



(86) Date de dépôt PCT/PCT Filing Date: 2008/06/27
(87) Date publication PCT/PCT Publication Date: 2009/01/08
(85) Entrée phase nationale/National Entry: 2009/11/02
(86) N° demande PCT/PCT Application No.: EP 2008/058318
(87) N° publication PCT/PCT Publication No.: 2009/003960
(30) Priorité/Priority: 2007/06/29 (EP07111403.7)

(51) Cl.Int./Int.Cl. *A23D 7/005* (2006.01),
A23L 1/035 (2006.01), *A23L 1/48* (2006.01),
A61K 8/06 (2006.01), *A61K 9/113* (2006.01),
B01F 17/00 (2006.01)
(71) Demandeur/Applicant:
NESTEC S.A., CH
(72) Inventeurs/Inventors:
FOLMER, BRITTA, CH;
MICHEL, MARTIN, CH;
GEHIN-DELVAL, CECILE, FR;
ACQUISTAPACE, SIMONE, CH;
LESER, MARTIN, CH;
SYRBE, AXEL, CH; ...

(54) Titre : EMULSIONS DOUBLES STABLES
(54) Title: STABLE DOUBLE EMULSIONS

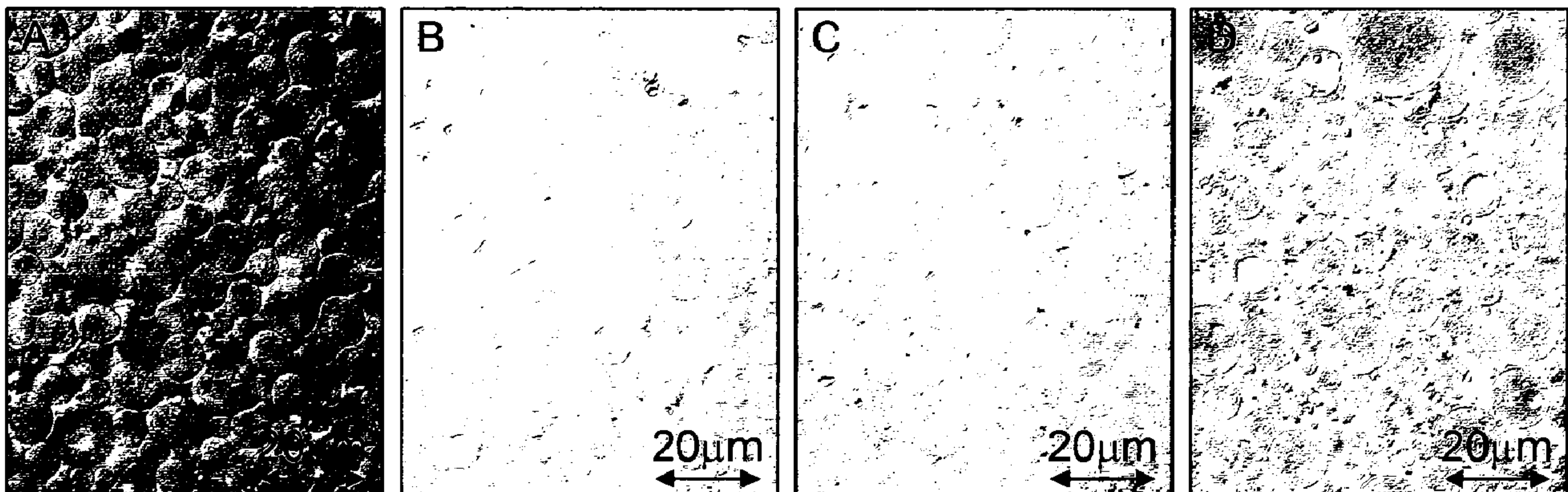


FIG. 1

(57) Abrégé/Abstract:

The invention relates to double emulsions, in particular double emulsions of the water-in-oil-in-water type, which are organoleptically similar to full-fat oil in water emulsions and which are stabilised by mixture of emulsifiers. The invention also relates to a method for producing said double emulsions, and to the use of a mixture of emulsifier for stabilising said emulsions.



(72) Inventeurs(suite)/Inventors(continued): MARZE, SEBASTIEN, FR

(74) Agent: BORDEN LADNER GERVAIS LLP

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
8 January 2009 (08.01.2009)

PCT

(10) International Publication Number
WO 2009/003960 A1

(51) International Patent Classification:

A23D 7/005 (2006.01) B01F 17/00 (2006.01)
A23L 1/48 (2006.01) A61K 8/06 (2006.01)
A23L 1/035 (2006.01) A61K 9/113 (2006.01)

(21) International Application Number:

PCT/EP2008/058318

(22) International Filing Date: 27 June 2008 (27.06.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

07111403.7 29 June 2007 (29.06.2007) EP

(71) Applicant (for all designated States except US): NESTEC S.A. [CH/CH]; Avenue Nestlé 55, CH-1800 Vevey (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): FOLMER, Britta [SE/CH]; Avenue de Rumine 66, CH-1005 Lausanne (CH). MICHEL, Martin [CH/CH]; Ch. de Verdonnet 12, CH-1010 Lausanne (CH). GEHIN-DELVAL, Cécile [FR/FR]; 4, Avenue de la Gare, F-25160 Labergement Sainte Marie (FR). ACQUISTAPACE, Simone [IT/CH]; Rte de Chailly 2, CH-1814 La Tour-de-Peilz (CH). LESER, Martin [CH/CH]; Ch. du Champ Petau 36, CH-1053 Bretigny-s/Morrens (CH). SYRBE, Axel [DE/CH]; Rue du Lac 178, CH-1815 Clarens (CH). MARZE, Sébastien [FR/FR]; Av. Vinet 8, F-1004 Lausanne (FR).

(74) Agent: THOMAS, Alain; Avenue Nestlé 55, CH-1800 Vevey (CH).

(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, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report

(54) Title: STABLE DOUBLE EMULSIONS

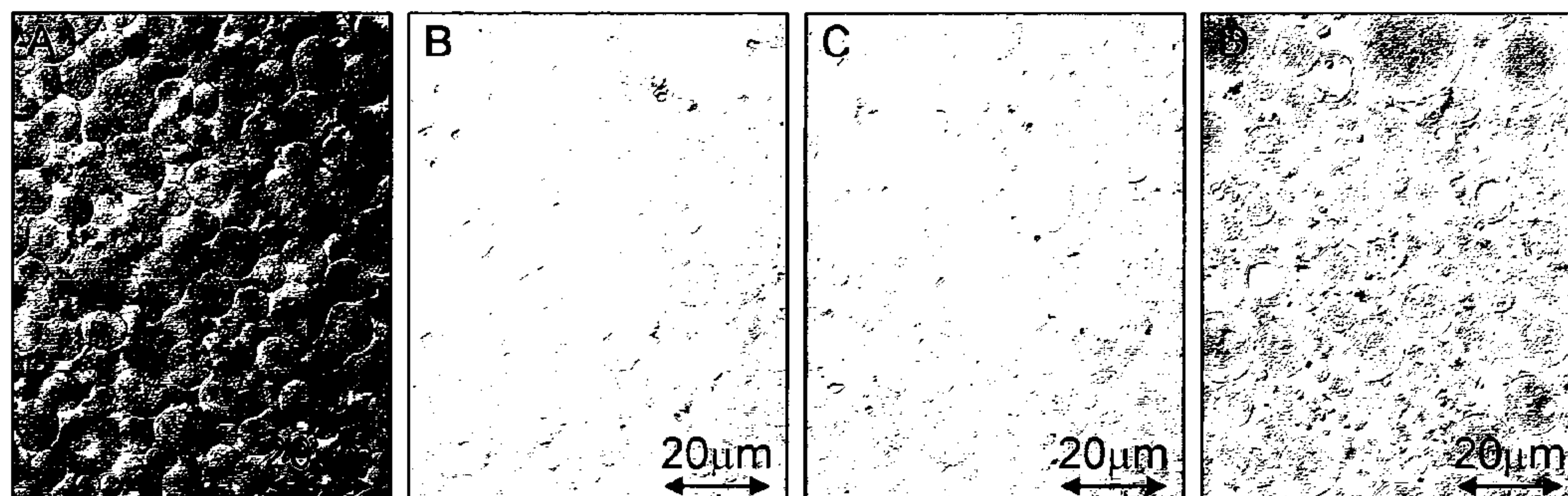


FIG. 1

(57) Abstract: The invention relates to double emulsions, in particular double emulsions of the water-in-oil-in-water type, which are organoleptically similar to full-fat oil in water emulsions and which are stabilised by mixture of emulsifiers. The invention also relates to a method for producing said double emulsions, and to the use of a mixture of emulsifier for stabilising said emulsions.

WO 2009/003960 A1

Stable double emulsions**Field of the invention**

The invention relates to double emulsions, in particular
5 double emulsions of the water-in-oil-in-water type, which
are organoleptically similar to full-fat oil in water
emulsions and which are stabilised by a selection of
emulsifiers. The invention also relates to a method for
producing said double emulsions, and to the use of a
10 selection of emulsifier for stabilising said emulsions.

Background of the invention

Double emulsions, also named multiple emulsions, can be
considered as an emulsion of an emulsion: the oil droplets
15 which are dispersed in an aqueous phase, contain
themselves small water droplets. Water-in-oil-in-water
(W/O/W) emulsions are interesting for fat reduction to
create low fat products. Indeed, the oil droplets in an
ordinary oil-in-water emulsion can be replaced by droplets
20 made of a water-in-oil emulsion. Low-fat products obtained
with multiple emulsions are described in EP 0 711 115, US
2004/0101613 (EP 1 565 076), EP 0 345 075. Multiple
emulsions are also often used in cosmetic applications.
For instance, EP 1 097 702, EP 0 614 660, EP 0 650 352, EP
25 0 648 102, EP 0 507 693 all describe cosmetic compositions
in the form of water in oil in water emulsions.

