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EPDLA's position paper on polymer dispersions, redispersible powders made thereof and nanomaterials

The 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 and redispersible powders made thereof, 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.

Nano Definition

The European Commission has updated their recommendation on the definition of a nanomaterial (2022/C 229/01)¹ as:

'Nanomaterial' means a natural, incidental or manufactured material consisting of solid particles that are present, either on their own or as identifiable constituent particles in aggregates or agglomerates, and where 50 % or more of these particles in the number-based size distribution fulfil at least one of the following conditions:

(a) one or more external dimensions of the particle are in the size range 1 nm to 100 nm;

- (b) the particle has an elongated shape, such as a rod, fibre or tube, where two external dimensions are smaller than 1 nm and the other dimension is larger than 100 nm;
- (c) the particle has a plate-like shape, where one external dimension is smaller than 1 nm and the other dimensions are larger than 100 nm.

For more details, see Annex II.

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 dispersion technology has been used safely and successfully for more than 70 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.

European Polymer Dispersion and Latex Association (EPDLA)
Rue Belliard 40, Box 15, B-1040 Brussels Belgium
Tel. +32.492345072 elm@cefic.be www.cefic.org





¹ https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=oj:JOC 2022 229 R 0001 Commission Recommendation of 10.6.2022 on the definition of nanomaterial



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Polymer dispersions are mixtures as defined under Article 3(2) of the REACH Regulation², consisting mainly of water and high molecular weight polymer droplets. The diameter of such polymer droplets can widely vary between ca. <100 nm (<0.1 μ m) and 10,000 nm (10 μ m) in diameter ³.

Polymer dispersions with a number particle diameter equal or below 100 nm may 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 embedded in the liquid matrix. They cannot be isolated as discrete "droplets" by simple separation techniques and do not exist without their waterborne environment, they're kind of bound in it. Polymer dispersions are stable under the normal or advised storage, transport and handling conditions.

According to the definition of Nanomaterials only solid particles should be considered. JRC have issued a guidance stating that only particles solid at 25°C and above can fall under this definition.⁴

Dispersion polymers are placed in the market in their dispersed form in water. EPDLA has established a method to measure the melting point of such dispersed film-forming polymers, the so-called MFFT/WPT method. For further details see the EPDLA position paper on Synthetic Polymer Microparticles (SPM)⁵.

The melting point of a dispersed film-forming polymer is reached when the coalescence of the polymer droplets into a film is completed and a clear film is created. This temperature is called the Minimum Film Formation Temperature.

Most polymer dispersions have a MFFT and thus melting point equal or below 25°C, which means the polymer is liquid in droplet form. 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 droplets (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. Commission Recommendation 3689(2022) also states that materials with a volume specific surface area less than $6m^2/cm^3$ should not be considered a nanomaterial. Specific surface area (SSA) is a property of solids.

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² 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

 $^{^{3}}$ nm = nanometer / μ m = micrometer

⁴ https://publications.jrc.ec.europa.eu/repository/handle/JRC132102

⁵ https://epdla.eu/policy/polymer-dispersions-and-synthetic-polymer-microparticles



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A liquid like a polymer dispersion in delivery form has a surface of 6 cm²/cm³. A JRC document⁶ states in chapter 7.1.2.7 on nano emulsions that "Being nanostructured materials, they can have external dimensions well above the nanoscale. The current position of the EC, as expressed in the SWD, is that such objects are not covered by the EC definition."

Measurement of the particle size distribution of Polymer Dispersions

In case a polymer droplet in a polymer dispersion falls under the definition of a nanomaterial (2022/C 229/01), e.g. if the melting point (determined by MFFT) is above 25 °C and the droplet size is below 100 nm. the droplet size / particle size can be determined by transmission electronic microscope (TEM).

Redispersible polymer powders

Redispersible polymer powders (RDP) are obtained through spray-drying of polymer dispersions with the help of a spray drying adjuvant polymer. Such spray drying adjuvant polymers are water soluble polymers. During spray drying larger particles in the micrometer range, typically >>1 μ m are formed as loose agglomerates of a few polymer dispersion droplets individually covered by the spray drying adjuvant polymer.

