[illegible], 2013, [illegible] 8, [illegible] 1



[illegible] 541.182; 678.762.2

# [illegible]

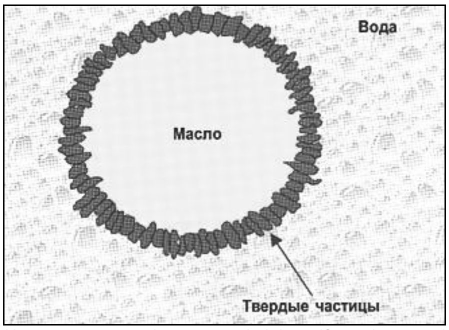
[illegible]

[illegible] 119571 [illegible]

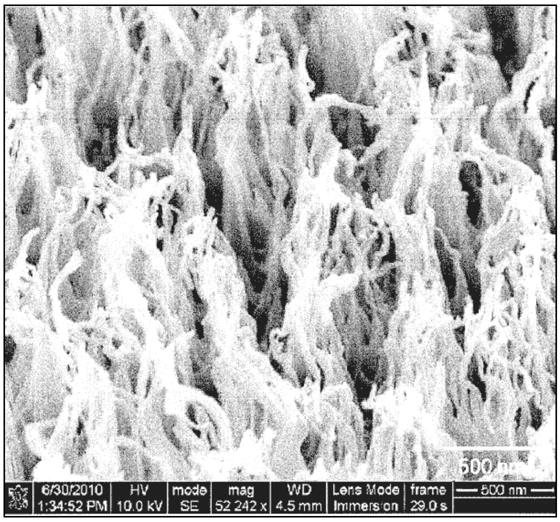
e-mail: pokidko2000@mail.ru

[illegible] in situ [illegible]

[illegible] [1, 2], [illegible] (supracolloidal structures), [illegible] [3]. [illegible] «[illegible]» (colloidosomes). [illegible] (hairy-rod nano-structures, [illegible] 2) [4], [illegible] [5], [illegible] CdSe [6], [illegible] [7] [illegible] [8].




[illegible] 1. [illegible]




[illegible] 2. SEM [illegible] [4].

[illegible] [9–13].

[illegible] [14], [illegible] [12], [illegible] [13], [illegible] [15], [illegible] [16], [illegible] [17], [illegible] [18], [illegible] [19], [illegible] [20] [illegible] [21].

[illegible] [22]. [illegible] [18]. [illegible] [19]. [illegible]

## 1. [illegible]

[illegible]

1) [illegible];

2) [illegible];

3) [illegible] [22].

[illegible] [18, 23].

[illegible] ($\theta$) [illegible] 0° [illegible] 180°, [illegible] $\theta$ [illegible] 90°, [illegible] $\theta > 90°$, [illegible] [8, 22]. [illegible] [24]. [illegible] [25] [illegible] [26], [illegible] [27]. [illegible] 48 % ($\theta$ ≥ 85°), [illegible] 71 % [illegible] $\theta$ ≥ 68° [28].

[illegible] $A_w$, [illegible] $A_o$. [illegible]

$$[illegible] = \frac{A_w}{A_o} = \frac{1+\cos\theta}{1-\cos\theta}. \qquad (1)$$

[illegible] [28].

[illegible] [29] [illegible] [30] [illegible] *in situ*

[31]. [24] 30 % 1.5 %

[32] 3 2. 1.5 % [33], 1.5 % 1 %

$S/V$ $\phi_V$ (2):

$$D = \frac{6V}{S} = \frac{6\phi_V V}{S}. \qquad (2)$$

$S$ [28]. [32], ($D$ = 39.7$C^{-0.76}$). [34], [35]. [19],

(2)

[28] 20 %

[illegible]

$$D = \frac{6\phi(\ldots)}{\rho\,\phi(\ldots)(1-\phi(\ldots))\cdot S} = \frac{6}{\rho\,S}\cdot\frac{(\ldots)}{(\ldots)}, \qquad (3)$$

[illegible]

$$S = C \cdot 0.006 \cdot \frac{S}{2}, \qquad (4)$$

[illegible]

