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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 January 2018 (11.01.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/007261 A1

(51) International Patent Classification:
A61K 8/26 (2006.01) *A61K 8/06* (2006.01)
A61Q 19/00 (2006.01)

(21) International Application Number:
PCT/EP2017/066320

(22) International Filing Date:
30 June 2017 (30.06.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
16001478.3 04 July 2016 (04.07.2016) EP

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, 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, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

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

WO 2018/007261 A1

(54) Title: EMULSION STABILIZED BY CLAY

(57) Abstract: The invention relates a composition in form of a stable oil-in-water emulsion comprising: a) at least one natural clay which belongs to the class of saponites clay minerals and has a cation exchange capability equal or lower than 40 meq per 100 g of dry clay, b) a dispersed oil component, and c) an aqueous continuous phase.

EMULSION STABILIZED BY CLAY

This invention relates to an oil-in-water emulsion, stabilized by smectite clay mineral which has excellent emulsion stability in a broad range of pH and salt concentration.

Emulsions are colloidal systems where droplets of one liquid are dispersed in a second non-miscible liquid. Though they are thermodynamically unstable and tend to separate, they can be stabilized by surfactants, amphiphilic molecules which adsorb at the liquid interface and reduce the interfacial tension between the immiscible liquids. Alternatively, solid particles can also be used to stabilize emulsions, provided that they fulfill the partial wetting conditions, that means, the particles are wetted by both liquids and therefore adsorb at the interface, leading to a reduction of the liquid interfacial area of the system. Specific benefit derived from the stabilization of emulsions by particles is the high resistance against coalescence due to the practically irreversible attachment of the particles at the interface. This feature becomes of special interest in application fields like enhanced oil recovery or agrochemical formulations, where high temperature and/or salinity dominates and surfactants usually show a lack of performance, as described in WO 2014/114538 and WO 2015/170099. Moreover, the formulation of “surfactant-free” emulsions allows to overcome adverse effects related to the use of surfactants in certain applications, like skin irritancy in topical formulations, as described in International Journal of Pharmaceutics 428 (2012) 1 - 7.

Clay minerals have a sheet-like structure and are composed of tetrahedral layers of silicate linked to octahedral layers of metal oxides. Depending on the number of layers linked together building a structural motif, clays are classified in 1:1 phyllosilicates, which consist of one tetrahedral layer of silica bond through oxygen atoms to one octahedral layer of metal (aluminium or magnesium) oxide, 2:1 phyllosilicates, which consist of octahedral metal (aluminium or magnesium) oxide layer sandwiched between 2 tetrahedral layers of silica, and 2:1 inverted ribbons, which present continuous fibrous-like tetrahedral sheets together with discontinuous octahedral sheets.

Smectites are a group of 2:1 phyllosilicates characterized by the partial substitution of cations in the layers by other cations of lower charge, thus originating an excess of negative charge in the layers which is compensated by cations intercalated between the sheets. Typically the degree of substitution and therefore of charge is low for the members of the smectite family. A further differentiation of smectites is made with regard to the oxygen atoms in the octahedral oxide layer which are either coordinated bridging two metal centers (dioctahedral smectites, the metal is typically Al^{3+}) or each oxygen atom is shared by three metal centers (trioctahedral smectites, the metal is typically Mg^{2+}).

Montmorillonite ($Z_X[Al_2^{3+}]^{oct}[Si_4]^{tetr}O_{10}(OH)_2$) is the main representative class of the dioctahedral smectites. It consists of an octahedral layer of aluminum oxide sandwiched between two silica tetrahedral lays platelet-like monocrystals with a constant thickness of 1.1 nm and a diameter between 50 - 1000 nm. The platelets are typically stacked in large piles. The substitution of aluminium atoms by magnesium atoms in the octahedral layer or silicon atoms by aluminum atoms in the tetrahedral layer creates a net negative charge in the crystals, which is balanced by the presence of counter ions (typically sodium or calcium) in the interlayer gallery. ($Z_X[Mg_3^{2+}]^{oct}[Si_4]^{tetr}O_{10}(OH)_2$) is the basic structure of trioctahedral smectites. When the magnesium ions are partially substituted by lithium ion, the clay is called laponite (or hectorite), while when the tetrahedral silicon are partially replaced by aluminium, the clay is called saponite.

FR 2976503 discloses oil-in-water emulsions stabilized by clay minerals previously treated with organic compounds in order to render the particles more hydrophobic and thus increase their affinity towards the oil phase. The pre-treatment of the clays with the organic compounds is an additional processing step. For environmental and economic reasons it would be of interest to find a clay which can stabilize oil-in-water emulsions without need of a hydrophobizing pre-treatment with organic compounds.

The stabilization of mixtures of monolinolein and different kind of oils (glycerol trioleate, R-(+)-limonene and styrene) by two unmodified smectites (purified Na^+-montmorillonite and synthetic laponite) is described in Journal of Colloid and Interface Sciences, 333 (2009) 563-569. The clays are claimed to act as cosurfactants in the sense that they support monolinolein, which is an amphiphilic molecule and act as emulsifier, to stabilize the oil-in-water emulsions. Either the emulsions can be stabilized in the absence of surfactant solely by the clays or the stability of the described emulsions is perturbed by the addition of electrolyte to the aqueous phase is not disclosed.

Stable emulsions of paraffin oil in water stabilized by combinations of smectites and non-ionic surfactants are disclosed in Applied Clay Science, 14 (1999) 83 - 103. Especially Na^+ montmorillonite with a cation exchange capacity of 103 meq per 100 g dry clay is mentioned to form stable emulsions. The addition of sodium chloride or calcium chloride to the aqueous phase is reported to stabilize the emulsions against coalescence. No information about the ability of the clays to stabilize the emulsions in absence of surfactants is disclosed.

Nevertheless there is an on-going need to provide solid materials able to stabilize oil-in-water emulsions in the absence of amphiphilic molecules. Such materials have to be economically competitive and environmentally sustainable, that means they must be easy to be produced and must not be classified as hazardous chemicals.

Unexpectedly it was found that natural clays which belong to the class of saponites or are natural blends of saponite and kerolite and have a cation exchange capacity equal or lower than 40 meq per 100 g of dry clay are able to stabilize oil-in-water emulsions without addition of any surfactant.

The clays disclosed in this invention are natural raw materials which due to their unexpected unique surface properties can efficiently adsorb at the oil-water interface and prevent oil droplets from coalescence without the need of a hydrophobizing pre-treatment with organophilic molecules.

Surprisingly, the clays being object of this invention stabilize oil-in-water emulsions without additional stabilizers such as surfactants being needed. Oil-droplet stabilization in the aqueous phase and prevention of coalescence and phase separation is fulfilled by the clays disclosed in this invention.

Furthermore it was also unexpectedly found that the clays disclosed in this invention are able to stabilize oil-in-water emulsions against coalescence at diverse pH values and salt concentrations.

The oil-in-water emulsion is considered to be stable if coalescence and phase separation does not occur for at least three months after preparation during storage at temperatures around room temperature (23 °C). Coalescence can be tracked by changes in the droplet size during time and phase separation can be visually evaluated.

The present invention is related to oil-in-water emulsions stabilized, preferably solely, by natural clays which belong to the class of saponites or are, preferably natural, blends of saponite and kerolite and have a cation exchange capability equal or lower than 40 meq per 100 g of dry clay.

The instant invention therefore relates to a composition in form of a stable oil-in-water emulsion comprising

a) at least one natural clay which belongs to the class of saponite clay minerals and has a cation exchange capability equal to or lower than 40 meq per 100 g of dry clay,

b) a dispersed oil component, and

c) an aqueous continuous phase

In a further aspect of the invention there is provided a process for the production of the composition of the invention comprising the steps of i) dispersing the at least one natural clay (component a) in water, ii) adding the oil phase to the aqueous clay dispersion of step i) and iii) homogenizing the composition in order to obtain a stable oil-in-water emulsion.

In yet a further aspect of the invention there is provided the use of a composition of the invention in personal care and/or cosmetic formulations; in agrochemical formulations, in emulsion paints, in cleaning formulations and/or in formulations for the oil and mining industry.

Figure 1 shows light microscope images of compositions of the invention containing 20 wt.-% oil and 1 wt.-% of clay and increasing concentrations of sodium chloride in the aqueous phase.

Figure 2 shows light microscope images of compositions of the invention containing 20 wt.-% of oil and 1 wt.-% of clay A (as described below).

Figures 3a and 3b show rheological properties of compositions of the invention containing 1 wt.-% of clay A (as described below), 20 wt.-% oil, 2.5 wt.-% glycerol, 1 wt.-% Phenonip® Me and 0.5 wt.-% Aristoflex® AVC, which are a flow curve after preparation and after 90 days of storage at 50 °C (Figure 3a) and a frequency sweep after preparation and after 90 days of storage at 50 °C (Figure 3b).

Natural clays are extracted from geological deposites. Natural clays occur typically as a mixture of diverse components, such as clay minerals, metal oxides and other weathered minerals. At least one natural clay according to the present invention belongs to the class of the saponites. Most preferred clays according to the present invention occur as a natural blend of saponite and kerolite.

Saponites are natural trioctahedral smectite clay minerals, where tetrahedral silicon atoms are partially replaced by aluminium atoms. They can be expressed by the formula $((Ca,Na)_x[Mg_3^{2+}]^{oct}[(Si,Al)_4]^{tetr}O_{10}(OH)_2)$.

The term kerolite is used for a nickel containing variety of talc that can be described as a mixture of saponite and serpentine (hydrous magnesium iron phyllosilicate mineral). It can be depicted by the formula $(Mg,Ni)_3Si_4O_{10}(OH)_2 \cdot H_2O$.

Preferred clays (component a) suitable to formulate compositions in accordance with the present invention have a cation exchange capacity from 1 to 35 meq per 100 g of dry clay. Particularly preferred clays have a cation exchange capacity from 15 to 35 meq per 100 g of dry clay.

