This invention relates to a process of manufacturing minute capsules en masse in a liquid manufacturing vehicle and to the capsule product, each capsule comprising a core and a seamless protecting wall surrounding the core. By “minute capsules” are meant capsules from a few microns to several thousand microns and possibly somewhat larger in average size.

This application is a continuation-in-part of United States patent application Ser. No. 13,725, filed Mar. 9, 1960, by Thomas C. Powell et al., now abandoned. The following is a related United States patent application directed to a specific process invention referred to herein, without limitation, as an example of a process employing the broader invention of this application and its above-identified parent application: Ser. No. 192,070, filed herewith by Thomas C. Powell et al., and now abandoned.

This preferred capsule-forming process of this invention involves the establishment of a system that is characterized as follows (these terms being defined below):

1. It is un-ionized;
2. It is in an agitated state;
3. It comprises the following three phases, characterized first of all by being mutually incompatible and further characterized, respectively, as being:
   a. a continuous liquid phase vehicle having a comple-
   mentary polymer (as defined hereafter) dissolved therein that constitutes at least about 75% by volume of the three phases in total,
   b. a discontinuous phase of minute, mobile entities of 
   core material, either solid or liquid, dispersed in the 
   vehicle and constituting about 5% or less by volume of the three phases in total, and
   c. a discontinuous phase of minute, mobile entities of 
   wall-forming material dispersed in the vehicle and 
   constituted by a solution of one or more hydrophobic 
   polymeric substances, the solution being capable of 
   wetting the core material and having a viscosity of 
   about from 1,000 to 4,000 centipoises.

This un-ionized, agitated system results without more in a deposit of the wall-forming material around the entities of core material. By reason of the viscosity and volume relation of the dispersed phase of wall-forming polymer solution, that phase is capable of deposit on the dispersed entities of core material and also is capable after deposit of maintaining itself as a wall against the shearing forces that exist as an incident of the required agitation of the system. The deposits quickly accumulate to a maximum thickness, which may be varied by varying the amount of the wall material provided and the degree and type of agitation used, which may vary in accordance with the need for protection of the core material and the protective characteristics of the wall-forming material selected for use.

Depending on the nature of the core material and that of the wall material, the capsules initially formed in the liquid vehicle by this system are more or less durable.

Various supplemental treatments of the capsules so formed may be employed to harden their walls and thereby impart to them greater durability and greater impermeability relative to the core material and the environment, among other properties.

In another aspect of the invention, two methods of hardening the walls of the capsules are described, and others are possible which either harden the polymeric material or concentrate the solution thereof. The methods described to illustrate this involve introducing into the liquid vehicle, usually after deposit of wall material on core entities has occurred, either a cross-linking or other hardening agent for some or all of the polymeric material in the wall-forming solution, together with a catalyst when needed, or another liquid which displaces the solvent component of the wall material in whole or in part and, being a poorer solvent or a non-solvent, and removable, concentrates the polymer solution and increases the viscosity and density of the walls. The cross-linking insolubilizes the polymer. The displacing liquid concentrates the polymer solution and also permits further concentration, by drying. Thus the displacing liquid is removable in a mild drying heat following recovery of the capsules from the vehicle, to leave the polymer in a more concentrated solution or a more permeable residual wall. These procedures are described more fully and are exemplified below. Another hardening procedure involves the introduction of a chelating agent which reversibly cross-links the polymer chains when they are of the known type susceptible to such action.

A further measure of protection is to cause deposit of an additional surrounding wall of polymeric material by a succeeding encapsulation step in which these initially-formed capsules, with or without hardening treatment, serve as the core entities.

This new process of making capsules en masse in a liquid vehicle by establishing a system as defined above differs from the previously-known system of United States Patents Nos. 2,800,457 and 2,800,458 (Reissue No. 24,899) in that the present system is un-ionized, and differs in some particulars with respect to the capsule materials that can constitute, and that preferably constitute, the vehicle, the capsule cores, and the capsule wall, respectively. This new process is applicable to the encapsulation of a wide range of core materials, including many that cannot be encapsulated by the processes described in those patents, and is applicable to the encapsulation of water-sensitive solids as well as non-water-sensitive solids, and also, through conjoint use of a further invention of Thomas C. Powell et al. respecting the use of polymeric material having special polar groups (described in United States patent application Ser. No. 192,070), is capable of encapsulating water and water-like liquid core materials.

Former specifically-disclosed processes employing a liquid manufacturing vehicle were incapable of usefully encapsulating water-sensitive solids and water or water-like liquids. Such known processes of making capsules en masse employed an aqueous vehicle and a three-compo-
nent system in which a deposit of hydrophilic wall-forming polymeric material around dispersed core entities would occur. This involved an aqueous vehicle and an aqueous solution of hydrophilic wall-forming polymeric material (e.g., a coacervate), which forbade the use of water-sensitive solids or aqueous materials. Very slightly water-soluble solids could be used only if the vehicle and the aqueous wall-forming solution were saturated with them.

