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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
02 February 2023 (02.02.2023)

WIPO | PCT

(10) International Publication Number
WO 2023/009514 A1

(51) International Patent Classification:
B01J 13/18 (2006.01) *B01J 13/20* (2006.01)
C11D 3/50 (2006.01)

(21) International Application Number:
PCT/US2022/038330

(22) International Filing Date:
26 July 2022 (26.07.2022)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
21187930.9 27 July 2021 (27.07.2021) EP

(71) Applicant: **INTERNATIONAL FLAVORS & FRAGRANCES INC.** [US/US]; 521 WEST 57TH STREET, NEW YORK, New York 10019 (US).

(72) Inventor; and
(71) Applicant: **GABBARD, Ronald** [US/US]; c/o International Flavors & Fragrances Inc., 1515 State Highway #36, Union Beach, New Jersey 07735 (US).

(72) Inventors: **AKEROYD, Niels**; c/o International Flavors & Fragrances Inc., 1515 State Highway #36, Union Beach, New Jersey 07735 (US). **STOICA, Sonia-Patricia**; c/o International Flavors & Fragrances Inc., 1515 State Highway #36, Union Beach, New Jersey 07735 (US). **ANQUETIN, Florine**; c/o International Flavors & Fragrances Inc., 1515 State Highway #36, Union Beach, New Jersey 07735 (US). **CAVERO, Pedro Garcia**; c/o International Flavors & Fragrances Inc., 1515 State Highway #36, Union Beach, New Jersey 07735 (US). **HUNTER, Robert Allan**; c/o International Flavors & Fragrances Inc., 1515 State Highway #36, Union Beach, New Jersey 07735 (US). **LEI, Yabin**; c/o International Flavors & Fragrances Inc., 1515 State Highway #36, Union Beach, New Jersey 07735 (US). **LUCA VILCIU, Florin**; c/o International Flavors & Fragrances Inc., 1515 State Highway #36, Union Beach, New Jersey 07735 (US). **POPPLEWELL, Lewis Michael**; c/o International Flavors & Fragrances Inc., 1515 State Highway #36, Union Beach, New Jersey 07735 (US). **WIELAND, Julie Ann**; c/o International Flavors & Fragrances Inc., 1515 State Highway #36, Union Beach, New Jersey 07735 (US). **XU, Li**; c/o International Flavors & Fragrances Inc., 1515 State Highway #36, Union Beach, New Jersey 07735 (US).

(74) Agent: **TSENG, Xufan**; c/o International Flavors & Fragrances Inc., 1515 State Highway #36, Union Beach, New Jersey 07735 (US).

(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, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, 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, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, 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,

(54) Title: BIODEGRADABLE MICROCAPSULES

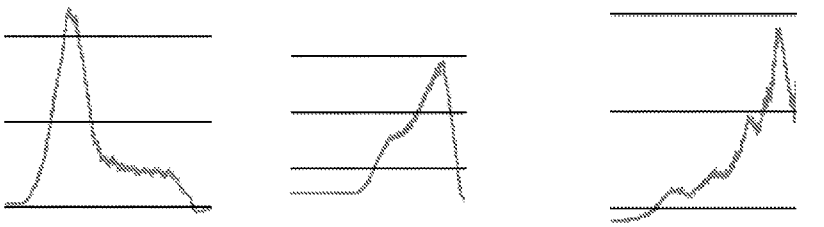

FIG. 1

(57) Abstract: Disclosed are biodegradable core-shell microcapsule slurries composed of microcapsules having a wall formed by self-condensation of an isocyanate in the presence of a denatured pea protein as dispersant. Also disclosed are consumer products containing such a core-shell microcapsule slurry and methods for producing core-shell microcapsule slurries.

WO 2023/009514 A1

[Continued on next page]

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

BIODEGRADABLE MICROCAPSULES

FIELD OF THE INVENTION

[0001] The present disclosure is directed towards biodegradable core-shell microcapsule slurries composed of microcapsules. More particularly, the microcapsules have walls formed by self-condensation of an isocyanate in the presence of a denatured pea protein as dispersant. Also disclosed are consumer products containing such a core-shell microcapsule slurry and methods for producing core-shell microcapsule slurries.

BACKGROUND OF THE INVENTION

[0002] Microcapsules are useful in a variety of applications where there is a need to deliver, apply, or release a fragrance or other active material in a time-delayed and controlled manner.

[0003] Conventional microcapsules each have a polymeric shell encapsulating an active material in a microcapsule core. The polymeric shell is typically formed *via* an interfacial polymerization reaction, namely, a polymerization that occurs at an interface between an aqueous phase and an oil phase. These microcapsules have been developed to provide good performance in various consumer products such as laundry detergents. See, *e.g.*, US 7,491,687, US 6,045,835, US 2014/0287008, and WO 2015/023961. Polyurea microcapsules have been developed for delivering fragrances. Their preparation involves the polymerization reaction between wall-forming materials, *e.g.*, a polyisocyanate and a polyamine. During the polymerization reaction, the polyisocyanate can react with many fragrance ingredients such as primary alcohols contained in a fragrance accord. The other wall-forming material polyamine is also reactive towards aldehyde fragrance ingredients. Primary alcohols and aldehydes are common ingredients in many fragrance accords. Such fragrances are not suitable to be encapsulated by conventional microcapsules. In addition, fragrance ingredients having a high-water solubility are also unsuitable for conventional encapsulation as these ingredients tend to stay in the aqueous phase instead of being encapsulated in the microcapsule oil core. Challenges remain in encapsulating fragrances and other active materials without losing reactive or water-soluble ingredients.

[0004] Methods to incorporate biodegradable polymers into microcapsule compositions have been described. For example, US 10,034,819 B2 and US 2019/0240124 A1 teach microcapsules with an inner shell and outer shell, wherein the outer shell is

produced by complex coacervation of first polyelectrolyte such as gelatin and a second polyelectrolyte such as carboxymethyl cellulose, sodium carboxymethyl guar gum, xanthan gum and plant gums.

[0005] Similarly, EP 2588066 B1 describes a coacervated capsule prepared with a coating layer composed of a protein, and optionally a non-protein polymer.

[0006] Further, EP 2811846 B1 describes the use of protein aggregates as an interface layer around a hydrophobic substance.

[0007] EP 1855544 B8 teaches the use of the encapsulation of an active ingredient in a matrix composed of 0.5-95 wt% of anionic polysaccharides and 0.5-95 wt% of peptides having a molecular mass within the range of 0.3-12 kDa.

[0008] EP 3746217 A1 and WO 2020/195132 A1 describe the preparation of core-shell microcapsules by cross-linking a protein into the wall of the microcapsule.

[0009] US 10,166,196 B2 discloses an agglomeration of primary microcapsules composed of a primary shell and outer shell, wherein the outer shell is the primary shell and outer shell are products of a complex coacervation reaction of a first protein such as a pea or soy protein and a second polymer such as an agar, gellan gum, gum Arabic, casein, cereal prolamine, pectin, alginate, carrageenan, xanthan gum, canola protein, dilutan gum, locus bean gum, or welan gum.

[0010] As such, these existing solutions still have limitations and do not adequately teach how to overcome the above-mentioned problems. Accordingly, there is still a need to develop a microcapsule composition suitable for encapsulating active materials having ingredients that are sustainable and biodegradable.

SUMMARY OF THE INVENTION

[0011] This invention is based, *inter alia*, on a core-shell microcapsule slurry composed of (a) microcapsules having a mean diameter of 1 to 100 microns, the core of the microcapsules comprises an active material (*e.g.,* at least one fragrance, pro-fragrance, malodor counteractive agent, or a combination thereof) and the shell of the microcapsules comprises a trimethylol propane-adduct of xylylene diisocyanate; (b) a dispersant comprising denatured pea protein; and (c) a hydrocolloid comprising gum Arabic added to an aqueous phase before an emulsification step during formation of the slurry.

[0012] Thus, in some aspects, the core-shell microcapsule slurry further includes at least one rheology modifier (*e.g.,* xanthan gum), preservative, emulsifier, or a combination thereof. In other aspects, the trimethylol propane-adduct of xylylene diisocyanate is present at 0.1 to 8% by weight of the core-shell microcapsule slurry. In a further aspect, the microcapsule shell of the microcapsules has a biodegradation rate of at least 20%, 30%, 40%, 50%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 98%, within 60 days according to OECD301F or OECD310, preferably of at least 20% within 60 days according to OECD301F or OECD310. In yet other aspects, the active material is a fragrance and the slurry has (a) less than 0.3% or 0.25% of a non-encapsulated fragrance, (b) a viscosity of less than 600 cps or less than 580 cps as measured at shear rate of 21 s^{-1}, or (c) a combination of (a) and (b). The present disclosure also provides a consumer product, *e.g.,* fabric softener, a fabric refresher, a liquid laundry detergent, a dry laundry detergent, personal wash, hair conditioner, hair shampoo, body lotion, deodorant, antiperspirant or fine fragrance is also provided.

[0013] The present disclosure also encompasses a method for producing a core-shell microcapsule slurry by (a) preparing an aqueous phase by (i) denaturing a pea protein, (ii) adjusting the pH to below 6 (*e.g.,* between 4.5 and 3.5), and (iii) adding gum Arabic as a hydrocolloid; (b) preparing an oil phase comprising an active material (*e.g.,* at least one fragrance, pro-fragrance, malodor counteractive agent, or a combination thereof) and a trimethylol propane-adduct of xylylene diisocyanate; (c) emulsifying the oil phase into the aqueous phase to form a slurry; and (d) curing the slurry at a temperature below 80°C (*e.g.,* in the range of 63°C to 67°C). In some aspects, the method further includes the addition of at least one rheology modifier, preservative, emulsifier, or a combination thereof. In other aspects, the rheology modifier (*e.g.,* xanthan gum) is added prior to step (c). In further aspects, the trimethylol propane-adduct of xylylene diisocyanate is present at a level between 0.1% and 8% based on the weight of the core-shell microcapsule composition.

[0014] All parts, percentages and proportions referred to herein and in the claims are by weight unless otherwise indicated.

[0015] The values and dimensions disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such value is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a value disclosed as "50%" is intended to mean

"about 50%" or alternatively, for example, about ± 2%, ± 5%, ± 10% or ± 15% of that value.

[0016] The details of one or more aspects of the disclosure are set forth in the description below. Each of the aspects and embodiments described herein are capable of being used together, unless excluded either explicitly or clearly from the context of the embodiment or aspect. These and other features, objects, and advantages of the disclosure will be apparent to those skilled in the art from the detailed description and the drawing in conjunction with the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] While the specification concludes with claims particularly pointing out and distinctly claiming the invention, it is believed that the invention will be better understood from the following description of the accompanying figure wherein:

[0018] FIG. 1 shows the force curve generated in a capsule breaking experiment for capsules prepared with whey protein according to Example 7 of WO 2020/131875 A2 with the addition of citric acid prior to curing to achieve a cure pH of 5; pea protein according to Example 2 herein; and pea protein with optimized cure temperatures and pH as described in Example 3 herein. This analysis indicated that capsule wall properties could be modified by the protein select and, more importantly, by optimizing the curing profile and pH of the capsule formation reaction.

[0019] FIG. 2 shows stable performance of ethyl vanillin in a base probe fragrance when encapsulated in microcapsules as described in Example 9.

DETAILED DESCRIPTION OF THE INVENTION

[0020] Definitions

[0021] As used herein, articles such as "a" and "an" when used in a claim, are understood to mean one or more of what is claimed or described.

[0022] As used herein, the terms "capsule" and "microcapsule" are used interchangeably.

[0023] As used herein, the terms "comprises", "comprised", "comprising" as used herein are synonymous with "includes", "included", "including" or "contains", "contained", "containing" and grammatical variants thereof, are inclusive or open-ended

and do not exclude additional, non-recited members, elements or method steps. The terms "comprises", "comprised" and "comprising", "includes", "included", "including", "contains", "contained", "containing" and grammatical variants thereof also include the term "consisting of".

[0024] As used herein, the terms "g," "mg," and "μg" refer to "gram," "milligram," and "microgram," respectively. The terms "L" and "mL" refer to "liter" and "milliliter," respectively.

[0025] Microcapsule Slurry

[0026] It has now been found that isocyanate, in particular a trimethylol propane-adduct of xylylene diisocyanate, when reacted with water to form a primary amine, will self-condense in the presence of a pea protein (as dispersant) and form a wall material suitable for encapsulation of active materials. Notably, the isocyanate does not cross-link with the protein. Rather, the pea protein appears to function as a scaffold to facilitate the self-condensation reaction of the isocyanate to form a wall polymer encapsulating the active material. Moreover, addition of gum Arabic prior to emulsification facilitates dissolution of pea protein in the aqueous phase thereby preventing aggregation of the same.