The cation exchange capacity of a clay (CEC) is a well-known parameter used to define the concentration of negatively charged sites on the clay sheets that can adsorb exchangeable cations. The higher the CEC value, the higher the anionic charge on the clay crystals. Typically, the CEC can be determined using the ammonium chloride method, as described for example in Clay Minerals, 44 (2009), 525 - 537 and is indicated in terms of miliequivalents per 100 g of dry clay.

The clays have preferably a specific surface area (BET-surface area) from 90 to 300 m^2/g. Particularly preferred clays have a BET-surface area from 105 to 275 m^2/g. Most preferred clays have a BET-surface area from 120 to 250 m^2/g. The specific surface area can be determined by the BET-method according to DIN 66131 (single point method using nitrogen).

Preferred clays have a surface free energy from 10 to 50 mN/m. Particularly preferred clays have a surface free energy from 20 to 45 mN/m. The surface free energy can be calculatedby applying the Owens-Wendt-Rabel-Kaelbe model as described in the experimental section.

The concentration of clay in the composition in accordance with the present invention is preferably from 0.01 % to 15 % by weight, more preferably from 0.1 % to 10 % by weight and most preferably from 0.3 % to 5 % by weight.

The compositions of the present invention contain at least one oil component (component b), which is any fatty substance which is liquid at room temperature (25 °C). Among the oils that can be used in the emulsion of the invention, mention may be made, for example, of plant oils such as sunflower, olive, soybean, rapeseed, canola, jojoba, palm, peanut, avocado, soft-almond, apricot and corn oils and the liquid fraction of karite butter; chemically modified plant oils such as methylated or ethylated seed oils and medium-chain triglycerides; hydrocarbon-based oils chosen from linear or branched hydrocarbons of mineral or synthetic origin, preferably from a volatile or nonvolatile liquid paraffin oil, hydrogenated isoparaffin, naphthalene oil, a totally or partially hydrogenated liquid polydecene, isoeicosane, a decene/butene copolymer, or a polybutene/polyisobutene copolymer, and mixtures thereof. Synthetic oils such as 2-ethylhexyl palmitate, isopropyl myristate, isononyl isononanoate and cetearyl octanoate; volatile or non-volatile silicone oils and fluorinated oils can also be used.

The concentration of the oil component in the composition in accordance with the present invention is preferably from 0.5 % to 60 % by weight, more preferably from 1 % to 45 % by weight and most preferably from 5 % to 30 % by weight.

It is known to the person skilled in the art that liphophilic active ingredients can be dissolved in the oil phase and be thus formulated in form of a stable oil-in-water emulsion in accordance with the presence invention. Among the active ingredients that can be formulated, mention may be made, for example, of cosmetic ingredients such as essential oils, UV-filters and anti-aging agents, and agrochemical agents such as pesticides.

In the aqueous phase (component c) of the emulsion different additives can be present, such as rheology modifiers, pH control agents, chelating agents, electrolytes, biocides and humectants.

The oil-in-water emulsions, preferably solely, stabilized by clays according to this invention are stable in a broad range of pH and electrolyte concentration. Stable means that there are almost no changes, preferably no more than 10 % increase,

in the droplet size of the dispersed oil phase when pH and/or salt concentration in the continuous aqueous phase of the emulsion is varied, and no phase separation is observed.

In the compositions of the present invention, typically there is no need for the presence of conventional emulsifiers in the form of amphiphilic molecules in order to achieve stabilization of the dispersed oil phase. If used, the amphiphilic molecules are present in an amount of at most 0.5 % by weight and most preferably at most at the critical micellar concentration, and they are incorporated in the formulation to optimize the wettability of the emulsion by lowering of the dynamic surface tension of the system.

In a preferred embodiment the compositions of the invention do not contain emulsifiers in the form of amphiphilic molecules.

In a further preferred embodiment the compositions of the invention do not contain monolinolein as a emulsifier in the form of an amphiphilic molecule.

In a further preferred embodiment of the invention the clays used according to the invention have not been treated with organic compounds in order to render the clay particles more hydrophobic, in particular not with the organic molecules disclosed in FR 2976503.

Another embodiment of the present invention is related to a process for the production of an oil-in-water emulsion with a composition according to the ones described above. The emulsion can be prepared by using any of the emulsification techniques described elsewhere, such as for example, high pressure homogenization, rotor-stator mixing, cavitation, membrane emulsification and microfluidic techniques. In a preferred manufacturing process, the clay (component a) is dispersed in water under high mechanical shear, preferably generated by a rotor-stator mixer. The oil phase is added to the aqueous clay dispersion and the composition is homogenized, preferably with a rotor-stator mixer, in order to obtain a stable oil-in-water emulsion.

The preferred droplet size of the emulsions can generally range from 1 µm to 200 µm. Specially preferred droplet size of the emulsion is in the range from 10 µm to 150 µm. Most preferred droplet size of the emulsion is in the range from 15 to 100 µm. This droplet size refers to the discontinuous phase of the emulsion and is determined by analysis of microscopic image of the emulsion.

A further embodiment of the present invention is related to the use of a composition according to the described above in personal care and cosmetics formulations, such as for example, hand creams, lotions, hair shampoos and conditioners and sunscreens; in agrochemical formulations such as pesticidal formulations, in emulsion paints, in cleaning formulations and formulations for use in the oil & mining industry.

The examples below are intended to illustrate the invention in detail without, however, limiting it thereto.

Examples

Characterization of the clays

The cationic exchange capacity (CEC) was determined following the NH_4Cl method. The clay material was dried at 150 °C for 2 h and the resulting material allowed to react under reflux with a large excess of aqueous NH_4Cl solution for 1 h. After standing at room temperature for 16 h, the material was filtered. The filter cake was washed, dried and ground, and the NH_4 content in the clay material was determined through measurement of the N content by elemental analysis using a CHN-Analyser Vario EL III by Elementar, Hanau (D).

The specific surface area was determined by the BET method (single-point method using nitrogen, according to DIN 66131) with an automatic nitrogen porosimeter by Micrometrics, type ASAP 2010.

The surface free energy was calculated applying the Owens-Wendt-Rabel-Kaelbe model using contact angles for water and diiodomethane obtained from powder contact angle measurements on the clays with a Krüss Force Tensiometer K100 following the Washburn method (Washburn, E.W., Phys. Rev. 17, 374 (1921)). For clays swelling rapidly in contact with water, ethanol was used instead of water for the contact angle measurements.

Clay	CEC (meq in 100 g)	BET-surface area (m^2/g)	Surface free energy (mN/m)	Mineral class
A	25	125	24	natural saponite
B	20	224	44	natural blend of saponite with kerolite
C (comparison)	52	239	55	natural blend of montmorillonite with amorphous silica
D (comparison)	94	83	48	natural montmorillonite
E (comparison)	49	67		natural montmorillonite

General procedure for preparation and characterization of emulsions

Clay particles are firstly dispersed in buffer solution by stirring at 800 rpm for 5 min with high shear mixer (Ultra Turrax T25-IKA® equipped with dispersing tool consisting of S25N shaft and 25G generator) and then the oil phase is added to the dispersion and homogenized at 6500 rpm for 5 min. The total mass of the emulsion is typically 100 g.

The emulsion type was determined by the drop test. A drop of the formed emulsion was added to water. Immediate dispersion of the droplets confirmed the presence of oil-in-water emulsion type.

The stability of the emulsion was evaluated from the visual inspection and assessed according to the volume of emulsion formed and the speed of phase separation after preparation and after 90 days at room temperature. According to the volume of each phase (especially the oil separation), the stability of the emulsion was assessed. More oil release pointed to the instability of the emulsion.

The morphology and size of the emulsion droplets was observed by optical microscope (Olympus DP26, Japan) and the droplet size determined by analysis of microscopic image of the emulsion.

For comparison of the emulsification efficiency, clays A, B, C, D and E were used at a concentration of 1 wt.-% in citrate buffer pH 5.5 to prepare emulsions of Myritol® 318 (medium chain triglyceride, BASF) at a volume fraction of 20 %. The volume of the existing phases (separated oil phase, (creamed) emulsion, aqueous phase and solid sediment) was recorded after preparation (D1) and after 90 days storage at room temperature (D90):

	A		B		C		D		E	
	D1	D90	D1	D90	D1	D90	D1	D90	D1	D90
oil phase (vol.-%)	0	0	0	0	7	13	48	48	2	4
emulsion (vol.-%)	81	56	49	40	34	31	0	0	37	33
aqueous phase (vol.-%)	18	44	40	51	52	49	52	12	61	48
sediment (vol.-%)	1	1	11	9	7	7	0	40	0	15

Clays A and B form very stable emulsions and no separation of oil was observed after 90 days at room temperature. Compression of the emulsion volumen due to creaming occured over the storage time which was due to the density differences

between the bulk and the dispersed phases, but the oil droplets remained dispersed indicating that the emulsion was stable.

For comparison, clay C and E showed oil separation after preparation, indicating that these clays were not as efficient for emulsion stabilization as A and B. Moreover, the volume of separated oil phase increased during storage. Clay D was not able at all to stabilize oil droplets and phase separation occurred after preparation.

To check the influence of salt on the stability of the emulsions, samples were prepared using the same conditions as mentioned before but adding increasing concentrations of sodium chloride. The droplet size of the resulting emulsions was compared.

NaCl (wt.-%)	Average droplet size (µm)		
	A	B	E
0	25	45	107
0.5	25	46	170
1.0	24	47	342

The droplet size of emulsions prepared with clays A and B remained almost invariable independently of the salt concentration in the aqueous phase, whereas the droplet size increased notably with the salt concentration for clay E (Figure 1). Figure 1 shows light microscope images of emulsions containing 20 % oil and 1 % of clay and increasing concentrations of sodium chloride in the aqueous phase (from left to the right, up to the bottom) Clay E - 0 % NaCl; Clay E - 0.5 % NaCl; Blay B - 0 % NaCl; Clay B - 0.5 % NaCl; Clay A - 0 % CaCl; Clay A - 0.5 % NaCl (scale bar 200 µm).