It has been discovered that, if the polymeric material of the capsule wall, the solvent therefor, and the vehicle
are selected to constitute an un-ionized system, while satisfying the further criteria set forth herein, not only is it possible to produce a system in which deposit of the dispersed wall-forming entities around the dispersed core entities can be achieved, but also this can be done with core materials that could not before be successfully encapsulated by any en masse process using a liquid manufacturing vehicle.

The further criteria which define the useful classes of materials for the vehicle and the wall-forming solution are these: (1) the polymeric material of the wall-forming solution should be hydrophobic; (2) the solution of polymeric materials which form the capsule wall must be capable of resisting the core material in order to deposit around the core entities, and, with regard to wetting properties, the polymeric wall material preferably should have naturally-occurring or artificially-supplied wetting groups such as --COOH; --OH; --COOR; --CN; Cl; and F, the wetting properties of which in certain instances may be enhanced by the solvent; (3) the solution of polymeric material should have a viscosity, preferably of about 1,000 to 4,000 centipoises, such that it may both deposit itself and also maintain itself deposited around the core entities despite the shearing forces of the agitation needed to maintain the dispersion; (4) the solution of polymeric materials with the viscosity of the total three-phase system, by volume, preferably about 15% to 20%, that it can exist as a dispersed phase of mobile entities; capable of deposit around the core entities; and (5) the core material, the solution of polymeric material, and the vehicle must be mutually incompatible.

The wetting action of polymeric materials in solution as regards a particular core material may be measured by the total contact-angle measurements, adsorption measurements, and, the like, and suitable selections may be made thereby, all in accordance with existing knowledge of this subject per se. The solvent for the polymeric material may in certain instances be selected to enhance the wetting action of a particular polymeric material solution with respect to a chosen core material. If a solvent is chosen that is too good a solvent for a particular polymer, which inhibits its wetting action with respect to the core material, then a higher molecular weight of the polymer may be used to reduce the solubility of the solvent used, or else a poorer solvent is substituted.

The term "non-aqueous" as used in the specification and claims includes those liquids having small amounts of water, provided, however, that the amount of water in the non-aqueous liquid is such that the compatibility or incompatibility of the liquid relative to other materials in the capsule-forming solution is not altered as compared to water-free non-aqueous liquids.

The stated criterion that the core material, the polymeric material solution, and the vehicle be mutually incompatible is used in the ordinary sense that their separate existence in the system must not be impaired by any reactivity or miscibility between them.

Prefabricated incomplete systems for use in carrying out the novel process may be established and stored for future use. Even unskilled operators may complete such systems by the addition of the missing components, with the required agitation, and heat if necessary, together with agents for hardening the walls, to make capsules at a later time. The missing component(s) may involve any of those three necessary to form an operative system, and the absence may be total or partial.

An un-ionized liquid system is characterized by electrical conductivity, the un-ionized systems employed in this novel process are characterized by being substantially non-conductive.

The preferred system is one in which the liquid used as the solvent for the wall-forming hydrophobic polymeric material is used as a major component of the manufacturing vehicle. The vehicle then must contain another material, in solution in it, which is complementary to the wall-forming material in the sense that it creates an immobility between the vehicle and the solution of wall-forming polymeric material. In other words, it completes a liquid system in which the suitably-viscous wall-forming solution of hydrophobic polymeric material can exist as a separate phase dispersed in the vehicle because of repulsive forces between the polymeric material of the wall-forming solution and the complementary material. Without the complementary material, if the vehicle included or consisted of the same liquid that is used as the solvent for the wall-forming polymer, the vehicle would be compatible with and would dilute the polymer solution, which then could not exist as a separate phase of proper viscosity. Thus the stated immobility between the vehicle and the wall-forming polymer solution connotes the presence of a complementary material as a constituent of the vehicle when the vehicle includes a liquid compatible with or identical to the solvent used in the wall-forming solution.

The nature of the core material is the primary guide to the selection of the polymeric wall-forming material and of its solvent, and also to the selection of the liquid vehicle if that is not to consist of or include as a solvent the same material that is used as the wall-forming polymer solvent. This is because the process conditions usually are chosen with the wall-forming polymer material in mind. Hence the polymer and its solvent must be incompatible with the core material, but capable of wetting and depositing around entities of it; and the polymeric material of the wall-forming solution must be hydrophobic rather than hydrophilic. From the class of polymers and solvents made eligible by this, the further choice is from among those polymer-solvent pairs which give an un-ionized system and which can form a solution having a viscosity of from 1,000 to 4,000 centipoises. When, as preferred, the vehicle is made up chiefly or wholly of the same material as the polymer solvent, the only further choice is with respect to the complementary material, which, again, must give an un-ionized system and meet the incompatibility requirement. The complementary material must be incompatible with the core material and must act to make it possible for the wall-forming polymeric material solution to exist as a separate phase.

