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Conductive Screen Printing Inks by Gelation of Graphene Dispersions

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This paper describes the gelation of highly concentrated graphene/polymer dispersions triggered by mild heating. The gel formation is only dependent on the concentration of graphene with 3.25 mg mL^{-1} as the minimum value for graphene network formation. The graphene gel is then utilized for the preparation of colloidally stable and highly concentrated (52 mg mL^{-1}) graphene pastes that demonstrate excellent performance in screen printing down to lines of $40 \text{ }\mu\text{m}$ in width. Printed patterns dried at $100 \text{ }^{\circ}\text{C}$ for only 5 min exhibit sheet resistances of $30 \text{ }\Omega \square^{-1}$ at $25 \text{ }\mu\text{m}$ thickness, thus, removing the need for long-time high temperature annealing, doping, or other treatments. Such a low drying temperature, high printing definition, and compatibility with industrially relevant plastic and paper substrates brings high-volume roll-to-roll application in printed flexible electronics within reach.

vital^[25] as it facilitates thick layers (of up to $100 \text{ }\mu\text{m}$) in a single pass, however, at the expense of a lower printing definition.

Following screen printing typically post-treatments such as drying, annealing, or top-coating are employed to maximize conductivities. The conditions of post-treatment define the substrate that can be used for printing. For example, ink annealing at $250 \text{ }^{\circ}\text{C}$ and higher for 30 min^[18,24,25] significantly limits the range of suitable substrates and fundamentally limits high speed R2R industrial realization. Thus, the design of graphene inks that meet the requirements of current R2R applications is still to be accomplished.

There are several reports on the preparation of graphene-based inks comprising either graphene oxide (GO),^[17,19,23,27–30] or graphite exfoliated with^[13,16,18,22,24,25] and without^[20] surface active agents. The preparation of inks based on GO is relatively simple. However, due to the low conductivity of GO these inks require harsh post-treatments that make them less relevant to industrial applications. Liquid-phase exfoliation of graphite with or without surfactant by ultrasonication,^[20,31–34] or high-shear mixing^[22,35] is a flexible, and in the latter case a scalable manufacturing approach.^[35] Nevertheless prolonged high shearing still requires separation of nonexfoliated graphite while the resulting dispersions consist mainly of small ($<500 \text{ nm}$) graphene sheets.^[33,34,36] Hence the quality^[20] is far from the one obtained by micromechanical cleavage.^[37] In contrast, expanded graphite (EG) demonstrates much better dispersibility than graphite due to significantly weakened van der Waals interactions on account of an increased distance between the layers.^[13,38–40] This results in much shorter times and smaller energy input to obtain well-exfoliated concentrated dispersions of typically large ($>1 \text{ }\mu\text{m}$) flake graphene.^[39,41] Colloidal stability, however, as for the exfoliation of graphite, requires the presence of surface active agents and can be adjusted accordingly. The quality of graphene in EG depends on the precursor used for expansion. For instance, EG obtained from GO exhibits a highly defective structure,^[41,42] whereas EG obtained from either donor- or acceptor-type intercalation compounds (IC) exhibits a much smaller amount of defects and, thus, is more suitable for highly conductive inks.^[39–41]

One of the approaches for ink preparation comprises stabilization of graphene dispersions by surfactants or surface active polymers on account of charge or van der Waals repulsion. This stabilization has been studied and reported by many research

1. Introduction

Low-cost high-throughput printing of solution processed electronics is a rapidly expanding field that already encompasses many large-scale applications such as roll-to-roll (R2R) printed solar cells,^[1–5] including current collecting grids,^[5,6] displays,^[7–9] and radio frequency identification devices.^[10–12] Current developments in the field result in the fabrication of devices with outstanding properties such as recyclability, flexibility, and light weight. Here, solution-processed graphene holds considerable promise for printed electronics as it is widely available, inexpensive, flexible, and most importantly, highly conductive. One may already distinguish graphene printing as a separate emerging field of printed electronics that comprises inkjet printing,^[13–22] gravure printing,^[23,24] and screen printing^[25,26] techniques. While inkjet^[18] and gravure^[24] printings of graphene offer patterning at high definition, screen printing shows the greatest potential for applications where low resistances are

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groups around the globe demonstrating its high application potential.^[13,14,16–18,24] However, this approach is not the only one. For example, a significant increase of the dispersion viscosity, which can be achieved via gelation, will minimize particle mobility. This gelation route has been applied to Ag-based inks,^[43] metal oxide nanoparticle dispersions,^[44–46] and GO dispersions,^[47] but not yet for nonfunctionalized graphene dispersions.