The same kind of experiment was repeated but changing the pH value, which was adjusted to 4 and 9 using respective citrate buffers. Again clays A and B were able

to stabilize the emulsions at both acidic and alkaline pH, whereas clay E was not able to form any emulsion at pH 9 and phase separation was immediately found after preparation.

In order to show the ability of the clays according to this invention to stabilize emulsions of diverse types of oils, quick emulsification tests were done by dispersing clay A in citric buffer pH 5.5 by vortex mixing (IKA 4 Digit) at 3000 rpm for 20 s, adding the oil and further mixing for 40 s at the same speed. Clay concentration was 1 wt.-% and the oil volumen fraction 20 %. Oils used were Solvesso® 200ND (mixture of aromatic hydrocarbons, Exxonmobil), canola based methylated seed oil (Oleon), tetradecane (Alfa Aesar) and sunflower oil. Stable emulsions were obtained for all type of oils (Figure 2).
Figure 2 shows the light microscope images of emulsions containing 20 % of oil and 1 % of Clay A (from left to the right, up to the bottom) Solvesso® 200 ND, canola based methylated seed oil, tetradecane and sunflower oil.

Furthermore, in order to show that the ability of stabilizing oil-in-water emulsions by the clays according to this invention is not affected by other typical components of a formulation, such as for example rheology modifiers, biocides and humectants, an oil-in-water emulsion containing 1 wt.-% of clay A, 20 wt.-% of medium chain triglyceride (Myritol® 318, BASF), 0.5 wt.-% of a copolymer of vinylpyrrolidone and 2-acrylamido-2-methylpropane sulfonic acid (Aristoflex® AVC, Clariant), 1 wt.-% of phenoxyethanol (Phenonip® ME, Clariant) and 2.5 wt.-% glycerol (Merck) was prepared as follows:

Glycerol was dissolved in desionized water and clay A was added and stirred at 800 rpm for 5 min with high shear mixer (Ultra Turrax T25-IKA® equipped with dispersing tool consisting of S25N shaft and 25G generator). Then Myritol® 318 was added to the dispersion and homogenized at 6500 rpm for 5 min. Aristoflex® AVC was then added and the mixture was homogenized for another 2 min at 9500 rpm. Finally, Phenonip® ME was added to the emulsion and gently stirred for 1 min.

The obtained emulsion had the texture of a typical cosmetic hand cream. The stability of the emulsion was investigated by comparison of the rheological properties of the sample after preparation and after 90 days storage at 50 °C.

All measurements were done with a rheometer MARS III (Thermofisher Scientific) with a cone (2°, 35 mm) / plate geometry.

The flow of the emulsion was evaluated by a shear controlled sweep between 0 and 1000 1/s at 23 °C. Frequency sweeps were carried out at 23 °C to characterize the viscoelastic properties of the emulsion. After pre-shearing steps at constant shear rate of 100 1/s for 2 min followed by 0.001 1/s for 30 min, a 0.01592 - 15.92 Hz Hz ramp at constant strain of 1 % (which was previously determined to be in the linear viscoelastic range via strain controlled amplitude sweep) was measured.

The measurements showed that the rheological properties of the emulsion remained almost constant during the storage, indicating that the system was highly stable and no changes occurred in the colloidal structure of the emulsion (Figures 3).
Figures 3a and 3b show rheological properties of emulsions containing 1 % clay A, 20 % oil, 2.5 % glycerol, 1 X Phenonip® ME and 0.5 % Arisoflex® AVC. Figure 3a shows the flow curve after preparation (filled squares) and after 90 days storage at 50°C (open circles). Figure 3b shows the frequency sweep after prepration (filled triangles up (storage module G') and down (loss module G")) and after 90 days storage at 50°C (open triangles up (G') and down (G")).

Patent claims

1. A composition in form of a stable oil-in-water emulsion comprising
a) at least one natural clay which belongs to the class of saponites clay minerals and has a cation exchange capability equal or lower than 40 meq per 100 g of dry clay,
b) a dispersed oil component, and
c) an aqueous continuous phase.

2. The composition according to claim 1, wherein the natural clay is a natural blend of saponite and kerolite.

3. The composition according to claim 1 and/or 2, wherein the cation exchange capacity is from 1 to 35 meq per 100 g of dry clay.

4. The composition according to one or more of the preceding claims, wherein the clay has a BET-surface area from 90 to 300 m^2/g.

5. The composition according to one or more of the preceding claims, wherein the clay has a surface free energy from 10 to 50 mN/m.

6. The composition according to one or more of the preceding claims, wherein the concentration of clay in the composition is in the range from 0.01 % to 15 % by weight.

7. The composition according to one or more of the preceding claims, wherein the oil component (b) is a fatty substance which is liquid at room temperature (25 °C).

8. The composition according to claim 7, wherein the oil component is made of plant oils, in particular sunflower, olive, soybean, rapeseed, canola, jojoba, palm, peanut, avocado, soft-almond, apricot and corn oils and the liquid fraction of karite

butter or chemically modified plant oils, hydrocarbon-based oils or synthetic oils or volatile or non-volatile silicone oils and fluorinated oils.

9. The composition according to one or more of the preceding claims, wherein the concentration of oil component in the composition is in the range from 0.5 % to 60 % by weight.

10. The composition according to one or more of the preceding claims, wherein liphophilic active ingredients are dissolved in the oil phase.

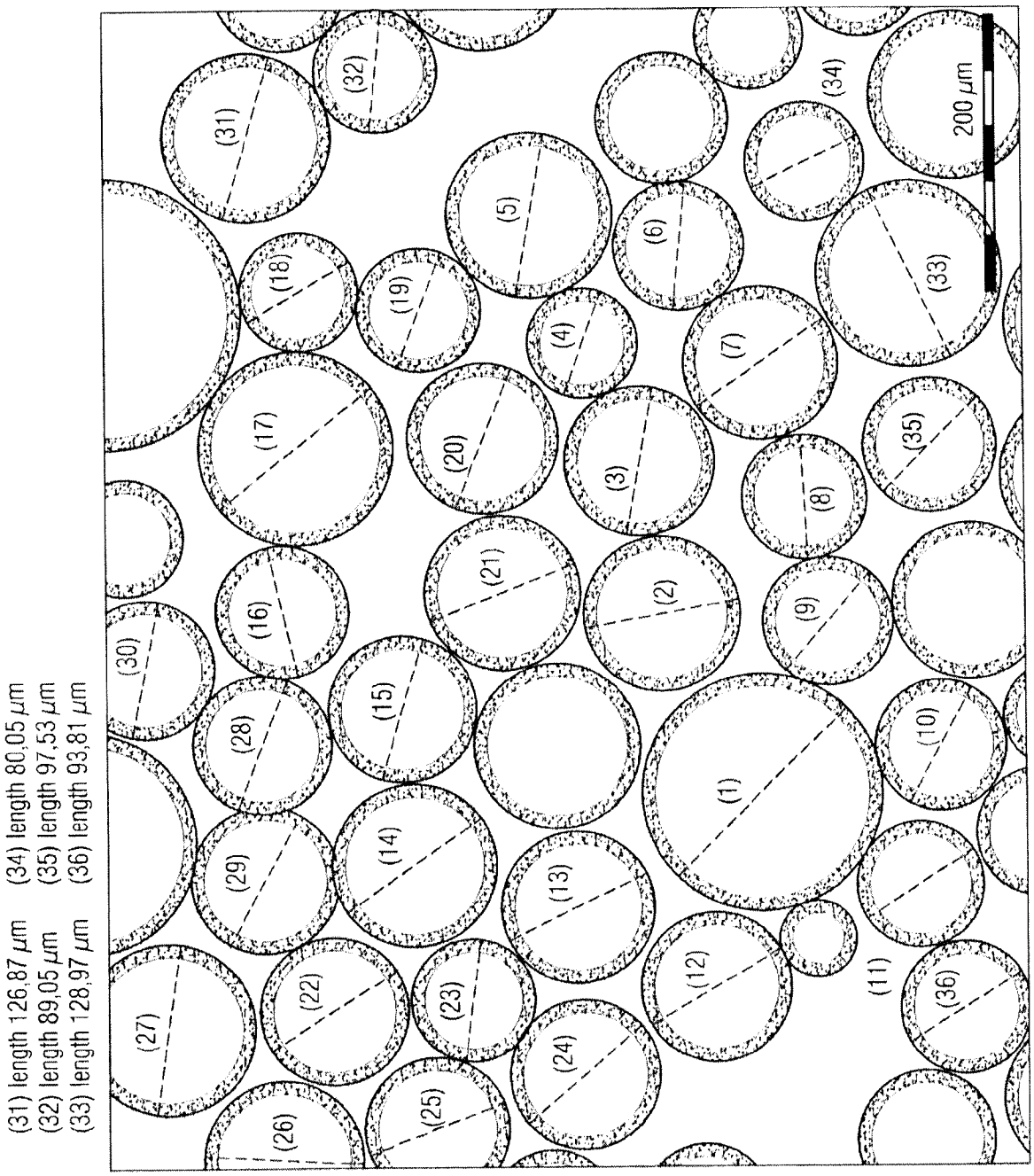
11. The composition according to one or more of the preceding claims, wherein the aqueous phase (c) comprises different additives, in particular rheology modifiers, pH control agents, chelating agents, electrolytes, biocides and/or humectants.

12. The composition according to one or more of the preceding claims, wherein the droplet size of the emulsions is in the range from 1 µm to 200 µm.

13. The use of a composition according to one or more claims 1 to 12 for personal care and cosmetics formulations, in agrochemical formulations, in emulsion paints, in cleaning formulations and formulations in the oil & mining industry.

14. A process for the production of the composition according to one or more of claims 1 to 12, comprising the steps of i) dispersing the at least one natural clay (component a) in water, ii) adding the oil phase to the aqueous clay dispersion of step i) and iii) homogenizing the composition in order to obtain a stable oil-in-water emulsion.