[0027] Accordingly, the present disclosure provides a core-shell microcapsule slurry composed of microcapsules, wherein the core of the microcapsules includes an active material and the shell of the microcapsules is formed by the self-condensation of a trimethylol propane-adduct of xylylene diisocyanate; a denatured pea protein as a dispersant; and gum Arabic as a hydrocolloid. Such a microcapsule slurry is shown to be an effective delivery system capable of delivering a fragrance in a consumer product such as a fabric conditioner. Additionally, the microcapsule slurry delivery system also finds utility in a wide range of consumer applications, *e.g.*, personal care products including shampoos, hair conditioners, hair rinses, hair refreshers; personal wash such as bar soaps, body wash, personal cleaners and sanitizers; fabric care such as fabric refreshers, softeners and dryer sheets, ironing water, industrial cleaners, liquid and powder detergent including unit dose capsules, rinse conditioners, and scent booster products; fine fragrances such as body mist and Eau De Toilette products; deodorants; roll-on products, and aerosol products.

[0028] The terms "microcapsule" and "capsule" are used herein interchangeably. The microcapsule wall of the core-shell microcapsules of the present disclosure is composed of

a single type of wall polymer, in particular an isocyanate, which self-condenses in the presence of water. In this regard, the wall of the core-shell microcapsule is formed from a single type of wall polymer that consists of or consists essentially of one or more isocyanates. In this regard, the wall is preferably not formed by the addition of a cross-linker, *e.g.,* a carbonyl, amine, polyamine, or polyalcohol crosslinker, and is therefore preferably devoid of an exogenous cross-linking agent.

[0029] *Isocyanates*. The terms "isocyanate," "multifunctional isocyanate," and "polyisocyanate" all refer to a compound having two or more isocyanate (-NCO) groups. Suitable isocyanates include, for example, 1,5-naphthylene diisocyanate, 4,4′-diphenylmethane diisocyanate (MDI), hydrogenated MDI (H12MDI), xylylene diisocyanate (XDI), tetramethylxylol diisocyanate (TMXDI), 4,4′-diphenyldimethylmethane diisocyanate, di- and tetraalkyldiphenylmethane diisocyanate, 4,4′-dibenzyl diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, the isomers of tolylene diisocyanate (TDI), optionally in a mixture, 1-methyl-2,4-diisocyanatocyclohexane, 1,6-diisocyanato-2,2,4-trimethylhexane, 1,6-diisocyanato-2,4,4-trimethylhexane, 1-isocyanatomethyl-3-isocyanato-1,5,5-trimethylcyclohexane, chlorinated and brominated diisocyanates, phosphorus-containing diisocyanates, 4,4′-diisocyanatophenylperfluoroethane, tetramethoxybutane 1,4-diisocyanate, butane 1,4-diisocyanate, hexane 1,6-diisocyanate (HDI), dicyclohexylmethane diisocyanate, cyclohexane 1,4-diisocyanate, ethylene diisocyanate, phthalic acid bisisocyanatoethyl ester, also polyisocyanates with reactive halogen atoms, such as 1-chloromethylphenyl 2,4-diisocyanate, 1-bromomethylphenyl 2,6-diisocyanate, and 3,3-bischloromethyl ether 4,4′-diphenyldiisocyanate. Sulfur-containing polyisocyanates are obtained, for example, by reacting hexamethylene diisocyanate with thiodiglycol or dihydroxydihexyl sulfide. Further suitable diisocyanates are trimethylhexamethylene diisocyanate, 1,4-diisocyanatobutane, 1,2-diisocyanatododecane, dimer fatty acid diisocyanate, or a combination thereof.

[0030] Other suitable commercially-available isocyanates sold under the tradenames LUPRANATE® M20 (PMDI, commercially available from BASF containing isocyanate group "NCO" 31.5 wt %), where the average n is 0.7; BAYHYDUR® N304 and BAYHYDUR® N305, which are aliphatic water-dispersible isocyanates based on hexamethylene diisocyanate; DESMODUR® N3600, DESMODUR® N3700, and

DESMODUR® N3900, which are low viscosity, polyfunctional aliphatic isocyanates based on hexamethylene diisocyanate; DESMODUR® 3600 and DESMODUR® N100 which are aliphatic isocyanates based on hexamethylene diisocyanate, commercially available from Bayer Corporation (Pittsburgh, PA); PAPI® 27 (PMDI commercially available from Dow Chemical having an average molecular weight of 340 and containing NCO 31.4 wt %) where the average n is 0.7; MONDUR® MR (PMDI containing NCO at 31 wt % or greater, commercially available from Bayer) where the average n is 0.8; MONDUR® MR Light (PMDI containing NCO 31.8 wt %, commercially available from Bayer) where the average n is 0.8; MONDUR® 489 (PMDI commercially available from Bayer containing NCO 30-31.4 wt %) where the average n is 1.0; poly[(phenylisocyanate)-co-formaldehyde] (Aldrich Chemical, Milwaukee, WI), other isocyanate monomers such as DESMODUR® N3200 (poly(hexamethylene diisocyanate) commercially available from Bayer), and TAKENATE® D110N (xylene diisocyanate adduct polymer commercially available from Mitsui Chemicals corporation, Rye Brook, NY, containing NCO 11.5 wt %), DESMODUR® L75 (an isocyanate base on toluene diisocyanate commercially available from Bayer), and DESMODUR® IL (another isocyanate based on toluene diisocyanate commercially available from Bayer).

[0031] In some aspects, the isocyanate used in the preparation of the capsules of the present disclosure is a single isocyanate. In other aspects the isocyanate is a combination of isocyanates. In some aspects, the combination of isocyanates includes an aliphatic isocyanate and an aromatic isocyanate. In particular, the combination of isocyanates is a biuret of hexamethylene diisocyanate and a trimethylol propane-adduct of xylylene diisocyanate. In certain aspects, the isocyanate is an aliphatic isocyanate or a combination of aliphatic isocyanate, free of any aromatic isocyanate. In other words, in these aspects, no aromatic isocyanate is used to prepare the capsule wall. In accordance with certain aspects of the present disclosure of a trimethylol propane-adduct of xylylene diisocyanate, the wall is formed form a single isocyanate, which is a trimethylol propane-adduct of xylylene diisocyanate.

[0032] The average molecular weight of certain suitable isocyanates varies from 250 Da to 1000 Da and preferably from 275 Da to 500 Da. In general, the range of the isocyanate concentration varies from 0.1% to 10%, preferably from 0.1% to 8%, more preferably from 0.2% to 5%, and even more preferably from 1.5% to 3.5% or 0.1% to 5%,

all based on the weight of the capsule delivery system. Ideally, the isocyanate is present at a level of less than 1% (*e.g.*, 0.99%, 0.98%, 0.97%, 0.96%, 0.95%, 0.94%, 0.93%, 0.92%, 0.91%, 0.90%, 0.85%, 0.80%, 0.70%, 0.60%, 0.50%, 0.4%, 0.3%, 0.2% or 0.1%) by weight of the biodegradable core-shell microcapsule composition.

[0033] *Microcapsule Formation Aids.* Most microcapsule formation aids are used as dispersants (namely, emulsifiers or surfactants). They facilitate the formation of stable emulsions containing nano- or micro-sized oil drops to be encapsulated. Further, microcapsule formation aids improve the performance of the microcapsule by stabilizing capsules and/or their deposition to the target areas or releasing to the environment. Performance is measured by the intensity of the fragrance release during various touchpoints of the user experience, such as the pre-rub and post-rub phases in a laundry experience. The pre-rub phase is the phase when the microcapsules have been deposited on the cloth, *e.g.,* after a fabric softener containing microcapsules has been used during the wash cycle. The post-rub phase is after the microcapsules have been deposited and the microcapsules are broken by friction or other similar mechanisms.

[0034] The amount of these microcapsule formation aids is anywhere from about 0.1% to about 40% by weight of the microcapsule, more preferably from 0.1% to about 10%, or more preferably 0.1% to 5% by weight.

[0035] Examples of microcapsule formation aids are polyvinyl pyrrolidone, polyvinyl alcohol, poly(styrene sulfonate), carboxymethyl cellulose, sodium salt of naphthalene sulfonate condensate, co-polymer of ethylene and maleic anhydride, an alginate, hyaluronic acid, poly(acrylic acid), carboxymethylcellulose, copolymers of acrylic acid and acrylamide, copolymer of acrylamide and acrylamidopropyltrimonium chloride, terpolymers of (acrylic acid, acrylamide, and acrylamidopropyltrimonium chloride), partially or completely hydrolyzed polyvinyl acetate polymers (*i.e.*, polyvinyl alcohol), or a combination thereof.

[0036] Other microcapsule formation aids include water-soluble salts of alkyl sulfates, alkyl ether sulfates, alkyl isothionates, alkyl carboxylates, alkyl sulfosuccinates, alkyl succinamates, alkyl sulfate salts such as sodium dodecyl sulfate, alkyl sarcosinates, alkyl derivatives of protein hydrolysates, acyl aspartates, alkyl or alkyl ether or alkylaryl ether phosphate esters, sodium dodecyl sulphate, phospholipids or lecithin, or soaps, sodium, potassium or ammonium stearate, oleate or palmitate, alkylarylsulfonic acid salts such as

sodium dodecylbenzenesulfonate, sodium dialkylsulfosuccinates, dioctyl sulfosuccinate, sodium dilaurylsulfosuccinate, poly(styrene sulfonate) sodium salt, isobutylene-maleic anhydride copolymer, sodium alginate, cellulose sulfate and pectin, isobutylene-maleic anhydride copolymer, gum Arabic, carrageenan, sodium alginate, pectic acid, tragacanth gum, almond gum and agar; semi-synthetic polymers such as sulfated cellulose, sulfated methylcellulose, carboxymethyl starch, phosphated starch, lignin sulfonic acid; and synthetic polymers such as maleic anhydride copolymers (including hydrolysates thereof), polyacrylic acid, polymethacrylic acid, acrylic acid butyl acrylate copolymer or crotonic acid homopolymers and copolymers, vinylbenzenesulfonic acid or 2-acrylamido-2-methylpropanesulfonic acid homopolymers and copolymers, and partial amide or partial ester of such polymers and copolymers, carboxymodified polyvinyl alcohol, sulfonic acid-modified polyvinyl alcohol and phosphoric acid-modified polyvinyl alcohol, phosphated or sulfated tristyrylphenol ethoxylates.

[0037] Commercially available surfactants include, but are not limited to, sulfonated naphthalene-formaldehyde condensates sold under the tradename MORWET® D425 (sodium salt of alkylnaphthalenesulfonate formaldehyde condensate, Akzo Nobel, Fort Worth, TX); partially hydrolyzed polyvinyl alcohols sold under the tradenames MOWIOL®, *e.g.*, MOWIOL® 3-83 (Air Products), or SELVOL® 203 (Sekisui), or polyvinyl alcohols such as Ultalux FP, Ultalux FA, Ultalux AD, OKS-8089 (Sourus); ethylene oxide-propylene oxide block copolymers or poloxamers sold under the tradenames PLURONIC®, SYNPERONIC® or PLURACARE® materials (BASF); sulfonated polystyrenes sold under the tradename FLEXAN® II (Akzo Nobel); ethylene-maleic anhydride polymers sold under the tradename ZEMAC® (Vertellus Specialties Inc.); copolymer of acrylamide and acrylamidopropyltrimonium chloride sold under the tradename SALCARE® SC 60 (BASF); and polyquaternium series such as Polyquaternium 11 ("PQ11;" a copolymer of vinyl pyrrolidone and quaternized dimethylaminoethyl methacrylate; sold by BASF as Luviquat PQ11 AT 1). Surfactant MOWIOL® 3-83 has a viscosity of 2-4 mPa·S (*e.g.*, 3 mPa·S), a degree of hydrolysis of 80-85% (*e.g.*, 83%), an ester value of 170-210 mg KOH/g (*e.g.*, 190 mg KOH/g), and a residual unhydrolyzed acetyl content of 13-18% (*e.g.*, 15%). In certain aspects, the surfactant or emulsifier is a sulfonated polystyrene, *e.g.*, the high molecular weight polystyrene sulfonate, sodium salt sold under the tradename FLEXAN® II.