## 2. [illegible]

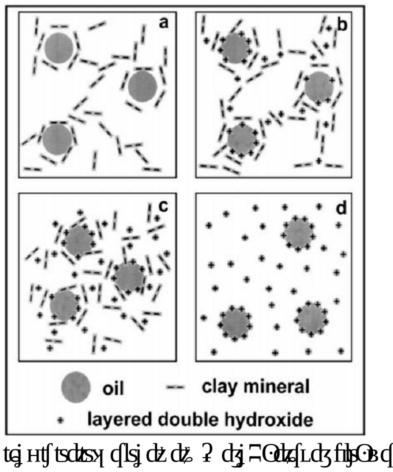
[illegible]

[illegible] [36] [illegible] [24]. [illegible] (confocal fluorescence microscopy). [illegible] 200 [illegible] [37], [illegible] [38].

[illegible] [39] [illegible]

[illegible] [40] [illegible]

[illegible] [39] [illegible] 3 [illegible] 4).

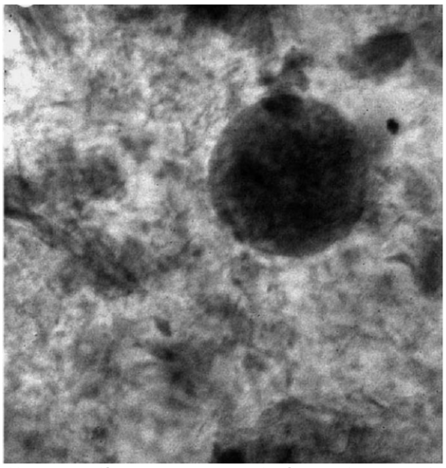



[illegible] 3. [illegible] 1 % [illegible] (a – 100 % [illegible], d – 100 % [illegible]) [39].

[illegible]

[illegible] (… 3, …), [illegible] (… 3, d). [illegible]

[illegible]



[illegible] 4. [illegible] (transmission X-ray microscopy) [39].

[illegible] [41], [illegible] $r$ [illegible] [42], [illegible] [43]:

$$E = \pi r^2 \sigma_{BM} (1 \pm \cos\theta)^2, \qquad (5)$$

[illegible] $\sigma_{BM}$ – [illegible], $\theta$ – [illegible], $r$ – [illegible].

[illegible] [17]: [illegible] ~ 2800 kT [illegible] $r$ ≈ 70 [illegible] $\sigma$ = 32.5 [illegible] $\theta$ = 30°. [illegible] kT).

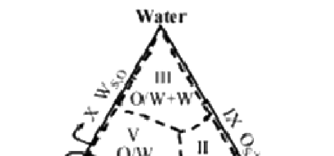
[illegible] [37] [illegible] 1 – 10 [illegible] $10^8$ – $10^9$ kT. [illegible]

[illegible] 1 – 10 kT [illegible]

[illegible] [42]. [illegible] (creaming) [43].

[illegible] 50% [illegible] [44]

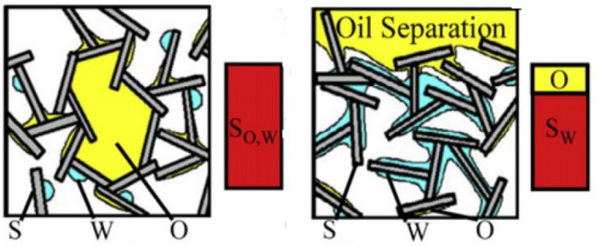
[illegible] [45]. [illegible] (… 5).




[illegible] 5. [illegible] I – [illegible] II – [illegible] 1 [illegible] III – [illegible] 2 [illegible] IV – [illegible] V – [illegible] 3 [illegible] VI – [illegible] 4 [illegible] [45].

[illegible]

[illegible]




[illegible] 6. [illegible] [45]

[illegible] [46].