Fig. 1a



(1) length 178,31 µm
(2) length 113,29 µm
(3) length 103,57 µm
(4) length 78,62 µm
(5) length 120,26 µm
(6) length 90,53 µm
(7) length 110,09 µm
(8) length 93,15 µm
(9) length 93,15 µm
(10) length 96,30 µm
(11) length 90,89 µm
(12) length 117,15 µm
(13) length 111,40 µm
(14) length 121,00 µm
(15) length 105,73 µm
(16) length 100,34 µm
(17) length 123,48 µm
(18) length 91,41 µm
(19) length 95,84 µm
(20) length 116,07 µm
(21) length 110,83 µm
(22) length 108,98 µm
(23) length 82,46 µm
(24) length 100,10 µm
(25) length 109,58 µm
(26) length 111,53 µm
(27) length 129,15 µm
(28) length 105,13 µm
(29) length 102,45 µm
(30) length 100,48 µm

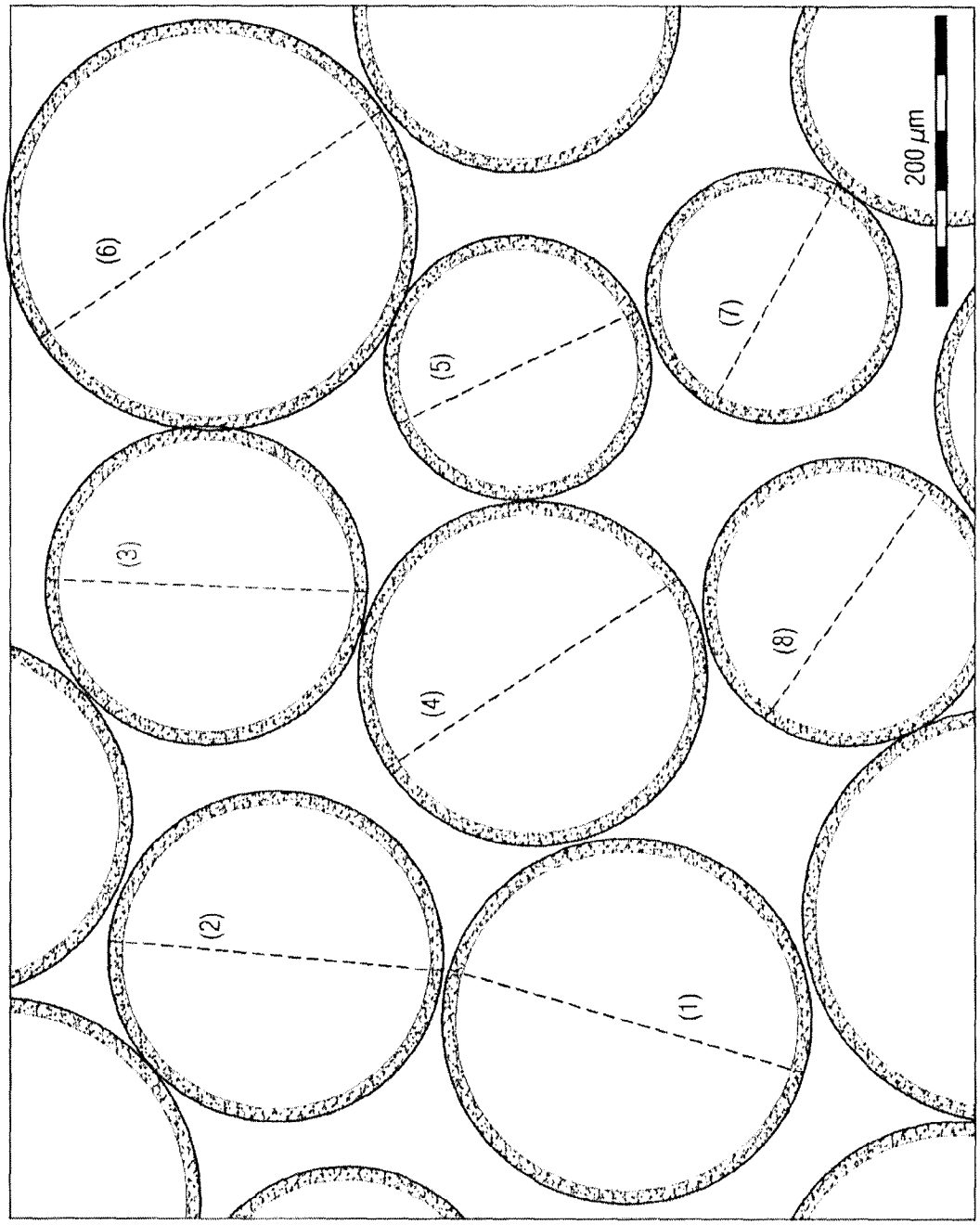


Fig. 1b

(1) length 254,62 µm
(2) length 228,53 µm
(3) length 219,12 µm
(4) length 242,97 µm
(5) length 185,65 µm
(6) length 281,75 µm
(7) length 176,89 µm
(8) length 203,35 µm

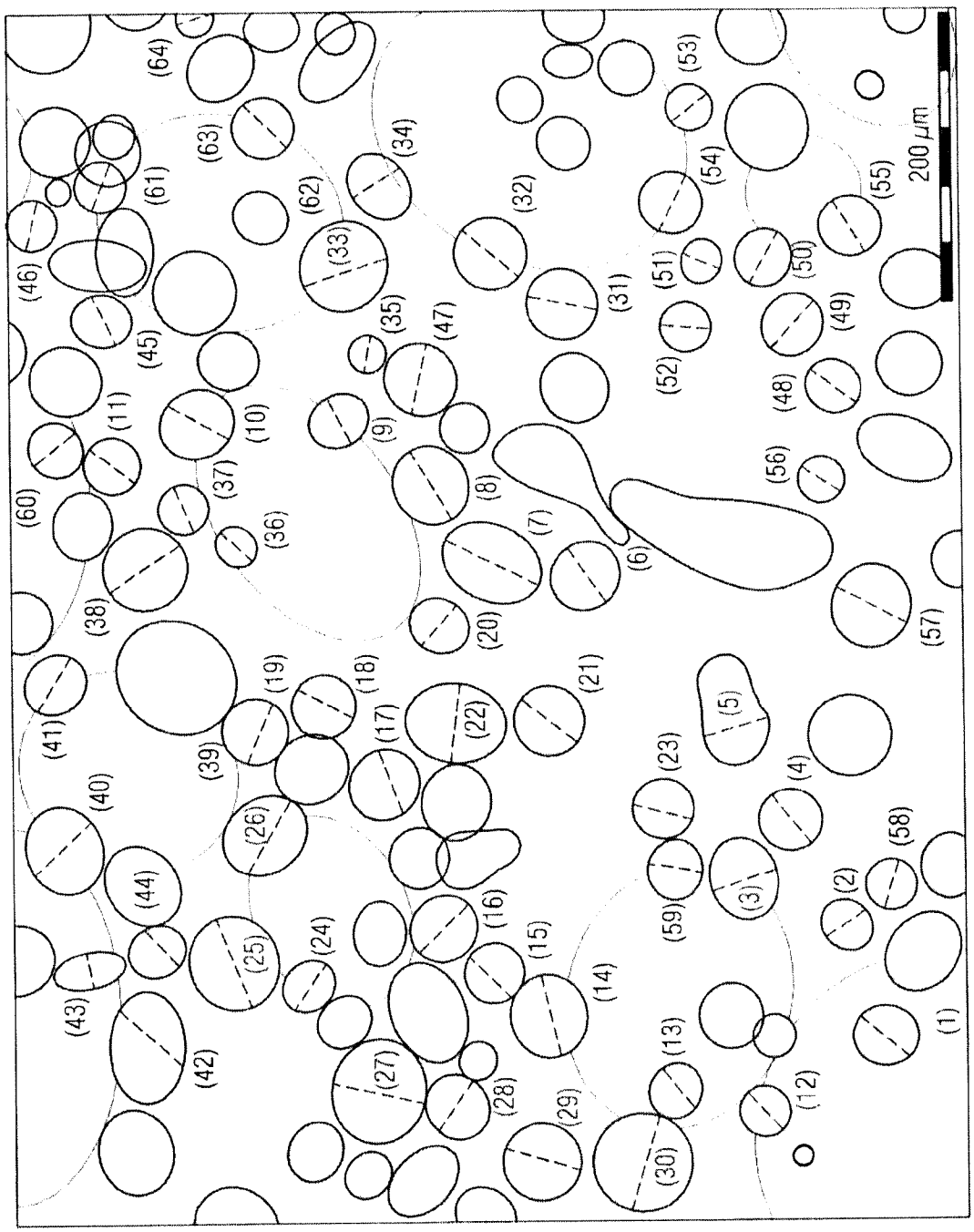


Fig. 1c

Fig. 1c'

(1) length 45,55 µm
(2) length 34,93 µm
(3) length 45,21 µm
(4) length 46,74µm
(5) length 42,34µm
(6) length 45,93 µm
(7) length 72,53 µm
(8) length 50,33 µm
(9) length 38,44 µm
(10) length 46,84 µm
(11) length 38,34 µm
(12) length 34,06 µm
(13) length 37,13 µm
(14) length 66,10 µm
(15) length 45,13 µm

(16) length 51,49 µm
(17) length 51,33 µm
(18) length 46,22 µm
(19) length 51,25 µm
(20) length 40,06 µm
(21) length 46,41 µm
(22) length 57,18 µm
(23) length 41,37µm
(24) length 39,65 µm
(25) length 64,15 µm
(26) length 64,41 µm
(27) length 60,96 µm
(28) length 43,92 µm
(29) length 53,59 µm
(30) length 63,26 µm

(31) length 44,59 µm
(32) length 48,33 µm
(33) length 63,64 µm
(34) length 40,85 µm
(35) length 24,70 µm
(36) length 30,31µm
(37) length 37,83 µm
(38) length 59,35 µm
(39) length 60,37µm
(40) length 50,28 µm
(41) length 43,82 µm
(42) length 58,68 µm
(43) length 32,58 µm
(44) length 36,86 µm
(45) length 40,30µm