Given these criteria of selection, not known before in total as the determinants of an operative encapsulation system, the classes of materials that are useful in constituting the vehicle and the wall-forming polymer solution of the present system are ascertained from existing knowledge and means of selecting the materials and solvents in respect of four properties; viz.:

(1) solubility of the polymer in various solvents;
(2) ability of the polymer solution to wet the given nucleus material, liquid or solid;
(3) ability to yield an un-ionized system with the particular solvent(s) and vehicle(s); and
(4) ability to exist in a separate solution phase of the stated viscosity in the vehicle liquid.

Materials thus selected are useful in the encapsulation of any incompatible and wettable core material, liquid or solid.

Polymer solutions which meet the requirement of incompatibility with the vehicle in an un-ionized system are known from the study of Dobry and Boyer-Kawenoki, published in "Journal of Polymer Science," volume 2, No. 1, pp. 90 to 100 (1947), concerning the incompatibility of different polymers when in solution in a common solvent, whereby separation into two solution phases occurs when not impeded by excessive viscosity of the system. That impeding viscosity does not exist under the conditions here defined with respect to the viscosity and volumetric proportion of the wall-forming polymer solution as a core material, and the other phases.

Thus, for cases where another polymeric material is used as the complementary incompatibilizing material in a sys-
tem in which the same liquid is used as the solvent for the wall-forming polymeric material and as the major liquid used in the wall-forming solution may be any polymer that has a greater affinity for the core material than does the polymer serving as the complementary material, so that the wall-forming polymeric material will deposit preferentially around the core entities.

The following useful polymeric wall materials, solvent vehicles therefor, complementary phase-separation-inducing materials, and core materials useful in practicing the invention are given as examples separately and in combination, but such are illustrative only and are not to be considered exhaustive:

**Wall-forming polymeric materials**

(A) Ethyl cellulose (preferably one having an ethoxyl content of about 47.5 by weight and a viscosity of 22 centipoises in a 5% concentration, by weight, in an 80/20 toluene-ethanol bath at 25 degrees centigrade).

(B) Cellulose nitrate (preferably of 11.8% to 12.2% nitrogen content).

(C) Cellulose acetate phthalate (preferably of 30% to 40% esterified phthaloyl and of 17% to 22% esterified acetyl content).

(D) Acrylonitrile-methyl methacrylate (about 100,000 to 150,000 molecular weight by viscometric measurement).

(E) Acrylonitrile-styrene copolymer (about 15/85 by weight).

(F) Polystyrene (about 80,000 to 100,000 molecular weight by viscometric measurement).

(G) Vinylidene chloride-acrylonitrile copolymer (a) — (78.8% by weight), or (b) — (90.2% by weight).

(H) Epoxy resin (viscosity of 100-160 poises at 25 degrees centigrade, epoxy equivalent 175-218).

(I) Polytolyl-formal (preferred 30,000 molecular weight, hydroxyl content expressed as percent polylvinyl alcohol 5-7, and acetate content expressed as 25% polylvinyl acetate).

**Solvents**

I. Toluene-ethanol

II. Methyl ethyl ketone

III. Toluene-ethanol-ethyl acetate

IV. Acetone

V. Benzene

VI. Toluene

VII. Nitropropane

VIII. Dioxane

IX. Tetrahydro-naphthalene.

**Complementary substances for inducing phase separation**

(M) Polybutadiene, 8,000 to 10,000 molecular weight as determined by the osmotic pressure method.

(N) Polydimethyl-siloxane, 500 centistokes viscosity.

(O) Phenyl-methyl siloxane, 475 to 525 centistokes viscosity.

(P) Methacrylic polymer, viscosity 325 centistokes in low-viscosity petroleum distillate.

**Three-phase systems (symbols as above)**

A-I-M F-V-N

A-II-M B-II-M

A-II-N B-VII-P

D-V-N G(a)-II-M

D-II-N G(b)-II-M

D-V-N H-VI-M

E-I-M I-VII-M

E-I-N II-VII-M

**Core materials**

Sodium amobarbital, penicillin acid, ascorbic acid, polyvinyl pyrrolidone, acetyl-d-p-amino phenol, bacillus thuringiensis, lead, titanium dioxide, zirconium hydride, iron, zinc, calcium hydride, acrylonic hydrochloride, sodium chloride, phthalic anhydride, magnesium hydride, ammonium dichromate, sodium bicarbonate, stannous fluoride, sodium pyrophosphate, quinidine sulfate, aspirin, mepyliene blue, vanillin, quinine glucoside, phloroglucinol, cyanuric acid, trichlorocyanuric acid, potassium penicillin, d-propoxyphenyl hydrochloride, d-desoxyephedrine hydrochloride, sulfamazine, crystal violet, pepin enzyme, riboflavin, thiamine chloride, quinidine sulfate, albumin, pancreatin, bacitracin, aluminum aspirin, calcium silicate, gelatin, gum arabic, magnesium hydroxide, barium, calcium hydride, iron, zinc, manganese, potassium chloride, potassium iodide, potassium erythromycin-arlyl sulfate, citric acid.