[illegible]

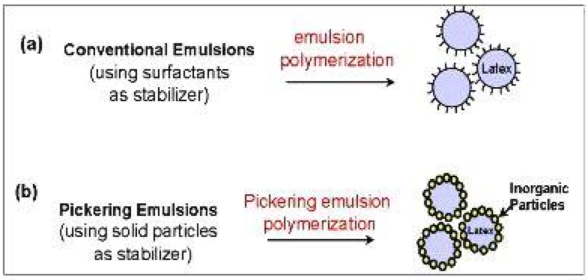
$$\sigma_B \bar{\gamma} = \nu \cdot U_{\min}. \tag{6}$$

[illegible] [47]:

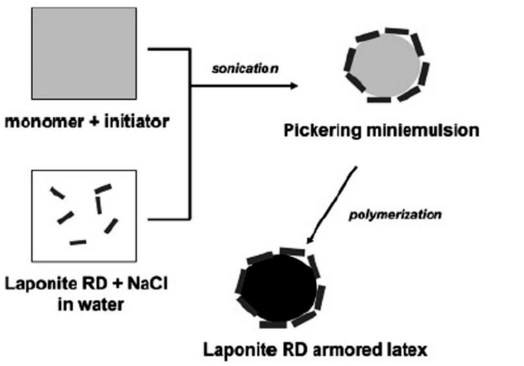
$$\sigma_B = \frac{24 U_{\min} \cdot \varphi^2}{\pi^2 (2a^3)}. \tag{7}$$

[illegible] [48] [illegible] [44].

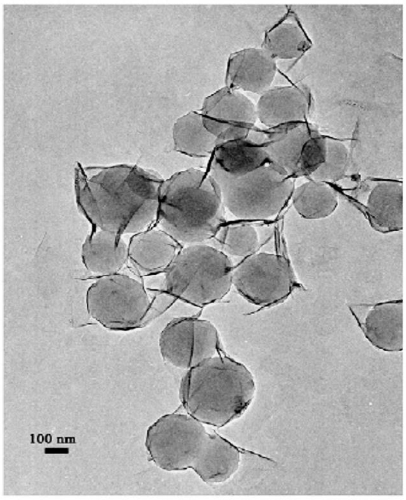
[illegible]


(a)
Conventional Emulsions
(using surfactants
as stabilizer)
emulsion
polymerization
Latex
(b)
Pickering Emulsions
(using solid particles
as stabilizer)
Pickering emulsion
polymerization
Inorganic
Particles
Latex

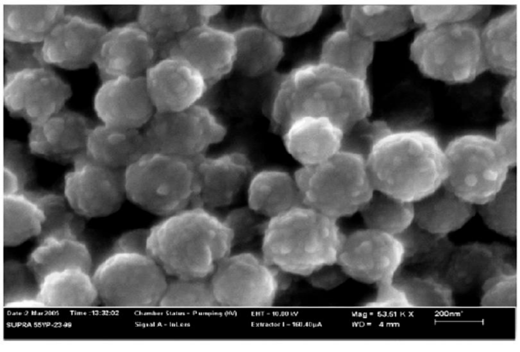
[illegible] (Fig. 8 [illegible] 9).




[illegible] 8. [illegible] [53].




а



в

[illegible] 9. [illegible]:
а – Na+-[illegible] [54],
в – [illegible] [10].

[illegible]

[illegible] [55] [illegible] 2-([illegible]).

[illegible] [56] [illegible] $TiO_2$ [illegible] $TiO_2$ [illegible]

[illegible] $SiO_2$ [57]. [illegible] 90°, [illegible]

[illegible]

[illegible]