The main problems encountered with double emulsions is
their stability. Most solutions proposed to date rely on
30 the proper choice of the emulsifiers used. For instance,
EP 0 731 685 describes a stable multiple emulsion obtained
by using emulsifiers having a HLB value less than 6. EP 0
631 774 also describes storage stable multiple emulsions
comprising particular hydrophobic and hydrophilic

emulsifiers. WO 03/049553 similarly relates to stable multiple emulsions obtained by selecting the appropriate emulsifiers used for the internal water-in-oil emulsion and for the external oil-in-water emulsion. There is
5 however still room for improvement. The FR Patent 2823450 concerns a final product which is a suspension, that means a solid product and not a liquid Water-in-oil-in-water emulsion. This is not a food product, but only a product for use in cosmetic. The WO patent application 03/049553
10 concerns a double emulsion in which the inner water phase contains a viscosifier, such as alginate. In this case, the objective is to obtain a gelified product, which is not the case for us.

15 **Object of the invention**

The object of the present invention is thus to provide stabilised double emulsions which can be used in a number of applications.

20 **Summary**

Accordingly, the present object is achieved by means of the features of the independent claims. The dependent claims develop further the central idea of the invention.

25 In a first aspect, the invention relates to a double emulsion comprising an internal aqueous phase dispersed in an oil phase forming a water-in-oil emulsion, said water-in-oil emulsion being dispersed in an external aqueous phase, wherein the water-in-oil emulsion comprises at
30 least one emulsifier, wherein at least the internal aqueous phase comprises solutes and wherein the external aqueous phase comprises at least one hydrophilic polymer or polymer aggregates.

A method for the preparation of a double emulsion comprising the steps of:

- a. Preparing an internal aqueous phase comprising solutes
- 5 b. Combining the internal aqueous phase with an oil phase comprising at least one emulsifier to obtain a stabilised water-in-oil emulsion
- c. Combining the water-in-oil emulsion with an external aqueous phase to form a double
10 emulsion,

wherein the external aqueous phase comprises at least one hydrophilic polymer or polymer aggregates,
and the double emulsion obtainable by said method both form part of the present invention.

15

A further aspect of the invention relates to the use of at least one emulsifier for stabilising a water-in-oil emulsion, wherein the water-in-oil emulsion is part of a double emulsion comprising said water-in-oil emulsion
20 dispersed in an external aqueous phase.

Finally, the use of the double emulsion of the invention in food products, clinical products, pharmaceutical products, nutricosmetics, cosmetics, agro-chemical or
25 other industrial products is also part of the invention.

Figures

The present invention is further described hereinafter with reference to some of its embodiments shown in the
30 accompanying drawings in which:

- Fig. 1 represents light microscopy pictures (DIC) of the double emulsion at different time points.
- Fig. 2a and 2b shows the rheological behaviour of the double emulsion of the invention

- Fig. 3 shows the influence of salt in the internal aqueous phase on the stability of the double emulsion

5 **Detailed description of the invention**

The double emulsions of the invention are preferably emulsions of the water-in-oil-in-water type. They comprise an aqueous phase (the inner aqueous phase) dispersed in an oil phase forming a water-in-oil emulsion. Said water-in-oil emulsion is dispersed in an external aqueous phase.

According to the invention, the inner aqueous phase is dispersed and stabilised by means of an emulsifier or emulsifier mixture in an oil phase. The inner aqueous phase also comprises solutes.

In one embodiment, the water-in-oil emulsion comprises at least two different emulsifiers having different molecular weights.

20

By emulsifiers having differing molecular weights is preferably to be distinguished between emulsifiers having a molecular weight of less than 2000g/mol and emulsifiers having a molecular weight of more than 700g/mol. In a preferred embodiment, at least one emulsifier has a molecular weight of less than 1800g/mol, more preferably less than 1500g/mol, even more preferably less than 1200g/mol, while at least a second emulsifier has a molecular weight of more than 800g/mol, preferably more than 1000g/mol, even more preferably more than 1200g/mol. Such emulsifiers may be termed "low-molecular weight" emulsifiers and "high-molecular weight" emulsifiers respectively. Preferably, the "low-molecular weight"

25
30

emulsifier has a molecular weight lower than the "high-molecular weight" emulsifier.

According to a preferred embodiment, at least one of the
5 emulsifier is selected from the group of low molecular weight emulsifiers consisting of fatty acids, sorbitan esters, propylene glycol mono- or diesters, pegylated fatty acids, monoglycerides, derivatives of monoglycerides, diglycerides, pegylated vegetable oils,
10 polyoxyethylene sorbitan esters, phospholipids, lecithin, cephalin, lipids, galactolipids, sugar esters, sugar ethers, sucrose esters, sorbitol anhydride monostearate, sorbitol anhydride monooleate, glycerol monooleate, or mixtures thereof and at least a second emulsifier is
15 selected from the group of high molecular weight emulsifiers consisting of polyglycerol esters, polyglycerol polyricinoleic acid (PGPR), cellulose and its derivatives such as ethylcellulose, oil soluble proteins or peptides or hydrolysates, protein-polysaccharide
20 complexes, coacervates or conjugates, food particles, fat particles, solid-lipid nanoparticles, micronised nutrient crystals, dietary fibres or mixtures thereof.

Accordingly, the emulsifier mixture preferably comprises
25 at least one "low-molecular weight" emulsifier and at least one "high-molecular weight" emulsifier.

If only one emulsifier is used , it is possible to use either the "low molecular weight" emulsifier or the "high
30 molecular weight" emulsifier, preferably the "high molecular weight" emulsifier.

Under protein-polysaccharide complexes, coacervates or conjugates, which can be used as a "high molecular weight" emulsifier in the invention is meant any protein-polysaccharide mixtures which forms interfacially active
5 supra-molecular aggregates, which are either physical complexes or which are chemically linked together via chemical bonds. These coacervates or conjugates have the properties of accumulating at the water-oil interface, reducing the interfacial tension and helping to disperse
10 the water droplets into an oil phase and to stabilise the obtained water-in-oil emulsion (w/o emulsion).

Furthermore, the food particles which can be used in the present invention as part of the "high-molecular weight"
15 emulsifier include seeds, spices, seasonings, spores, cloves, pepper, fennel, cumin, coriander, nutmeg, poppy grains, paprika, cinnamon, talcum, pollen of flowers, wheat germs, wheat bran, saffron, coconut, cacao, melanoidins, sugar crystals, protein aggregates, ginger,
20 curry, titanium dioxide polymeric particles, calcium carbonate polymeric particles, microcrystalline cellulose, or a mixture thereof. The particles may already be surface active on their own or may get their surface active properties after grinding of the particle material and/or
25 by addition of a "low molecular weight" emulsifier which adsorbs onto the surface of the particles. The interfacial activity of the particles of this invention (adsorption onto the water-oil interface or desorption from the water-oil interface) can be followed using classical surface
30 tensiometry, such as the Wilhelmy plate or Drop shape or Drop volume or Bubble pressure tensiometry (R. Miller et al., SÖFW-Journal 130, 2-10 (2004)). The adsorption/attachment of the interfacially active particles to the water droplets can be followed by light

and/or electron microscopy. Especially polarized light or fluorescent microscopy is a suitable technique to visualise the attachment of interfacially active particles at the air-bubble surface.

5

The term 'interfacially active particles' is used herein to describe colloidal particles, i.e. supra-molecular aggregates, having a diameter between 0.5 nm up to 100 microns, preferably 0.5-50 microns, which act in many ways like emulsifiers in the sense that they are able to adsorb or attach to a water-oil interface. The unique feature of the adsorbed particles is that their attachment at the water-oil interface is irreversible. This is clearly not observed using commonly used emulsification agents, such as low molecular surfactants, which are adsorbed in a reversible way and desorb again after a certain time (an adsorption/desorption equilibrium between the water-oil is established). The irreversible attachment of the particles to the water-oil interface gives the water droplets the remarkable stability against coalescence or Ostwald ripening.

According to the present invention, the interfacially active particles can be created in different ways: one way to create interfacially active particles is by using "low molecular weight" emulsifiers, heating the aqueous dispersion above their Krafft temperature and cooling the dispersion down again to room temperature while stirring. During the cooling step, the particles are formed. The emulsification of the internal aqueous phase into the oil phase can be done during the cooling step or just after the system is cooled down to room temperature. The used emulsifier can be a mixture of different emulsifiers or can be used singly.

Similarly fat particles can be made from fat sources selected from sunflower oil, palm oil, rapeseed oil, cotton seed oil, soy bean oil, maize oil, shea oil, cocoa
5 butter, or fractions thereof or in their hardened form or as fraction of the hardened oil or as partially hydrolysed oil rich in diglycerides or monoglycerides or as mixtures thereof. The particles are micronised and their interfacial activity and emulsification properties can be
10 tuned by adding a "low molecular weight" emulsifier, similarly as described above for creating interfacially active food particles.

Under solid-lipid nanoparticles is to be understood
15 particulate systems with mean particle diameters ranging from 50 up to 1000 nm. They are mainly known as drug delivery systems and formed by homogenisation as described by Dong Zhi Hou, Chang Sheng Xie, Kai Jin Huang, Chang Hong Zhu in Biomaterials 24 (2003) 1781-1785. Their
20 interfacial activity and emulsification properties can be tuned by adding a "low molecular weight" emulsifier, similarly as described above for creating interfacially active food particles.

25 Finally, micronised nutrient crystals such as phytosterols, hesperidin, or lycopene crystals can also be used as one of the "high-molecular weight" emulsifier. It concerns all nutrients which are insoluble both in water and oil phases and, as a consequence, forming crystals.
30 Their interfacial activity and emulsification properties can be tuned by adding a "low molecular weight" emulsifier, similarly as done for creating interfacially active food particles.

Most preferably, the mixture of emulsifiers used to stabilise the inner water-in-oil emulsion is a mixture of PGPR and glycerol monooleate (GMO). It is also possible to use only PGPR or only GMO.

5

It has been found that using simply a "low-molecular weight" emulsifier, or alternatively using simply a "high-molecular weight" emulsifier can be enough to stabilise the inner water/oil interface. By using a mixture of emulsifiers according to the present invention, a product having the desired consistency and stability is obtained.