The invention includes a particular procedure for establishing the defined system. This particular procedure involves the formation of an ionized solution system comprising two different polymeric materials and a common solvent, one polymeric material being the intended wall former, and a separation of this system into two separate solution phases, one containing chiefly one polymeric material and the other containing chiefly the other polymeric material, by a phenomenon of phase separation known in itself from the work of Dobry et al. cited above but not before known to be useful in a system of encapsulation. The two polymeric materials and the solvent may be assembled in any order to effect the phase separation, but it is preferable first to form a dilute solution of a polymeric material that is intended to be in the capsule-wall-forming phase, and then to induce the phase separation by addition of the second, or complementary, polymeric material, the only role of which is to induce and maintain the phase separation.

The second polymeric material in that case is one that has either no affinity or a lesser affinity for the nucleus material, so that the solution of the first polymeric material (the intended wall former) will be the one that preferentially deposits around the dispersed nucleus entities. This second polymeric material is referred to as a "complementary polymeric material."

The addition of the complementary polymeric material to an initial dilute solution of the wall-forming polymeric material permits easier control of the phase separation to yield a wall-forming solution phase of the proper viscosity (1,000 to 4,000 centipoises) and relative volume (about 15% to 20% of the total), especially in an initial operation before the procedure is standardized quantitatively for any particular polymeric materials and common solvent. In such an initial operation, the attainment of the desired viscosity in the wall-forming solution phase may be ascertained by microscopic observation of an agitated sample of the system containing dispersed core material, the criterion being that, when a useful wall-forming solution is present, it is seen that discrete entities with liquid walls are formed. A confirmation and basis for quantitative statement can be had by allowing the two separated solution phases to stratify and then measuring the viscosity and relative volume of the phase containing the intended wall-forming polymeric material. If the viscosity is too low, addition of more of the complementary material will cause additional concentration of the wall-forming phase to occur, with a consequent increase of viscosity of that phase, until the desired viscosity is attained.

The proper volume relation of the wall-forming phase (of proper viscosity) can be predetermined to a close enough approximation by calculation from readily-ascertained data on the relation of viscosity to concentration for a solution of the intended wall-forming polymer in the chosen solvent.

The order of addition can be reversed, or the two polymeric materials and the solvent can be brought together at one time, once the proper quantitative relations are established for the particular materials being used, since the resulting volume and viscosity (concentration) of the two separate phases are independent of the order of assembly.
The core material, always a minor component of the total volume of the system, can be added either before or during or after the formation of the solution or its separation into two solution phases. Similarly, the agitation of the system can be begun before, during, or after either of these steps. It is preferred, however, to agitate before, during, and after the phase separation, and to introduce the core material after the phase separation has taken place.

The direction of the agitation is made such as to reduce the core material to the desired entity size, if such is necessary, and, in any event, to assure thorough dispersion of it in the vehicle. The core entity size is pre-selected to give the desired capsule size after allowance for encapsulating wall thickness. With solid core materials, the entity size can be predetermined and obtained by any suitable grinding or milling.

When the three-phase capsule-forming system is established in this way, the continuous or vehicle phase consists of more dilute and less viscous solution containing the great part of the complementary polymeric material; and that polymeric material is the material which imparts the necessary incompatibility between the vehicle and the wall-forming solution phase and permits the latter to exist as a separate dispersed phase. The small amount of complementary polymeric material that may pass into the separated wall-forming solution phase by entrainment or otherwise is not objectionable.

Another alternative procedure is to pre-form a solution of hydrophobic wall-forming polymeric material having the desired viscosity within the stated range, and then to disperse it in a vehicle which is a liquid that is immiscible with this polymeric material solution and with the core material. This avoids any phase separation step such as is necessary when the wall-forming polymeric material is initially present in dilute solution and has to be driven out in a more concentrated solution as a separate phase having the desired viscosity.

In the following examples, the novel process will be disclosed in detail as applied to the encapsulation of various materials.

**Example I**

In this, the preferred example, there will be considered the encapsulation of ammonium nitrate particles in ethyl cellulose, the whole process being carried on in a 200-milliliter beaker at 25 to 50 degrees centigrade, with the materials being agitated constantly. There is introduced into the beaker 50 grams of a 2%, by weight, solution of ethyl cellulose in an 80/20 toluene-ethyl alcohol solvent, the particular ethyl cellulose having a viscosity grade of 22 centipoises and an ethoxyl content of 47.5%, by weight, the viscosity being determined when the ethyl cellulose is dispersed dry in a 5% concentration, by weight, in an 80/20 toluene-ethyl alcohol bath at 25 degrees centigrade. Into the ethyl cellulose is introduced 4 grams of ammonium nitrate particles which have a 200-micron average dimension, followed by the introduction of 25 grams of polybutadiene having a molecular weight of 8,000 to 10,000 as determined by the osmotic pressure method, such being a liquid and introduced over a period of fifteen to thirty minutes, during which time the ethyl cellulose in viscous solution separates from the rest of the system as small liquid entities which deposit on and surround each ammonium nitrate particle individually, such being brought about mechanically by the agitation and chemically by the wetting substituent groups of the ethyl cellulose. The phase separation of the ethyl cellulose as a liquid includes the carrying with it of a part of its original solvent, and in this particular example such mostly consists of the ethyl component and a small part of the toluene component. The liquid deposits are hardened by introducing into the system, after the liquid walls have been formed, 15 grams of toluene disiocyanate over a period of a minute or two, the toluene disiocyanate seemingly combining with the ethanol of the deposited wall material, forming plasticized self-supporting firm ethyl cellulose walls which are substantially water-impermeable. Water-sensitivity of the core material is not a requirement necessary for the practice of the invention, as materials not sensitive to water may be encapsulated thereby.