## [illegible]:


1. Ramsden W. Separation of solids in the surface-layers of solutions and suspensions // Proc. Royal Soc. London. 1903. V. 72. С. 156–164.
2. Pickering S.U. Emulsions // J. Chem. Soc. 1907. V. 91. С. 2001–2021.
3. Velev O.D., Furusava K., Nagayama K. Assembly of latex particles by using emulsion droplets. 1. Microconstructed Hollow spheres // Langmuir. 1996. V. 12. С. 2374–2384.
4. Noble P.F., Cayre O.J., Alagrova R.G., Velev O.D., Paunov V.N. Fabrication of «hairy» colloidosomes with shells of polymeric microrods // J. Am. Chem. Soc. 2004. V. 126. С. 8092–8093.
5. Kaiser A., Liu T., Richtering W., Schmidt A.M. Magnetic capsules and Pickering emulsions stabilized by core-shell particles // Langmuir. 2009. V. 25. № 13. P. 7335–7341.
6. Miesch C., Kosif I., Lee E., Kim J.-[illegible]., Russell T.P., Hayward R.C., Emrick T. Nanoparticle-stabilized double emulsions and compressed droplets // Angew. Chem. Int. Ed. 2012. V. 51. № 1. P. 145–149.
7. He J., Zhang Q., Gupta S., Emrick T., Russell T.P., Thiyagarajan P. Drying droplets: A window into the behavior of nanorods at interfaces // Small. 2007. V. 3. С. 1214–1217.
8. [illegible] // [illegible]. 2008. Т. 77. № 8. С. 729–756.
9. Polymer Nanocomposites by Emulsion and Suspension Polymerization / Ed. V. Mittal. – London: RSC Nanosci. & Nanotechnol., 2011. 317 с. http://pubs.rsc.org/en/Content/eBook/978-1-84755-225-9.
10. Cauvine S., Colver P.J., Bon S.A.F. Pickering stabilized miniemulsion polymerization: Preparation of clay armored latexes // Macromolecules. 2005. V. 38. С. 7887–7889.
11. Kim Y.J., Liu Y.D., Choi H.J., Park S.J., Facile fabrication of Pickering emulsion polymerized polystyrene/laponite composite nanoparticles and their electrorheology // J. Colloid Interface Sci. 2012 doi: 10.1016/j.jcis.2012.12.040.
12. Yang J., Hasell T., Wanget W.X., Li J, Brown PD, Poliakoff M. Preparation of hybrid polymer nanocomposite microparticles by a nanoparticle stabilized dispersion polymerization // J. Mater. Chem. 2008. V. 18. С. 998–1002.
13. Gao Q., Wang C., Liu H., Wang C., Liu, X. Tong, Z. Suspension polymerization based on inverse Pickering emulsion droplets for thermo-sensitive hybrid microcapsules with tunable supracolloidal structures // Polymer. 2009. V. 50. С. 2587–2594.
14. Dai L.L. Advanced core-shell composite nanoparticles through Pickering emulsion polymerization. In: The Delivery of Nanoparticles / Ed. A.A. Hashim. – InTech, 2012. Chap. 12. http://www.intechopen.com/books/the-delivery-of-nanoparticles.
15. Giermanska-Kahn J., Shmitt V., Binks B.P., Leal-Calderon F. A new method to prepare monodisperse Pickering emulsions // Langmuir. 2003. V. 18. С. 2515–2518.
16. He Y.J. A novel emulsion route to sub-micrometer polyaniline/nano-ZnO composite fibers // Appl. Surface Sci. 2005. V. 249. С. 1–6.
17. Yang F., Nui Q., Lan Q., Sun D.J. Effect of dispersion pH on the formation and stability of Pickering emulsions stabilized by layered double hydroxides // J. Colloid Interface Sci. 2007. V. 306. С. 285–295.
18. Lagaly G., Reese M., Abend S. Smectites as colloidal stabilizers of emulsions. I. Preparation and properties of emulsions with smectites and nonionic surfactants // Appl. Clay Sci. 1999. V. 14. С. 83–103.
19. Chen J., Vogel R., Werner S., Heinrich G. Clausse D. Dutschk V. Influence of the particle type on the rheological behavior of Pickering emulsions // Colloids & Surfaces A: Physicochem. Eng. Aspects. 2011. С. 238–245.
20. Sacanna S., Kegel W.K., Philipse A.P. Thermodynamically stable Pickering emulsions // Phys. Rev. Lett. 2007. V. 98. С. 158–301.
21. Fujii S., Murakami R. Smart particles as foam and liquid marble stabilizers // KONA Powder & Particle J. 2008. № 26. С. 153–166.
22. Aveyard R., Binks B.P., Clint J.H. Emulsion stabilized solely by colloidal particles // Adv. Colloid Interface Sci. 2003. V. 100-102. С. 503–546.
23. Binks B.P., Whitby C.P. Silica particle-stabilized emulsions of silicone oil and water: Aspects of emulsification // Langmuir. 2004. V. 20. С. 1130–1137.

24. Whitby C.P., Fornasiero D., Ralston J. Effect of adding anionic surfactant on the stability of Pickering emulsions // J. Colloid Interface Sci. 2009. V. 329. ţ. 173ï 181.

