

## POLYMER DISPERSIONS AND NANO-TECHNOLOGY

EPDLA (European Polymer Dispersion and Latex Association, a Cefic Sector Group) is dedicated to promote the safe manufacture, transportation, distribution, handling and use of waterborne polymer dispersions, in compliance with regulatory requirements and industry guidelines.

EPDLA members are committed to Responsible Care® principles and have implemented risk management according to the precautionary principles.

### Polymer dispersions

Polymer dispersions are used as binders in many waterborne applications, e.g. adhesives, coatings and paints, carpets, non-woven, paper and paperboard coatings, plasters and textile finishing agents. Polymer dispersions technology has been used safely and successfully for more than 50 years and has contributed to a significant reduction in the release of organic solvents in the environment. Common to all dispersions covered by this paper is a film forming process during application.

Polymer dispersions are mixtures as defined under Article 3(2) of the REACH Regulation<sup>1</sup>, consisting mainly of water and high molecular weight polymer droplets. Based on polymer weight and chemical nature, the polymer droplets can be solid or highly viscous. The particle size of such polymer droplet can widely vary between ca. <100 nm (<0.1 µm) and 10,000 nm (10 µm)<sup>2</sup> in diameter.

This makes the low end of the polymer particle size distribution fall into the domain of the nanomaterials definition, and this paper is meant to address user questions about safety and regulatory status of polymer dispersions from this specific nanomaterial point of view.

The polymer droplets are dispersed and stabilized in water and regarded as bound in the liquid matrix. They cannot be isolated as discrete particles by simple separation techniques and do not exist without their waterborne environment. Polymer dispersions are stable under the normal or advised storage, transport and handling conditions. By evaporation of the water a separation between the aqueous and the polymeric phase is enacted and leads to the film formation via coalescence of the polymer droplets. Coalescence is the process where discrete droplets lose their identity, which is a property that isolated inorganic nanoparticles lack under ambient conditions.

The polymer droplets are formed by a polymerization reaction in liquid phase or by special emulsifying techniques that naturally generate a size distribution. The nano scaled polymer particles (if present) are neither intentionally added to the water phase nor intended to be extracted or released from the polymer dispersion even during further processing.

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<sup>1</sup> Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC

<sup>2</sup> nm = nanometre / µm = micrometre

### Film forming process

On application, polymer dispersions are converted to a dry film, the properties of which usually determine the performance of the final product. The film forming process might be supported e.g. by film forming agents or elevated temperature if appropriate.

The film forming process can be divided in four phases (see Annex I):

1. The water evaporates and the polymer droplets close up in the diminishing liquid volume until the particles form a dense packing.
2. Further evaporation of water results in high capillary forces, causing particle attraction and filling of void space in between the polymer droplets.
3. The polymer droplets deform and converge to produce a continuous polymer-film<sup>3</sup> (see also phase III in Annex I to this paper)
4. Further fusion by inter-diffusion of macromolecules from adjacent particles imparts mechanical strength.

### Exposure to polymer dispersions

EPDLA recognizes that regulators, NGOs, the academic community as well as the media pay increased attention to the toxicological and environmental behaviour of nanomaterials.

The polymer droplets in polymer dispersions - including those at the nanoscale – are not individually available during recommended application conditions. In these systems the polymer droplet is formed in water and delivered as such, then coalescence takes place to form a (polymeric) film.

### Consequently:

- The release of isolated nanoparticles, if present at all, from the polymer dispersion is very unlikely during film formation and can be excluded for the final polymer film.
- All polymer droplets in a polymer dispersion do not exist without their waterborne environment; thus they are bound in water.
- Individual particles irreversibly lose their identity during the application process (film formation) and the polymer dispersion no longer exists.

Any exposure of humans and environment to polymer dispersions droplets cannot be totally excluded during production and processing. Polymer dispersions are stable under the normal or advised storage, transport and handling conditions and the release of isolated polymer particles and consequently any human or environmental exposure to isolated particles is highly unlikely. Therefore, no concerns due to nanoparticles in polymer dispersions are anticipated in the life cycle of polymer dispersions or in the application of polymer dispersion-based waterborne products, like e.g. paints or adhesives, under advised conditions.