According to a preferred embodiment, the external aqueous phase comprises a hydrophilic polymer or polymer aggregates. Thus, the oil droplets (which contain the dispersed inner aqueous phase) are stabilised in the external aqueous phase. Examples of such polymers or aggregates of polymers are amidated low methoxy pectin, caseinate, whey proteins, milk proteins, egg proteins, egg yolk, soy proteins, acacia gum, starch derivatives or other o/w emulsion stabilizing proteins or polysaccharides, or hydrophilic particles made out of protein aggregates, polysaccharide aggregates, hydrophilic particles made out of protein-surfactant aggregates, hydrophilic particles made out of protein-polysaccharide mixtures, hydrophilic particles made out of polysaccharide-polysaccharide mixtures, hydrophilic particles made out of polysaccharide-protein phase separating mixtures, or any mixtures thereof.

30

By hydrophilic particles is meant particles which are dispersible into an aqueous phase and show an interfacial activity. The term "interfacially active particles" is as defined above.

Preferably, protein-polysaccharide mixtures, coacervates, conjugates, hybrids or particles are used as hydrophilic polymer in the present invention.

5

Most preferably, the hydrophilic polymer is taken in the group consisting of whey protein isolate, amidated low methoxy pectin, egg yolk or a mixture thereof.

10 The inner aqueous phase preferably comprises solutes selected from salts, polyols and/or sugars. Any water soluble salts, including organic salts, polyols or sugars can be used. Salts may be, for instance, sodium chloride, potassium chloride, calcium chloride, magnesium chloride,
15 zinc chloride etc. Polyols or sugars which can be used in the present invention comprise any mono-, di- and oligosaccharides, starch, degradation products of starch, maltodextrins, dextran, glucose, sucrose, fructose, glycerol, polyglycerol, ethyleneglycol, propylene glycol
20 etc.

The presence of solutes in the inner aqueous phase creates initially an osmotic pressure gradient between the inner aqueous phase and the outer aqueous phase. Thus, the
25 internal water-in-oil emulsion of the present invention is under osmotic pressure. This causes a swelling of the inner aqueous phase over time such that a textured double emulsion may be obtained. This is only achieved when the inter water-oil interface is efficiently stabilised by the
30 used emulsifiers. The texture and consistency of the double emulsion of the invention can be modulated and regulated from low viscous (pourable) to highly viscous (spreadable) by, for instance, choosing a suitable type and amount of solute.

Thus, by the present invention, it is not necessary to introduce a gelling agent i.e. a viscosifier at concentrations above the gel point, in the external aqueous phase to obtain the desired texture and consistency. The external aqueous phase is not gelified. If a gelling agent would be present, it is present in the amount of less than 5 %, preferably of less than 2 %.

Furthermore, referring to fig. 3, it can be seen that the presence of solutes (e.g. salt) in the inner aqueous phase has an impact on the stability of the double emulsion. The light microscopy images show the difference in stability directly after preparation (1), 1 hour after preparation (2), 3-7 days after preparation (3) for a double emulsion comprising salt in the inner water phase (A) and a double emulsion not comprising salt in the inner water phase (B). The images show that A is very stable over time whereas B is not stable at all.

20

The double emulsion of the present invention may comprise from 1 to 55%, preferably 2 to 45%, more preferably 3 to 35% oil. This depends on the desired product. For instance, by varying the amount of oil, the double emulsions of the invention may vary in consistency and texture from fluid, to viscous, to full-fat mayonnaise-like textures.

30

Another way to vary the final product consistency is by varying the amount of aqueous solute phase droplets in the inner w/o emulsion. Increasing the amount of the aqueous solute phase in the w/o emulsion transforms the consistency and texture of the final double emulsion of the invention from fluid to viscous and mayonnaise-like

while keeping the overall fat content in the double emulsion constant.

In one embodiment, a viscosifier is also present in the double emulsion in order to fine tune the final texture and consistency of the double emulsion product. Preferably, the viscosifier is present in the external aqueous phase. The presence of a viscosifier may enhance the viscosity of said product and the stability of the emulsion against creaming and/or phase separation. This is particularly advantageous when low-fat double emulsions are produced.

Viscosifiers which can be used in the present invention may be selected from amidated low methoxy pectin, pectin, alginates, carrageenan, locust bean gum, guar gum, tragacanth, Acacia gum, xanthan gum, Karaya gum, gellan gum, polydextrose, dextrin, modified starch, oxidized starch, cellulose derivatives, or mixtures thereof.

20

When amidated low methoxy pectin is already used as part of the hydrophilic polymer for stabilising the oil phase in the external aqueous phase, a further viscosifier is not needed, but may be added.

25

The double emulsions of the present invention may be used in food products, clinical products, pharmaceutical products, nutricosmetics, cosmetics, agro-chemical or other industrial products. Depending on the application, they may be freeze-dried or spray-dried. The dried form may be rehydrated in solution without losing the double emulsion texture.

30

Preferably, they are used in food products selected from salad dressing, mayonnaise-type products, sauces, spreads, soups, desserts, creams etc. The consistency and texture of these products may be tailored such that fluid, viscous
5 or even thick textures are possible. In a preferred embodiment, the product may be a low-fat food product having the same sensory properties as the respective full fat version of the same product.

10 Referring to figure 2, it can be seen that the texture of the double emulsion of the present invention is close to the texture of a standard product "Thomy mayonnaise à la française", especially in terms of yield stress before stirring (Fig. 2a) and viscosity at high shear rate (Fig.
15 2b). Indeed, the present double emulsion has a yield stress of 318Pa at 0.9 of strain, versus a yield stress of 294Pa at 0.6 of strain for the standard mayonnaise product. Similarly, the viscosity at 160s^{-1} shear rate is 1.425 for the present emulsion versus 2.16 for the
20 standard product.

A tasting session has also revealed that the present double emulsions have been perceived as neutral, with a good texture similar to the full-fat mayonnaise. The
25 double emulsion gave an impression of palate full-fat coating such as a mayonnaise.

The double emulsion of the invention is very stable over time, with no phase separation or texture change over at
30 least 1 month. Indeed, referring to fig. 1, these images of the double emulsion of the invention are taken after sample preparation (A), 1 hour later (B), 1 week later (C), 1 month later (D). It can be seen that there is no structural change of the double emulsion over 1 month. The

double emulsion consists of spherical droplets of oil in water emulsion of 1 to 10 microns in diameter. These droplets are almost close packed into the aqueous solution.

5

The present double emulsion may further comprise additional water-soluble molecules in the inner or in the outer aqueous phase of the double emulsion. The addition of these compounds does not compromise the texture of the final products enabling the production of a large variety of products, in particular low-fat products.

10

The double emulsions according to the invention are obtainable by a method described in the following.

15

The present method for the preparation of a double emulsion comprises, in a first step, the preparation of an internal aqueous phase comprising solutes. The solutes may be selected from salts, polyols and/or sugars. Typical salts include organic salts, sodium chloride, potassium chloride, calcium chloride, magnesium chloride, zinc chloride etc. Polyols or sugars which can be used in the present invention comprise any mono-, di- or oligosaccharides, starch, degradation products of starch, maltodextrins, dextran, glucose, sucrose, fructose, glycerol, polyglycerol, ethyleneglycol, propylene glycol etc.

20

25

The solutes concentration in the internal aqueous phase is preferably between 0.1 up to 30% by weight, more preferably 1% to 20% by weight, even more preferably 3% to 15% by weight.

30

To the internal aqueous phase is then added an oil phase comprising at least one emulsifier to obtain a well stabilised water-in-oil emulsion.

- 5 In the case of the use of a mixture of emulsifiers, it is such that each emulsifier has a differing molecular weight such that at least one emulsifier has a molecular weight of less than 2000g/mol and at least a second emulsifier has a molecular weight of more than 700g/mol. Preferably,
10 at least one emulsifier has a molecular weight of less than 1800g/mol, more preferably less than 1500g/mol, even more preferably less than 1200g/mol, while at least a second emulsifier preferably has a molecular weight of more than 800g/mol, more preferably more than 1000g/mol,
15 even more preferably more than 1200g/mol.

- More preferably, the emulsifiers are such that at least one of the emulsifier is selected from the group of "low molecular weight" emulsifiers consisting of fatty acids,
20 sorbitan esters, propylene glycol mono- or diesters, pegylated fatty acids, monoglycerides, derivatives of monoglycerides, diglycerides, pegylated vegetable oils, polyoxyethylene sorbitan esters, phospholipids, lecithin, cephalin, lipids, galactolipids, sugar esters, sugar
25 ethers, sucrose esters, sorbitol anhydride monostearate, sorbitol anhydride monooleate, glycerol monooleate, or mixtures thereof and at least a second emulsifier is selected from the group of high molecular weight emulsifiers consisting of polyglycerol esters,
30 polyglycerol polyricinoleic acid (PGPR), cellulose and its derivatives such as ethylcellulose, oil soluble proteins or peptides or hydrolysates, protein-polysaccharide complexes, coacervates or conjugates, food particles, fat

particles, solid-lipid nanoparticles, micronised nutrient crystals, dietary fibres or mixtures thereof.

Most preferably, the emulsifier used to stabilise the
5 inner water-in-oil emulsion is PGPR, glycerol monooleate (GMO) or a mixture thereof.

In a preferred embodiment, the amount of emulsifiers used to stabilise to water-in-oil emulsion is less than 5%,
10 preferably less than 3%, more preferably less than 1% of the water-in-oil emulsion obtained.

The ratio of "low-molecular weight" emulsifier to "high-molecular weight" emulsifier is between 1:10 to 10:1 by
15 weight. Preferably, it is between 1:5 and 5:1. Most preferably it is 4:1.

The weight percentage of the aqueous, solute containing phase in the water-in-oil emulsion may be from 1% to 80%,
20 preferably, from 5% to 60%, and most preferable from 10% to 50%.