25. Rao S.R. Surface Chemistry of Froth Flotation. V. 2. ï NY: Plenum Publishers, 2004. 758 ţ.

26. Tsamantakis C., Masliyah J., Yeung A., Gentzis T. The behavior of micro-bitumen drops in aqueous clay environments // J. Colloid Interface Sci. 2005. V. 288. ţ. 129ï 139.

27. Rousseau D. Fat crystals and emulsion stability // Food Res. Intl. 2000. V. 33. ţ. 3ï 14.

28. Frelichowska J., Bolzinger M.-A., Chevalier Y. Effect of solid particles content on properties of O/W Pickering emulsions // J. Colloid Interface Sci. 2010. V. 351. ţ. 348ï 356.

29. Shulman J.H., Leja J. Control of contact angles at the oil-water-solid interfaces. Emulsions stabilized by solid particles ($BaSO_4$) // Trans. Faraday Soc. 1954. V. 50. ţ. 598ï 605.

30. Hassander H., Johansson B., Tornell B. The mechanism of emulsion stabilization by small silica (Ludox) particles // Colloids Surf. 1989. V. 40. ţ. 93ï 105.

31. Subramaniam A.B., Mejean C., Abkarian M., Stone H.A. Microstructure, morphology, and lifetime of armored bubbles exposed to surfactants // Langmuir. 2006. V. 22. ţ. 5986ï 5990.

32. Cui Y., Therelfall M., van Duijneveldt J.S. Optimizing organoclay stabilized Pickering emulsions // J. Colloid Interface Sci. 2011. V. 356. ţ. 665ï 671.

33. Ashby N.P., Binks B.P. Pickering emulsions stabilized by laponite clay particles // Phys. Chem. Chem. Phys. 2000. V. 2. ţ. 5640ï 5646.

34. Arditty S., Schmitt V., Lequeux F. Leal-Calderon. Interfacial properties in solid-stabilized emulsions // Eur. Phys. J. E. 2005. V. 44. ţ. 381ï 393.

35. Yan Y., Masliyah J.H. Solids-stabilized oil-in-water emulsion: Scavenging of emulsion droplets by fresh oil addition // Colloids Surf. A. 1993. V. 75. ţ. 123ï 132.

36. Whitby C.P., Fischer F.E., Fornasiero D., Ralston J. Shear-induced coalescence of oil-in-water Pickering emulsions // J. Colloid Interface Sci. 2011. V. 361. ţ. 170ï 177.

37. Marinova K.G., Alargova R.G., Denkov N.D., Velev O.D., Petsev D.N., Ivanov I.B., Borwankar R.P. Charging of oil-water interfaces due to spontaneous adsorption of hydroxyl ions // Langmuir. 1996. V. 12. ţ. 2045ï 2051.

38. Wang X., Alvarado V. Effect of salinity and pH on Pickering emulsion stability // Rep. at SPE Annual Technical Conference and Exhibition, 21ï 24 Sept. 2008. Denver, Colorado, USA. ţ. 17ï 19.

39. Abend S., Bonnke N., Gutschner U., Lagaly G. Stabilization of emulsions by heterocoagulation of clay minerals and layered double hydroxides // Colloid Polym. Sci. 1998. V. 276. ţ. 730ï 737.

40. Li C., Liu Q., Mei Z. Pickering emulsions stabilized by paraffin wax and laponite clay // J. Colloid Interface Sci. 2009. V. 336. ţ. 314ï 321.

41. Wang S., He Y., Zou Y. Study of Pickering emulsion stabilization by mixed particles of silica and calcite // Particuology. 2010. V. 8. ţ. 390ï 393.

42. Lin Y., Skaff H., Emrick T., Dinsmore A.D., Russell T.P. Nanoparticle assembly and transport at liquid-liquid interfaces // Science. 2003. V. 299. ţ. 226ï 229.

43. Binks B.P., Rodrigure J.A. Types of phase inversion of silica particle stabilized emulsions containing triglyceride oil // Langmuir. 2003. V. 19. ţ. 4905ï 4912.

44. Binks B.P., Lumsdon S.O. Effects of oil type and aqueous phase composition on oil-water mixtures containing particles of intermediate hydrophobicity // Phys. Chem. Chem. Phys. 2000. V. 2. ţ. 2959ï 2967.

