(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 October 2015 (01.10.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/145393 A2

(51) International Patent Classification:
C11D 3/50 (2006.01)

(21) International Application Number:
PCT/IB2015/052267

(22) International Filing Date:
27 March 2015 (27.03.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1087/MUM/2014 27 March 2014 (27.03.2014) IN

(72) Inventor; and
(71) Applicant : **KABRA, Puneet** [IN/IN]; 192, Sharmistha, Tarangan Towers, Near Korum Mall, Thane West, Thane 400606 (IN).

(74) Agent: **KHURANA & KHURANA, ADVOCATES AND IP ATTORNEYS**; E-13, UPSIDC, Site-IV, Behind-Grand Venice, Kasna Road, UP, National Capital Region, Greater Noida 201310 (IN).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

WO 2015/145393 A2

(54) **Title**: MICROENCAPSULATION OF MICROENCAPSULATION OF PERMETHRIN OR PYRETHROID CLASS OF COMPOUNDS FOR APPLICATION IN COSMETIC, INDUSTRIAL & TECHNICAL TEXTILES AND SURFACE COATINGS

(57) **Abstract**: This invention provides a method for preparing aminoplast microcapsules from a urea- formaldehyde or melamine-formaldehyde polymer with high methylol/butylol content and a second polymer which is an initiator that is used in conjunction which is a copolymer of one or more anhydrides, preferably ethylene maleic anhydride (EMA).

MICROENCAPSULATION OF MICROENCAPSULATION OF PERMETHRIN OR PYRETHROID CLASS OF COMPOUNDS FOR APPLICATION IN COSMETIC, INDUSTRIAL & TECHNICAL TEXTILES AND SURFACE COATINGS

BACKGROUND:

Microencapsulation may be used in different applications where a compound needs to be delivered or applied to a target area, and/or protected from its environment, and/or released in a time-delayed way and/or only after a treatment has been applied that triggers release. Various techniques for preparing microcapsules are known in the art and are used, depending on the contents to be encapsulated, the environment in which the microcapsules should retain their integrity and the desired release mechanism.

The following prior arts describe various methods of such encapsulation.

In the US patent US7238655, the inventor, Jeremy Nicholas Ness, describes a process for preparing microcapsules with perfume molecules in the core of the microcapsule and the wall material being a melamine-formaldehyde polymer and a second polymer comprising a polymer or copolymer of one or more anhydrides which improves the perfume retention of the shell.

The European patent EP 0238184 B1 describes that pesticidal formulation for application on a surface over which crawling insect or acarine pests crawl. The formulation comprises a microencapsulated Pyrethroid and a non-microencapsulated Pyrethroid, wherein in relation to the total amount of Pyrethroid in the formulation, the proportion which is non-microencapsulated Pyrethroid is at least 5%.

The European patent application EP 2204155 A1 narrates, that in the process of formation of microencapsulation, it is particularly advantageous if the capsules are cured by heating to a temperature between 60 deg C to 100 deg C for several hours with moderate stirring. It also specifies that typically 10-30% additional melamine and/or urea can be added at this stage to reduce the formaldehyde concentration in the final product and increase the wall thickness. Post curing, the temperature is reduced to 50 deg C and the dispersion is neutralized before being adjusted to a pH around 9.5.

The European patent EP 1797947 B1 discloses that addition of urea scavengers is preferred over formaldehyde scavengers during encapsulation.

In situ polycondensation is a known technique for preparing microcapsules and versatile microcapsule wall materials are used including Polyurea and Polyurethanes. Polyurea and polyurethane microcapsules are often used for rugged applications, such as for encapsulation of agrochemicals, e.g., herbicides and pesticides, where slow time-release is desired to set the agents free. For such applications, the microcapsules also require a relatively high mechanical strength.

Such wall materials are produced by having a first phase which is water-immiscible and includes a polyfunctional isocyanate, i.e., a diisocyanate and/or a polyisocyanate, and a second aqueous phase that may include a polyfunctional alcohol or amine, i.e., a diol and/or polyol, for obtaining a polyurethane capsule wall or a diamine and/or polyamine having —NH2 and/or —NH groups.