In this paper, we describe, the gelation of highly concentrated graphene dispersions for the preparation of colloiddally stable high-volume fraction graphene pastes. Moreover, the use of EG prepared from an acceptor-type IC of graphite as the graphene source is advocated due to its high quality and almost effortless dispersibility. We implemented the gelation process to formulate a graphene paste for screen printing applications designed for typical mesh screens for Ag-based inks, and tested the printing definition, morphology, and conductive properties of printed patterns. To the best of our knowledge, this is the first report on gelation in graphene dispersions opening a route to a simple, cost-effective, and up-scalable method for 2D materials ink preparation and deposition.

2. Results and Discussion

Exfoliation of graphite starts with acceptor-type intercalation followed by thermal expansion and high-shear mixing (see the Supporting Information) as shown in **Figure 1a**. The remarkable feature of the intercalation step is its reversibility,^[39,48–50] that in combination with subsequent thermal expansion allows

an increase in interlayer distance with a minimum amount of defects introduced in the graphene sheets.

Changes to the material during processing were monitored by C_{1s} X-ray photoelectron spectroscopy (XPS, **Figure 1b**) and Raman spectroscopy (**Figure 1c**). The XPS spectrum of starting graphite shows only the characteristic asymmetric peak of sp^2 carbon. However, in the spectrum of the graphite intercalation compound (GIC), along with the peak of sp^2 carbon that can be fitted with the reference spectrum, we clearly observe the presence of another peak that is attributed to the C–OR single bond,^[51,52] where R might be either hydrogen or a residue of the intercalant. The C_{1s} spectrum of thermally EG shows only one major sp^2 carbon component. Interestingly, we did not observe the presence of a sp^3 carbon component verifying that intercalation and thermal expansion proceeds without breaking of the σ -bonds. The remaining minor components seen in the spectrum might be originating from either residual functional groups present on the graphene due to incomplete microwave-assisted expansion or from adventitious carbon^[51] deposited during sample processing. Similar conclusions are obtained by Raman spectroscopy (**Figure 1c**). The raw graphite source has a typical spectrum as also reported by others^[37,49,53] with the ratio $I(D)/I(G)$ between zero in the plane and ≈ 0.1 – 0.2 when measured on edges and at grain boundaries. The intercalation leads to an increase of $I(D)$ and $I(D')$, where the $I(D)/I(G)$ ratio reaches 0.8 – 1.0 , indicating an increase in charge scattering sites or defects within the graphene planes. Charge transfer from the graphite matrix also causes a significant shift of the G-band to 1612 – 1618 cm^{-1} .^[50] After thermal expansion, however, the Raman spectrum closely resembles raw graphite with

Figure 1. Preparation of graphene dispersion starting from raw graphite. a) Scheme of i) graphite intercalation, ii) thermal expansion of GIC, iii) preparation of graphene dispersion and subsequent gelation; b) C_{1s} X-ray photoelectron spectra of (from left to right) starting graphite, GIC, and EG; c) Raman spectra (633 nm) of (from bottom to top) graphite, GIC, and EG.

a $I(D)/I(G)$ ratio of about 0.1–0.2 demonstrating almost complete restoration of the initial properties. (Due to the structure of EG no in-plane spectrum can be reliably measured as many edges will be always present within the probed area). From both XPS and Raman analyses it is concluded that the obtained EG has very few defects and that intercalation is basically reversible. The quality of the EG, which can be readily dispersed, is comparable with, e.g., graphene obtained by prolonged ultrasonication of graphite.^[18,20,24,25,32–36,54] Taking into account the good dispersibility,^[13,39] and overall time and energy costs of preparation, the presented route seems to be competitive, if not advantageous, for large-scale preparation of graphene dispersions from graphite in particular due to the large sheet sizes (from 2 μm up to 10 μm) that are obtained when natural graphite is used as a source.