The conditions for forming the water-in-oil emulsions are standard conditions known to the skilled person. For
25 instance, the mixture of oil and water is homogenised using high pressure or shear or a membrane or ultrasound, by mixers known in the art. The homogenisation speed and the duration of the shearing or mixing have an influence on the size of the water droplets inside the oil droplets,
30 and thereby, on the texture and consistency of the final double emulsion.

Preferably, the conditions are such that the water droplets have a size between 70nm and 20 microns. The size

of the water droplets influences the consistency of the final double emulsion and may be adjusted accordingly. In a most preferred embodiment, the size of the water droplets is between 100nm and 10 microns.

5

The last step in the present method is the mixing of the water-in-oil emulsion with an external aqueous phase to form a double emulsion. Preferably, the external aqueous phase comprises a hydrophilic polymer or polymer mixture
10 or aggregate. In this way, the oil phase is stabilised in the external aqueous phase by said hydrophilic polymer.

Examples of such hydrophilic polymers or aggregates of polymers are amidated low methoxy pectin, caseinate, whey
15 proteins, milk proteins, egg proteins, soy proteins, acacia gum, starch derivatives or other o/w emulsion stabilizing proteins or polysaccharides, or hydrophilic particles made out of protein aggregates, polysaccharide aggregates, hydrophilic particles made out of protein-
20 surfactant aggregates, hydrophilic particles made out of protein-polysaccharide mixtures, hydrophilic particles made out of polysaccharide-polysaccharide mixtures, hydrophilic particles made out of polysaccharide-protein phase separating mixtures, or any mixtures thereof.

25

By hydrophilic particles is meant particles which are dispersible into an aqueous phase and show an interfacial activity. The term 'interfacially active particles' is described above.

30

Preferably, protein-polysaccharide mixtures, coacervates, conjugates, hybrids or particles are used as hydrophilic polymer in the present invention.

Most preferably, the hydrophilic polymer is taken in the group consisting of whey protein isolate, amidated low methoxy pectin, egg yolk or a mixture thereof.

- 5 The amount of external aqueous phase added to the water-in-oil emulsion is in the range of 15:85 up to 95:5. Preferably, it is in the range of 20:80 up to 80:20. More preferably, it is in the range of 30:70 up to 70:30.
- 10 In the present method, water-soluble molecules may further be included in the inner or in the outer aqueous phase of the double emulsion. The addition of these compounds does not compromise the texture of the final products enabling the production of a large variety of products, in
- 15 particular low-fat products.

In a preferred embodiment of the present invention, the double emulsion obtained is allowed to set such as to form a textured double emulsion. This is due to the fact that

20 the concentration of solutes in the internal aqueous phase is such that an osmotic pressure gradient is created between the internal and the external aqueous phases. Typically, several hours are needed for osmotic equilibration to occur between the phases. This final

25 texture is found to be very stable over time and does no longer change. Thus, the double emulsion of the invention may be produced in a liquid form and poured or filled into a packaging without problem before the final viscosity is obtained. This provides a great advantage regarding ease

30 of processing.

According to the present invention, the final consistency is controlled by a number of factors such as the amount and type of solutes present in the inner and outer aqueous

phase, the amount of oil phase, the amount of inner water phase in the oil droplets, the size of the inner water phase droplets, the oil droplets size, the amount and type of emulsifier mixture used to stabilise the inner aqueous phase and the type of polymer used to stabilise the outer oil/water interface.

Most importantly, it has been found by the present invention that the type of emulsifiers used to stabilise the water-in-oil emulsion is crucial when stability of the whole double emulsion is concerned.

Thus, the use of least one emulsifier for stabilising a water-in-oil emulsion, wherein the water-in-oil emulsion is part of a double emulsion comprising said water-in-oil emulsion dispersed in an external aqueous phase also forms part of the present invention.

The emulsifiers are such as those described above with respect to the double emulsions and their method of production.

Most preferably, the emulsifiers are a mix of glycerol monooleate and polyglycerol polyricinoleic acid (PGPR).

25

The present invention thus provides a way in which double emulsions may be produced which are stable over time and which display consistencies which may be tailored to the desired use. In particular, low fat double emulsion may be obtained having the organoleptic properties of full fat products. In this way, a 10% fat mayonnaise-type product can be made using a double emulsion of the present invention, which is perceived as an 80% fat standard mayonnaise.

30

The present invention is further illustrated by means of the following non-limiting examples.

5 **EXAMPLES**

The following procedure was used to form a number of products having mayonnaise-like textures, spread-like consistencies (e.g. Nutella type) or salad-dressing like
10 consistencies.

A polymer is mixed into water with a rotor-stator mixer (Kinematic AG, Switzerland) at room temperature for 5 minutes to form an external aqueous phase. The solution is
15 kept under agitation.

A homogeneous solution of sugar and/or salt in water is prepared at room temperature. A mixture of oil and emulsifiers is added to the solution at room temperature
20 and the mixture is submitted to high shear (speed 3 to 10) with the rotor-stator mixer for 1 to 8 minutes to form a water-in-oil emulsion. The external aqueous phase is added to the water-in-oil emulsion or vice-versa, i.e. the water-in-oil emulsion is added to the external aqueous
25 phase, and they are mixed together at room temperature under low shear (speed 3) for 1 minute. The sample is then stored at 4°C for at least 1 to 6 hours prior to utilisation. During this time, the final consistency of the double emulsion evolves.

30

The samples may be sterilised and/or pasteurised using standard methods.

Mayonnaise-like textures

Example 1	Water-in-oil emulsion	Outer aqueous phase
Salt	25% aqueous 1M NaCl	–
Sugar	5% glucose	–
Emulsifiers	8% PGPR 2% GMO	–
Oil	60% sunflower	–
Polymer	–	5% WPI 2% ALMP
Amount	20%	80%

Example 2	Water-in-oil emulsion	Outer aqueous phase
Salt	29% aqueous 1M NaCl	–
Sugar	5% glucose	–
Emulsifiers	4% Ethocel 2% GMO	–
Oil	60% sunflower	–
Polymer	–	5% WPI 2% ALMP
Amount	20%	80%

Example 3	Water-in-oil emulsion	Outer aqueous phase
Salt	24% aqueous 1M NaCl	–
Sugar	4% glucose	–
Emulsifiers	8% TiO ₂ polymeric particles 4% GMO	–
Oil	60% sunflower	–
Polymer	–	5% WPI 2% ALMP
Amount	20%	80%

Example 4	Water-in-oil emulsion	Outer aqueous phase
Salt	16% aqueous 2M NaCl	-
Sugar	5% glucose	-
Emulsifiers	2% PGPR 2% GMO	-
Oil	75% sunflower	-
Polymer	-	6.25% WPI 2.5% ALMP
Amount	20%	80%

Example 5	Water-in-oil emulsion	Outer aqueous phase
Salt	25% aqueous 1M NaCl	-
Sugar	5% glucose	-
Emulsifiers	8% PGPR 2% GMO	-
Oil	60% sunflower	-
Polymer	-	6.25% WPI
Amount	30%	70%

Example 6	Water-in-oil emulsion	Outer aqueous phase
Salt	25% aqueous 1M NaCl	-
Sugar	5% glucose	-
Emulsifiers	8% PGPR 2% GMO	-
Oil	60% sunflower	-
Polymer	-	6.25% WPI
Amount	40%	60%

Example 7	Water-in-oil emulsion	Outer aqueous phase
Salt	5% aqueous 1M NaCl	-
Sugar	1% glucose	-
Emulsifiers	1.6% PGPR 0.4% GMO	-
Oil	92% sunflower	-
Polymer	-	6.25% WPI 2.5% ALMP
Amount	40%	60%

Example 8	Water-in-oil emulsion	Outer aqueous phase
Salt	10% aqueous 1M NaCl	-
Sugar	2% glucose	-
Emulsifiers	3.2% PGPR 0.8% GMO	-
Oil	60% sunflower	-
Polymer	-	6.25% WPI 2.5% ALMP
Amount	30%	70%

Example 9	Water-in-oil emulsion	Outer aqueous phase
Salt	8% aqueous 4M NaCl	-
Sugar	5% glucose	-
Other	6.75% vinegar (10%) 1.25% water	0.37% vinegar (10%) 2.5% mustard 5% egg yolk water solution
Emulsifiers	2% PGPR 2% GMO	-
Oil	75% sunflower	-
Polymer	-	6.25% WPI 2.5% ALMP
Amount	30%	70%

Example 10	Water-in-oil emulsion	Outer aqueous phase
Salt	3% NaCl	-
Sugar	-	-
Other	1.5% vinegar (10%) 25.5% water	10% vinegar (10%) 10% mustard 39% FGEM egg yolk
Emulsifiers	0.6% PGPR	-
Oil	69.4% sunflower	-
Polymer	-	-
Amount	65%	35%

Example 11	Water-in-oil emulsion	Outer aqueous phase
Salt	3% NaCl	-
Sugar	-	-
Other	1.5% vinegar (10%) 25.5% water	10% vinegar (10%) 10% mustard 39% FGEM egg yolk
Emulsifiers	0.5% PGPR	-
Oil	69.5% sunflower	-
Polymer	-	1% ALMP
Amount	70%	30%

Spread-like consistencies

5

Example 12	Water-in-oil emulsion	Outer aqueous phase
Salt	10% aqueous 1M NaCl	-
Sugar	2% glucose	-
Emulsifiers	3.2% PGPR 0.8% GMO	-
Oil	84% sunflower	-
Food-grade polymer	-	6.25% WPI 2.5% ALMP
Amount	40%	60%

Salad-dressing like consistencies

Example 13	Water-in-oil emulsion	Outer aqueous phase
Salt	5% aqueous 1M NaCl	-
Sugar	1% glucose	-
Emulsifiers	1.6% PGPR 0.4% GMO	-
Oil	92% sunflower	-
Polymer	-	6.25% WPI 2.5% ALMP
Amount	20%	80%