If the active material to be encapsulated is hydrophobic, it will be included in the water-immiscible phase; thereafter the two phases are mixed by high shear mixing to form an oil-in-water emulsion. In this emulsion, the polycondensation reaction will take place. Thus, the small droplets of the water-immiscible phase will be surrounded by the microcapsule wall formed by polycondensation of the isocyanate and the polyalcohol or polyamine as starting materials. Conversely, if the material to be encapsulated is hydrophilic, it will be included in the aqueous phase and the mixture of the two phases converted into a water-in-oil emulsion. The polycondensation reaction will then form microcapsule walls surrounding the droplets of water-miscible phase. Suitable emulsifiers are often utilized to aid in the preparation and stabilization of the emulsion.

The present invention describes microencapsulation of Permethrin or Pyrethroid class of compounds.

Typically, method of formation of microcapsules, keeping Pyrethroid molecules stable which may be introduced into the micro-capsules optionally in combination with one or more other chemicals.

Typically, these microcapsules are added as a functional finishing agent during textile/yarn manufacturing or finishing process, in home or commercial laundry or in paints and surface coating agents as an additive.

SUMMARY OF THE INVENTION:

In an embodiment, this invention provides a method for preparing aminoplast microcapsules from a urea-formaldehyde or melamine-formaldehyde polymer with high methylol/butylol content and a second polymer which is an initiator that is used in conjunction which is a copolymer of one or more anhydrides, preferably ethylene maleic anhydride. The method comprises the steps of,

Preparing aqueous solution of urea-formaldehyde or melamine-formaldehyde polymer with high methylol/butylol content;

agitating the aqueous mixture at approximately 50-200 rpm for approximately 5-30 minutes to obtain a substantially homogenous mixture;

adding a second polymer which is a copolymer of one or more anhydrides, preferably ethylene maleic anhydride EMA to the aqueous solution in conjunction with urea-formaldehyde or melamine-formaldehyde polymer with high methylol/butylolcontent;

agitating the mixture at speeds of 50-200 rpm for approximately 5-60 minutes to make the mixture homogenous;

maintaining pH of the aqueous mix at approximately 4.0 to 6.0 using a weak acid; and

initiating cross-linking of urea-formaldehyde or melamine-formaldehyde polymer with high methylol/butylol content and the copolymer EMA to form a double walled shell material.

Typically, approximately 0.1 to 20% by weight of urea-formaldehyde or melamine-formaldehyde polymer with high methylol/butylol content is added, preferably 1 to 10% by weight of urea-formaldehyde or melamine-formaldehyde polymer with high methylol/butylol content is added which helps in cross-linking to form single walled microcapsule.

Typically, approximately 0.1 to 25% by weight of copolymer EMA is added, preferably 0.5 to 20% by weight of copolymer EMA is added which is responsible for the second wall formation during encapsulation.

DETAILED DESCRIPTION:

In an embodiment, this invention provides a method for preparing aminoplast microcapsules from a urea-formaldehyde or melamine-formaldehyde polymer high methylol/butylol content and a second polymer which is an initiator that is used in conjunction which is a copolymer of one or more anhydrides, preferably ethylene maleic anhydride (EMA). The method comprises the steps of,

preparing aqueous solution of urea-formaldehyde or melamine-formaldehyde polymer with high methylol/butylol content;

agitating the mixture at speeds of 50-200 rpm for approximately 5-60 minutes to make the mixture homogenous;

adding a second polymer which is a copolymer of one or more anhydrides, preferably ethylene maleic anhydride EMA to the aqueous solution in conjunction with urea-formaldehyde or melamine-formaldehyde polymer with high methylol/butylol content;

agitating the mixture at speeds of 50-200 rpm for approximately 5-60 minutes to make the mixture homogenous;

maintaining pH of the aqueous mix at approximately 4.0 to 6.0 using a weak acid;

initiating cross-linking of urea-formaldehyde or melamine-formaldehyde polymer with high methylol/butylol content and the copolymer EMA to form a double walled shell material.

Typically, approximately 0.1 to 20% by weight of urea-formaldehyde or melamine-formaldehyde polymer with high methylol/butylol content is added, preferably 1 to 10% by weight of urea-formaldehyde or melamine-formaldehyde polymer with high methylol/butylol content is added for a single wall formation during encapsulation.

Typically, approximately 0.1 to 25% by weight of copolymer EMA is added, preferably 0.5 to 20% by weight of copolymer EMA is added which is responsible for the second wall formation during encapsulation.

In an embodiment of the invention, the copolymer EMA has a molecular weight ranging from 60,000 to 1,000,000, and preferably ranging from 60,000 to 600,000.