Dispersions containing EG and a copolymer of polyvinylpyrrolidone (PVP) and polyvinyl acetate (PVAc) (for simplicity further called binder) in isopropanol were prepared by high-shear mixing.^[13] These dispersions were found to thicken and eventually gelate upon mild heating as has been earlier reported for aluminum oxide and iron oxide particles.^[44] Interestingly,

without heating the liquid dispersions (Figure 2a) do not form a gel spontaneously. To investigate this phenomenon in detail we performed oscillatory shear rheological studies in a closed cell to prevent evaporation of the solvent. We probed gel formation at a sufficiently low strain ($\gamma = 0.001$) to keep the network intact.

Heating of a dispersion with a graphene concentration of 13 mg mL^{-1} and a graphene:binder mass ratio of 1:3 resulted in gel formation that is characterized by a drastic build-up of storage modulus up to 100 Pa with a gel onset temperature of $\approx 40 \pm 3^\circ\text{C}$ (Figure 2b, triangles). When keeping the gel at 75 $^\circ\text{C}$ we found no signs of gel structure degradation. This shows that the gel microstructure is thermally stable at least up to 75 $^\circ\text{C}$. A further increase of a temperature is not practical due to solvent boiling (boiling point of isopropanol is 82–83 $^\circ\text{C}$) that may disturb the network. After ageing for 400 s the gel was cooled down to 20 $^\circ\text{C}$. We observed no breakdown of the gel structure suggesting that the gel is stable upon cooling. The flow curve (Figure 2c) revealed that the gelled graphene network behaves as a pseudoplastic fluid with an apparent viscosity of more than 100 Pa s at low shear rates, e.g., 0.001 s^{-1} , and less than 1 Pa s at shear rate of 1 s^{-1} . The gel is stable for

Figure 2. Rheological behavior and gel formation for graphene dispersions with a concentration of 13 mg mL^{-1} and varying graphene-to-binder ratios a–c), i.e., 1:2 (squares), 1:3 (circles), and 1:4 (triangles). a) Shear viscosity curves for starting dispersions; b) storage moduli curves at constant strain $\gamma = 0.001$, and constant angular frequency $\omega = 6.28 \text{ rad s}^{-1}$ as functions of ageing time when subjected to a heating cycle (continuous line); c) shear viscosity curves for gelled dispersions, and with varying graphene concentrations d–f) i.e., 3.25 mg mL^{-1} (squares), 6.5 mg mL^{-1} (circles), 13 mg mL^{-1} (triangles with top up), and 26 mg mL^{-1} (triangles with top down) and graphene-to-binder ratio of 1:3. d) Shear viscosity curves for starting dispersions; e) Storage moduli curves at constant strain $\gamma = 0.001$, and constant angular frequency $\omega = 6.28 \text{ rad s}^{-1}$ as functions of ageing time when subjected to a heating cycle (continuous line); f) shear viscosity curves for gelled dispersions.

considerable time (up to several days), however, once a high shear is applied, e.g., by means of ultrasonication or high-shear mixing, the gel network is broken and a liquid dispersion again obtained. Interestingly, the gelation and consequent gel breakdown is repeatable for at least three times.

To investigate the influence of the polymeric binder on gel properties we analyzed samples with a constant graphene concentration of 13 mg mL^{-1} and varying graphene-to-binder ratios of 1:2, 1:3, and 1:4 (Figure 2a–c). Surprisingly, we did not observe significant differences, neither in storage moduli, nor in gel onset temperatures, between the various graphene:binder ratios. On the contrary, the consistency of the storage moduli curves, with almost identical gel onset temperatures, led us to the conclusion that the concentration of the binder does not play a critical role in gelation, except that the graphene-to-binder ratio must be kept equal or below 1:2 to maintain colloidal stability of the liquid dispersions for longer than a day. Above this ratio the dispersions are not stable, and agglomeration and phase separation rather than gel formation is observed.

To study the role of graphene in the gel formation process we analyzed samples with different graphene concentrations while keeping the graphene-to-binder ratio constant at 1:3 (Figure 2d–f). Oscillatory shear measurements revealed significant differences between the gel onset temperatures, as well as differences in storage moduli curves, proving the importance of the graphene concentration in the gelation process (Figure 2e). It can be seen that the gel onset temperature for the dispersions decreases and the storage modulus increases with increasing graphene concentration. In addition, viscosities for the starting dispersions (Figure 2d) and the corresponding gels (Figure 2f) at comparable shear rates are more than one order of magnitude higher. However, at high shear rates, for example, 100 s^{-1} , when the gel microstructure is broken down, viscosities of the starting dispersion and the gel fall back to the initial range.