The finished capsules may be recovered from their liquid environment and dried for their end use, one of the uses being to act as core entities to receive a second wall of the same material or another material applied by the method of this invention or by any other en masse method, or by coating, spraying, or rolling.

**Example II**

To 196 grams of toluene add 4 grams of ethyl cellulose, as specified in Example I, and stir at 25 degrees centigrade until a clear solution is formed. Disperse there-in 16 grams of the desired core material reduced to any desired particle size between 40 and 5,000 microns, and, with agitation, slowly add, over a period of fifteen minutes, 40 grams of polybutadiene of 8,000 to 10,000 molecular weight, as obtained by the osmotic pressure method, which addition induces phase separation of the ethyl cellulose in solution of proper viscosity and the encapsulation of the core particles with it. The capsule walls may be hardened by the addition to the agitated system of 0.2 gram of tetrabutyl titanate.

**Example III**

Prepare a solution of 4 grams of ethyl cellulose as specified in Example I, in 196 grams of cyclohexane, stirring at 80 degrees centigrade. Add 16 grams of particles of intended core material (e.g., iron powder), and, with continued agitation, add, over a period of five minutes, 20 grams of polybutadiene, as specified in Example II, during which the system is allowed to cool to 50 degrees centigrade. The further cooling to room temperature, with stirring, results in a hardening of the capsule walls.

**Example IV**

Stir 4 grams of cellulose nitrate (11.8% to 12.2% nitrogen content) into 196 grams of methyl ethyl ketone at 25 degrees centigrade until a clear solution is formed, and then add 4 grams of the particulate intended core material (e.g., titanium dioxide). To the still-stirred solution add 50 grams of the polybutadiene specified in Example IV to form liquid-walled embryonic capsules. The capsule walls are hardened by stirring in 0.2 gram of tetrabutyl titanate.

**Example V**

Make a solution of 10 grams of vinylidene chloride-acrylonitrile copolymer, having a component ratio of 78.8/21.2, in 196 grams of tetrahydrofuran at 25 degrees centigrade until a clear solution is formed. Stir in 16 grams of the selected core material particles, and, with agitation, add 30 grams of polybutadiene of 8,000 to 10,000 molecular weight specified in Example II, to cause a polymer phase separation and the deposit of it on the core particles. The capsule walls may be hardened by the addition of tetrabutyl titanate in an amount of 0.4 gram with stirring.

**Example VI**

Add 10 grams of cellulose acetate phthalate (preferably of 30% to 40% esterified phthaloyl and 17% to 22% acetyl content) to 190 grams of dioxane at 25 degrees centigrade to form a clear solution. To this is added, as an exemplary coloring material, 20 grams of ammonium dichromate having a particle size of 250 to 800 microns, and add 72 grams of polybutadiene of 8,000 to 10,000 molecular weight as determined by the osmotic pressure method, which addition, with
continued agitation, forms capsules with liquid walls which may be hardened by extraction of the solvent with petroleum distillate.

Example VII

This process, particularly adapted to the encapsulation of aqueous solutions, is begun by introducing into a 500-ml beaker, at room temperature, 100 grams of a 5%, by weight, solution of a specially-modified copolymeric material having the general structure

![Formula](image)

dissolved in ethylene dichloride. Next, 10 grams of a 10%, by weight, solution of sodium ferrocyanide in water is introduced, with agitation to reduce it to the desired drop size, to furnish the capsule core material ingredient.

This preferred core material is exemplary of a colorless water solution of a color reactant. To the agitated mixture (which may be termed a water-in-oil emulsion) there is added slowly, as a phase-separation-inducing polymeric material, 15 grams of polydimethyl siloxane of, for instance, 500-centistoke viscosity, the addition preferably being made drop by drop over a period of three or four minutes to prevent agglomeration of the modified polyvinyl chloride wall-forming material as it separates out, thus permitting it to break up into small entities which deposit evenly over the droplets of nuclear material.

With continued agitation, the so-formed liquid-walled embryonic capsules are treated by the addition to the agitated system of 0.2 gram of tetraetyl titanate, drop by drop, which results in the cross-linking of the polymeric material content of the deposited liquid wall material, to a dense self-supporting condition, within a matter of a few minutes. If the drop size of the core material is of an average diameter of 100 microns, the capsules will have walls of 1 to 5 microns in thickness, such thickness being governed largely by the ratio of wall material to nuclear material that is used in a given vehicle system.