10

Example 14	Water-in-oil emulsion	Outer aqueous phase
Salt	5% aqueous 1M NaCl	–
Sugar	1% glucose	–
Emulsifiers	1.6% PGPR 0.4% GMO	–
Oil	92% sunflower	–
Polymer	–	6.25% WPI 2.5% ALMP
Amount	30%	70%

Example 15	Water-in-oil emulsion	Outer aqueous phase
Salt	10% aqueous 1M NaCl	–
Sugar	2% glucose	–
Emulsifiers	3.2% PGPR 0.8% GMO	–
Oil	84% sunflower	–
Polymer	–	6.25% WPI 2.5% ALMP
Amount	20%	80%

Example 16	Water-in-oil emulsion	Outer aqueous phase
Salt	10% aqueous 1M NaCl	–
Sugar	2% glucose	–
Emulsifiers	2% PGPR 0.5% GMO	–
Oil	85.5% sunflower	–
Food-grade polymer	–	6.25% WPI
Amount	20%	80%

Example 17	Water-in-oil emulsion	Outer aqueous phase
Salt	25% aqueous 1M NaCl	–
Sugar	5% glucose	–
Emulsifiers	2% PGPR 0.5% GMO	–
Oil	67.5% sunflower	–
Food-grade polymer	–	6.25% WPI
Amount	30%	70%

PGPR: polyglycerol polyricinoleic acid (PGPR 90)

Ethocel 45: Ethylcellulose from Dow Chemicals

GMO: glycerol monooleate (Dimodan MO90, Danisco)

TiO₂: Titanium dioxide particles

5 WPI: whey protein isolate (Bipro, U.S.)

ALMP: amidated low methoxy pectin (Grinsted Pectin LA040)

FGEM egg yolk : factory grade enzyme modified egg yolk.

Claims

1. Double emulsion comprising an internal aqueous phase
5 dispersed in an oil phase forming a water-in-oil
emulsion, said water-in-oil emulsion being dispersed
in an external aqueous phase,
wherein the water-in-oil emulsion comprises at least
one emulsifier, wherein at least the internal
10 aqueous phase comprises solutes and wherein the
external aqueous phase comprises at least one
hydrophilic polymer or polymer aggregates.
2. Double emulsion according to claim 1, wherein the
15 water-in-oil emulsion comprises at least two different
emulsifiers having different molecular weights.
3. Double emulsion according to claim 1 or 2, wherein
at least one emulsifier has a molecular weight of less
20 than 2000g/mol and at least a second emulsifier has a
molecular weight of more than 700g/mol.
4. Double emulsion according to any of claims 1 to 3,
wherein at least one emulsifier has a molecular weight
25 of less than 1800g/mol, preferably less than 1500g/mol,
more preferably less than 1200g/mol, and at least a
second emulsifier has a molecular weight of more than
800g/mol, preferably more than 1000g/mol, more
preferably more than 1200g/mol.
- 30 5. Double emulsion according to any of claims 1 to 4,
wherein at least one emulsifier is selected from the
group of low molecular weight emulsifiers consisting of
fatty acids, sorbitan esters, propylene glycol mono- or

diesters, pegylated fatty acids, monoglycerides, derivatives of monoglycerides, diglycerides, pegylated vegetable oils, polyoxyethylene sorbitan esters, phospholipids, lecithin, cephalin, lipids, sugar
5 esters, sugar ethers, sucrose esters, sorbitol anhydride monostearate, sorbitol anhydride monooleate, glycerol monooleate, or mixtures thereof and at least a second emulsifier is selected from the group of high molecular weight emulsifiers consisting of polyglycerol
10 esters, polyglycerol polyricinoleic acid (PGPR), cellulose and its derivatives such as ethylcellulose, oil soluble proteins or peptides or hydrolysates, protein-polysaccharide complexes, coacervates or conjugates, food particles, fat particles, solid-lipid
15 nanoparticles, micronised nutrient crystals, dietary fibres or mixtures thereof.

6. Double emulsion according to claim 1, wherein the polymer or aggregate is selected from amidated low
20 methoxy pectin, caseinate, whey proteins, milk proteins, egg proteins, egg yolk, soy proteins, acacia gum, starch derivatives or other o/w emulsion stabilizing proteins or polysaccharides, or hydrophilic particles made out of protein aggregates,
25 polysaccharide aggregates, hydrophilic particles made out of protein-surfactant aggregates, hydrophilic particles made out of protein-polysaccharide mixtures, hydrophilic particles made out of polysaccharide-polysaccharide mixtures, hydrophilic particles made out
30 of polysaccharide-protein phase separating mixtures, or any mixtures thereof.

7. Double emulsion according to claim 6, wherein the polymer is whey protein isolate, amidated low methoxy pectin, egg yolk or a mixture thereof.
- 5 8. Double emulsion according to any of the preceding claims, wherein the solutes are salts, polyols and/or sugars.
- 10 9. Double emulsion according to any of the preceding claims, wherein the internal aqueous phase is under osmotic pressure.
- 15 10. Double emulsion according to any of the preceding claims, wherein the external aqueous phase is not gelified.
- 20 11. Double emulsion according to any of the preceding claims, wherein said double emulsion comprises 1% to 55%, preferably 2 to 45%, more preferably 3 to 35% oil.
- 25 12. Double emulsion according to any of the preceding claims, wherein the double emulsion comprises a viscosifier selected from amidated low methoxy pectin, pectin, alginates, carrageenan, locust bean gum, guar gum, tragacanth, Acacia gum, xanthan gum, Karaya gum, gellan gum, polydextrose, dextrin, modified starch, oxidized starch, cellulose derivatives, or mixtures thereof.
- 30 13. Method for the preparation of a double emulsion comprising the steps of:
 a. Preparing an internal aqueous phase comprising solutes

b. Combining the internal aqueous phase with an oil phase comprising at least one emulsifier to obtain a stabilised water-in-oil emulsion

5 c. Combining the water-in-oil emulsion with an external aqueous phase to form a double emulsion, wherein the external aqueous phase comprises at least one hydrophilic polymer or polymer aggregates.

10 14. Method according to claim 13, wherein the solutes concentration in the internal aqueous phase is such that an osmotic pressure gradient is created between the internal and the external aqueous phases.

15 15. Method according to any of claims 13 or 14, wherein the double emulsion obtained in step c is allowed to set such as to form a textured double emulsion.

20 16. Method according to any of claims 13 to 15, wherein the at least one emulsifier has a molecular weight of less than 2000 g/mol and at least a second emulsifier has a molecular weight of more than 700 g/mol.

25 17. Method according to any of claims 13 to 16, wherein at least one emulsifier has a molecular weight of less than 1800g/mol, preferably less than 1500g/mol, more preferably less than 1200g/mol, and at least a second emulsifier has a molecular weight of more than 800g/mol, preferably more than 1000g/mol, more preferably more than 1200g/mol.

30 18. Method according to any of claims 13 to 17, wherein at least one emulsifier is selected from the group of low molecular weight emulsifiers consisting of fatty acids, sorbitan esters, propylene glycol mono- or

diesters, pegylated fatty acids, monoglycerides, derivatives of monoglycerides, diglycerides, pegylated vegetable oils, polyoxyethylene sorbitan esters, phospholipids, lecithin, cephalin,
5 lipids, galactolipids, sugar esters, sugar ethers, sucrose esters, sorbitol anhydride monostearate, sorbitol anhydride monooleate, glycerol monooleate, or mixtures thereof and at least a second emulsifier is selected from the group of high molecular weight
10 emulsifiers consisting of polyglycerol esters, polyglycerol polyricinoleic acid (PGPR), cellulose and its derivatives such as ethylcellulose, oil soluble proteins or peptides or hydrolysates, protein-polysaccharide complexes, coacervates or conjugates,
15 food particles, fat particles, solid-lipid nanoparticles, micronised nutrient crystals, dietary fibres or mixtures thereof.

19. Method according to any of claims 13 to 18, wherein
20 the solutes are selected from salts, polyols and/or sugars.

20. Method according to any of claims 13 to 20, wherein the external aqueous phase comprises a viscosifier
25 selected from amidated low methoxy pectin, pectin, alginate, carrageenan, locust bean gum, guar gum, tragacanth, Acacia gum, xanthan gum, Karaya gum, gellan gum, polydextrose, dextrin, modified starch, oxidized starch, or mixtures thereof.

30

21. Method according to any of claims 13 to 21, wherein the double emulsion is spray-dried or freeze-dried.

22. Double emulsion obtainable by the method of any of claims 13 to 22.

23. Use of a mixture of at least two different emulsifiers having differing molecular weights for stabilising a water-in-oil emulsion, wherein the water-in-oil emulsion is part of a double emulsion comprising said water-in-oil emulsion dispersed in an external aqueous phase.

10

24. Use according to claim 24, wherein at least one emulsifier has a molecular weight of less than 2000g/mol and at least a second emulsifier has a molecular weight of more than 700g/mol.

15

25. Use according to any of claims 24 or 25, wherein at least one emulsifier has a molecular weight of less than 1800g/mol, preferably less than 1500g/mol, more preferably less than 1200g/mol, and at least a second emulsifier has a molecular weight of more than 800g/mol, preferably more than 1000g/mol, more preferably more than 1200g/mol.

20

26. Use according to any of claims 24 to 26, wherein at least one emulsifier is selected from the group of low molecular weight emulsifiers consisting of fatty acids, sorbitan esters, propylene glycol mono- or diesters, pegylated fatty acids, monoglycerides, derivatives of monoglycerides, diglycerides, pegylated vegetable oils, polyoxyethylene sorbitan esters, phospholipids, lecithin, cephalin, lipids, galactolipids, sugar esters, sugar ethers, sucrose esters, sorbitol anhydride monostearate, sorbitol anhydride monooleate, glycerol monooleate, or mixtures thereof and at least a

25

30

second emulsifier is selected from the group of high molecular weight emulsifiers consisting of polyglycerol esters, polyglycerol polyricinoleic acid (PGPR), cellulose and its derivatives such as ethylcellulose, oil soluble proteins or peptides or hydrolysates, protein-polysaccharide complexes, coacervates or conjugates, food particles, fat particles, solid-lipid nanoparticles, micronised nutrient crystals, dietary fibres or mixtures thereof.