45. Nonomura Y., Kobayashi N. Phase inversion of the pickering emulsions stabilized by plate-shaped clay particles // J. Colloid Interface Sci. 2009. V. 330. ţ. 463ï 466.

46. Torres L.G., Iturbe R., Snowden M.J., Chowdhry B. Z., Leharne S. A. Preparation of o/w emulsions stabilized by solid particles and their characterization by oscillatory rheology // Colloids Surf. A: Physicochem. Eng. Aspects. 2007. V. 302. ţ. 439ï 448.

47. Stancik E.J., Kouhkan M., Fuller G.G. Coalescence of particle-laden fluid interfaces // Langmuir. 2004. V. 20. ţ. 90ï 94.

48. Ross-Murphy S.B. Rheology of biopolymer solutions and gels / In: New Physico-Chemical Techniques for the Characterization of Complex Food Systems / Ed. E. Dickinson. ï London: Blackie, 1995. ţ. 139ï 156.

49. Hohenstein W.P. The method of polymerization in suspension // Polymer Bull. 1945. V. 1. ţ. 13ï 16.

50. Voorn D.J., Ming W., van Herk A.M. Polymer-clay nanocompiste latex particles by inverse Pickering emulsion polymerization stabilized with hydrophobic montmorillonite plates // Macromolecules. 2006. V. 39. ţ. 2137ï 2143.

51. Ianchis R., Donescu D., Petcu C. Surfactant-free emulsion polymerization of styrene in the presence of silylated montmorillonite // Appl. Clay Sci. 2009. V. 45. ţ. 164ï 170.

52. Khatana S., Dhibar A.K., Ray S. Sinha, Khatua B.B. Use of pristine clay platelets as a suspension stabilizer for the synthesis of poly(methyl methacrylate)/clay nanocomposite // Macromol. Chem. Phys. 2009. V. 210. ţ. 1104ï 1113.

53. Bon S.A.F., Colver P.J. Pickering emulsion polymerization using laponite clay as a stabilizer // Langmuir. 2007. V. 23. P. 8316–8322.

54. Guillot S., Bergaya F., de Azevedo C., Warmont F., Tranchant J.F. Internally structured Pickering emulsions stabilized by clay mineral particles // J. Colloid Interface Sci. 2009. V. 333. P. 563–569.

55. Sedlakova Z., Plestil J., Baldrian J., Slouf M., Holub P. Nanostructured hybrid materials prepared via in-situ emulsion polymerization // Polym. Bull. 2009. V. 63. P. 365–384.

56. Chen T., Colver P.J., Bon S.A.F. Organic–inorganic hybrid hollow spheres prepared from $TiO_2$-stabilized Pickering emulsion polymerization // Advanced Materials. 2007. V. 19. № 17. P. 2286–2289.

57. Zhang W.H., Fan X.D., Tian W., Fan W.W. Polystyrene/nano-$SiO_2$ composite microspheres fabricated by Pickering emulsion polymerization: Preparation, mechanisms and thermal properties // eXPRESS Polymer Lett. 2012. V. 6. № 7. P. 532–542.

## PICKERING EMULSIONS AND THEIR USE IN PRODUCTION OF POLYMER NANOSTRUCTURED MATERIALS

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*In this article both types of Pickering emulsions – oil/water and water/oil – and their applications in the synthesis of different polymers have been considered. Pickering emulsions are dispersions stabilized by solid particles adsorbed at oil-water interface instead of conventional emulsifier. The influence of various solid particles, their amount and interaction on emulsions formation, stability and morphology with various suspended solid particles have been considered. Phase inversion phenomena and factors (such as wettability of solid particles) affecting them have been described. The interest to Pickering emulsions for the last decade is highly fueled by eco-friendly and cost-effective manufacture of hybrid polymer particles and nanocomposites with supracolloidal structures. The Pickering emulsion polymerization or suspension polymerization allows preparing in situ reinforced nanostructural polymer composites, unusual latexes and microcapsules with unique properties.*

***Key words:*** *adsorption, contact angle, emulsion stability, latexes, Pickering emulsion polymerization, polymer nanocomposites, surfactants, wetting.*