Other core materials, of a watery or aqueous nature, that can be encapsulated in place of the solution of sodium ferrocyanide in water are similar solutions of solids either in water, or ethylene glycol, and glycerine or their solutions with water or other materials, or solids which are not soluble in the liquid system, and all of the various materials heretofore mentioned as core materials.

Example VIII

This example is the same as Example VII except that the polymeric material intended for the capsule walls is a copolymer of vinyl chloride and acrylonitrile with acrylic acid groups, and having the general formula

![Formula](image)

Typical solvents to be used with the above wall-forming material are cyclohexane or methylisobutyl ketone, in the same amounts and in place of ethylene dichloride. The materials are used in the same ratio as in Example VII.

Example IX

Example VIII is followed, except that the wall-forming polymeric material is a copolymer of vinylidene chloride and acrylonitrile with acrylic acid groups having the general structure

![Formula](image)

and used in the same amount.

Example X

Example VIII is followed, except that the wall-forming polymeric material is of the structure

![Formula](image)

and used in the same amount.

Examples VII, VIII, IX and X exhibit the use of polymeric wall-forming materials that have special water-wetting groups thereon to facilitate the encapsulation of watery nuclei, but such property does not exclude them from use in the encapsulation of non-watery materials according to the broad aspects of the invention. However, the use of these special materials will be claimed in the Powell et al. application Ser. No. 192,070, filed herewith.

What is claimed is:

1. The process of forming minute capsules en masse which comprises

(a) establishing an agitated, un-ionized system consisting of a liquid vehicle forming a continuous first phase, a second phase dispersed therein consisting of minute mobile entities of core material, and a third phase dispersed therein consisting of minute, mobile liquid entities of a wall-forming solution of a hydrophobic polymeric material, the said core material being wettable by said wall-forming solution, the said three phases being mutually incompatible, the third phase constituting such a part of the total three-phase system, by volume, that it can exist as a dispersed phase of minute mobile entities capable of sufficient in amount to deposit around the core entities, and wherein said third phase has been formed by introducing a sufficient amount of polymeric complementary material in the presence of the wall-forming polymeric material and a solvent therefor to thereby effect a phase separation, whereby said wall-forming solution deposits on and around said core entities to form a liquid protective wall; and

(b) further curing the walls so formed.

2. The process of claim 1 in which the first phase is a non-aqueous organic liquid.

3. The process of claim 1 in which the core material is a liquid.

4. The process of claim 1 in which the core material is a solid.

5. The process of claim 1 in which the core material is partly liquid and partly solid.

6. The process of claim 1 in which the core material is water-sensitive but insoluble in the other components of the system.

7. The process of claim 1 in which the polymeric material is ethyl cellulose of about 47.5% ethoxy content, by weight.

8. The process of claim 1 in which the core material is ammonium nitrate.

9. The process of claim 1 in which the liquid vehicle is an 80/20 toluene-ethanol solvent.
The process of claim 1 in which the liquid vehicle is selected from the group consisting of toluene, ethanol, and benzene.

The process of claim 1 wherein the wall-forming polymer is hardened by reaction with a cross-linking agent for it.

The process of claim 11 in which the polymeric material is ethyl cellulose of an ethoxy content of about 47.5% by weight, the liquid vehicle is an 80/20 toluene-ethanol solvent, and the cross-linking agent is toluene diisocyanate.

The process of claim 11 in which the hydrophobic polymeric material is selected from the group consisting of ethyl cellulose, cellulose nitrate and poly methyl methacrylate.

The process of claim 11 wherein the walls so formed are hardened by displacing the solvent of said wall-forming solution, after deposit, with a solvent of greater volatility and thereafter removing a substantial part of said displacing solvent by evaporation.

The process of establishing a system capable of forming minute capsules en masse comprising establishing an agitated un-ionized system consisting of a liquid vehicle constituting at least 75% of the said system by volume and forming a continuous liquid first phase, a second phase dispersed therein consisting of minute, mobile liquid entities of core material, and a third phase dispersed therein consisting of minute, mobile liquid entities of a wall-forming solution of a hydrophobic polymeric material having a viscosity of about 1,000 to 4,000 centipoises and in sufficient amount to form a protective wall on said core material, said third phase being formed by introducing a polymeric complementary material of lower affinity for said core material in the presence of the wall-forming polymeric material and a solvent therefore and effecting a phase separation yielding said third phase, the said core material being wettable by said wall-forming solution and the three phases being mutually incompatible whereby said wall-forming solution deposits on and around said core entities.

The process of claim 15 in which the said system is established by

(a) forming a solution of a wall-forming polymeric material,

(b) introducing a complementary polymeric material of lower affinity for said core material, thereby effecting a phase separation yielding said vehicle phase as a solution containing chiefly said complementary polymeric material and said third phase as a separate phase containing chiefly said wall-forming polymeric material,

(c) introducing said second phase with agitation to cause the stated dispersion of said second and third phases.