10

27. Use according to any of claims 24 to 27, wherein the emulsifiers are glycerol monooleate and polyglycerol polyricinoleic acid (PGPR).

15

28. Use of a double emulsion according to any of claims 1 to 12, in food products, clinical products, pharmaceutical products, nutricosmetics, cosmetics, agro-chemical or other industrial products.

20

29. Use according to claim 29, wherein the food product is selected from salad dressing, mayonnaise-type products, sauces, spreads, soups, desserts, creams etc.

1 / 2

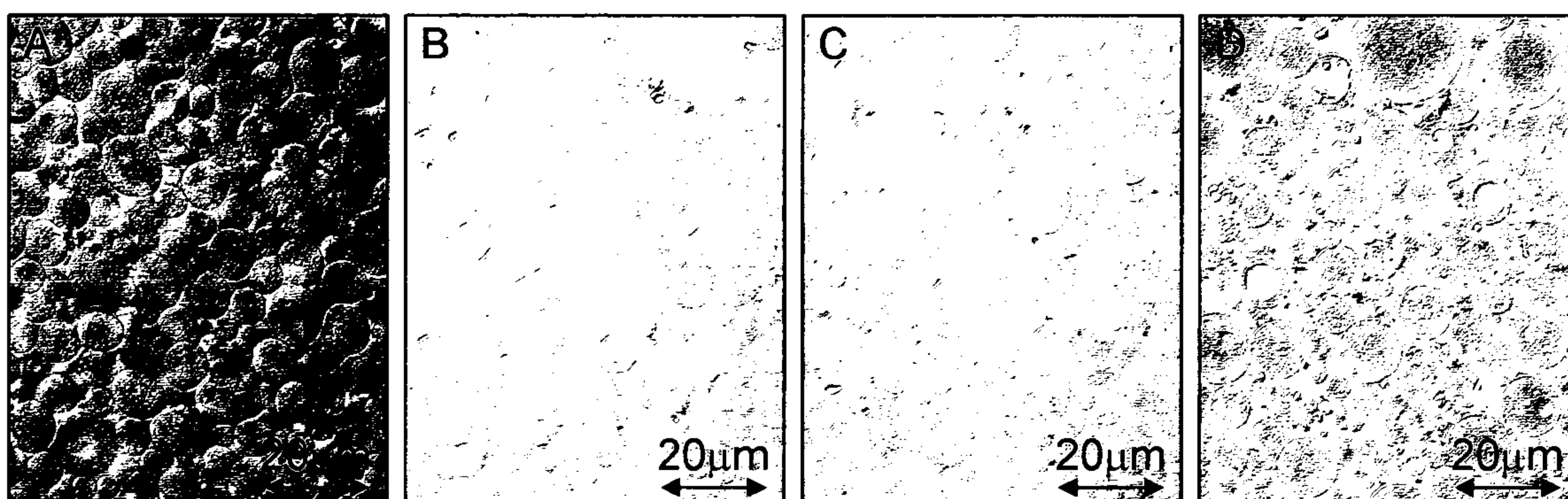


FIG. 1

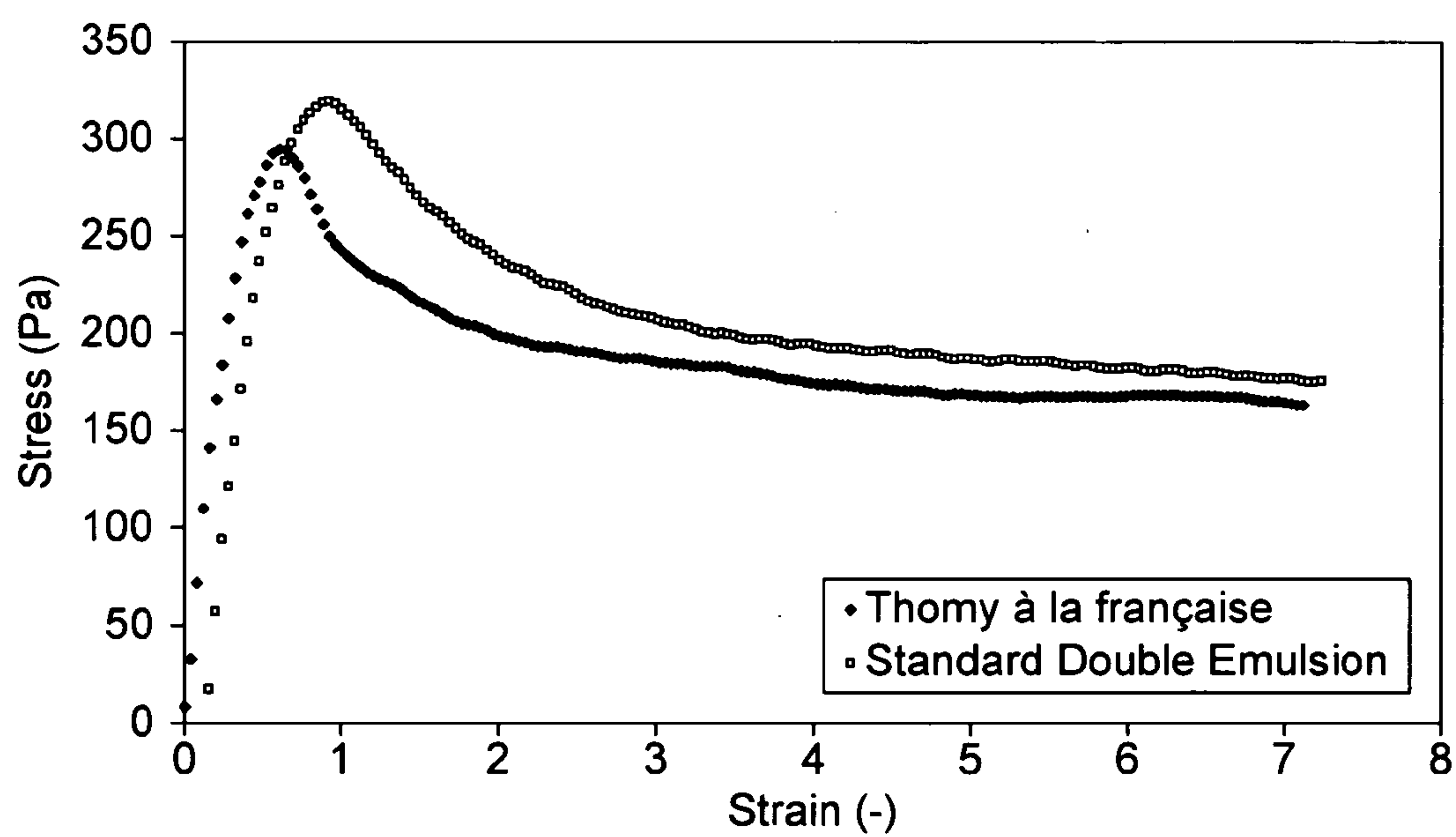