[0038] In other aspects, the capsule formation aid is a processing aid such as a hydrocolloid, which improves the colloidal stability of the slurry against coagulation, sedimentation and creaming. In accordance with the present disclosure, the hydrocolloid is added to the aqueous phase before an emulsification step during formation of the slurry. The term "hydrocolloid" refers to a broad class of water-soluble or water-dispersible polymers having anionic, cationic, zwitterionic or non-ionic character. Hydrocolloids useful in the present disclosure include, but are not limited to, polycarbohydrates, such as starch, modified starch, dextrin, maltodextrin, and cellulose derivatives, and their quaternized forms; natural gums such as alginate esters, carrageenan, xanthan, agar-agar, pectins, pectic acid, gum Arabic, gum tragacanth and gum karaya, guar gums and quaternized guar gums; gelatin, protein hydrolysates and their quaternized forms; synthetic polymers and copolymers, such as poly(vinyl pyrrolidone-co-vinyl acetate), poly(vinyl alcohol-co-vinyl acetate), poly((met)acrylic acid), poly(maleic acid), poly(alkyl(meth)acrylate-co-(meth)acrylic acid), poly(acrylic acid-co-maleic acid)copolymer, poly(alkyleneoxide), poly(vinylmethylether), poly(vinylether-co-maleic anhydride), and the like, as well as poly-(ethyleneimine), poly((meth)acrylamide), poly(alkyleneoxide-co-dimethylsiloxane), poly(amino dimethylsiloxane), Ultrez 20 (Acrylates/C10-30 Alkyl Acrylate Crosspolymer), cross-linked homopolymer of acrylic acid polymerized in a cyclohexane and ethyl acetate co-solvent system sold under the tradename CARBOPOL® Ultrez 30, acrylates copolymer sold under the tradename ACULYN® Excel (Acrylates Copolymer), crosslinked polyacrylic acid polymer sold under the tradename CARBOPOL® 981 (Carbomer), and the like, and their quaternized forms. In certain aspects, the microcapsule slurry is prepared in the presence of gum Arabic as a hydrocolloid.

[0039] The capsule formation aid can also be used in combination with carboxymethyl cellulose ("CMC"), polyvinylpyrrolidone, polyvinyl alcohol, alkylnaphthalenesulfonate formaldehyde condensates, and/or a surfactant during processing to facilitate capsule formation. Examples of surfactants that can be used in combination with the capsule formation aid include, but are not limited to, cetyl trimethyl ammonium chloride (CTAC), poloxamers sold under the tradenames PLURONIC® (*e.g.*, PLURONIC® F127), PLURAFAC® (*e.g.*, PLURAFAC® F127), or Miranet-N, saponins sold under the

tradename Q-NATURALE® (National Starch Food Innovation); or a gum Arabic such as Seyal or Senegal.

[0040] In certain aspects, the CMC polymer has a molecular weight range between about 90,000 Daltons to 1,500,000 Daltons, preferably between about 250,000 Daltons to 750,000 Daltons and more preferably between 400,000 Daltons to 750,000 Daltons. The CMC polymer has a degree of substitution between about 0.1 to about 3, preferably between about 0.65 to about 1.4, and more preferably between about 0.8 to about 1.0. The CMC polymer is present in the capsule slurry at a level from about 0.1% to about 2% and preferably from about 0.3% to about 0.7%. in other aspects, polyvinylpyrrolidone used in this invention is a water-soluble polymer and has a molecular weight of 1,000 to 10,000,000. Suitable polyvinylpyrrolidone are polyvinylpyrrolidone K12, K15, K17, K25, K30, K60, K90, or a combination thereof. The amount of polyvinylpyrrolidone is 2-50%, 5-30%, or 10-25% by weight of the capsule delivery system. Commercially available alkylnaphthalenesulfonate formaldehyde condensates include MORWET® D-425, which is a sodium salt of naphthalene sulfonate condensate by Akzo Nobel, Fort Worth, TX.

[0041] In some aspects, a food-grade dispersant is used. The term "food-grade dispersant" refers to a dispersant having a quality as fit for human consumption in food. They can be natural or non-natural products. A natural product or surfactant refers to a product that is naturally occurring and comes from a nature source. Natural products/surfactants include their derivatives which can be salted, desalted, deoiled, fractionated, or modified using a natural enzyme or microorganism. On the other hand, a non-natural surfactant is a chemically synthesized surfactant by a chemical process that does not involve an enzymatic modification.

[0042] Natural dispersants include quillaja saponin, lecithins, gum Arabic, pectin, carrageenan, chitosan, chondroitin sulfate, modified cellulose, cellulose gum, modified starch, whey protein, pea protein, egg white protein, silk protein, gelatin of fish, proteins of porcine or bovine origin, ester gum, fatty acids, or a combination thereof. In certain aspects, the microcapsule composition is prepared in the presence of denatured protein, *e.g.*, a denatured pea protein, as a dispersant.

[0043] Plant storage proteins are proteins that accumulate in various plant tissues and function as biological reserves of metal ions and amino acids. Plant storage proteins can be classified into two classes: seed or grain storage proteins and vegetative storage proteins.

Seed/grain storage proteins are a set of proteins that accumulate to high levels in seeds/grains during the late stages of seed/grain development, whereas vegetative storage proteins are proteins that accumulate in vegetative tissues such as leaves, stems and, depending on plant species, tubers. During germination, seed/grain storage proteins are degraded and the resulting amino acids are used by the developing seedlings as a nutritional source. In some aspects, the dispersant used in the preparation of a microcapsule is a leguminous storage protein, in particular a protein extracted from soy, lupine, pea, chickpea, alfalfa, horse bean, lentil, haricot bean, or a combination thereof. Preferably, the denatured protein is a denatured pea protein, in particular a denatured pea protein isolate.

[0044] In particular, the denatured pea protein is intended to include a pea protein isolate, pea protein concentrate, or a combination thereof. Pea protein isolates and concentrates are generally understood to be composed of several proteins. For example, pea protein isolates and concentrates can include legumin, vicilin and convicilin proteins. The term "pea protein" is also intended to include a partially or completely modified or denatured pea protein. Individual storage polypeptides (*e.g.,* legumin, vicilin, or convicilin) can also be used in the preparation of microcapsules of this invention. Individual proteins can be isolated and optionally purified to homogeneity or near homogeneity, *e.g.,* 90%, 92%, 95%, 97%, 98%, or 99% pure.

[0045] Ideally, the pea protein of the present disclosure is denatured, preferably without causing gelation of the pea protein. Exemplary conditions for protein denaturation include, but are not limited to, exposure to heat or cold, changes in pH, exposure to denaturing agents such as detergents, urea, or other chaotropic agents, or mechanical stress including shear. In some aspects, the pea protein is partially denatured, *e.g.,* 50%, 60%, 70%, 80% or 85% (w/w) denatured. In other aspects, the pea protein is substantially or completely denatured, *e.g.,* at least 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, 99% or 100% (w/w) denatured. For example, when an 8% pea storage protein solution (w/v) is used, the solution can be treated at a temperature of 80°C to 90°C for 20 to 30 minutes (or preferably 85°C for 25 minutes) to yield a substantially denatured pea storage protein. Accordingly, depending on the degree of denaturation desired, it will be appreciated that higher temperatures and shorter times can also be employed.

[0046] In particular, it has been found that chaotropic agents are particularly useful in providing a denatured protein of use in the preparation of the biodegradable microcapsules of the present disclosure. As is conventional in the art, a chaotropic agent is a compound which disrupts hydrogen bonding in aqueous solution, leading to increased entropy. Generally, this reduces hydrophobic effects which are essential for three dimensional structures of proteins. Chaotropes can be defined by having a positive chaotropic value, *i.e.,* kJ kg^{-1} mole on the Hallsworth Scale. Examples of chaotropicity values are, for example, $CaCl_2$ +92.2 kJ kg^{-1}, $MgCl_2$ kJ kg^{-1} +54.0, butanol +37.4 kJ kg^{-1}, guanidine hydrochloride +31.9 kJ kg^{-1}, and urea +16.6 kJ kg^{-1}. In certain aspects, the chaotropic agent is a guanidinium salt, *e.g.,* guanidinium sulphate, guanidinium carbonate, guanidinium nitrate or guanidinium chloride. In particular aspects, the pea protein is partially or completely denatured with guanidine carbonate.

[0047] In addition to natural dispersants, non-natural dispersants are of use in the preparation of the microcapsules of the present disclosure. Non-natural dispersants include N-lauroyl-L-arginine ethyl ester, sorbitan esters, polyethoxylated sorbitan esters, polyglyceryl esters, fatty acid esters, or a combination thereof.

[0048] Other food safe dispersants can also be used in the microcapsule of the present disclosure. Examples include ammonium phosphatides, acetic acid esters of mono- and diglycerides (Acetem), lactic acid esters of mono- and diglycerides of fatty acids (Lactem), citric acid esters of mono and diglycerides of fatty acids (Citrem), mono and diacetyl tartaric acid esters of mono and diglycerides of fatty acids (Datem), succinic acid esters of monoglycerides of fatty acids (SMG), ethoxylated monoglycerides, sucrose esters of fatty acids, sucroglycerides, polyglycerol polyricinoleate, propane-1,2-diol esters of fatty acids, thermally oxidized soybean oil interacted with mono- or diglycerides of fatty acids, sodium stearoyl lactylate (SSL), calcium stearoyl lactylate (CSL), stearyl tartrate, polyglycerol esters of interesterified castor oil acid (E476), sodium stearoyllatylate, sodium lauryl sulfate, polyoxyethylated hydrogenated castor oil (for instance, such sold under the tradename CREMO-PHOR®), block copolymers of ethylene oxide and propylene oxide (for instance as sold under the tradename PLURONIC®, polyoxyethylene fatty alcohol ethers, and polyoxyethylene stearic acid ester.

[0049] *Encapsulation Methods.* As demonstrated herein, an isocyanate, when reacted with water to form a primary amine, will self-condense in the presence of a pea protein as

dispersant and form a wall material suitable for encapsulation of active materials in a core-shell microcapsule. Not wishing to be bound by theory, it is posited that the pea protein provides a scaffold that facilitates self-condensation of the isocyanate. Advantageously, the inclusion of pea protein provides for the use of reduced levels of isocyanate and improves the sustainability and biodegradability of the core-shell microcapsules. Moreover, desirable microcapsule properties such as good dry performance, low discoloration and/or reduced aggregation or agglomeration can be achieved by adjusting the pH of the emulsion to below 6 and/or curing the microcapsule slurry at a temperature below 80°C.

[0050] Accordingly, the present disclosure provides methods for producing core-shell microcapsule slurries, which are biodegradable. "Biodegradable" as used herein with respect to a material, such as a microcapsule shell as a whole and/or a polymer (*e.g.*, biodegradable polymer or prepolymer) of the microcapsule shell, has no real or perceived health and/or environmental issues, and is capable of undergoing and/or does undergo physical, chemical, thermal, microbial, biological and/or UV or photo-degradation. Ideally, a microcapsule shell and/or polymer is deemed "biodegradable" when the microcapsule shell and/or polymer passes one or more of the following tests including: a respirometry biodegradation method in aquatic media, available from Organization for Economic Cooperation and Development (OECD), International Organization for Standardization (ISO) and the American Society for testing and Material (ASTM) tests including, but not limited to OECD 301F or 310 (Ready biodegradation), OECD 302 (inherent biodegradation), ISO 17556 (solid stimulation studies), ISO 14851 (fresh water stimulation studies), ISO 18830 (marine sediment stimulation studies), OECD 307 (soil stimulation studies), OECD 308 (sediment stimulation studies), and OECD 309 (water stimulation studies). Preferably, the microcapsules are readily biodegradable as determined using a respirometry biodegradation method in aquatic media, the OECD 301F or OECD 310 test. More preferably, the shell and/or polymer of the microcapsules are biodegradable if the shell and/or polymer has a biodegradation rate of at least 20%, 30%, 40%, 50%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 98%, within 60 days according to the OECD301F or OECD310 tests, or most preferably a biodegradability of at least 20% within 60 days according to OECD301F test.

[0051] Generally, the present disclosure provides a method for producing a biodegradable core-shell microcapsule slurry, which involves the step of polymerizing a

wall material consisting of an isocyanate in the presence of a denatured pea protein, wherein the isocyanate is present at a level of less than 1% by weight of the biodegradable core-shell microcapsule slurry. For the purposes of the present disclosure, the polymerization step is a self-condensation reaction where the isocyanate acts both as the electrophile and the nucleophile.

[0052] More particularly, the present disclosure provides a method for producing a core-shell microcapsule slurry by (a) preparing an aqueous phase by (i) combining a pea protein with guanidine carbonate to denature the pea protein, (ii) adjusting the pH to below 6, and (iii) adding gum Arabic as a hydrocolloid; (b) preparing an oil phase composed of an active material and a trimethylol propane-adduct of xylylene diisocyanate, wherein the trimethylol propane-adduct of xylylene diisocyanate is preferably present at a level between 0.1% and 8% based on the weight of the core-shell microcapsule slurry; (c) emulsifying the oil phase into the aqueous phase to form a slurry; and (d) curing the slurry at a temperature below 80°C for a predetermined period of time.