The process of making en masse, minute capsules each having a seamless wall of hydrophobic polymeric material enclosing and retaining a particle of water-sensitive core material, comprising the steps of

(a) forming a liquid solution of hydrophobic polymeric material adapted to wet the core material when in such solution,

(b) disposing in solution (a) particles of incompatible core material, by agitation;

(c) with continued agitation adding a second polymeric material that is incompatible with the hydrophobic polymeric material and dissolved in the solvent for the hydrophobic polymeric material to induce separation of said hydrophobic polymeric material as a dense liquid solution phase dispersed, by the agitation, as small mobile liquid entities which deposit on the particles of core material to form seamless walls of hydrophobic polymeric material liquid solution; and

(d) treating the deposited walls to make them self-sustaining by a process of densification.

The process of claim 17 in which a plasticizer for the polymeric material is introduced into solution (a) before step (c),

(a) forming a solution of the intended wall material in a non-aqueous solvent;

(b) dispersing said particles of core material in said solution;

(c) adding to said solution, with agitation, a second polymeric miscible with the non-aqueous solvent but incompatible with the wall-forming polymeric material, whereby a dense solution of the wall-forming polymeric material is induced to separate out as a separate phase of small dispersed entities, which dense solution entities deposit on said particles individually to form liquid walls; and

(d) hardening the deposited wall material.

The process of claim 19 wherein the wall-forming polymeric material is ethyl cellulose and the second polymeric material is liquid polybutadiene.

In the establishment of an agitated three-phase capsule-forming system comprising (a) a liquid vehicle of a first phase, (b) minute, mobile liquid entities of core material dispersed in said vehicle as a second phase, and (c) minute, mobile entities of a solution of hydrophobic polymeric wall-forming material as a third phase, the said phases being mutually incompatible, the process of producing the said third phase solution with a viscosity of about 1,000 to 4,000 centipoises which comprises bringing together a solution of the wall-forming polymeric material and a solvent therefor in a proportion in which alone they form a less viscous solution, and a complementary polymeric material that is incompatible with the wall-forming polymeric material having a lower affinity for the core material and a greater affinity for said solvent than the said polymeric wall-forming material so that said complementary polymeric material preferentially dissolves in said solvent, whereby to rob the wall-forming solution of solvent and yield, as a separate phase, a solution of said polymeric wall-forming material having a higher viscosity, in the range stated.

The process of forming minute capsules en masse which comprises

(a) establishing an agitated, un-ionized system consisting of a liquid vehicle constituting a major portion of the said system by volume and forming a continuous liquid first phase, a second phase dispersed in said first phase consisting of minute, mobile liquid entities of a wall-forming solution of a hydrophobic polymeric material, said third phase being a minor but substantial portion by volume of the total system and having a viscosity such that the wall-forming solution deposits around individual core entities and remains there, the said core material being wettable by said wall-forming solution, the said three phases being mutually incompatible, and wherein said third phase has been formed by introducing a polymeric complementary material in the presence of the wall-forming polymeric material and a solvent therefor to thereby effect a phase separation yielding said third phase, whereby a protective wall is formed about said core entities, and

(b) hardening the walls so formed.

The process for forming minute capsules en masse which comprises

(a) establishing an agitated, un-ionized system consisting of a non-aqueous liquid vehicle constituting a
The process of making en masse, minute capsules each having a seamless wall of hydrophobic polymeric material enclosing and retaining a particle of water-sensitive core material, comprising the steps of
(a) forming a liquid solution of hydrophobic polymeric material adapted to wet the core material when in such solution;
(b) dispersing in solution (a) particles of incompatible core material, by agitation;
(c) with continued agitation adding a second polymeric material that is incompatible with the hydrophobic polymeric material and dissolved in the solvent for the hydrophobic polymeric material to induce separation of said hydrophobic polymeric material as a dense liquid solution phase dispersed, by the agitation, as small mobile liquid entities which deposit on the particle of core material to form seamless walls of hydrophobic polymeric material liquid solution; and
(d) treating the deposited walls to make them self-sustaining by a process of densification by the addition of a material that effects a molecular linking of the hydrophobic polymer of the wall-forming solution or by the addition of a liquid that extracts the solvent from the wall-forming polymer solution.

27. A process of making en masse minute capsules each having a wall of hydrophobic polymeric material enclosing and retaining a particle of non-aqueous material insoluble in and wettable by a solution of said wall-forming polymeric material in a non-aqueous solvent, consisting of the steps of
(a) forming a solution of the intended wall material in a non-aqueous solvent;
(b) dispersing said particles of core material in said solution;
(c) adding to said solution, with agitation, a second polymer miscible with the non-aqueous solvent but incompatible with the wall-forming polymeric material, whereby a dense solution of the wall-forming polymeric material is induced to separate out as a separate phase of small dispersed entities, which dense solution entities deposit on said particles individually to form liquid walls; and
(d) hardening the deposited wall material by the addition of a material that effects a molecular linking of the hydrophobic polymer of the wall-forming solution or by the addition of a liquid that extracts the solvent from the wall-forming polymer solution.

