, Acrinathrin, Bifenthrin,
Cyfluthrin, Gamma-Cyhalothrin, Lambda-Cyhalothrin, Cypermethrin, Alpha-
Cypermethrin, Beta-Cypermethrin, Theta-Cypermethrin, Zeta-Cypermethrin,
Deltamethrin, Fenfluthrin, Fenpropothrin, Fenvalerate, Eufenvalerate, Permethrin,
Resmethrin, Bioresmethrin, Tefluthrin, Tetramethrin, Tralomethrin, Transfluthrin,
Etofenprox, Flufenprox, Halfenprox, Pyrimidifen, Chlorfenapyr, Spiromesifen,
Diafenthiuron, Sulcofon Sondum, Hydramethlynon, Isoprothiolane, Malonoben,

21. The process according to claim 20, wherein said material comprises metalaxyl-M.

22. The process according to claim 20, wherein said material comprises difenoconazole.
23. The process according to claim 20, wherein said material comprises myclobutanil.

24. The process according to claim 20, wherein said material comprises cyprodinil.

25. The process according to claim 20, wherein said material comprises propaconazol.

26. The process according to claim 20, wherein said material comprises thiamethoxam.

27. The process according to claim 20, wherein said material comprises lambda-cyhalothrin.

28. The process according to claim 20, wherein said material comprises clothianidin.