We tentatively attribute the phenomenon of graphene gelation to polymer desorption induced–graphene interactions. In our system, we utilize a binder to exfoliate and stabilize the EG resulting in good colloidal stability of the final dispersions.^[13] While the mechanism of interaction between the co-polymer of PVP–PVAc and graphene is not fully understood, the stabilization effect is most likely achieved by steric hindrance of polymeric chains adsorbed on the surface of graphene. However, once heat is applied to the dispersion, partial desorption of the binder from the surface of graphene occurs thus reducing the surface coverage, and hence, increasing the possibilities for interaction between neighboring graphene sheets, while concomitantly increasing the concentration of polymer in solution. This, in turn, along with a sufficiently high particle mobility, large sheet size and small interparticle distances, leads to a partial destabilization of the colloidal system, forcing the graphene to minimize the surface energy by attaching to neighboring sheets. The latter process may be facilitated by depletion interactions.^[55–58] This results in partial overlap of the graphene sheets via attractive van der Waals forces leading to the formation of a 3D network. Gelation rather than agglomeration is ensured by the excessive presence of the polymer that still interacts with most of the graphene sheet surface. Hence, a relatively strong irreversible network of graphene sheets connected to each other is formed.

The observed strong dependence of gelation on the graphene concentration can be explained through overlap distance considerations. In general, the higher the graphene concentration, the higher the chance of overlap between two neighboring sheets with concomitant increase of interparticle interactions. In particular, we estimated the mean overlap distance for graphene dispersions using the radius of gyration and the mean interparticle distance as described in detail in the Supporting Information. Thus, for dispersions with concentrations of 26 and 13 mg mL^{-1} we obtained a mean overlap distance of 712 and 447 nm, respectively (Table S1, Supporting Information), suggesting that the graphene sheets indeed overlap, thereby facilitating attractive interparticle interactions. In the case of the graphene dispersion with a concentration of 3.25 mg mL^{-1} , that forms the weakest gel among the four dispersions (Figure 2e,f, squares), the mean overlap distance is estimated to be $\approx 309 \text{ nm}$ (see the Supporting Information) and this is the smallest value within the set, suggesting the weakest interparticle interaction. It also suggests that this concentration is close to the minimum gelation threshold value for these dispersions. While this tentative explanation is backed up with simple model considerations, further proof, either by experiments or by modeling is necessary, but outside the scope of the present paper.

Blank experiments for binder solutions without graphene showed no evidence of thickening or gel formation (Figures S1a, S1b, and S2, Supporting Information). This again confirms the primary role of graphene in the gel formation processes.

Gelated graphene dispersions, referred to from here onward as gels, can be dried in air without a significant shrinkage being observed. To investigate the gel microstructure we performed cross-sectional scanning electron microscopy (SEM) of the gel prepared from 13 mg mL^{-1} graphene dispersion with a graphene-to-binder ratio of 1:3 (Figure 3; Figure S3 (Supporting Information)). For this gel a uniform network of partially overlapping graphene sheets without any apparent preferential orientation is observed, similar to GO-based gels.^[47,59,60] Raman spectra of printed and dried layers (data not shown) indicate that the material consists mainly of few layer graphene.

As discussed above, the graphene gel demonstrates shear thinning behavior with structure restoration after mild shear, i.e., $<10 \text{ s}^{-1}$, and structure breakdown at high shear rates, i.e., 100 s^{-1} . Such properties are very desirable in many applications such as printing, as shear thinning enables the deposition of material at low viscosity into a pattern of interest as long as it is flowing. However, once the shear is removed the ink stops to flow and, thus, excessive spreading on the substrate is avoided leading to a good print definition. The gel described in this paper has high viscosity at high graphene content, thus it holds great promise as an ink for screen printing. However, the solvent (isopropanol) used for exfoliation and gelation is not suitable for screen printing purposes due to its low boiling point and high evaporation rate. Therefore, we performed an exchange^[16,61] of the gel solvent from isopropanol to the methyl ether of dipropylene glycol (DPM) to prepare a suitable screen printing ink. DPM is an environmentally safe industrial solvent combining both hydrophobic and hydrophilic properties. More importantly, it is fully compatible with our formulation and has a boiling point of 190°C , enabling screen printing of graphene

Figure 3. Scanning electron micrographs of dried graphene gel (cross-section). a) An overview; b) high magnification micrograph.

without ink drying on the screen. Notably, the final viscosity of the resulting ink (graphene paste) can be tuned by the amount of DPM that is added during solvent exchange.