[0053] In accordance with some aspects, the aqueous phase of the method above is adjusted to a pH at or below 6 or more preferably below 5.5. Ideally, the pH of the aqueous phase is adjusted to a pH in the range of 2 to 6, 3 to 5.5, preferably between 3.5 and 4.5, or most preferably between 5.8 and 4.2.

[0054] In accordance with other aspects, the microcapsules prepared according to the method above are cured at a temperature below 80°C, or preferably below 70°C. Ideally, the slurry is cured at a temperature in the range of 15°C to 80°C (*e.g.,* 55°C to 65°C, or 55°C to 70°C, or 55°C to 80°C) for 1 minute to 10 hours (*e.g.*, 0.1 hours to 5 hours, 0.2 hours to 4 hours and 0.5 hours to 3 hours). Preferably, the microcapsules slurry is cured at a temperature between 67-63°C, or more preferably at 65°C.

[0055] Depending on the nature of the microcapsule, the slurry can be heated to a target cure temperature at a linear rate of 0.5 to 2°C per minute (*e.g.*, 1 to 5°C per minute, 2 to 8°C per minute, and 2 to 10°C per minute) over a period of 1 to 60 minutes (*e.g.,* 1 to 30 minutes). The following heating methods can be used: conduction for example via oil, steam radiation *via* infrared, and microwave, convection *via* heated air, steam injection and other methods known by those skilled in the art. The target cure temperature used herein refers to the minimum temperature in degrees Celsius at which the capsule slurry is cured to retard leaching.

[0056] In aspects of the present disclosure, the microcapsules produced by such a method typically have a mean particle size in the range of from 0.1 to 1000 microns (*i.e.*, μm) in diameter (*e.g.*, 0.5 to 500 microns, 1 to 200 microns, 1 to 100 microns, 2 to 50 microns, 5 to 25 microns, and 1 to 10 microns). The microcapsules produced by the method of this invention are single microcapsules (*i.e.,* not agglomerated), and can have a size distribution that is narrow, broad, or multi-modal.

[0057] *Active Materials*. The microcapsule slurries of the present disclosure have one or more active materials encapsulated therein. Non-limiting examples include those described in WO 2016/049456. These active materials include a fragrance, pro-fragrance, flavor, malodor counteractive agent, vitamin or derivative thereof, anti-inflammatory agent, fungicide, anesthetic, analgesic, antimicrobial active, anti-viral agent, anti-infectious agent, anti-acne agent, skin lightening agent, insect repellent, animal repellent, vermin repellent, emollient, skin moisturizing agent, wrinkle control agent, UV protection agent, fabric softener active, hard surface cleaning active, skin or hair conditioning agent, flame retardant, antistatic agent, taste modulator, cell, probiotic, antioxidant, self-tanning agent, dihydroxyacetone, cooler, sensate, malodor reactive material, cosmetic active, or a combination thereof. Cosmetic actives include vitamins, sun filters and sunscreens, anti-aging agents, anti-wrinkle agents, antioxidants, lifting agents, firming agents, anti-spot agents, anti-redness agents, thinning agents, draining agents, moisturizers, soothing agents, scrubbing or exfoliating agents, mattifying agents, sebum regulating agents, skin-lightening actives, self-tanning actives, tanning accelerators, or a combination thereof. In addition to the active materials listed above, the products of this invention can also contain dyes, colorants or pigments, naturally obtained extracts (for example paprika extract and black carrot extract), and aluminum lakes. Notably, the microcapsules of the present disclosure are of use in encapsulating natural extracts, and/or essential oils. In certain aspects, the microcapsule slurry has less than 0.3% or 0.25% of a non-encapsulated fragrance.

[0058] *Rheology Modifiers*. One or more rheology modifiers or viscosity control agents can be added to the microcapsule slurry to achieve a desired viscosity of the composition so that the microcapsule is dispersed in the slurry for a pro-longed period of time. During capsule preparation, the rheology modifier is preferably added prior to the emulsification of the aqueous phase and oil phase and is typically disperses

homogeneously in the microcapsule slurry and outside of the microcapsule wall of the microcapsules in the composition of the present disclosure. Suitable rheology modifiers include an acrylate copolymer, a cationic acrylamide copolymer, a polysaccharide, or a combination thereof. Preferably, the addition of a rheology modifier to the slurry provides a slurry having a viscosity of less than 600 cps or less than 580 cps as measured at shear rate of 21 s^{-1}.

[0059] Commercially available acrylate copolymers include those under the tradename ACULYN® (from Dow Chemical Company) such as ACULYN® 22 (a copolymer of acrylates and steareth-20 methacrylate), ACULYN® 28 (a copolymer of acrylate and beheneth-25 methacrylate), ACULYN® 33 (a copolymer of acrylic acid and acrylate), ACULYN® 38 (a cross polymer of acrylate and vinyl neodecanoate), and ACULYN® 88 (a cross polymer of acrylate and steareth-20 methacrylate). Particularly useful acrylate copolymers are anionic acrylate copolymer such as ACULYN® 33, an alkali-soluble anionic acrylic polymer emulsion (ASE), which is synthesized from acrylic acid and acrylate comonomers through emulsion polymerization. Acrylate copolymers sold under the tradename CARBOPOL® are also suitable for use in this invention. Examples are CARBOPOL® ETD 2020 polymer (a cross polymer of acrylate and C_{10}-C_{30} alkyl acrylate), CARBOPOL® ETD 2691, and CARBOPOL® ETD 2623 (a crosslinked acrylate copolymer).

[0060] Polysaccharides are another class of agents suitable as rheology modifiers. In certain aspects, polysaccharides that are useful as rheology modifiers include starches, pectin, and vegetable gums such as alginin, guar gum, locust bean gum, and xanthan gum, *e.g.*, xanthan gum sold under the tradename KELTROL® T (80-mesh food-grade), commercially available from CP Kelco, Atlanta, GA. Preferably, the at least one rheology modifier is a xanthan gum.

[0061] In certain aspects, the microcapsules of the present disclosure include a fragrance as the active material and the slurry has (a) less than 0.3% or 0.25% of a non-encapsulated fragrance, (b) a viscosity of less than 600 cps or less than 580 cps as measured at shear rate of 21 s^{-1} or (c) a combination of (a) and (b).

[0062] *Adjunct Core Materials.* In addition to the active materials, the present disclosure also provides for the incorporation of adjunct materials including solvents, emollients, and core modifier materials in the core encapsulated by the capsule wall. Other

adjunct materials are nanoscale solid particulate materials, polymeric core modifiers, solubility modifiers, density modifiers, stabilizers, humectants, viscosity modifiers, pH modifiers, or a combination thereof. These modifiers can be present in the wall or core of the capsules, or outside the capsules in delivery system. Preferably, they are in the core as a core modifier.

[0063] The one or more adjunct material can be added in the amount of from 0.01% to 25% (*e.g.*, from 0.5% to 10%) by weight of the capsule.

[0064] Suitable examples of adjunct materials include those described in WO 2016/049456 and US 2016/0158121.

[0065] *Deposition Aids.* A capsule deposition aid from 0.01% to 25%, more preferably from 5% to 20% can be included by weight of the capsule. The capsule deposition aid can be added during the preparation of the capsules or it can be added after the capsules have been made.

[0066] These deposition aids are used to aid in deposition of capsules to surfaces such as fabric, hair or skin. These include anionically, cationically, nonionically, or amphoteric water-soluble polymers. Suitable deposition aids include polyquaternium-4, polyquaternium-5, polyquaternium-6, polyquaternium-7, polyquaternium-10, polyquaternium-16, polyquaternium-22, polyquaternium-24, polyquaternium-28, polyquaternium-39, polyquaternium-44, polyquaternium-46, polyquaternium-47, polyquaternium-53, polyquaternium-55, polyquaternium-67, polyquaternium-68, polyquaternium-69, polyquaternium-73, polyquaternium-74, polyquaternium-77, polyquaternium-78, polyquaternium-79, polyquaternium-80, polyquaternium-81, polyquaternium-82, polyquaternium-86, polyquaternium-88, polyquaternium-101, polyvinylamine, polyethyleneimine, polyvinylamine and vinylformamide copolymer, an acrylamidopropyltrimonium chloride/acrylamide copolymer, a methacrylamidopropyltrimonium chloride/acrylamide copolymer, polymer comprising units derived from polyethylene glycol and terephthalate, polyester, polymer derivable from dicarboxylic acids and polyols, or a combination thereof. Other suitable deposition aids include those described in WO 2016/049456, pages 13-27. Additional deposition aids are described in US 2013/0330292, US 2013/0337023, and US 2014/0017278.

[0067] *Preservatives.* One or more preservatives can be added to the microcapsule slurry to prevent damage or inadvertent growth of microorganisms for a specific period of

time thereby increasing shelf life. The preservative can be any organic preservative that does not cause damage to the microcapsule slurry. Suitable water-soluble preservatives include organic sulfur compounds, halogenated compounds, cyclic organic nitrogen compounds, low molecular weight aldehydes, parabens, propanediol materials, isothiazolinone, quaternary compounds, benzoates, Examples include low molecular weight alcohols, dehydroacetic acids, phenyl and phenoxy compounds, or a combination thereof.

[0068] A non-limiting example of commercially available water-soluble preservative is a mixture of about 77% 5-chloro-2-methyl-4-isothiazolin-3-one and 23% 2-methyl-4-isothiazolin-3-one. Additional antibacterial preservatives include a 1.5% aqueous solution under the tradename KATHON® CG of Rohm &Haas; 5-bromo available under the tradename BRONIDOX L® of Henkel; 2-bromo-2-nitro-1,3-propanediol available under the tradename BRONOPOL® of Inorex; 1,1'-Hexamethylenebis (5-(p-chlorophenyl) biguanide) and salts thereof, such as acetates and digluconates; 1,3-bis (hydroxy) available under the tradename GLYDANT PLUS® from Ronza; glutaraldehyde; ICI Polyaminopropylbiguanide; dehydroacetic acid; and 1,2-Benzisothiazolin-3-one sold under the tradename PROXEL® GXL.

[0069] *Microcapsule Delivery System Formulations*. The microcapsule slurry can be formulated into a capsule delivery system (*e.g.,* a microcapsule composition) for use in consumer products.

[0070] The capsule delivery system can be a microcapsule slurry suspended in an external solvent (*e.g.*, water, ethanol, or a combination thereof), wherein the capsule is present at a level 0.1% to 80% (*e.g.*, 70-75%, 40-55%, 50-90%, 1% to 65%, and 5% to 45%) by weight of the capsule delivery system.

[0071] Alternatively, or in addition to, the capsule and its slurry prepared in accordance with the present disclosure is subsequently purified. See US 2014/0017287. Purification can be achieved by washing the capsule slurry with water until a neutral pH is obtained.

[0072] *Additional Components*. The capsule delivery system can optionally contain one or more other delivery system such as polymer-assisted delivery compositions (see US 8,187,580), fiber-assisted delivery compositions (US 2010/0305021), cyclodextrin host guest complexes (US 6,287,603 and US 2002/0019369), pro-fragrances (WO 2000/072816

and EP 0922084), or a combination thereof. The capsule delivery system can also contain one or more (*e.g.*, two, three, four, five or six or more) different capsules including different capsules of the present disclosure and other capsules such as such as aminoplasts, hydrogel, sol-gel, polyurea/polyurethane capsules, and melamine formaldehyde capsules. More exemplary delivery systems that can be incorporated are coacervate capsules (see WO 2004/022221) and cyclodextrin delivery systems (see WO 2013/109798 and US 2011/03085560).

[0073] Any compound, polymer, or agent discussed above can be the compound, polymer, or agent itself as shown above, or its salt, precursor, hydrate, or solvate.

[0074] Certain compounds, polymers, and agents have one or more stereocenters, each of which can be in the R or S configuration, or a combination thereof. Further, some compounds, polymers, and agents possess one or more double bonds wherein each double bond exists in the E (trans) or Z (cis) configuration, or a combination thereof. The compounds, polymers, and agents include all possible configurational stereoisomeric, regioisomeric, diastereomeric, enantiomeric, and epimeric forms as well as a combination thereof. As such, lysine used herein includes L-lysine, D-lysine, L-lysine monohydrochloride, D-lysine monohydrochloride, lysine carbonate, and so on. Similarly, arginine includes L-arginine, D-arginine, L-arginine monohydrochloride, D-arginine monohydrochloride, arginine carbonate, arginine monohydrate, etc. Guanidine includes guanidine hydrochloride, guanidine carbonate, guanidine thiocyanate, and other guanidine salts including their hydrates. Ornithine include L-ornithine and its salts/hydrates (*e.g.*, monohydrochloride) and D-ornithine and its salts/hydrates (*e.g.*, monohydrochloride).