Permethrin is a common synthetic chemical, widely used as insecticide, acaricide, or insect repellent. It functions as a neurotoxin, affecting neuron membranes by prolonging sodium channel activation. It is not known to rapidly harm most mammals or birds, but is highly toxic to cats and fish. It has a low mammalian toxicity and is poorly absorbed by mammalian skin.

Pyrethroid is an organic compound similar to the natural pyrethrins produced by the flowers of pyrethrums such as *Chrysanthemum cinerariaefolium* and *Chrysanthemumcoccineum*. Pyrethroids now constitute the majority of commercial household insecticides. In the concentrations used in such products, they may also have insect repellent properties and are harmless to human beings in low doses. They are usually unstable in sunlight and disintegrate in one or two days and thus do not significantly affect groundwater quality. Permethrin is the dichlorovinyl derivative of pyrethrin.

Permethrin or Pyrethroid class of insecticides or repellent encapsulated by this method are hydrophobic and thus insoluble in water. These compounds mayoptionally be blended with one or more compounds which are also insoluble in water.

Fragrance oils are a composition and blends of various chemical and natural ingredients and which are highly volatile. The top notes of these fragrance oils vaporises as soon as they are exposed to the environment. These fragrance oils are developed with specifications such that they can be encapsulated and give better performance and longevity when applied onto the substrate/surface.

Essential oils are natural extracts without any modification. These essential oils are proven to have natural cure on humans in the science of aromatherapy. These essential natural oils are volatile in nature and vaporises as soon as they are exposed to the environment. These oils when encapsulated, give better performance and longevity when applied onto the substrate/surface.

Anti Bacterials are natural extracts as well as synthetically developed to exhibit antibacterial properties. They inhibit the growth of bacteria and some are bactericidal. In the effort to make them more durable and long lasting, they are encapsulated before they are applied onto the substrate/surface.

The compound of Permethrin or Pyrethroid class is added in to the aqueous mixture before film formation in presence of a high speed homogenizer which regulates the particle size as the microcapsules are formed. 10 to 40% by weight, preferably 20 to 35% by weight of the Permethrin or Pyrethroid compounds added. One or more compounds may be added with the Permethrin or Pyrethroid class of compounds. The high reactivity of the double walled shell material initiates the encapsulation process and the double walled shell materials cross-link with the Permethrin or Pyrethroid class of compounds to form microcapsules.

Typically, the particle size of the microcapsules is in the range of 1 to 100 microns, and preferably is in the range of 5 to 50 microns, and more preferably in the range of 10-20 microns.

The release profile of the microcapsules is both friction and diffusion based. The agitation speed and time during the encapsulation process helps in maintaining the proportion of friction and diffusion based microcapsules. The slight to no porosity for diffusion, is however, achieved due to the polymer and co-polymers used as a wall material.

Typically, the pH is regulated at every step and is maintained between 4.0 to 6.0 using a weak acid.

Typically, the time range for the encapsulation process is approximately between 2 minutes to 60 minutes and is dependent on the amount of Permethrin or Pyrethroid class of compounds and their respective grades.

In an embodiment of the invention, the curing process follows the encapsulation process which allows better cross-linkages of the polymers and strengthens the double walled shell and core structure microcapsule.

Typically, the curing process is done at temperatures ranging between 50 to 100 deg C, and preferably between 70-80 deg C.

Typically, the curing time ranges from 1 to 4 hrs, and preferably from 2 to 3 hrs, under moderate agitation.

Typically, the pH for curing is regulated from 4.0 to 6.0 using a weak acid, for better cross-linkages and better strengthening of the microcapsule walls.

In an embodiment of the invention, the free formaldehyde from the final product is removed by addition of formaldehyde scavenger, urea, melamine or any combination thereof. The formaldehyde scavenger is added after curing process is complete under moderate stirring.

In an embodiment of the invention, the encapsulation process gives free un-encapsulated compounds of approximately <0.5% of the weight of the product. Addition of a free un-encapsulated compound is added in a proportion ranging from 1 to 2% of the final product so that the application of this new final product provides immediate applicability.

In an embodiment of the invention, microcapsules with the Permethrin or Pyrethroid class of compounds, optionally in combination of one or more other compounds is used as an additive in textile/yarn manufacturing and finishing, in home and commercial laundry and in paints or surface coating agents.

In an embodiment of the invention, the textile substrate in the cosmetic, industrial and technical textiles may comprise but is not limited to cotton, polyester, polyamide, wool, silk, acrylic fibres and their blends which is treated with the functional microcapsules during various fabric/fibre processing stages at dosages ranging from 0.5 to 15%.