Due to their decisive influence on cement, lime or gypsum based finished drymix mortar products, as well as on cement free and mineral-binder free systems, they are mainly used as building material additives in construction-applications to provide e.g. adhesion to many types of surfaces and substrates or waterproofing.

The RDPs are usually free-flowing fine powders, with a particle-size distribution in the micrometer-range, which excludes them from falling under the nanomaterial definition. Moreover, the RDPs contain a sort of liquid core (the original Polymer droplets) in a shell of a dried water-soluble polymer. In contact with water, the RDP particles disappear as the soluble polymer dissolves and release the individual dispersion droplets in their original state again. This redispersed polymer powder has the same properties as the original polymer dispersion.

Polymer Dispersions with a size distribution between 1-100 nm are differently stabilized, namely by emulsifiers, compared to those stabilized by a soluble polymer (usually, the individual droplet size in such cases is > 500 nm). Spray-drying such fine-particle polymer dispersions leads to polymer powders in the micrometer range, which are not redispersible.

<u>In summary:</u> Redispersible polymer powders (RDP) will normally not fall under the nanomaterial definition.

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⁶ https://publications.jrc.ec.europa.eu/repository/handle/JRC91377 (Amenta V, Aschberger K, Boix Sanfeliu A, Calzolai L, Emons H, Gaillard C, Gibson P, Holzwarth U, Koeber R, Linsinger T, Rasmussen K, Sokull-Kluettgen B, Stamm H, authors Roebben G, Rauscher H, editors. Towards a review of the EC Recommendation for a definition of the term "nanomaterial" Part 2: Assessment of collected information concerning the experience with the defintion. EUR 26744. Luxembourg (Luxembourg): Publications Office of the European Union; 2014. JRC91377)



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Film forming process

On application, polymer dispersions and redispersed polymer powders are converted to a dry film, the properties of which usually determine the performance of the final product. The film forming process depends on the melting point of the polymer (determined as WPT or MFFT) and might be supported e.g. by film forming agents or elevated temperature if appropriate, in case the MFFT is higher than 25°C.

The film forming process can be divided in four phases (see Annex I)³:

- 1. The water evaporates and the polymer droplets close up in the diminishing liquid volume until the droplets form a dense packing.
- 2. Further evaporation of water results in high capillary forces, causing droplet attraction and polymer droplets deform, filling of void space in between the polymer droplets.
- 3. The (deformed) droplets converge to produce a continuous polymer-film⁷, a process called coalescence (see also phase III in Annex I to this paper)
- 4. Further fusion by inter-diffusion of macromolecules from adjacent droplets 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 properties of nanomaterials.

The polymer droplets in polymer dispersions and in redispersed polymer powders - 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:

- Polymers in polymer dispersions are to be considered liquid at temperatures above the minimum film formation temperature (MFFT). If MFFT of a dispersion is above 25°C, the film forming polymer in the dispersion is not a solid particle within the nano material definition and therefore does not fall under this regime⁸
- The release of isolated nanoparticles, if present at all, from a polymer dispersion (or redispersed polymer powders) is not expected during film formation as these are then permanently incorporated in the polymer film. All polymer droplets in a polymer dispersion

European Polymer Dispersion and Latex Association (EPDLA) Rue Belliard 40, Box 15, B-1040 Brussels Belgium

Tel. +32.492345072 elm@cefic.be www.cefic.org
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⁷ "Untersuchung der Filmbildung aus Polymerdispersionen mit Hilfe der forcierten Rayleighstreuung" –Dissertation Thilo Jahr, Johannes-Gutenberg University, Mainz (2002)

⁸ Please note, that the temperature to decide if a material is a solid in context of being a Synthetic Polymer Microparticle is 20°C, whereas the temperature to decide if a material is solid in context of being a nanomaterial per JRC guidance (see ref. 4) is 25°C



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do not exist without their waterborne environment, but are embedded and kind of bound in water.

 Individual droplets irreversibly lose their identity during the application process through film formation.