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<sup>3</sup> „Untersuchung der Filmbildung aus Polymerdispersionen mit Hilfe der forcierten Rayleighstreuung“ –Dissertation Thilo Jahr, Johannes-Gutenberg University, Mainz (2002)

Studies<sup>4</sup> showed that the release of particles from paints depends greatly on the substrate and the paint itself, but not primarily on the fact that nanoparticles (e.g. from fillers and pigments) are incorporated. It was also shown that the release of particles with a diameter below 100 nm is negligibly low compared to normal indoor and outdoor air content of particles in the nano range. These findings were accordingly highlighted in a factsheet from the Umweltbundesamt<sup>5</sup>. These results should be transferable to polymer dispersions, given that they are the basis for such paints and waterborne mixtures. Therefore, the risk linked with exposure by inhalation to particles released by dispersions in the typical conversion settings is regarded as extremely low<sup>6</sup>. This concurs with the findings of the scientific study carried out in 2012 “Short-Term Rat Inhalation Study With Aerosols of Acrylic Ester-Based Polymer Dispersions Containing a Fraction of Nanoparticles”<sup>7</sup>. In this study, none of the tested preparations of acrylic ester polymers elicited any adverse effect at the end of the inhalation or post-inhalation periods. No shift in toxicity could be observed by an increased proportion of nano-sized polymer particles.

The EU Scientific Committee on Consumer Products has addressed already dermal contact with Nanomaterials in the case of sunscreens, which are also dispersions of solids in a liquid matrix. There is no evidence of a direct hazard if healthy skin is exposed to nanoparticles in the order of 20 nm or above from e.g. sunscreens<sup>8</sup>. Intensive, direct contact of polymer particles in dispersions with skin would be an exception and not intended in most of the applications of polymer dispersions, so that this study might serve as a worst case. Finally, swallowing can be excluded as likely route of exposure.

In general, there is increasing scientific evidence that regarding both human toxicity and potential environmental effects of nanomaterials no statements can be made on nanomaterials per se but that for nanoscale substances a risk assessment on a case-by-case basis is needed – like for all other substances.<sup>9;</sup>  
10; 11

A study on Migration of Nanoparticles from Plastics into Foods has not shown any evidence that Nanoparticles would migrate from the LDPE host polymer into food simulants even under very severe test

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<sup>4</sup> Göhler, D., Stintz, M., Hillemann, L., Vorbau, M. (2010): Characterization of nanoparticle release from surface coatings by the simulation of sanding process. *Ann. Occup. Hyg.*, 54 (6), 615-624, 2010.  
<http://annhyg.oxfordjournals.org/content/54/6/615.abstract>

<sup>5</sup> [https://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/use\\_of\\_nanomaterials\\_in\\_coatings\\_0.pdf](https://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/use_of_nanomaterials_in_coatings_0.pdf)

<sup>6</sup> 10 Years of Research: Risk Assessment, Human and Environmental Toxicology of Nano-materials, Status paper issued by DEHEMA / VCI Working Group “Responsible Production and Use of Nano-Materials, October 2011;  
[http://www.dechema.de/dechema\\_media/Downloads/Positionspapiere/Nanomaterials+Risk+Assessment.pdf](http://www.dechema.de/dechema_media/Downloads/Positionspapiere/Nanomaterials+Risk+Assessment.pdf)

<sup>7</sup> *International Journal of Toxicology* (2012, Volume 31, No 1, pp 46-57)

<sup>8</sup> Scientific Committee on Consumer Products SCCP Opinion on safety of Nanomaterials in Cosmetic Products from December 2007  
[http://ec.europa.eu/health/ph\\_risk/committees/04\\_sccp/docs/sccp\\_o\\_123.pdf](http://ec.europa.eu/health/ph_risk/committees/04_sccp/docs/sccp_o_123.pdf), p. 12 & 36

<sup>9</sup> Donaldson, K and Poland, CA; Nanotoxicity: challenging the myth of nano-specific toxicity; *Current Opinion in Biotechnology* 2013, 24:724–734

<sup>10</sup> Krug, H.: “Nanosafety Research — Are We on the Right Track?”; *Angewandte Chemie Intern. Ed.*, Special Issue: Nanotechnology & Nanomaterials, Nanotoxicology & Nanomedicine, Vol. 53, Issue 46, pp 12304–12319, Nov. 10, 2014, <http://dx.doi.org/10.1002/anie.201403367>

<sup>11</sup> Wagner, S., Gondikas, A., Neubauer, E., Hofmann, T. und Frank von der Kammer: „Spot the Difference: Engineered and Natural Nanoparticles in the Environment — Release, Behavior, and Fate“; *Angew. Chemie Intern. Ed.*, Vol. 53, Issue 46, pp 12398–12419, Nov. 10, 2014, <http://dx.doi.org/10.1002/anie.201405050>

conditions.<sup>12</sup> We would expect the same findings for a migration experiment from a film obtained by drying a polymer dispersion, which e.g. originates from an adhesive used in food packaging.