In an embodiment of the invention, the cosmetic, industrial and technical textiles are treated with microcapsules in industrial processes, commercial laundry and washing processes. The dosages of microcapsules range from 0.5 to 15%.

In an embodiment of the invention, the paint may comprise but is not limited to water base and oil base, preferably acrylic emulsion, distemper, varnishes, lustre in which the microcapsules are added in doses ranging from 0.5 to 10%, and preferably ranging from 2 to 5% is mixed before the surface coating process.

In an embodiment of the invention, microcapsule present in the base paints or surface coatings may range from 0.5 to 3%, and preferably from 1 to 2%, wherein the microcapsules are homogenized and then coated on the surface.

In an embodiment of the invention, the microcapsule dosing in the middle paints or surface coatings may range from 0.5 to 5%, and preferably from 1 to 3%, wherein the microcapsules are homogenized and then coated on the surface.

In an embodiment of the invention, the microcapsule dosing in the top paint coat range from 0.5 to 7%, and preferably from 2 to 5%, wherein the microcapsules are homogenized and then coated on the surface.

According to one embodiment, the dosing of 3-10% w/w of Microencapsulated Permethrin of the present invention will be durable and perform longer as compared to the direct application in Nylon/Polyester/HDPE Net such as mosquito net. For example, non-Encapsulated Permethrin which is emulsified and dosed at 2% w/w of Mosquito Net which is made up of Nylon/Polyester or HDPE will show repellency against mosquitoes for 2 months. And, microencapsulated Permethrin of the present invention which is dosed at 5% (active content: 33%) w/w of Mosquito Net which is made up of Nylon/Polyester or HDPE will show repellency against mosquitoes for 9 months

In an embodiment of the invention, the micro-capsules may contain other compounds or molecules or chemicals such as but not limited to fragrance oil, essential natural oil, antimicrobials, or the like.

Fragrances, Essential natural oils, Anti bacterials and other actives which are to be encapsulated are an oily medium.

In an embodiment of the invention, the formulations of the micro-capsules formed reduces or eliminates or repels insects and arthropods such as but not limited to mosquitoes, cockroaches, house flies or the like. These organisms come in contact with the substrate/surface incorporated with the functional micro-capsules which breaks the nervous system of the organisms which may also kill the organisms.

EXAMPLES:

Example 1: Compositions of the present invention

Components	**Composition A (in wt. %)**	**Composition B (in wt. %)**	**Composition C (in wt. %)**	**Composition D (in wt. %)**
Water	62	65	65	65
Melamine Formaldehyde	3.33	0	2.33	1.67

EMA Copolymer	1.33	1.33	1.33	1.33
Permethrin	30	30	30	30
Formaldehyde Scavenger	0.33	0.33	0.33	0.33
Caustic Soda	3	3	3	3

Example 2:

This example illustrates the performance and stability of the microcapsules using different grades of initiators and resins.

	Capsule A	Capsule B	Capsule C	Capsule D
Highly Methylated MF Resin	3.33	3.33	-	-
Partially Methylated MF Resin	-	-	3.33	3.33
EMA [M_w: 60,000-300,000]	-	3.33	3.33	-
EMA [M_w: 300,000-1,000,000]	3.33	-	-	3.33
Permethrin	30	30	30	30

The performance of the microcapsules and its stability is the best in Capsule D which uses melamine formaldehyde resin with moderate degree of alkylation and a relatively higher molecular weight EMA.

Permethrin used has a cis/trans ratio of 25:75.

Example 3

This example illustrates the performance of a Composition A in paint application on surfaces using application in different coats. Combination 1, 2 and 3 are the different combinations of Composition A used for the application on paint surfaces.

	Combination 1	Combination 2	Combination 3
Base Coat	-	-	2%
Middle Coat	-	3%	3%

Top Coat	6%	3%	3%

The performances of the three combinations were tested. The results of Combination 1 showed better repellency data than the other combinations tested.

Example 4:

In a Fabric Conditioner, microencapsulated Permethrin in accordance to the present invention dosed at 1-3% will be wash durable for a single wash in the fabric industrial/commercial/consumer laundry post laundering and post-machine drying as compared to a Non-Encapsulated dosed in the fabric conditioner/ fabric afterwash.