(46) length 38,51 µm
(47) length 52,44 µm
(48) length 37,90 µm
(49) length 48,81 µm
(50) length 42,60 µm
(51) length 26,41 µm
(52) length 29,49 µm
(53) length 38,97 µm
(54) length 29,96 µm
(55) length 50,94 µm
(56) length 31,89 µm
(57) length 54,79 µm
(58) length 35,05 µm
(59) length 36,80 µm
(60) length 40,75µm

(61) length 34,40 µm
(62) length 45,86 µm
(63) length 41,89 µm
(64) length 22,98µm

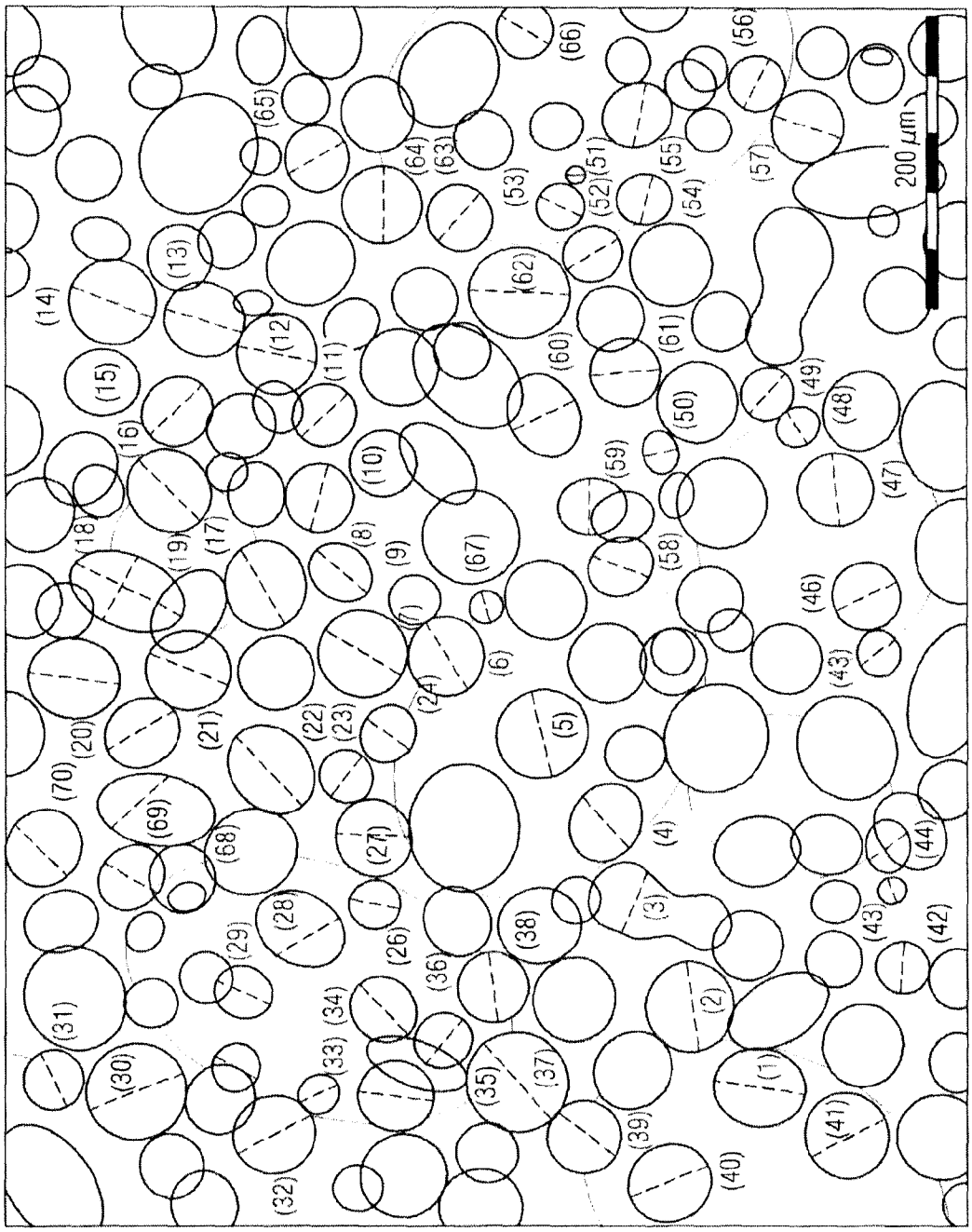


Fig. 1d

Fig. 1d'

(1) length 62,17 µm
(2) length 60,58 µm
(3) length 50,68 µm
(4) length 47,20 µm
(5) length 60,53 µm
(6) length 54,89 µm
(7) length 58,96 µm
(8) length 59,02 µm
(9) length 44,18 µm
(10) length 46,45 µm
(11) length 44,08 µm
(12) length 52,63 µm
(13) length 46,23 µm
(14) length 61,57 µm
(15) length 50,78 µm
(16) length 61,23 µm
(17) length 75,90 µm
(18) length 47,81 µm
(19) length 62,70 µm
(20) length 55,04 µm
(21) length 59,28 µm
(22) length 68,82 µm
(23) length 37,83 µm
(24) length 37,99 µm
(25) length 51,61 µm
(26) length 33,18 µm
(27) length 54,59 µm
(28) length 38,57 µm
(29) length 34,38 µm
(30) length 65,53 µm
(31) length 41,72 µm
(32) length 58,68 µm
(33) length 29,66 µm
(34) length 48,92 µm
(35) length 320,1 µm
(36) length 40,38 µm
(37) length 65,21 µm
(38) length 44,19 µm
(39) length 47,77 µm
(40) length 57,76 µm
(41) length 50,73 µm
(42) length 32,20 µm
(43) length 18,37 µm
(44) length 32,65 µm
(45) length 28,29 µm
(46) length 47,54 µm
(47) length 56,99 µm
(48) length 29,68 µm
(49) length 39,45 µm
(50) length 26,61 µm
(51) length 9,81 µm
(52) length 31,94 µm
(53) length 37,04 µm
(54) length 33,89 µm
(55) length 48,89 µm
(56) length 28,83 µm
(57) length 49,29 µm
(58) length 40,99 µm
(59) length 40,79 µm
(60) length 48,43 µm
(61) length 44,19 µm
(62) length 69,69 µm
(63) length 43,16 µm
(64) length 48,36 µm
(65) length 45,94 µm
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(67) length 18,98 µm
(68) length 43,05 µm
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(70) length 48,34 µm

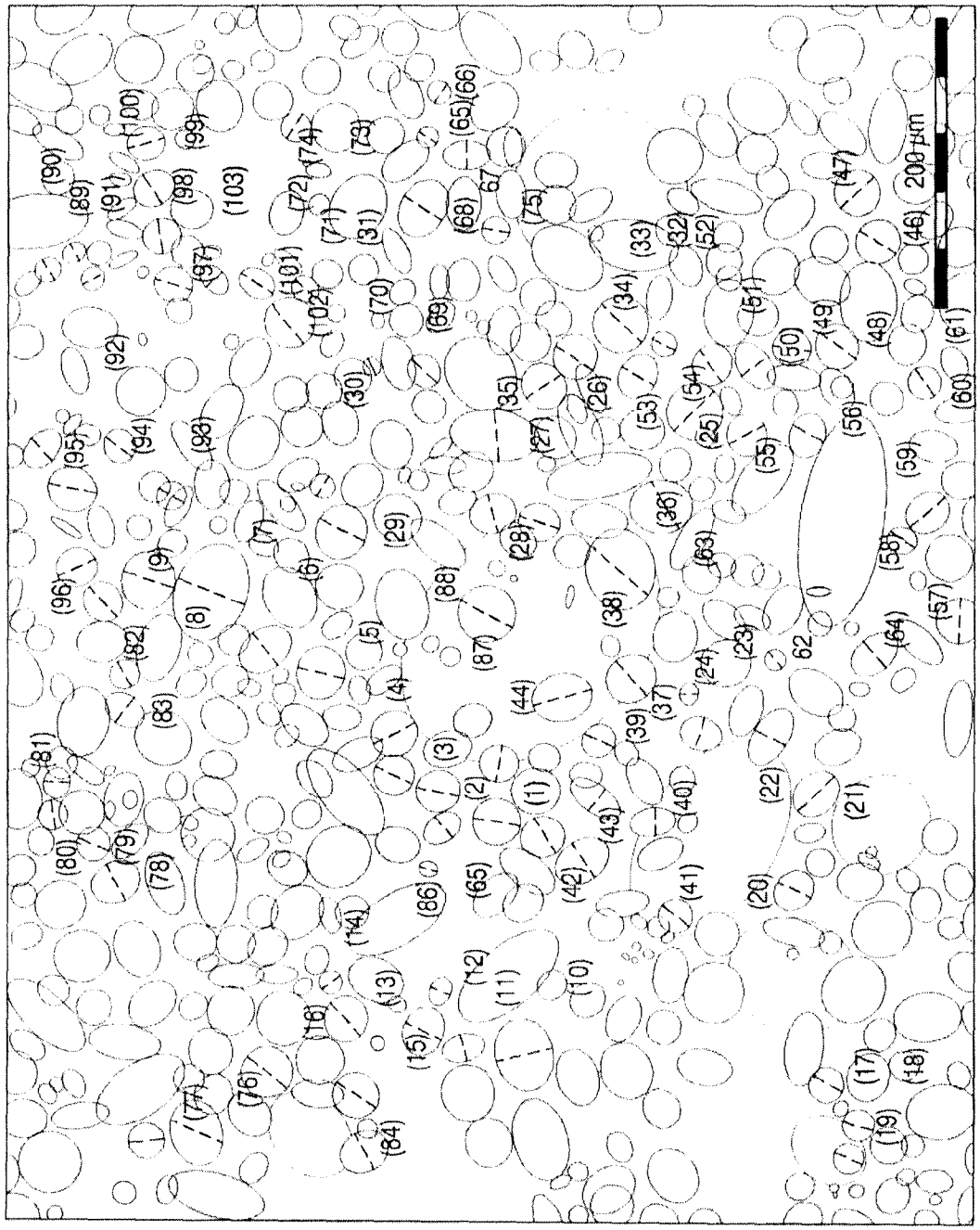


Fig. 1e

Fig. 1e'