[0075] *Applications.* The delivery systems of the present disclosure are well-suited for use, without limitation, in the following products:

a) Household products.

i. Liquid or Powder Laundry Detergents which can use the present disclosure include those systems described in US 5,929,022, US 5,916,862, US 5,731,278, US 5,565,145, US 5,470,507, US 5,466,802, US 5,460,752, US 5,458,810, US 5,458,809, US 5,288,431, US 5,194,639, US 4,968,451, US 4,597,898, US 4,561,998, US 4,550,862, US 4,537,707, US 4,537,706, US 4,515,705, US 4,446,042, and US 4,318,818

ii. Unit Dose Pouches, Tablets and Capsules such as those described in EP 1431382 A1, US 2013/0219996 A1, US 2013/0284637 A1, and US 6,492,315. These unit

dose formulations can contain high concentrations of a functional material (*e.g.*, 5-100% fabric softening agent or detergent active), fragrance (*e.g.*, 0.5-100%, 0.5-40%, and 0.5-15%), and flavor (*e.g.*, 0.1-100%, 0.1-40%, and 1-20%). They can contain no water to limit the water content as low as less than 30% (*e.g.*, less than 20%, less than 10%, and less than 5%).

iii. Scent Boosters such as those described in US 7,867,968, US 7,871,976, US 8,333,289, US 2007/0269651 A1, and US 2014/0107010 A1.

iv. Fabric Care Products such as Rinse Conditioners (containing 1 to 30 weight % of a fabric conditioning active), Fabric Liquid Conditioners (containing 1 to 30 weight % of a fabric conditioning active), Tumble Drier Sheets, Fabric Refreshers, Fabric Refresher Sprays, Ironing Liquids, and Fabric Softener Systems such as those described in US 6,335,315, US 5,674,832, US 5,759,990, US 5,877,145, US 5,574,179, US 5,562,849, US 5,545,350, US 5,545,340, US 5,411,671, US 5,403,499, US 5,288,417, US 4,767,547 and US 4,424,134

Liquid fabric softeners/fresheners contain at least one fabric softening agent present, preferably at a concentration of 1 to 30% (*e.g.*, 4% to 20%, 4% to 10%, and 8% to 15%). The ratio between the active material and the fabric softening agent can be 1:500 to 1:2 (*e.g.*, 1:250 to 1:4 and 1:100 to 1:8). As an illustration, when the fabric softening agent is 5% by weight of the fabric softener, the active material is 0.01% to 2.5%, preferably 0.02% to 1.25% and more preferably 0.1% to 0.63%. As another example, when the fabric softening agent is 20% by weight of the fabric softener, the active material is 0.04% to 10%, preferably 0.08% to 5% and more preferably 0.4% to 2.5%. The active material is a fragrance, malodor counteractant or a combination thereof. The liquid fabric softener can have 0.15% to 15% of capsules (*e.g.*, 0.5% to 10%, 0.7% to 5%, and 1% to 3%). When including capsules at these levels, the neat oil equivalent (NOE) in the softener is 0.05% to 5% (*e.g.*, 0.15% to 3.2%, 0.25% to 2%, and 0.3% to 1%).

Suitable fabric softening agents include cationic surfactants. Non-limiting examples are quaternary ammonium compounds such as alkylated quaternary ammonium compounds, ring or cyclic quaternary ammonium compounds, aromatic quaternary ammonium compounds, diquaternary ammonium compounds, alkoxylated quaternary ammonium compounds, amidoamine quaternary ammonium compounds, ester quaternary ammonium compounds, or a combination thereof. Fabric softening compositions, and

components thereof, are generally described in US 2004/0204337 and US 2003/0060390. Suitable softening agents include esterquats sold under the tradename REWOQUAT® WE 18 commercially available from Evonik Industries and STEPANTEX® SP-90 commercially available from Stepan Corporation.

v. Liquid dish detergents such as those described in US 6,069,122 and US 5,990,065

vi. Automatic Dish Detergents such as those described in US 6,020,294, US 6,017,871, US 5,968,881, US 5,962,386, US 5,939,373, US 5,914,307, US 5,902,781, US 5,705,464, US 5,703,034, US 5,703,030, US 5,679,630, US 5,597,936, US 5,581,005, US 5,559,261, US 4,515,705, US 5,169,552, and US 4,714,562

vii. All-purpose cleaners including bucket dilutable cleaners, toilet cleaners, bathroom cleaners, and bath tissue.

viii. Other products including: rug deodorizers, candles (including scented candles), room deodorizers, floor cleaners, disinfectants, window cleaners, garbage bags/trash can liners, air fresheners (including car deodorizer, sprays, scented oil air freshener, automatic spray air freshener and neutralizing beads), moisture absorber, household devices (including paper towels and disposable wipes) and moth balls/traps/cakes.

b) Baby Care Products. Suitable examples include: diaper rash cream/balm, and baby powder.

c) Baby Care Devices. Suitable examples include: diapers, bibs, and wipes.

d) Oral Care Products. Tooth care products (as an example of preparations according to the present disclosure used for oral care) generally include an abrasive system (abrasive or polishing agent), for example silicic acids, calcium carbonates, calcium phosphates, aluminum oxides and/or hydroxylapatites, surface-active substances, for example sodium lauryl sulfate, sodium lauryl sarcosinate and/or cocamidopropylbetaine, humectants, for example glycerol and/or sorbitol, thickening agents, for example carboxymethyl cellulose, polyethylene glycols, carrageenan and/or Laponite®, sweeteners, for example saccharin, taste correctors for unpleasant taste sensations, taste correctors for further, normally not unpleasant taste sensations, taste-modulating substances (for example inositol phosphate, nucleotides such as guanosine monophosphate, adenosine monophosphate or other substances such as sodium glutamate or 2-phenoxypropionic acid), cooling active

ingredients, for example menthol derivatives, (for example L-menthyllactate, L-menthylalkylcarbonates, menthone ketals, menthane carboxylic acid amides), 2,2,2-trialkylacetic acid amides (for example 2,2-diisopropylpropionic acid methyl amide), icilin and icilin derivatives, stabilizers and active ingredients, for example sodium fluoride, sodium monofluorophosphate, tin difluoride, quaternary ammonium fluorides, zinc citrate, zinc sulfate, tin pyrophosphate, tin dichloride, combinations of various pyrophosphates, triclosan, cetylpyridinium chloride, aluminum lactate, potassium citrate, potassium nitrate, potassium chloride, strontium chloride, hydrogen peroxide, flavorings and/or sodium bicarbonate or taste correctors.

i. Toothpaste. An exemplary formulation as follows: calcium phosphate 40-55%, carboxymethyl cellulose 0.8-1.2%, sodium lauryl sulfate 1.5-2.5%, glycerol 20-30%, saccharin 0.1-0.3%, flavor oil 1-2.5% and water q.s. to 100%. A typical procedure for preparing the formulation includes the steps of (i) mixing by a blender according to the foregoing formulation to provide a toothpaste, and (ii) adding a composition of the present disclosure and blending the resultant mixture till homogeneous.

ii. Other oral care products include: tooth powder, dental floss, toothbrush, oral rinse, tooth whiteners, and denture adhesive.

e) Health Care Devices. Suitable examples include respirators and scented/flavored condoms.

f) Feminine Hygiene Products. Suitable examples include tampons, feminine napkins and eipes, and pantiliners.

g) Personal Care Products: Cosmetic or pharmaceutical preparations, *e.g.*, a "water-in-oil" (W/O) type emulsion, an "oil-in-water" (O/W) type emulsion or as multiple emulsions, for example of the water-in-oil-in-water (W/O/W) type, as a PIT emulsion, a Pickering emulsion, a micro-emulsion or nano-emulsion; and emulsions which are particularly preferred are of the "oil-in-water" (O/W) type or water-in-oil-in-water (W/O/W) type. More specifically, personal cleansers (bar soaps, body washes, and shower gels), in-shower conditioner, sunscreen and tattoo color protection (sprays, lotions, and sticks), insect repellents, hand sanitizer, anti-inflammatory (including balms, ointments, and sprays), antibacterial ointments and creams, and sensate. Other suitable examples include deodorants and antiperspirants including aerosol and pump spray antiperspirant, stick antiperspirant, roll-on antiperspirant, emulsion spray antiperspirant, clear emulsion

stick antiperspirant, soft solid antiperspirant, emulsion roll-on antiperspirant, clear emulsion stick antiperspirant, opaque emulsion stick antiperspirant, clear gel antiperspirant, clear stick deodorant, gel deodorant, spray deodorant, roll-on, and cream deodorant.

Other suitable examples include wax-based deodorant. An exemplary formulation as follows: paraffin wax 10-20%, hydrocarbon wax 5-10%, white petrolatum 10-15%, acetylated lanolin alcohol 2-4%, diisopropyl adipate 4-8%, mineral oil 40-60%, and preservative (as needed). The formulation is prepared by (i) mixing the above ingredients, (ii) heating the resultant composition to 75°C until melted, (iii) with stirring, adding 4% cryogenically ground polymer containing a fragrance while maintaining the temperature 75°C, and (iv) stirring the resulting mixture in order to ensure a uniform suspension while a composition of the present disclosure is added to the formulation.

Other suitable examples include glycol/soap type deodorant. An exemplary formulation as follows: propylene glycol 60-70%, sodium stearate 5-10%, distilled water 20-30%, and 2,4,4-Trichloro-2′-Hydroxy Diphenyl Ether, manufactured by the Ciba-Geigy Chemical Company 0.01-0.5%. The ingredients are combined and heated to 75°C with stirring until the sodium stearate has dissolved. The resulting mixture is cooled to 40°C followed by addition of a composition of the present disclosure.

h) Body lotion, facial lotion, and hand lotion, body powder and foot powder, toiletries, body spray, aerosol or non-aerosol body spray (WO 2014/014705 and WO 2016/205023), shave cream and male grooming products, bath soak, and exfoliating scrub. Other suitable examples include personal care devices, including facial tissues and cleansing wipes.

i) Hair Care Products. Suitable examples include: shampoos (liquid and dry powder), hair conditioners (*e.g.*, rinse-out conditioners, leave-in conditioners, and cleansing conditioners), hair rinses, hair refreshers, hair perfumes, hair straightening products, hair styling products, hair fixative and styling aids, hair combing creams, hair wax, hair foam, hair gel, nonaerosol pump spray, hair bleaches, dyes and colorants, perming agents, and hair wipes.

j) Beauty Care. Suitable examples include: fine fragrance—alcoholic. Compositions and methods for incorporating fragrance capsules into alcoholic fine fragrances are described in US 4,428,869. Alcoholic fine fragrances can contain the following: ethanol

(1-99%), water (0-99%), a suspending aide including but not limited to: hydroxypropyl cellulose, ethyl cellulose, silica, microcrystalline cellulose, carrageenan, propylene glycol alginate, methyl cellulose, sodium carboxymethyl cellulose or xanthan gum (0.1-1%), and optionally an emulsifier or an emollient can be included, *e.g.,* those listed above. Other suitable examples include: solid perfume, lipstick/lip balm, make-up cleanser, skin care cosmetic such as foundation, pack, sunscreen, skin lotion, milky lotion, skin cream, emollients, skin whitening, make-up cosmetic including manicure, mascara, eyeliner, eye shadow, liquid foundation, powder foundation, lipstick and cheek rouge.

k) Consumer goods packaging such as fragranced cartons, fragranced plastic bottles/boxes.

l) Pet care products. Suitable examples include: cat litter, flea and tick treatment products, pet grooming products, pet shampoos, pet toys, treats, and chewables, pet training pads, and pet carriers and crates.