Nevertheless workers should always refer to the corresponding Safety Data Sheet before handling polymer dispersions and apply the recommended safety measures, e.g. dust masks when spray drying or using gloves when open handling.

### **Risk Assessment according recognized tools**

EPDLA evaluated the potential risk from polymer dispersions and determined the risk classes for polymer dispersions applying two well known scientific tools, namely

- *Stoffenmanager Nano Module* (Dutch tool)<sup>13</sup>
- *Développement d'un outil de gestion graduée des risques spécifique au cas des nanomatériaux* (Anses, French tool)<sup>14</sup>

In both cases polymer dispersions ended up in the lowest risk category.

This is confirmed by the fact that manufacturing and use of polymer dispersions is a well established technology which has proven to be safe for decades, long before any discussion on nanomaterials was started.

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<sup>12</sup> Bott, J.; Störmer, A. Franz, R.: "A comprehensive study into the migration potential of nano silver particles from food contact polyolefins" Chemistry of Food, Food Supplements, and Food Contact Materials: From Production to Plate. Chapter 5, pp 51–70. (2014) *ACS Symposium Series*, Vol. 1159. Chapter DOI: 10.1021/bk-2014-1159.ch005 // Bott, J.; Störmer, A. Franz, R.: "Investigation into the migration of nanoparticles from plastic packaging materials containing carbon black into foodstuffs" *Food Additiv. Contam.* Vol. 31 (10) 1769-1782 (2014). DOI: 10.1080/19440049.2014.952786. // Bott, J.; Störmer, A. Franz, R.: "A model study into the migration potential of nanoparticles from plastics nanocomposites for food contact". *Food Packaging and Shelf Life*2 (2) 73-80 (2014). DOI: 10.1016/j.fpsl.2014.08.0001.

<sup>13</sup> <http://nano.stoffenmanager.nl/Default.aspx>

<sup>14</sup> <http://www.afssa.fr/Documents/AP2008sa0407.pdf>

### Disclaimer

- The present position paper has been developed by EPDLA members in good faith, to the best of its knowledge and following the latest scientific evidence.
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#### About EPDLA

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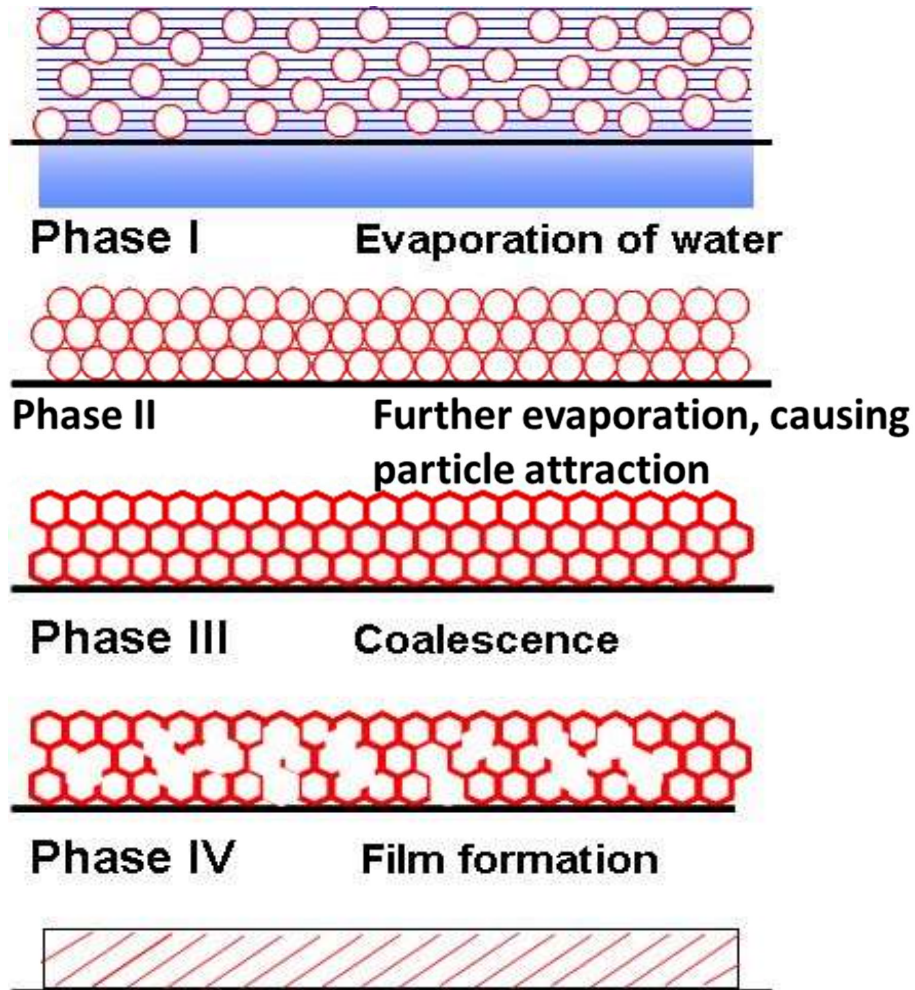
A sector group of Cefic 