(1) length 28,72 µm
(2) length 26,78 µm
(3) length 20,89 µm
(4) length 32,08 µm
(5) length 28,96 µm
(6) length 20,77 µm
(7) length 49,61 µm
(8) length 31,96 µm
(9) length 25,19 µm
(10) length 36,92 µm
(11) length 16,66 µm
(12) length 22,80 µm
(13) length 28,40 µm
(14) length 14,67 µm
(15) length 30,77 µm
(16) length 35,52 µm
(17) length 25,64 µm
(18) length 22,43 µm
(19) length 21,63 µm
(20) length 21,79 µm

(21) length 36,59 µm
(22) length 20,21 µm
(23) length 23,85 µm
(24) length 19,29 µm
(25) length 46,90 µm
(26) length 28,90 µm
(27) length 32,25 µm
(28) length 35,56 µm
(29) length 37,11 µm
(30) length 15,43 µm
(31) length 23,14 µm
(32) length 40,27 µm
(33) length 30,11 µm
(34) length 27,62 µm
(35) length 37,98 µm
(36) length 49,73 µm
(37) length 36,39 µm
(38) length 41,68 µm
(39) length 24,78 µm
(40) length 15,40 µm

(41) length 24,32 µm
(42) length 31,10 µm
(43) length 30,39 µm
(44) length 26,54 µm
(45) length 21,07 µm
(46) length 31,97 µm
(47) length 32,15 µm
(48) length 32,72 µm
(49) length 27,94 µm
(50) length 20,54 µm
(51) length 26,73 µm
(52) length 17,76 µm
(53) length 25,67 µm
(54) length 38,96 µm
(55) length 30,22 µm
(56) length 25,00 µm
(57) length 33,47 µm
(58) length 19,76 µm
(59) length 30,14 µm
(60) length 21,76 µm

(61) length 23,73 µm
(62) length 13,67 µm
(63) length 13,46 µm
(64) length 27,12 µm
(65) length 15,60 µm
(66) length 15,33 µm
(67) length 25,64 µm
(68) length 34,78 µm
(69) length 24,40 µm
(70) length 16,99 µm
(71) length 12,50 µm
(72) length 19,67 µm
(73) length 13,74 µm
(74) length 22,12 µm
(75) length 19,46 µm
(76) length 34,11 µm
(77) length 23,03 µm
(78) length 27,95 µm
(79) length 19,19 µm
(80) length 19,16 µm

(81) length 18,15 µm
(82) length 16,46 µm
(83) length 24,67 µm
(84) length 27,94 µm
(85) length 14,95 µm
(86) length 12,73 µm
(87) length 14,04 µm
(88) length 13,25 µm
(89) length 12,72 µm
(90) length 19,25 µm
(91) length 15,49 µm
(92) length 22,81 µm
(93) length 18,67 µm
(94) length 34,65 µm
(95) length 22,09 µm
(96) length 30,18 µm
(97) length 25,78 µm
(98) length 24,53 µm
(99) length 24,44 µm
(100) length 23,07 µm
(101) length 22,64 µm
(102) length 36,50 µm
(103) length 14,64 µm

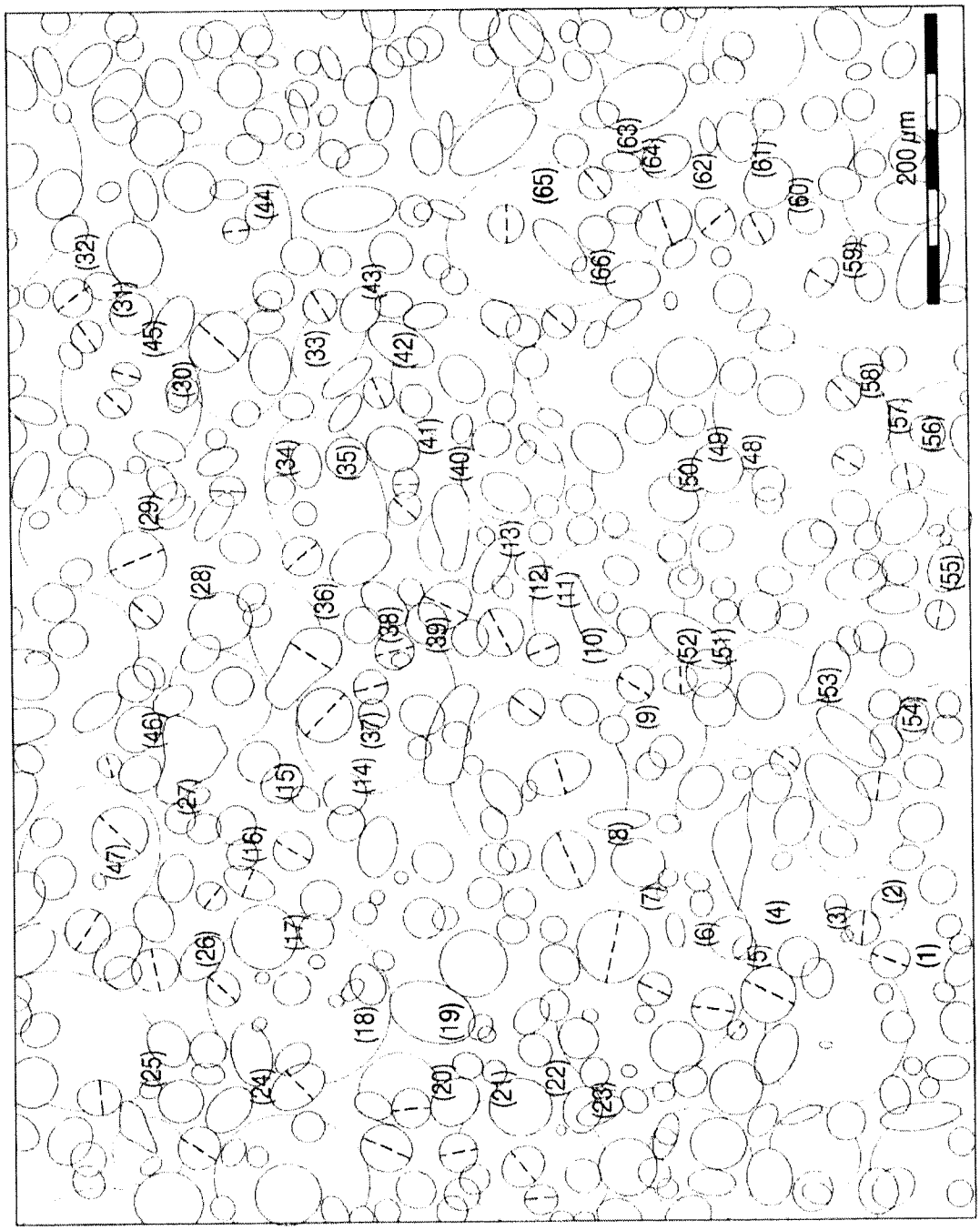


Fig. 1f

Fig. 1f

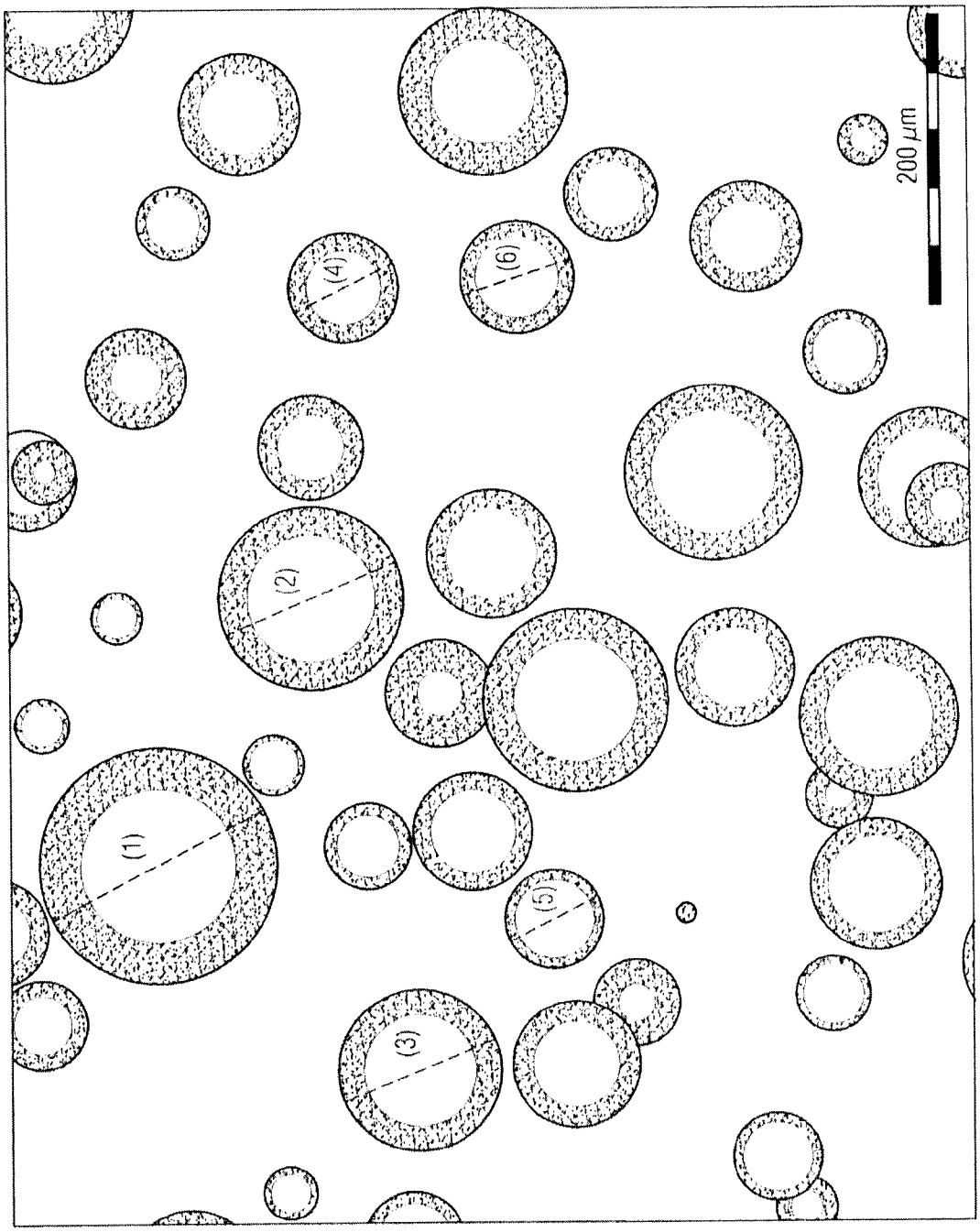
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(8) length 39,38 µm
(9) length 28,26 µm
(10) length 21,63 µm
(11) length 19,29 µm
(12) length 30,90 µm
(13) length 27,48 µm
(14) length 26,30 µm
(15) length 21,29 µm