m) Confectionaries. Suitable examples include: chocolate, chocolate bar products, other products in bar form, fruit gums, hard and soft caramels and chewing gum. Gum may comprise the following formulation: gum base (natural latex chicle gum, most current chewing gum bases also presently include elastomers, such as polyvinyl acetate (PVA), polyethylene, (low or medium molecular weight) polyisobutene (PIB), polybutadiene, isobutene-isoprene copolymers (butyl rubber), polyvinyl ethyl ether (PVE), polyvinyl butyl ether, copolymers of vinyl esters and vinyl ethers, styrene-butadiene copolymers (styrene-butadiene rubber, SBR), or vinyl elastomers, for example based on vinyl acetate/vinyl laurate, vinyl acetate/vinyl stearate or ethylene/vinyl acetate, as well as a combination thereof of the mentioned elastomers (see EP 0242325, US 4,518,615, US 5,093,136, US 5,266,336, US 5,601,858 or US 6,986,709) 20-25%, powdered sugar 45-50%, glucose 15-17%, starch syrup 10-13%, plasticizer 0.1% and flavor 0.8-1.2%. The components for the gum formulation are kneaded by a kneader according to the foregoing formulation to provide a chewing gum. Encapsulated Flavor or sensate is then added and blended till homogeneous. Other suitable examples include: breath fresheners, orally dissolvable strips, chewable candy and hard candy.

n) Baked products can include bread, dry biscuits, cakes, and other cookies.

o) Snack foods can include baked or fried potato chips or potato dough products, bread dough products and corn or peanut-based extrudates. Suitable examples include: potato, tortilla, vegetable, or multigrain chips, popcorn, pretzels, and extruded stacks.

p) Cereal Products can include breakfast cereals, muesli bars and precooked finished rice products.

q) Alcoholic and non-alcoholic beverages can include coffee, tea, wine, beverages containing wine, beer, beverages containing beer, liqueurs, schnapps, brandies, sodas containing fruit, isotonic beverages, soft drinks, nectars, fruit and vegetable juices and fruit or vegetable preparations; instant beverages can include instant cocoa beverages, instant tea beverages and instant coffee beverages. Suitable examples include: ready to drink liquid drinks, liquid drink concentrates, powder drinks, coffee (including instant cappuccino), tea and alcoholic beverages.

r) Spice blends and consumer prepared foods. Suitable examples include: powder gravy, sauce mixes, condiments and fermented products.

s) Ready to heat foods: ready meals and soups can include powdered soups, instant soups, precooked soups. Suitable examples include: soups, sauces, stews, and frozen entrees.

t) Dairy Products. Milk products can include milk beverages, ice milk, yogurt, kefir, cream cheese, soft cheese, hard cheese, powdered milk, whey, butter, buttermilk and partially or fully hydrolyzed milk protein-containing products, or flavored milk beverages. Suitable examples include: yogurt, ice cream, and cheese.

u) Soy protein or other soybean fractions can include soy milk and products produced therefrom, soy lecithin-containing preparations, fermented products such as tofu or tempeh or products produced therefrom, bean curd and soy sauces.

v) Meat products can include ham, fresh or raw sausage preparations, and seasoned or marinated fresh or salt meat products.

w) Eggs or egg products can include dried egg, egg white, or egg yolk.

x) Oil-based products, or emulsions thereof, can include mayonnaise, remoulade, dressings, and seasoning preparations.

y) Fruit preparations can include jams, sorbets, fruit sauces and fruit fillings; vegetable preparations can include ketchup, sauces, dried vegetables, deep-frozen vegetables, precooked vegetables, vegetables in vinegar and preserved vegetables.

z) Flavored pet foods.

[0076] The invention is described in greater detail by the below non-limiting examples. Without further elaboration, it is believed that one skilled in the art can, based on the description herein, utilize the present invention to its fullest extent. All publications cited herein are incorporated by reference in their entirety.

EXAMPLES

[0077] The following examples are provided to further illustrate the invention and are not to be construed as limitations of the invention, as many variations of the present invention are possible without departing from its spirit or scope.

[0078] **Example 1**: Synthesis of Reference Microcapsules

[0079] As described in Example 1 of US 2012/0093899, melamine formaldehyde capsules were prepared. Briefly, 80 parts by weight of Helion fragrance (International Flavors & Fragrance Inc., Union Beach, NJ) was admixed with 20 parts by weight of caprylic/capric triglyceride solvent sold under that tradename NEOBEE® M-5 by Stepan Corp. (Chicago, IL) thereby forming a fragrance/solvent composition. The uncoated capsules were prepared by creating a polymeric wall to encapsulate fragrance/solvent composition droplets. A copolymer of acrylamide and acrylic acid (sold under the tradename ALCAPSOL® 200) was first dispersed in water together with a methylated melamine formaldehyde resin (sold under the tradename CYMEL® 385). These two components were allowed to react under acidic conditions for at least one hour.

[0080] The fragrance/solvent composition was then added to the wall polymer solution and droplets of the desired size were achieved by high shear homogenization. For the microcapsule slurry, curing of the polymeric layer around the fragrance/solvent composition droplets was carried out at 125°C. After cooling to room temperature, ethylene urea was added into the microcapsule slurry. Additionally, a rheology modifier and a preservative were added. The pH was adjusted using NaOH. The components of the slurry are listed in Table 1. The slurry contained an overall fragrance load of 28.0%.

[0081] Table 1 – Composition of the Slurry

Ingredient	Amount (grams)	Weight %
Fragrance	182	28

Caprylic/capric triglyceride	45.5	7
Copolymer of acrylamide and acrylic acid	73.9	11.4
Methylated melamine formaldehyde resin	9.9	1.5
Ethylene Urea	13.3	2.0
Acetic Acid	2.4	0.4
Sodium hydroxide	1.1	0.2
Acrylates copolymer [1]	6.5	1
1,2-Benzisothiazolin-3-one [2]	0.7	0.1
Water	314.8	48.4
Total	**650**	**100%**

[1] available as ACULYN® 33A.
[2] available as PROXEL® GXL.

[0082] **Example 2**: Preparation of Isocyanate Capsules in the Presence of Pea Protein, Modified Starch/Polystyrene Sulfonate, and Sodium Salt

[0083] An oil phase was prepared by mixing 80 parts by weight of Helion fragrance with 20 parts by weight of caprylic/capric triglyceride solvent sold under that tradename NEOBEE® M-5 by Stepan Corp. (Chicago, IL) thereby forming a fragrance/solvent composition.

[0084] A water phase was prepared by dispersing pea protein powder (15.4 weight %) in water. Guanidine carbonate, as a denaturing agent, was added and pH was adjusted to 5 using citric acid. These components were allowed to react for 15 minutes.

[0085] Modified starch sold under the tradename PURITY GUM® Ultra (Ingredion, Westchester, IL) and high molecular weight polystyrene sulfonate, sodium salt sold under the tradename FLEXAN® II were then added to the water phase as emulsifiers and the mixture was allowed to mix for 15 minutes. Tanal-02 (a high molecular weight general purpose hydrolysable tannin; Ajinomoto Natural Specialties, Tokyo, Japan) was subsequently added to the water phase.

[0086] A polyisocyanate (trimethylol propane-adduct of xylylene diisocyanate commercially available under the tradename TAKENATE® D110N, Mitsue Chemicals Inc., Japan) was added to the oil phase at 5 weight %. The oil phase was then emulsified into the aqueous phase to form an oil-in-water emulsion under a shearing rate of 7400 revolutions per minute ("RPM") for 3 minutes. For the microcapsule slurry, curing of the polymeric layer around the fragrance/solvent composition droplets was carried out at 55°C for 3.5 hours and 80°C for 30 minutes. Subsequently, a rheology modifier and a

preservative were added. The components of the slurry are listed in Table 2. The slurry contained an overall fragrance load of 31.2%.

[0087] Table 2 – Composition of the Slurry

Ingredient	Amount (grams)	Weight %
Fragrance	187.2	31.2
Caprylic/capric triglyceride	46.8	7.8
Pea protein	17.5	2.9
Guanidine Carbonate	7.6	1.3
Citric Acid	7.3	1.2
High molecular weight polystyrene sulfonate, sodium salt [1]	2.9	0.5
Modified Starch [2]	5.9	1.0
Trimethylol propane-adduct of xylylene diisocyanate [3]	5.85	1
Tanal-02	2.9	0.5
Xanthan gum	0.5	0.08
1,2-Benzisothiazolin-3-one [4]	0.7	0.1
Water	309	51.5
Total	**600**	**100%**

[1] available as FLEXAN® II.
[2] available as PURITY GUM® Ultra.
[3] available as TAKENATE® D110N.
[4] available as PROXEL® GXL.

[0088] **Example 3**: Preparation of Isocyanate Capsules in the Presence of Pea Protein, Modified Starch/Polystyrene Sulfonate, Sodium Salt at pH 4 and a Cure Temperature of 65°C

[0089] The general procedure of Example 2 was followed with the following changes: the pH of the aqueous phase was adjusted to 4 instead of 5 and curing was carried out at 65°C for 4 hours. The components of the slurry are listed in Table 3. The slurry contained an overall fragrance load of 31.2%.

[0090] Table 3 – Composition of the Slurry

Ingredient	Amount (grams)	Weight %
Fragrance	187.2	31.2
Caprylic/capric triglyceride	46.8	7.8
Pea protein	17.5	2.9
Guanidine Carbonate	7.6	1.3
Citric Acid	14.0	2.3
High molecular weight polystyrene sulfonate, sodium salt [1]	2.9	0.5
Modified Starch [2]	5.9	1.0
Trimethylol propane-adduct of xylylene diisocyanate [3]	5.85	1

Tanal-02	2.9	0.5
Xanthan gum	0.5	0.08
1,2-Benzisothiazolin-3-one [4]	0.7	0.1
Water	302.3	50.4
Total	**600**	**100%**

[1] available as FLEXAN® II.
[2] available as PURITY GUM® Ultra.
[3] available as TAKENATE® D110N.
[4] available as PROXEL® GXL.

[0091] **Example 4**: Preparation of Capsules with Reduced Levels of Pea Protein

[0092] The general procedure of Example 3 was carried out with a reduced concentration of pea protein. The components of the slurry are listed in Table 4. The slurry contained an overall fragrance load of 31.2%.

[0093] Table 4 – Composition of the Slurry

Ingredient	Amount (grams)	Weight %
Fragrance	187.2	31.2
Caprylic/capric triglyceride	46.8	7.8
Pea protein	11	1.8
Guanidine Carbonate	7.6	1.3
Citric Acid	14.0	2.3
High molecular weight polystyrene sulfonate, sodium salt [1]	2.9	0.5
Modified Starch [2]	5.9	1.0
Trimethylol propane-adduct of xylylene diisocyanate [3]	5.85	1
Tanal-02	2.9	0.5
Xanthan gum	0.5	0.08
1,2-Benzisothiazolin-3-one [4]	0.7	0.1
Water	308.8	51.5
Total	**600**	**100%**

[1] available as FLEXAN® II.
[2] available as PURITY GUM® Ultra.
[3] available as TAKENATE® D110N.
[4] available as PROXEL® GXL.

[0094] **Example 5**: Preparation of Capsules Under Reduced pH Conditions

[0095] The general procedure of Example 3 was carried out but the pH was reduced from 4 to 3. The components of the slurry are listed in Table 5. The slurry contained an overall fragrance load of 30.3%.

[0096] Table 5 – Composition of the Slurry

Ingredient	Amount (grams)	Weight %

Fragrance	187.2	30.3
Caprylic/capric triglyceride	46.8	7.6
Pea protein	17.5	2.8
Guanidine Carbonate	7.6	1.2
Citric Acid	21.5	3.5
High molecular weight polystyrene sulfonate, sodium salt [1]	2.9	0.5
Modified Starch [2]	5.9	1.0
Trimethylol propane-adduct of xylylene diisocyanate [3]	5.85	0.9
Tanal-02	2.9	0.5
Xanthan gum	0.5	0.08
1,2-Benzisothiazolin-3-one [4]	0.7	0.1
Water	311.7	50.5
Total	**616.9**	**100%**

[1] available as FLEXAN® II.
[2] available as PURITY GUM® Ultra.
[3] available as TAKENATE® D110N.
[4] available as PROXEL® GXL.

[0097] **Example 6**: Preparation of Capsules with Reduced pH (Phosphoric Acid)

[0098] The general procedure of Example 3 was carried out with phosphoric acid instead of citric acid to reduce pH. The components of the slurry are listed in Table 6. The slurry contained an overall fragrance load of 32.2%.

[0099] Table 6 – Composition of the Slurry

Ingredient	Amount (grams)	Weight %
Fragrance	187.2	32.2
Caprylic/capric triglyceride	46.8	8.1
Pea protein	17.5	3.0
Guanidine Carbonate	7.6	1.3
Phosphoric acid	9.4	1.5
High molecular weight polystyrene sulfonate, sodium salt [1]	2.9	0.5
Modified Starch [2]	5.9	1.0
Trimethylol propane-adduct of xylylene diisocyanate [3]	5.85	1
Tanal-02	2.9	0.5
Xanthan gum	0.5	0.08
1,2-Benzisothiazolin-3-one [4]	0.7	0.1
Water	302.3	52
Total	**581**	**100%**

[1] available as FLEXAN® II.
[2] available as PURITY GUM® Ultra.
[3] available as TAKENATE® D110N.
[4] available as PROXEL® GXL.