Combination 1 and 2 are the different combinations of Composition A used for application in fabric conditioner/ fabric afterwash

	Combination 1	Combination 2
Cationic Softener	98	98
Composition A	2	0
Emulsified Non-encapsulated Permethrin	0	2

Performance in case of Combination 1 is much better than in case of Combination 2. The fabric becomes single wash durable.

In the description, any or all numbers disclosed are deemed to be approximate values, regardless whether the word "about" or "approximate" is used in connection therewith. They may vary by 1 percent, 2 percent, 5 percent, or, sometimes, 10 to 20 percent. Whenever a numerical range with a lower limit, RL and an upper limit, Ru, is disclosed, any number falling within the range shall be specifically disclosed. In particular, the following numbers within the range are specifically disclosed: R=RL+k*(Ru-R), wherein k is a variable ranging from 1 percent to 100 percent with a 1 percent increment, i.e., k is 1 percent, 2 percent, 3 percent, 4 percent, 5 percent,..., 50 percent, 51 percent, 52 percent,..., 95 percent, 96 percent, 97 percent, 98 percent, 99 percent, or 100 percent. Moreover, any numerical range defined by two R numbers as defined in the above is also specifically disclosed.

The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used herein, the singular forms "a", "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises" or "comprising," when used in this specification, specify the presence of stated features, integers, steps, operations, elements, or components, but do not preclude or rule out the presence or addition of one or more other features, integers, steps, operations, elements, components, or groups thereof.

The process steps, method steps, protocols, or the like may be described in a sequential order, such processes, methods, and protocol may be configured to work in alternate orders. In other words, any sequence or order of steps that may be described does not necessarily indicate a requirement that the steps be performed in that order. The steps of processes described herein may be performed in any order practical. Further, some steps may be performed simultaneously, in parallel, or concurrently.

The aim of this specification is to describe the invention without limiting the invention to any one embodiment or specific collection of features. A person skilled in the relevant art may realize the variations from the specific embodiments that will nonetheless fall within the scope of the invention, and such variations are deemed to be within the scope of the current invention.

It may be appreciated that various other modifications and changes may be made to the embodiment described without departing from the spirit and scope of the invention.

CLAIMS

I claim:

1. A method for preparing aminoplast microcapsules comprising the steps of
   a) preparing an aqueous solution of urea-formaldehyde or melamine-formaldehyde polymer with high methylol/butylol content;
   b) agitating the aqueous solution at50-200 rpm for 5-30 minutes to obtain a substantially homogenous mixture;
   c) adding ethylene maleic anhydride (EMA) to the homogenous mixture in conjunction with said urea-formaldehyde or said melamine-formaldehyde polymer with high methylol/butylol content;
   d) agitating the mixture at speed of 50-200 rpm for 5-60 minutes to make the mixture homogenous;
   e) maintaining pH of the mixture at 4.0 to 6.0 using a weak acid; and
   f) initiating cross-linking of said urea-formaldehyde or said melamine-formaldehyde polymer with high methylol/butylol content and said EMA to form a double walled shell material.
2. The method of claim 1, wherein said urea-formaldehyde or said melamine-formaldehyde is present in a range from 0.1 to 20% by weight of the microcapsules.
3. The method of claim 1, said ethylene maleic anhydride is present in a range from 0.1 to 10% by weight of the microcapsules.
4. The method of claim 1, wherein the method further comprises the steps of:
   (a) adding10 to 35% by weight of Permethrin or one or more compounds from Pyrethroid class of compounds into the mixture in presence of a high speed homogenizer; and
   (b) initiating cross-linking of said Permethrin or one or more compounds from Pyrethroid class of compounds with the double walled shell material to form microcapsules.
5. The method of claim 4, wherein particle size of the microcapsules range from 1 to 100 microns.
6. The method of claim 4, wherein the method further comprises the step of curing at a temperature ranging from 50 to 100 deg C for 1 to 4 hrs.
7. The method of claim 1 or 4, wherein the method further comprises the step of adding fragrance oil, essential natural health oil and antimicrobials.

8. A water based acrylic or plastic paint comprising the microcapsules formed in claim 4 in an amount ranging from 0.5 to 10% w/w of the paint.
9. A Nylon, Polyester or HDPE net comprising the microcapsules formed in claim 4 in an amount of 1-10% w/w of the mosquito net.
10. A mosquito repellent fabric conditioner or after wash conditioner comprising the microcapsules formed in claim 4 in an amount ranging from 1 to 5% w/w of the conditioner.