Any exposure of humans and the environment to individual polymer dispersion droplets is unlikely during production and processing. Polymer dispersions are stable under the normal or advised storage, transport and handling conditions and the release of isolated polymer droplets and consequently human or environmental exposure to isolated droplets is not expected. 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, e.g. paints or adhesives, under advised conditions. Nevertheless, for the sake of environmental protection, polymer dispersions and redispersible polymer powders should never be emitted into the environment and should not be put into (waste) water streams.

Workers should always refer to the corresponding Safety Data Sheet (Section 8 Exposure control/personal protection) before handling polymer dispersions or redispersible polymer powders and apply the recommended safety measures, e.g. dust masks when spray drying or using gloves when open handling.

According to the amended Annex II of REACH (Regulation (EU) 2020/878) after evaluation of each product a phrase can be added in Section 1 of the SDS depending on the outcome:

'This mixture does not contain nanoforms' or 'This mixture contains nanoforms'. If the specific nanoform has an impact on the overall classification of the product, it will be mentioned separately in section 3 of the SDS.

Please refer to Annex II below for further information on risk evaluations.

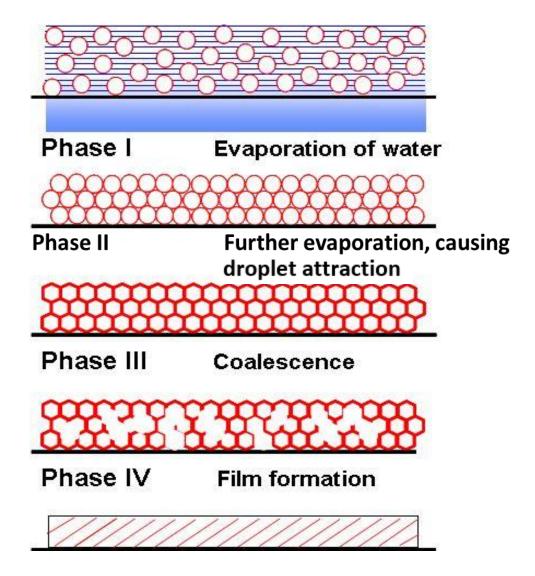
- The present position paper has been developed by EPDLA members in good faith, to the best of its knowledge and following the latest scientific evidence.
- The position paper is offered to all EPDLA members for further use. Each producer might add additional information in the communications towards customers, depending on the specific situation.
- Normal or reasonable foreseeable conditions of use of a polymer dispersion product are defined by the respective producer for each specific product. Polymer dispersions should always be applied as recommended by the producer.
- EPDLA commits to update this document in view of any new relevant available information.





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Annex I - Film forming process of polymer dispersions⁹



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⁹ 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).



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Annex II – European Union - Commission Recommendation, of 10.6.2022 on the definition of nanomaterial (2022/C 229/01)¹

Excerpt of the definition:

"'Nanomaterial' means a natural, incidental or manufactured material consisting of solid particles that are present, either on their own or as identifiable constituent particles in aggregates or agglomerates, and where 50 % or more of these particles in the number-based size distribution fulfil at least one of the following conditions:

(a) one or more external dimensions of the particle are in the size range 1 nm to 100 nm; However, a material with a specific surface area by volume of < 6 m2/cm3 shall not be considered a nanomaterial."

<u>EPDLA Conclusion:</u> Polymer dispersions and redispersed polymer powders are out of the scope of the EC Recommendation (**2022/C 229/01**). The polymer droplets are dispersed in water, embedded and stabilized in the liquid matrix. The existence of the waterborne environment is a prerequisite for the polymer droplets to exist. The dispersed phase wouldn't be stable without the other. Moreover during further processing the polymer particles will converge to form a continuous film or matrix via coalescence.

The recommendation also clearly states that "The definition should exclude non-solid (i.e. liquid and gaseous) particles, i.e. polymer dispersions with melting point below 25°C (determined via MFFT). This should ensure that the highly dynamic nature of the external dimensions of non-solid particles, such as micelles or nanoscale droplets in emulsions or sprays does not prevent the use of the external dimension as the defining qualifier in the definition."

Due to their particle size in the micrometer range, most redispersible polymer powders are out of the scope of the EC Recommendation (2022/C 229/01).

For more information please contact:

Eleonora Mancinelli, Secretary General, EPDLA, + 32. 492345072 or elm@cefic.be.

About EPDLA

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