[00100] **Example 7**: Preparation of Capsules with Increased Fragrance Load

[00101] The general procedure of Example 3 was followed with a reduced amount of water. The components of the slurry are listed in Table 7. The slurry contained an overall fragrance load of 34.6%.

[00102] Table 7 – Composition of the Slurry

Ingredient	Amount (grams)	Weight %
Fragrance	187.2	34.6
Caprylic/capric triglyceride	46.8	8
Pea protein	17.5	3.0
Citric Acid	5.7	1.0
High molecular weight polystyrene sulfonate, sodium salt [1]	2.9	0.5
Modified Starch [2]	5.9	1.0
Trimethylol propane-adduct of xylylene diisocyanate [3]	5.85	2.0
Tanal-02	5.8	1.0
Xanthan gum	0.5	0.09
1,2-Benzisothiazolin-3-one [4]	0.7	0.1
Water	296.3	51.0
Total	**581**	**100%**

[1] available as FLEXAN® II.
[2] available as PURITY GUM® Ultra.
[3] available as TAKENATE® D110N.
[4] available as PROXEL® GXL.

[00103] **Example 8**: Preparation of Capsules with a Higher Concentration of Surfactants

[00104] The general procedure of Example 3 was followed with a greater amount of surfactant solution. The components of the slurry are listed in Table 8. The slurry contained an overall fragrance load of 28.6%.

[00105] Table 8 – Composition of the Slurry

Ingredient	Amount (grams)	Weight %
Fragrance	187.2	28.6
Caprylic/capric triglyceride	46.8	7.2
Pea protein	17.5	2.7
Citric Acid	5.2	0.8
High molecular weight polystyrene sulfonate, sodium salt [1]	4.4	0.7
Modified Starch [2]	8.9	1.4
Trimethylol propane-adduct of xylylene diisocyanate [3]	5.85	0.9
Tanal-02	2.9	0.4
Xanthan gum	0.5	0.08
1,2-Benzisothiazolin-3-one [4]	0.7	0.1
Water	320.05	53.3
Total	**600**	**100%**

[1] available as FLEXAN® II.
[2] available as PURITY GUM® Ultra.
[3] available as TAKENATE® D110N.
[4] available as PROXEL® GXL.

[00106] **Example 9**: Capsules Prepared with Pea Protein and Gum Arabic

[00107] An oil phase was prepared by mixing 80 parts by weight of Helion fragrance with 20 parts by weight of caprylic/capric triglyceride solvent sold under that tradename NEOBEE® M-5 by Stepan (Chicago, IL) thereby forming a fragrance/solvent composition.

[00108] An aqueous phase was prepared by dispersing 12.43 grams of pea protein powder in 124 grams of water and adjusting the pH to 9-9.5 using 0.3 grams of 25% sodium hydroxide solution. To facilitate dissolution and inhibit aggregation of the pea protein isolate (Liu, et al. (2010) *Food Res. Internatl.* 43:489-495), 85 grams of a gum Arabic Instant AA (Nexira, Somerville, NJ; 10% solution) was included as a hydrocolloid. The mixture was high sheared for 20 seconds at 7400 rpm. High molecular weight polystyrene sulfonate, sodium salt sold under the tradename FLEXAN® II (15 grams of a 10% solution) was added and the mixture was high sheared for 20 seconds at 7400 rpm. In a separate beaker, 38 grams guanidine carbonate solution (20%) was pH to 4 adjusted using 31 grams of a 50% solution of citric acid and the solution was allowed to foam out. The guanidine citrate solution was added to the protein mix and allowed to react for 15 minutes at room temperature. Forty-eight grams of a 1% solution of xanthan gum was subsequently added to the water phase followed by 10 grams of a 30% solution of Tanal-02.

[00109] A polyisocyanate (trimethylol propane-adduct of xylylene diisocyanate commercially available under the tradename TAKENATE® D110N, Mitsue Chemicals Inc., Japan) was added to the oil phase at 5 weight %. The oil phase was then emulsified into the aqueous phase to form an oil-in-water emulsion under a shearing rate of 7400 rpm for 3 minutes.

[00110] For the microcapsule slurry, curing of the polymeric layer around the fragrance/solvent composition droplets was carried out at 65°C for 4 hours. Additionally, a preservative was added. The components of the slurry are listed in Table 9. The slurry contained an overall fragrance load of 31.2%.

[00111] Table 9 – Composition of the Slurry

Ingredient	Amount	Weight %

	(grams)	
Fragrance	187.2	31.2
Caprylic/capric triglyceride	46.8	7.8
Pea protein	12.4	2
Citric Acid	15.5	2.5
High molecular weight polystyrene sulfonate, sodium salt [1]	1.5	0.25
Gum Arabic	8.5	1.4%
Trimethylol propane-adduct of xylylene diisocyanate [2]	5.85	0.97
Tanal-02	3	0.5
Xanthan gum	0.5	0.08
1,2-Benzisothiazolin-3-one [3]	0.7	0.1
Water	318.05	53
Total	**600**	**100**

[1] available as FLEXAN® II.
[2] available as TAKENATE® D110N.
[4] available as PROXEL® GXL.

[00112] Identical capsules were prepared without gum Arabic. However, without gum Arabic the emulsion completely failed and a capsule was not formed. As such, a capsule including a polyisocyanate and pea protein could not be formed in the absence of gum Arabic.

[00113] **Example 10**: Fabric Conditioner Samples Containing Microcapsules

[00114] An un-fragranced model fabric conditioner having a 10% hole in the formulation was used to allow for water and capsules to be added. Microcapsules as described in Examples 1-3 were pre-mixed with water and then added to the model fabric conditioner. The samples were homogenized using an overhead agitator at 300 rpm. The finished fabric conditioner samples contained 0.2% neat oil equivalent resulting in 0.65 weight % encapsulated fragrance for the microcapsules in Examples 2 and 3 and 0.72 weight % encapsulated fragrance for the control microcapsules in Example 1.

[00115] Thirty-five grams of finished fabric conditioners containing the above-referenced dosage of microcapsule were added to a front load Miele Professional PW 6065 Vario washing machine. The wash load contained 2.2 kg of laundry including eight big towels, two t-shirts, two pillow cases, two dish towels, and two mini-towels for evaluation. The washing temperature was set to 40°C with 15.5 L of water used for the main wash and 34 L of total water for two rinses. The total washing cycle was 60 minutes. Some towels were kept for damp evaluation and the rest were line dried at room temperature for dry evaluation.

[00116] Randomly selected damp samples were evaluated by several experts using the intensity scale 0-5, where 0 is "no performance" and 5 is "strong performance." The evaluation was performed "blind," such that each sample had a randomly allocated number. The dry evaluation was performed the day following the damp and was performed by the same experts using the same intensity scale of 0-5. Sensory scores were recorded before and after, each of the randomly selected cloths (contained in a separate polyethylene bag) was gently handled. The results of these analyses are presented in Table 10.

[00117] Example 3, which is the pea protein/isocyanate capsules with low pH and low curing temperature, performs better by providing a strong fragrance burst during dry evaluation (post-handling) than both melamine formaldehyde capsules (Example 1) and pea protein/isocyanate capsules with high pH and high curing temperature (Example 2). Furthermore, Example 3 capsules demonstrate that they survive the damp stage on cloth, even though they are relatively weak compared to the Example 2 capsules. Moreover, Example 3 capsules have improved processability, no aggregate formation and improved slurry color when compared to Examples 1 and 2 capsules.

[00118] Table 10 – Sensory Evaluation Results

Exemplary Capsule	Damp Evaluation	Dry Evaluation	
		Pre-Handling	Post-Handling
1	3.56	3.19	4.05
2	3.88	3.36	3.74
3	3.60	3.29	4.13

[00119] **Example 11**: Analytical Evaluation of Different Capsules

[00120] Characteristics including fragrance load, encapsulation efficiency, free oil, viscosity and size of the microcapsules produced in Examples 1, 3, 4, 5, 6 and 9 were determined. The results of these analyses are presented in Table 11.

[00121] Table 11 – Analytical Evaluation Results

Exemplary Capsule	Fr. Load [1] %	EE [2] %	Free Oil %	Viscosity [3] (cps; 21 s-1)	PSD [4] (Mean/Mode)
1	28	>95	0.39	625	6.7/5.4
3	31.2	>95	0.3-1.9	574	22.1/15.6
4	31.2	>95	0.2	605	34.5/16.2
5	30.3	>95	0.4	495	24.5/18.9
6	32.2	>95	0.2	530	22.9/16.7

9	31.2	>95	0.18	357	23.3/24.3

[1] Fr. Load = Fragrance Load.
[2] EE = Encapsulation Efficiency.
[3] Viscosity was measured on a hake plate rheometer using 5, 21, and 64 sec shear rates.
[4] PSD = particle size distribution. Tbm, to be measured.

[00122] In addition, wall strength was determined for capsules prepared in Example 9 as compared to whey capsules prepared in accordance with Example 7 in WO 2020/131875 A2 or capsules prepared in accordance with Example 2. This analysis, presented in FIG. 1, indicates that the choice of protein had a smaller influence on the wall strength and flexibility of the capsules. The pH and cure profile have a stronger effect on the wall strength while maintaining the flexibility of the wall (deformation). This combination allows for the minimal damp performance but very strong burst with minimal friction on the dry stages. The wall strength is so weak that minimal energy breaks the wall but the flexibility is sufficient to survive the wash cycle in a EU washing machine and the damp stage on cloth. Even though the isocyanate/pea protein-based capsules are relatively weak compared to the whey capsules or melamine formaldehyde capsules, isocyanate/pea protein-based capsules have good stability in product and processability of the slurry is maintained.

[00123] **Example 12**: Malodor Absorption Capabilities

[00124] To test the malodor absorption capabilities of the capsules disclosed herein, diethyl phthalate and caprylic/capric triglyceride solvent sold under that tradename NEOBEE® M-5 by Stepan Corp. (Chicago, IL) were encapsulated according to the methods presented in Example 1 (melamine formaldehyde) and Example 9 (isocyanate capsule prepared with pea protein and gum Arabic) to generate odorless capsules.

[00125] The capsules were exposed to malodor and the reduction of the malodor concentration was measured via headspace analysis. More specifically, 100 grams of 1.5% malodor solution was placed into a jar and allowed to equilibrate for 30 minutes. A towel was "activated" by rubbing the towel five times with a tongue depressor on a side marked with an "X." The "activated" towel, with "X" side up, was placed in a second jar (16 oz.) fitted with a septa injection lid. With a 100 mL gas tight syringe, 100 mL of malodor vapor was transferred into the second jar containing the towel sample. The towel sample was stored

for 1.5 hours and headspace was subsequently analyzed using a SKC pump with 150 ml/min flow, sampling for 10 minutes on to a tenax tube.

[00126] The results of this analysis (Table 12) indicate that isocyanate capsules prepared with pea protein and gum Arabic have malodor absorption capabilities comparable to melamine formaldehyde capsules.

[00127] Table 12 – Malodor Absorption Evaluation Results

Malodor	Mean Area		
	Blank	Example 1	Example 9
Iso valeraldehyde	2805176984	1640184599	1370641528
Acetyl methyl carbinol	1990840968	302635768	168033889.5
Methyl pyrazine	1800621600	318617731	176231698
Heptanal	935200716	558749725.5	545558189

[00128] **Example 13**: Capsules Prepared with Oils Containing a High Concentration of Natural Components

[00129] The performance of capsules incorporating natural fragrances (*i.e.*, extracts from plants or distillation products) or naturally derived fragrances (*i.e.*, natural fragrances that have been chemically modified) was also assessed (Table 13). These capsules were prepared in accordance with the method described in Example 9.