28. The process of forming minute capsules en masse which comprises
(a) establishing an agitated, un-ionized system consisting of a liquid vehicle forming a continuous first phase, a second phase dispersed therein consisting of minute mobile entities of core material, and a third phase dispersed therein consisting of minute, mobile liquid entities of a wall-forming solution of a hydrophobic polymeric material, the said core material being wettable by said wall-forming solution, the said three phases being mutually incompatible, the third phase constituting a part of the total three-phase system, by volume, that it can exist as a dispersed phase of minute mobile entities capable of and sufficient in amount to deposit around the core entities, and wherein said third phase has been formed by introducing into the system a sufficient amount of polymeric complementary material in the presence of the wall-forming polymeric material and a solvent therefor to thereby effect a phase separation whereby said wall-forming solution deposits on and around said core entities to form a continuous liquid protective wall, and
(b) hardening the walls so formed by the addition of a material that effects a molecular linking of the hydrophobic polymer of the wall-forming solution, or by the addition of a liquid that extracts the solvent from the wall-forming polymer solution.
or by the addition of a liquid that extracts the solvent from the wall-forming polymer solution.

29. The process for forming minute capsules en masse which comprises
(a) establishing an agitated, un-ionized system consisting of a non-aqueous liquid vehicle constituting a major portion of the said system by volume and forming a continuous liquid first phase, a second phase dispersed in said first phase consisting of minute, mobile entities of core material, and a third phase dispersed in said first phase consisting of minute, mobile liquid entities of a wall-forming solution of a hydrophobic polymeric material, said third phase being a minor but substantial portion by volume of the total system and having a viscosity such that the wall-forming solution deposits on the individual core entities to build up a capsule wall therearound, the said core material being wettable by said wall-forming solution, the said three phases being mutually incompatible, and wherein said third phase has been formed by introducing a polymeric complementary material in the presence of the wall-forming polymeric material and a solvent therefor to thereby effect a phase separation yielding said third phase, whereby a liquid wall is formed about said core entities, and
(b) hardening the walls so formed by the addition of a material that effects a molecular linking of the hydrophobic polymer of the wall-forming solution or by the addition of a liquid that extracts the solvent from the wall-forming polymer solution.

30. The process for forming minute capsules en masse which comprises
(a) establishing an agitated, un-ionized system consisting of a non-aqueous liquid vehicle constituting at least about 75% of the said system by volume and forming a continuous liquid first phase, a second phase dispersed in said first phase consisting of minute, mobile liquid entities of core material, and a third phase dispersed in said first phase consisting of minute, mobile liquid entities of a wall-forming solution of a hydrophobic polymeric material, said third phase constituting about 15% to 20% by volume of the total system and having a viscosity of about 1,000 to 4,000 centipoises such that the wall-forming solution deposits on and around individual core entities to form capsule walls, the said core material being wettable by said wall-forming solution, the said three phases being mutually incompatible, and wherein said third phase has been formed by introducing a polymeric complementary material in the presence of the wall-forming polymeric material and a solvent therefor to thereby effect a phase separation yielding said third phase, whereby a liquid protective wall is formed about said core entities, and
(b) hardening the walls so formed.

31. The process of forming minute capsules en masse which comprises
(a) establishing an agitated, un-ionized system consisting of a liquid vehicle having a complementary polymer dissolved therein forming a continuous first phase, a second phase dispersed therein consisting of minute, mobile entities of core material, and a third phase dispersed therein consisting of minute, mobile liquid entities of a wall-forming solution of a hydrophobic polymeric material, the said core material being wettable by said wall-forming solution, the said three phases being mutually incompatible, the third phase constituting such a part of the total three phase system, by volume, that it can exist as a dispersed phase of minute, mobile entities capable of and sufficient in amount to deposit around the core entities, and thereby forming a liquid protective wall,
(b) hardening the walls so formed by the addition of a material that effects a molecular linking of the hydrophobic polymer of the wall-forming solution or by the addition of a liquid that extracts the solvent from the wall-forming polymer solution.

32. The process of forming minute capsules en masse which comprises:
(a) establishing an agitated, un-ionized system consisting of a liquid vehicle forming a continuous first phase, a second phase dispersed therein consisting of minute mobile entities of core material, and a third phase dispersed therein consisting of minute, mobile liquid entities of a wall-forming solution of a hydrophobic polymeric material, the said core material being wettable by said wall-forming solution, the said three phases being mutually incompatible, the third phase constituting such a part of the total three-phase system, by volume, that it can exist as a dispersed phase of minute mobile entities capable of and sufficient in amount to deposit around the core entities, and wherein in said system there is present a polymeric complementary material sufficient in amount to effect the formation of said third phase, and
(b) hardening the walls so formed.

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