European Chemical Industry Council - Cefic aisbl

EU Transparency Register n° 64879142323-90



### Annex I - Film forming process of polymer dispersions<sup>15</sup>



<sup>15</sup> Compare M.A. Winnik, The Formation and Properties of Latex Films in Emulsion Polymerization and Emulsion Polymers, P.A. Lovell und M.S. El-Aasser (Eds.), Wiley, New York, S. 467 (1997). and Error! Bookmark not defined.(page 17)

### **Annex II - Consideration of waterborne Polymer Dispersions towards different nanomaterial definitions or regulations**

#### **European Union - Commission Recommendation, October 2011 (2011/696/EU)**

*Excerpt of the definition:*

*“Nano-material means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm – 100 nm”.*

EPDLA Conclusion: Polymer dispersions are out of the scope of the EC Recommendation (2011/696/EU). The polymer droplets are dispersed in water, embedded and stabilized in the liquid matrix and thus bound in water. Furthermore, the existence of the waterborne environment is a prerequisite. Moreover during further processing the polymer droplets will converge to form a continuous film or matrix.

#### **France - Ministerial Order on Annual declaration of substances with nanoparticle status, 06.08.2012**

*Excerpt of the definition:*

*“Substance at nano scale”: substance as defined in article 3 of EC regulation no. 1907/2006, intentionally produced at nanometric scale, containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for a minimum proportion of particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm.”*

*“Substance at nano scale contained in a mixture without being linked to it”: substance at nano scale intentionally introduced in a mixture from which it is likely to be extracted or released under normal or reasonably foreseeable conditions of use.*

EPDLA Conclusion: Polymer dispersions are out of scope of the French Ministerial Order on annual declaration of substances with nanoparticles. According to REACH and the Q&A No. 20-bis of the French decree<sup>16</sup> waterborne polymer dispersions are mixtures. They are consisting out of at least two substances, namely water and polymer.

During the manufacturing process of waterborne polymer dispersions at no point in time nano scaled substances are intentionally added to the mixture.

Thus, neither a nano scaled substance was intentionally added to a mixture nor is the resulting mixture a substance according to REACH and Q&A No. 20-bis of the French decree, nor is the mixture a material/article according to REACH and Q&A No. 20-bis of the French decree out of which a nano scaled substance may be released under reasonable and foreseeable conditions of use: waterborne polymer dispersions are therefore not covered by the French decree so that no declaration/registration is needed.

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<sup>16</sup> Q&A published on 12 March 2013 by the Ministry of Ecology, Sustainable Development, Transport and Housing on articles R 523-12 to R. 523-21 of the French decree no. 2012-232 of 17 February 2012 (<https://www.r-nano.fr/>)



### Denmark – Statutory Order 644 of 13 June 2014

*Excerpt of scope:*

*“§ 2. The reporting requirement to the nano product register includes mixtures and articles that are intended for sale to the general public and which contain nanomaterials, where the nanomaterial itself is released under normal or reasonably foreseeable use of the mixture or article or where the nanomaterial itself is not released but substances in soluble form that are classified as CMRs or environmentally dangerous substances are released from the nanomaterial; ....”*

EPDLA Conclusion: Polymer dispersions are out of scope of the Danish Statutory Order 644 because no polymeric particles of nano scale are released under reasonably foreseeable use. Besides, the polymer droplets are dispersed in water, embedded and stabilized in the liquid matrix. Furthermore, the existence of the waterborne environment is a prerequisite.

### Belgium Federal Public Service for Public Health, Food Chain Safety and Environment – Royal decree regarding the placement on the market of substances manufacture at the nanoscale, 27 May 2014

*Excerpt of the definition:*

*“Substance produced in nanoparticle state: a substance that contains particles being in an unbound state or as an aggregate or as an agglomerate and from which minimum 50 % of the particles have a quantified size distribution with one or more external dimensions in the range of one to hundred nanometer, ...”*

EPDLA Conclusion: Polymer dispersions are out of the scope of Belgium Royal Decree. The polymer droplets are dispersed in water, embedded and stabilized in the liquid matrix and hence bound in water. Furthermore, the existence of the waterborne environment is a prerequisite. Moreover during further processing the polymer particles will converge to form a continuous film or matrix.