(16) length 18,30 µm
(17) length 25,05 µm
(18) length 28,59 µm
(19) length 26,23 µm
(20) length 34,28 µm
(21) length 28,50 µm
(22) length 23,72 µm
(23) length 20,77 µm
(24) length 25,21 µm
(25) length 26,57 µm
(26) length 28,50 µm
(27) length 37,20 µm
(28) length 24,23 µm
(29) length 40,87 µm
(30) length 21,66 µm

(31) length 20,30 µm
(32) length 26,29 µm
(33) length 38,25 µm
(34) length 23,55 µm
(35) length 25,22 µm
(36) length 36,71 µm
(37) length 41,27 µm
(38) length 23,26 µm
(39) length 24,78 µm
(40) length 14,74 µm
(41) length 16,79 µm
(42) length 20,38 µm
(43) length 23,33 µm
(44) length 19,03 µm
(45) length 20,36 µm

(46) length 17,28 µm
(47) length 31,67 µm
(48) length 17,74 µm
(49) length 29,78 µm
(50) length 21,61 µm
(51) length 20,43 µm
(52) length 24,36 µm
(53) length 22,04 µm
(54) length 21,76 µm
(55) length 20,99 µm
(56) length 18,83 µm
(57) length 21,15 µm
(58) length 25,68 µm
(59) length 17,81 µm
(60) length 23,02 µm

(61) length 25,45 µm
(62) length 32,19 µm
(63) length 25,68 µm
(64) length 25,39 µm
(65) length 25,27 µm
(66) length 24,15 µm



(1) length 163.66 µm
(2) length 126.07 µm
(3) length 110.94 µm
(4) length 72.91 µm
(5) length 68.94 µm
(6) length 75.44 µm

Fig. 2a

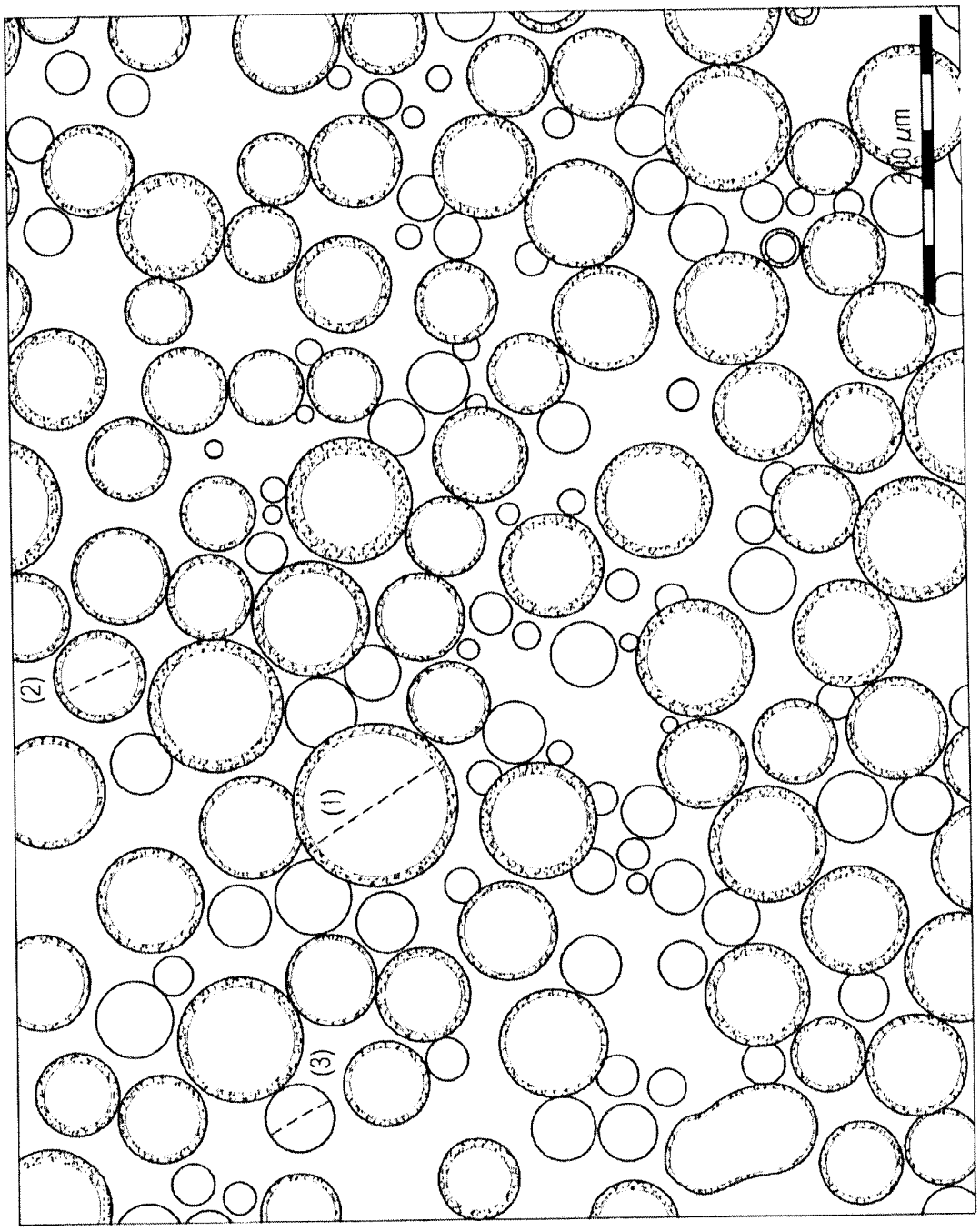
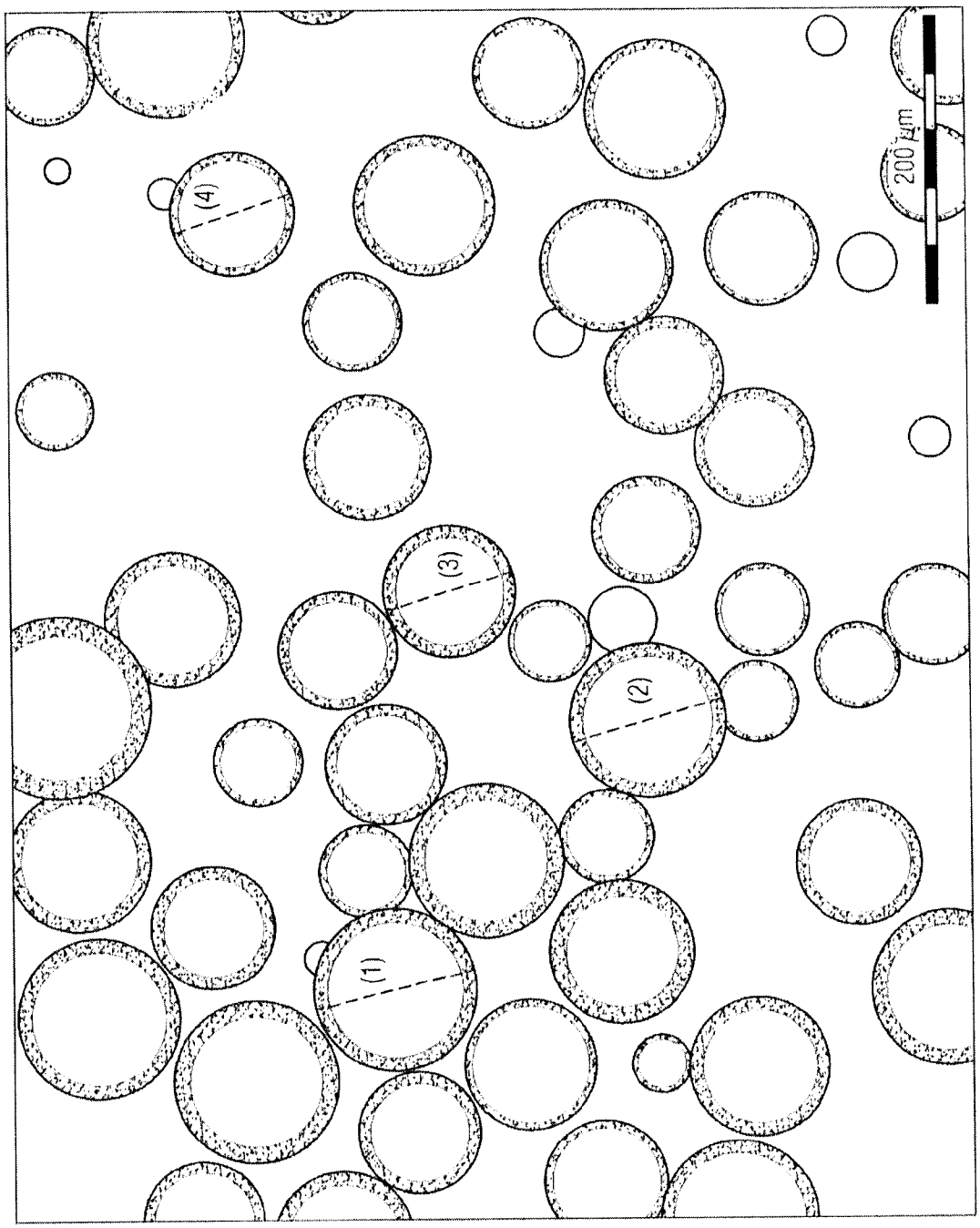