[00130] **Table 13** – Evaluation Results

Fragrance	% Naturals & Naturally derived	Free Oil (%)	Viscosity (cps) (5 s-1) (21 s-1) (106 s-1)	Performance		Leakage at 5 weeks (%)
				at fresh	at 4 weeks	
Tea Leaves	23.5% (15.5% Essential Oils)	0.25	476 293 214	++	++	<10
Apple 2	17% (3.5% Essential Oils)	0.22	584 358 273	++	++	<10
Bamboo 2	(3.2% Essential Oils)	0.44	569 315 175	++	++	<10
Clean Linen	18% (8% Essential Oils)	0.23	451 270 190	++	++	<10

Rose	15% (5% Essential oils)	0.52	476 281 197	++	++	<10
Rose litchi	14.5% (3% Essential Oils)	0.35	465 265 174	++	++	<10
Mango	69.55% (16,68% Essential Oils)	0.46	462 299 231	++	-	<10
Watermelon	22.3% naturally derived/ 3.7% natural	0.41	479 308 239	+	+/-	16
Lavender Blackberry	51.09% (9.82% Essential Oils)	0.48	513 331 254	-	n/a	n/a
Lavender	100% (45% Essential Oils)	0.35	536 325 245	++	++	<10
Tubereuz	13.3% naturals & 23% naturally derived	0.67	484 284 196	++	++	14
Eau d'Oranger	45% naturally derived & 10.3% natural	0.37	516 304 214	+	+	<10
Citrus Spicy	100% (74.58% Essential Oils)	0.52	502 283 173	-	n/a	n/a
Xmas Tree	99% (23.5% Essential Oils)	0.52	704 472 388	+	+	n/a

"++" represents excellent performance burst and hedonics on dry.
"+" represents good performance with burst on dry and hedonics.
"-" represents poor performance on dry and hedonics
.n/a, not available.

[00131] Leakage of fragrance from the capsules prepared in accordance with the method described in Example 9 was evaluated after storage at 37°C in fabric conditioner. The

results of this analysis (Table 14) show stable encapsulation of oils containing high amounts of natural extracts and essential oils.

[00132] The performance of isocyanate capsules prepared in accordance with the method described in Example 9 were compared to melamine formaldehyde capsules (Example 1) at damp, dry pre, dry GH and dry post stages. Fragrance intensity was determined on a scale of 0-5, where 0 is no performance and 5 is maximum. Strength and hedonics were assessed by perfumers and scent design managers.

[00133] Table 14 – Evaluation Results

Fragrance	Capsule	Damp	Dry Pre	Dry GH	Dry Post
Tea Leaves	Ex. 9	++	++	++	++
	Ex. 1 (ref)	+	+/-	+/-	+/-
Apple 2	Ex. 9	++	+	+	+
	Ex. 1 (ref)*	++	++	++	++
Lavender	Ex. 9	++	++	++	++
	Ex. 1 (ref)	++^	++^	++^	++^

*, Failed, due to high viscosity in process.
++, stable performance and hedonics.
+, stable performance, but less character.
+/-, less performance and character.
^, Difference in release profile, but acceptable.

[00134] The expert evaluation with scent design managers and perfumers indicated that the hedonics was stable for capsules produced by the method described in Example 9 for the oils containing high level of naturals (Table 14). By comparison, melamine formaldehyde capsules did not show good encapsulation or stable performance overtime in the product.

[00135] The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

[00136] Every document cited herein, including any cross referenced or related patent or application and any patent application or patent to which this application claims priority or benefit thereof, is hereby incorporated herein by reference in its entirety unless expressly

excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

[00137] While particular embodiments of the present disclosure have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the disclosure. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this disclosure.

CLAIMS

What is claimed is:

1. A core-shell microcapsule slurry comprising:

(a) microcapsules having a mean diameter of 1 to 100 microns, the core of the microcapsules comprises an active material and the shell of the microcapsules comprises a trimethylol propane-adduct of xylylene diisocyanate;

(b) a dispersant comprising denatured pea protein; and

(c) a hydrocolloid comprising gum Arabic added to an aqueous phase before an emulsification step during formation of the slurry.

2. The core-shell microcapsule slurry of claim 1, further comprising least one rheology modifier, preservative, emulsifier, or a combination thereof.

3. The core-shell microcapsule slurry of claim 2, wherein the rheology modifier comprises xanthan gum.

4. The core-shell microcapsule slurry of any one of the preceding claims, wherein the microcapsules comprise a microcapsule shell having a biodegradation rate of at least 20%, 30%, 40%, 50%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 98%, within 60 days according to OECD301F or OECD310, preferably of at least 20% within 60 days according to OECD301F or OECD310.

5. The core-shell microcapsule slurry of any one of the preceding claims, wherein the trimethylol propane-adduct of xylylene diisocyanate is present at 0.1% to 8% by weight of the core-shell microcapsule slurry.

6. The core-shell microcapsule slurry of any one of the preceding claims, wherein the active material comprises at least one fragrance, pro-fragrance, malodor counteractive agent, or a combination thereof.

7. The core-shell microcapsule slurry of claim 6, wherein the active material is a fragrance and the slurry has (a) less than 0.3% or 0.25% of a non-encapsulated fragrance, (b) a viscosity of less than 600 cps or less than 580 cps as measured at shear rate of 21 s^{-1}, or (c) a combination of (a) and (b).

8. A consumer product comprising the core-shell microcapsule slurry of any one of claims 1 to 7, preferably the consumer product is a fabric softener, a fabric refresher, or a liquid laundry detergent.

9. A method for producing a core-shell microcapsule slurry of claim 1 comprising:

(a) preparing an aqueous phase by

(i) denaturing a pea protein,

(ii) adjusting the pH to below 6, and

(iii) adding gum Arabic as a hydrocolloid;

(b) preparing an oil phase comprising an active material and a trimethylol propane-adduct of xylylene diisocyanate;

(c) emulsifying the oil phase into the aqueous phase to form a slurry; and

(d) curing the slurry at a temperature below 80°C.

10. The method of claim 9, wherein the pH in (a)(ii) is adjusted to between 4.5 and 3.5.

11. The method of claim 9 or 10, wherein the slurry in (d) is cured at a temperature in the range of 63°C to 67°C.

12. The method of any one of claims 9 or 11, wherein the active material comprises at least one fragrance, pro-fragrance, malodor counteractive agent, or a combination thereof.

13. The method of any one of claims 9 or 12, further comprising adding at least one rheology modifier, preservative, emulsifier, or a combination thereof.

14. The method of claim 13, wherein the rheology modifier is added prior to step (c), preferably the rheology modifier is xanthan gum.

15. The method of any one of claims 9 to 14, wherein the trimethylol propane-adduct of xylylene diisocyanate is present at 0.1% to 8% by weight of the core-shell microcapsule composition.

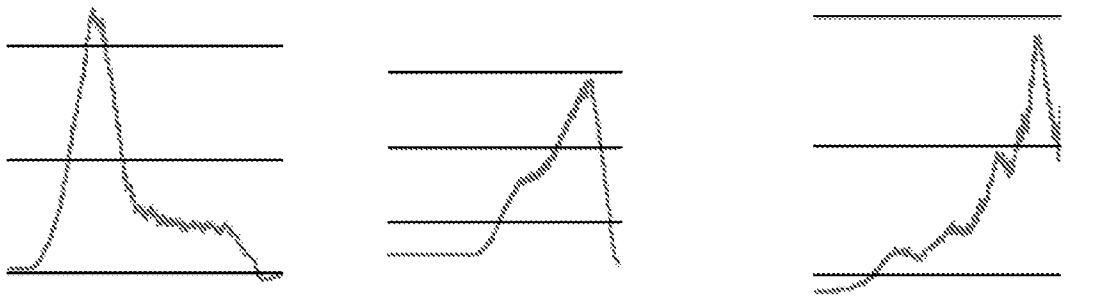
WHEY
PEA
TEMPERATURE AND pH
OPTIMIZED PEA

FIG. 1

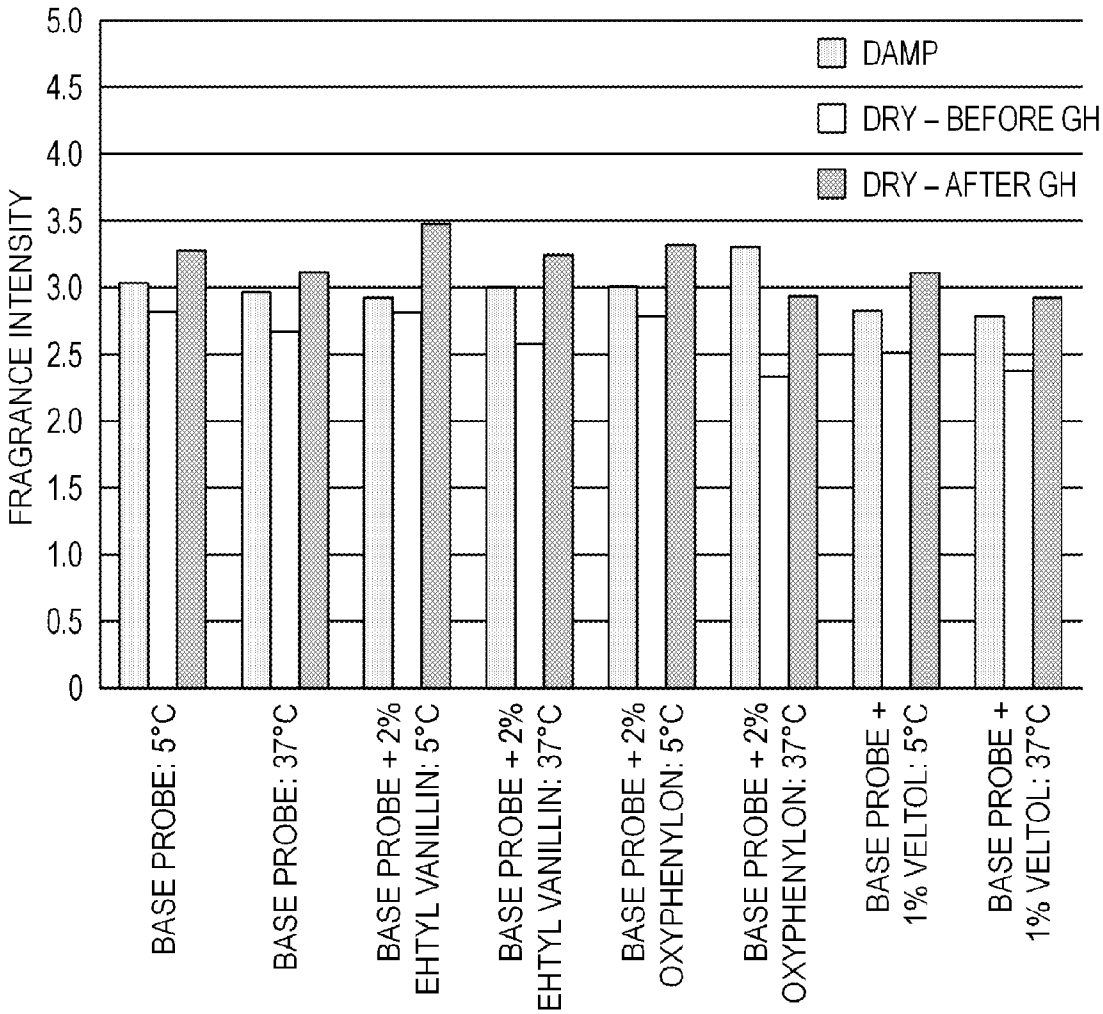
FRAGRANCE INTENSITY
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
DAMP
DRY – BEFORE GH
DRY – AFTER GH
BASE PROBE: 5°C
BASE PROBE: 37°C
BASE PROBE + 2% EHTYL VANILLIN: 5°C
BASE PROBE + 2% EHTYL VANILLIN: 37°C
BASE PROBE + 2% OXYPHENYLON: 5°C
BASE PROBE + 2% OXYPHENYLON: 37°C
BASE PROBE + 1% VELTOL: 5°C
BASE PROBE + 1% VELTOL: 37°C

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2022/038330

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J13/18 C11D3/50 B01J13/20
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2020/131879 A2 (INT FLAVORS & FRAGRANCES INC [US]) 25 June 2020 (2020-06-25) claims 1-4, 8-9 paragraphs [0021], [0028], [0033], [0035], [0043] - [0046], [0079], [0121] - [0122], [0163] -----	1-15
A	WO 2019/243426 A1 (FIRMENICH & CIE [CH]) 26 December 2019 (2019-12-26) the whole document -----	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 September 2022	26/09/2022

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Tarallo, Anthony

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2022/038330

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2020131879 A2	25-06-2020	BR 112021011819 A2	31-08-2021
		BR 112021011936 A2	08-09-2021
		CN 113438939 A	24-09-2021
		CN 113453656 A	28-09-2021
		EP 3897523 A2	27-10-2021
		EP 3897524 A2	27-10-2021
		US 2022071865 A1	10-03-2022
		WO 2020131875 A2	25-06-2020
		WO 2020131879 A2	25-06-2020
WO 2019243426 A1	26-12-2019	CN 111801155 A	20-10-2020
		EP 3746217 A1	09-12-2020
		JP 2021528223 A	21-10-2021
		SG 11202008071Y A	29-09-2020
		US 2021106966 A1	15-04-2021
		WO 2019243426 A1	26-12-2019