FIG. 2a

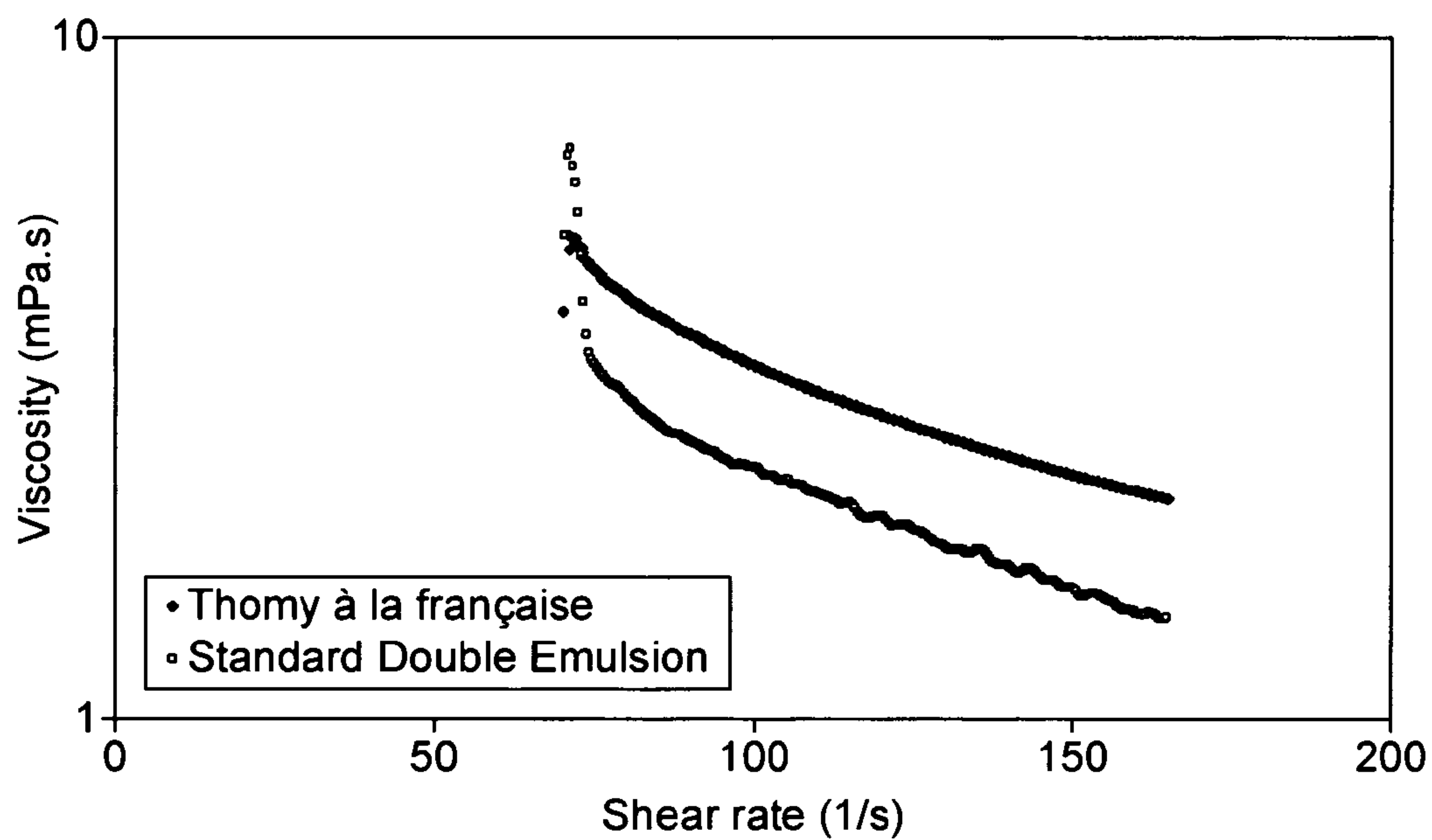


FIG. 2b

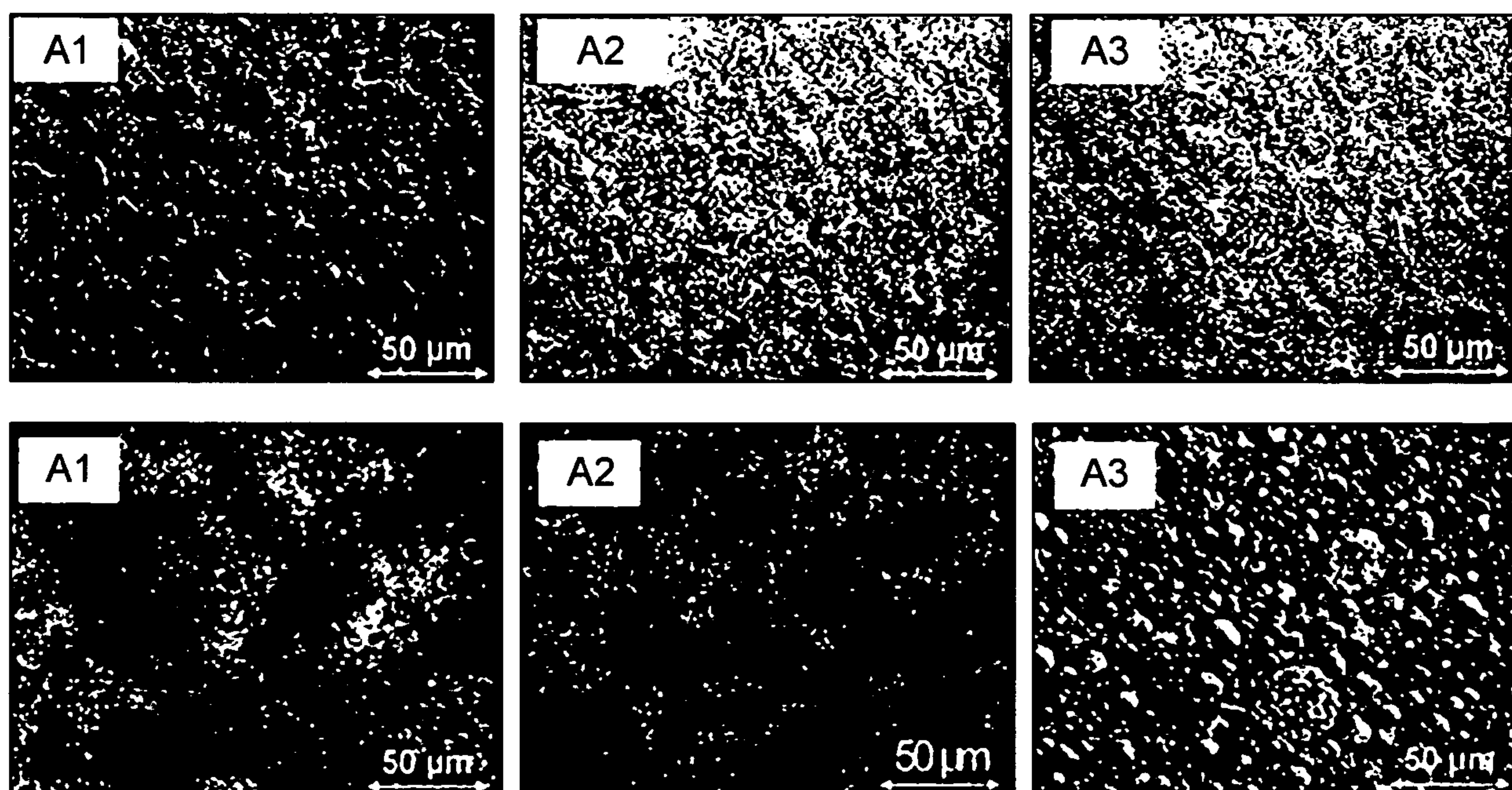


FIG. 3

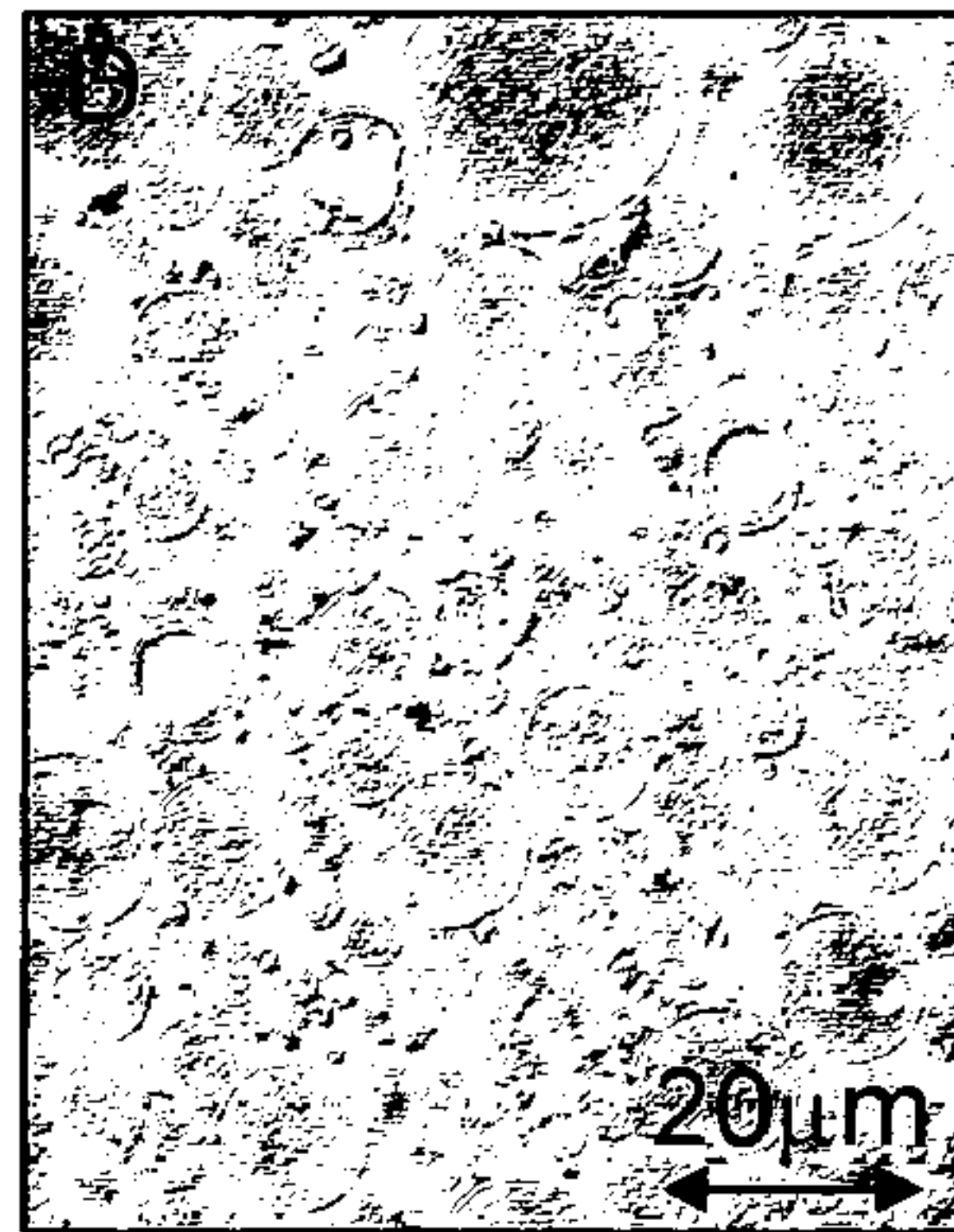
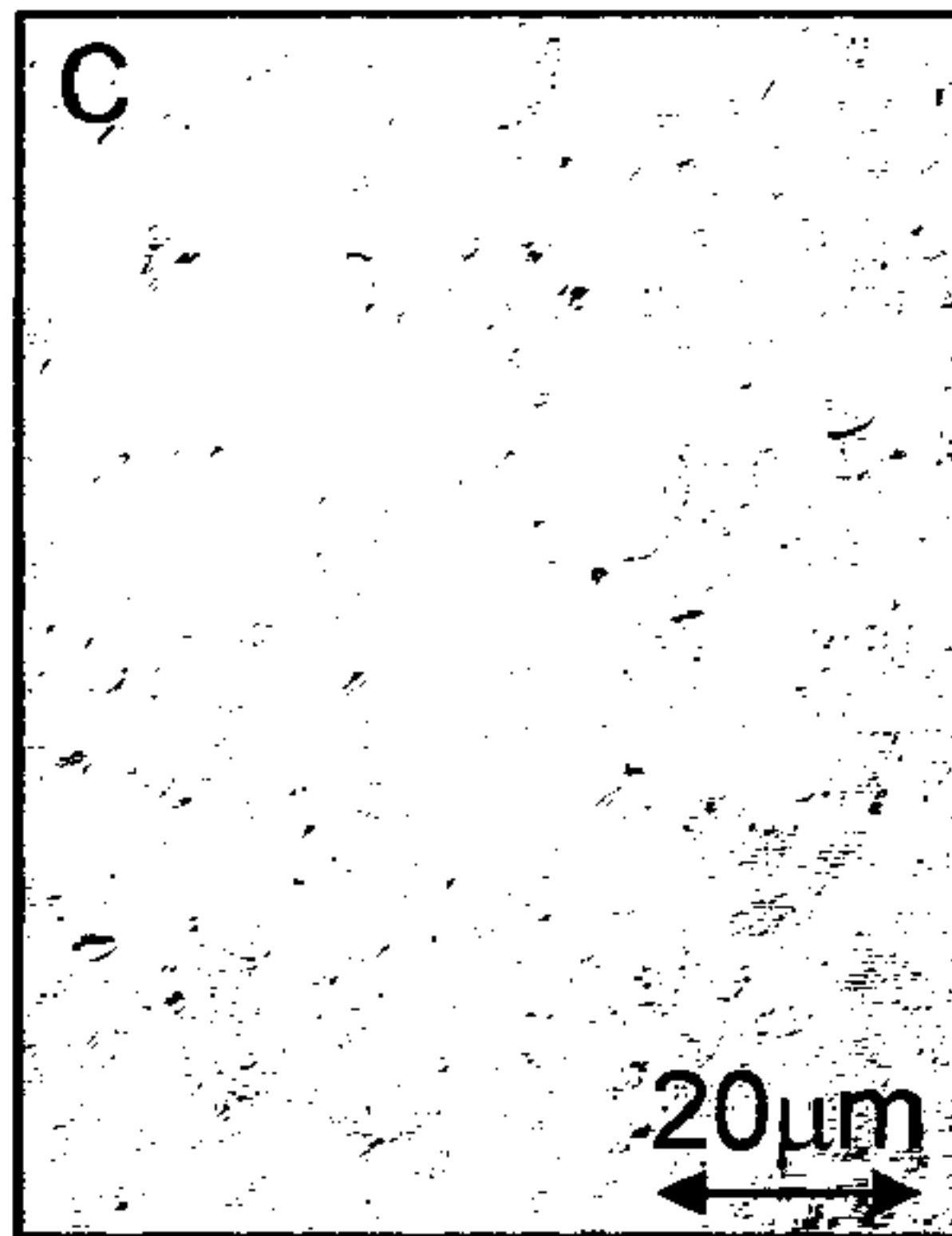
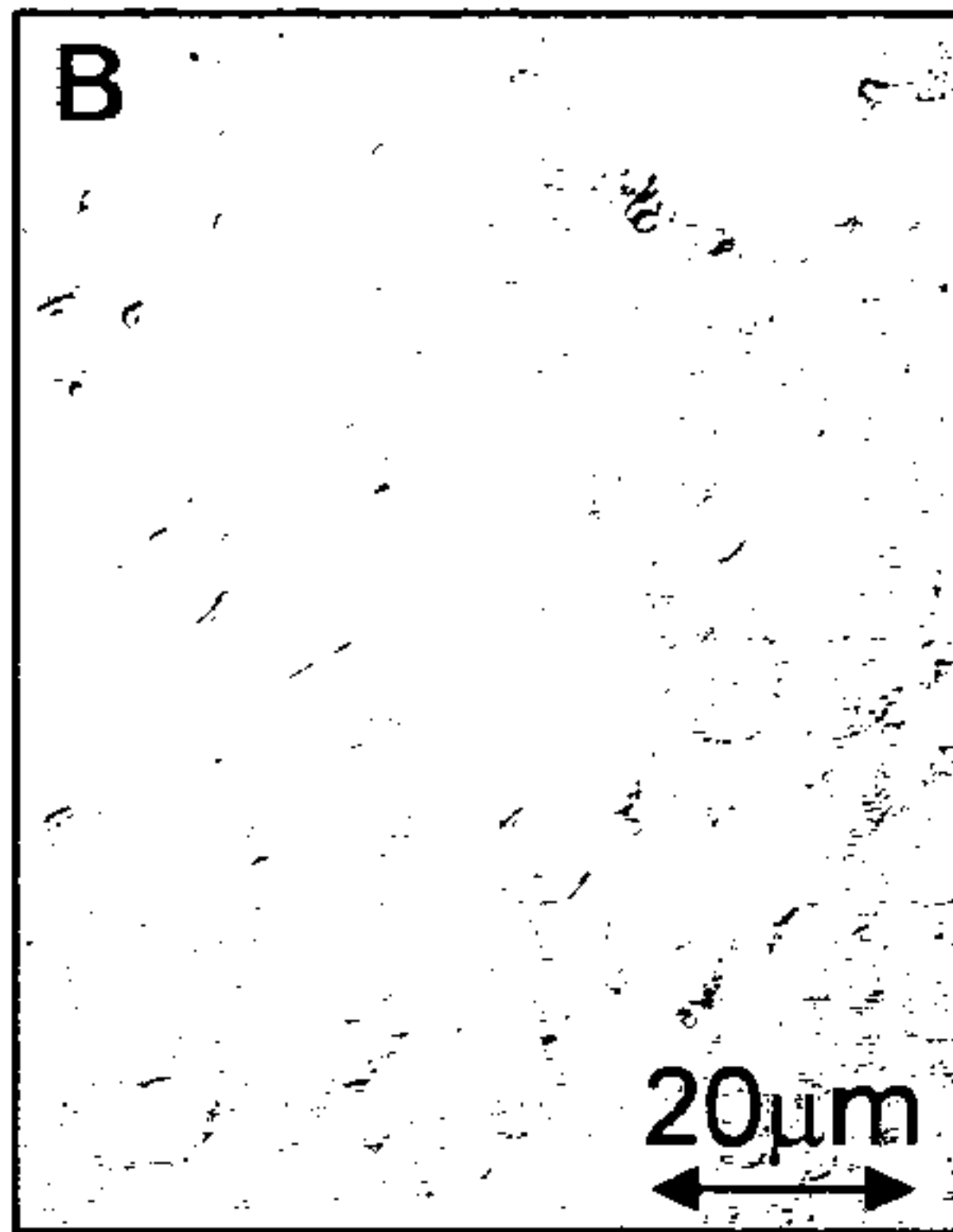
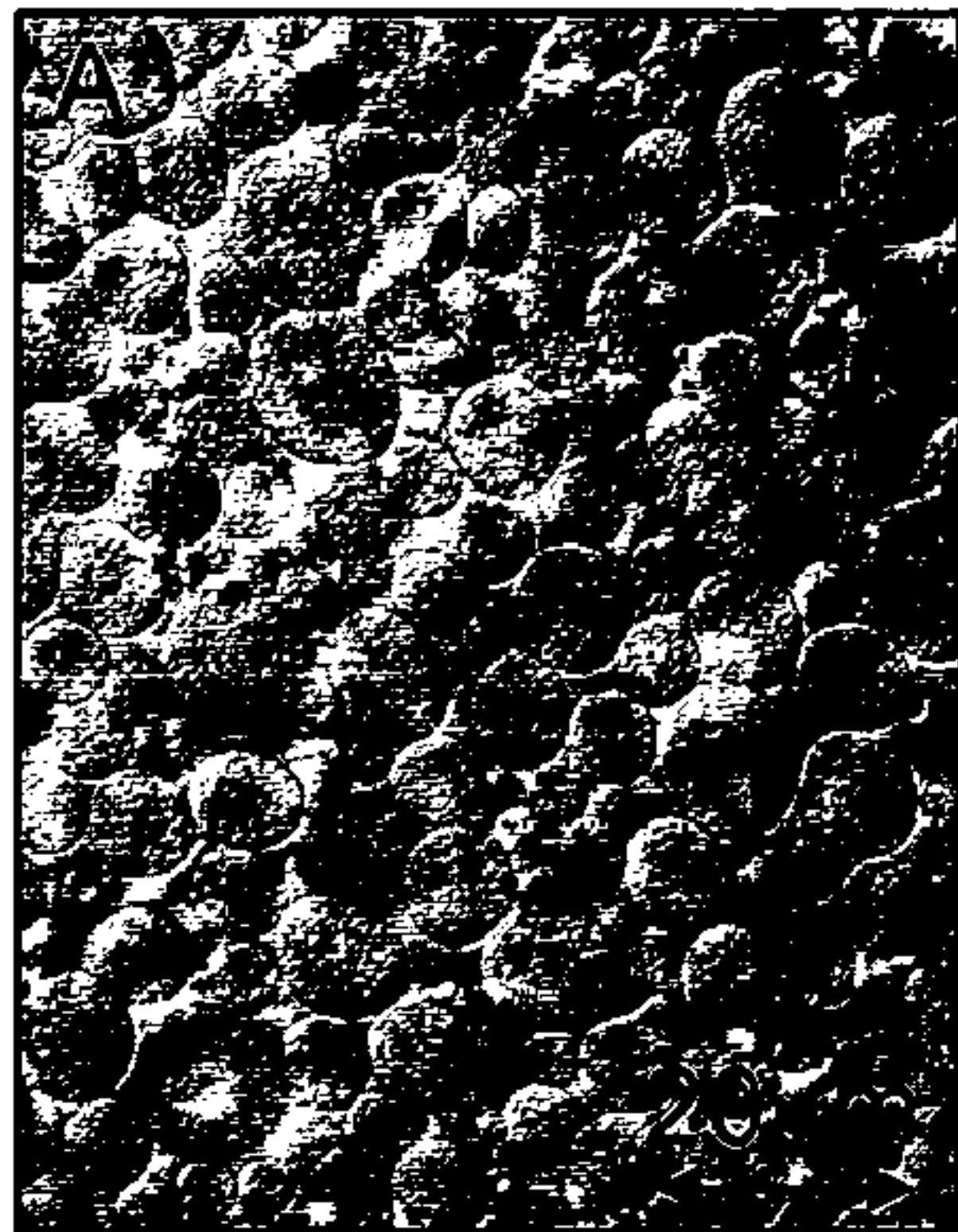


FIG. 1