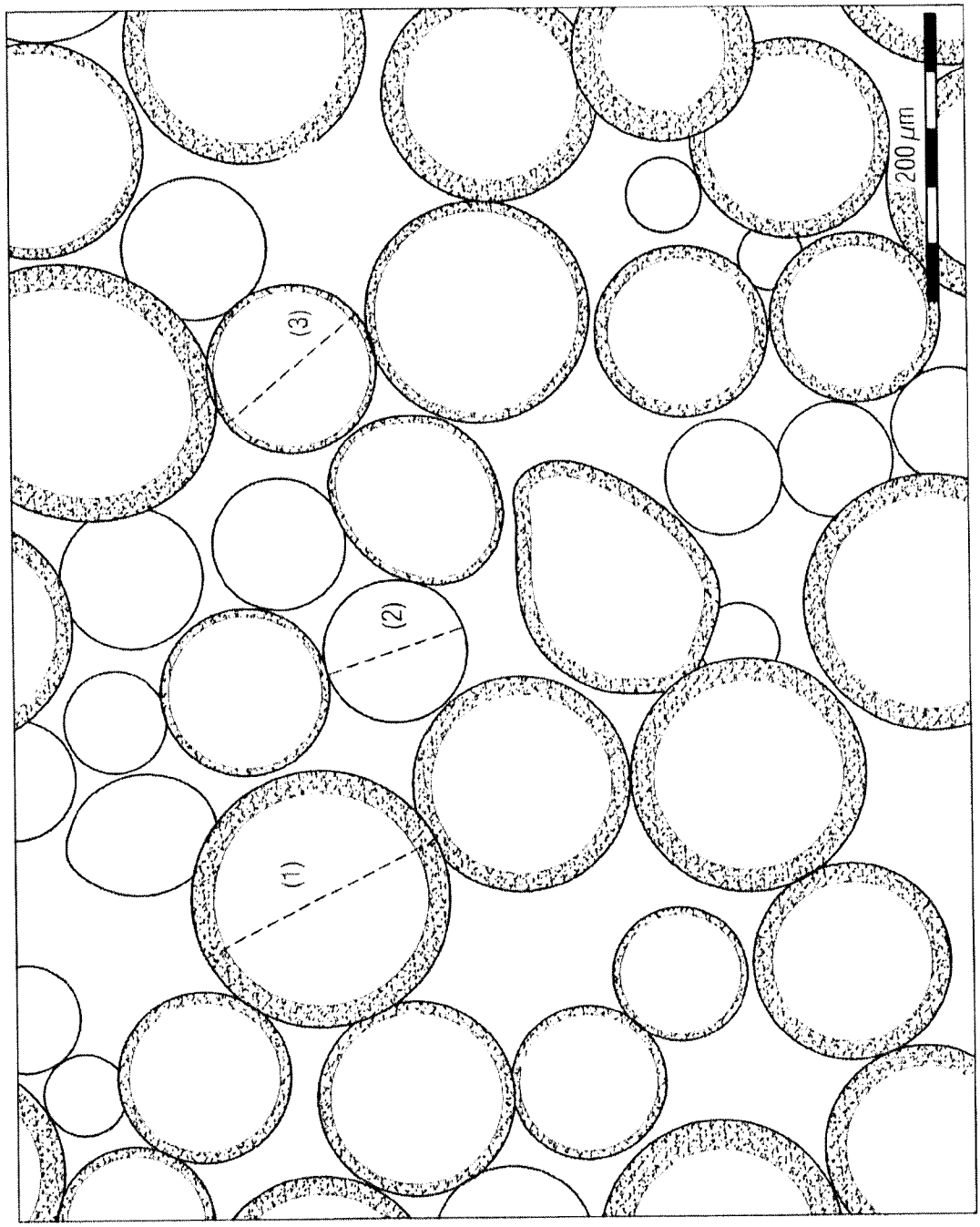
Fig. 2b

(1) length 108,00 µm
(2) length 60,25 µm
(3) length 46,65 µm



(1) length 103,85 µm
(2) length 102,96 µm
(3) length 86,49 µm
(4) length 85,58 µm

Fig. 2c



(1) Länge 176,50 µm
(2) length 97,71 µm
(3) length 111,81 µm

Fig. 2d

Fig. 3a

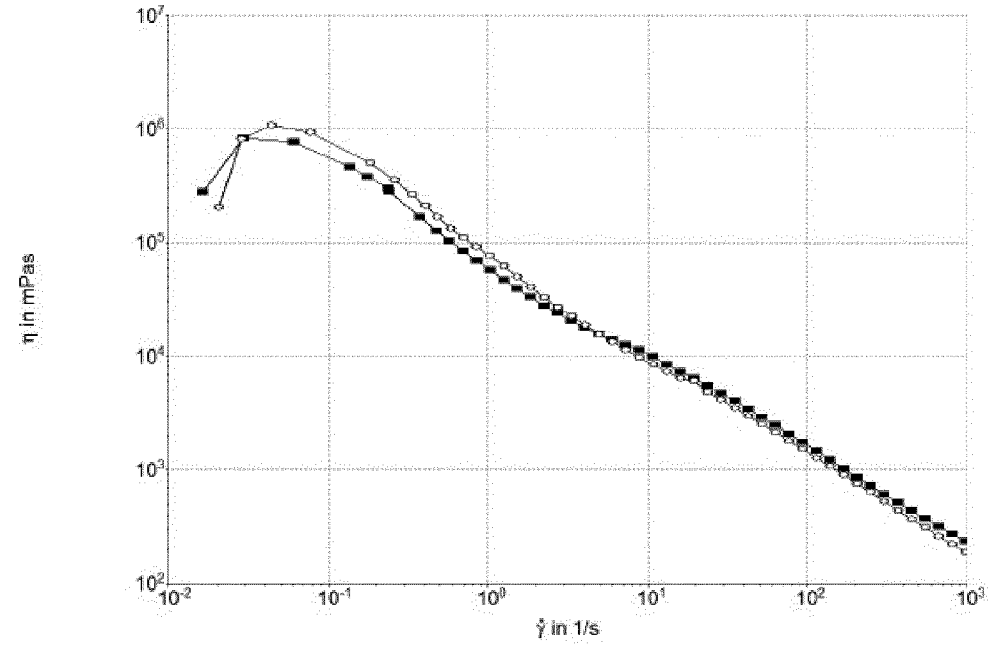
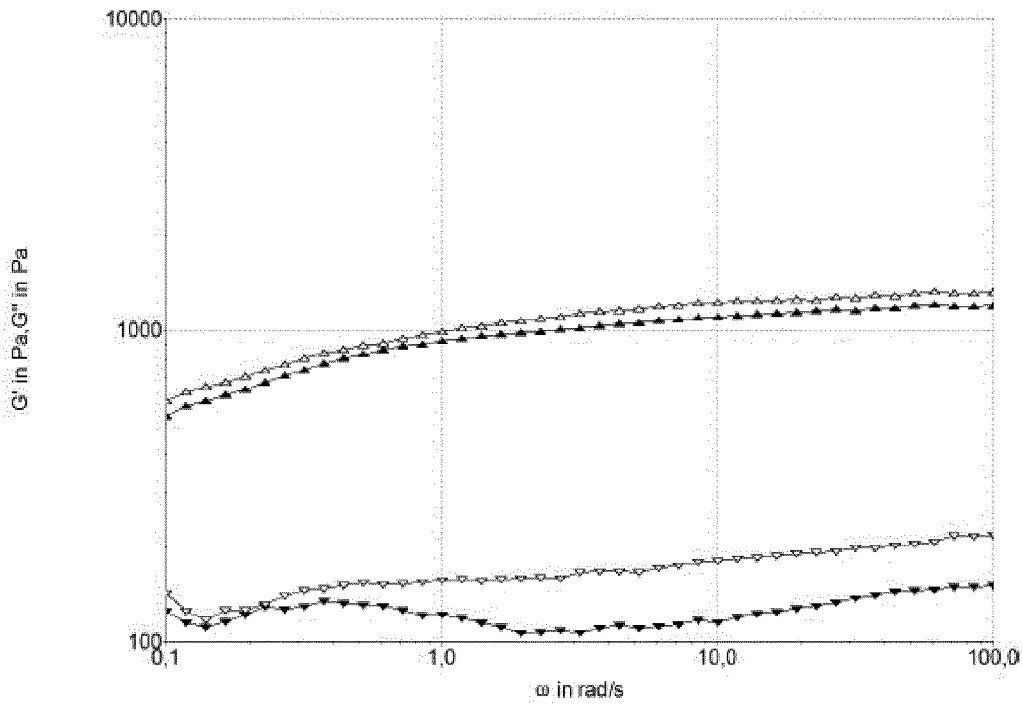

η in mPas
10^7
10^6
10^5
10^4
10^3
10^2
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3
$\dot{\gamma}$ in 1/s

Fig. 3b


G' in Pa,G'' in Pa
10000
1000
100
0,1
1,0
10,0
100,0
ω in rad/s

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/066320

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61K8/26 A61Q19/00 A61K8/06
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)
A61K A61Q

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	JP H03 32733 A (MIZUSAWA INDUSTRIAL CHEM) 13 February 1991 (1991-02-13) abstract	1-14
X	EP 2 559 423 A2 (SHISEIDO CO LTD [JP]) 20 February 2013 (2013-02-20) paragraphs [0009], [0021] table 1 example 2	1-14
X	WO 2012/137940 A1 (KAO CORP [JP]; MURATA TAKESHI [JP]) 11 October 2012 (2012-10-11) abstract	1-13

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

☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
1 August 2017	18/08/2017

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	Verrucci, Marinella

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2017/066320

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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