Modern screen printing equipment can process various inks within a wide range of viscosities: from low viscosity inks to highly viscous pastes. The example in **Figure 4a** of a highly viscous ink (paste is a more appropriate term) with exchanged solvent demonstrates shear thinning behavior within the range of 300–1 Pa s at shear of 5 s⁻¹ and is considered suitable for screen printing. This stable paste has a glossy and uniform surface and can hold its shape after being mildly sheared (**Figure 4b**). Experimentally, we found that the most suitable formulation for screen printing paste preparation starts from a dispersion with a graphene concentration of 13 mg mL⁻¹ and a graphene-to-binder ratio of 1:3 in isopropanol. The first reason for this specific composition is that the starting dispersion has a relatively low viscosity and, thus, is readily processable by high-shear mixing. Second, the graphene-to-binder ratio of 1:3

ensures a high exfoliation efficiency and good colloidal stability of the dispersion. Third, a higher amount of binder (e.g., 1:4) will lead to a decrease in the inks conductive properties due to the insulating properties of the polymer.

We successfully printed our formulated graphene paste with a graphene concentration of 52 mg mL⁻¹ in DPM into test patterns using a semiautomatic screen printer (DEK) and a 40/25 mesh emulsion test screens. We demonstrated the possibility to print large area patterns on both poly(ethylene terephthalate) (PET) foils (**Figure 4c**) and on special application paper (**Figures S4 and S5**, Supporting Information). The printing tests showed that print lines as thin as 40 μm (**Figure S6** (Supporting Information), 2 μm thick) can be reproducibly realized with a typical woven mesh screen (not optimized for graphene inks) used in industry, essentially verifying the high printing definition. We also printed test patterns with an array of lines separated by open spaces (**Figure 4d**; **Figures S7 and S8**, Supporting Information). Again, no significant line protrusion or overlap (due to ink spreading) was found, confirming the high printing definition. Using SEM, large-area graphene printed structures were analyzed in detail. In **Figure 4e,f**, it can be seen that the graphene paste covers the surface uniformly giving rise to a dense layer of 2D sheets. Remarkably, in **Figure 4f** it is clearly seen that the graphene sheets organize into a tile-like structure, close to what would be expected from the stacking of 2D platelets.

The printed structures were dried in a conventional oven at 80–100 °C for several minutes. Such a mild thermal post-treatment shows neither binder degradation nor any other adverse effect. Dried structures can withstand sticky-tape pull-off tests demonstrating good substrate adhesion and layer cohesion suggesting that the binder is distributed uniformly. We performed four-point probe sheet resistance (R_s) measurements for films dried at 100 °C for 5 min and found that printed layers demonstrate an R_s of 30 Ω □⁻¹ extrapolated to a thickness of 25 μm (see **Table S3** in the Supporting Information). Such good performance renders the described graphene paste, which only contains graphene, binder, and solvent (no dopants!), an alternative to already existing graphene ink formulations;^[18,24,25] especially after taking into account the simplicity of ink preparation, absence of centrifugation steps, and high performance already after drying at 100 °C. The mild post-treatment conditions bring graphene inks closer to high-speed R2R application, thus, opening the route for large-scale perspectives.

3. Conclusion

In summary, we describe an approach for graphene dispersion preparation utilizing the intercalation of graphite that is basically reversible in nature, followed by thermal expansion as an intermediate step. EG, the precursor for the dispersion preparation, exhibits a very small number of defects, as proven by Raman scattering and XPS, which is responsible for the preservation of its initial electrical properties. Highly concentrated graphene dispersions are prepared by high-shear mixing in the presence of a polymeric binder. We have, we believe, for the first time, demonstrated and described the gelation of graphene/binder dispersions triggered by mild heating. We hypothesize that the polymer desorption is the driving force

Figure 4. Graphene paste and screen printing results. a) Shear viscosity of graphene paste (52 mg mL^{-1} in DPM); b) image of graphene paste on a spatula; c) bent PET foil with a test pattern screen printed with graphene paste; d) SEM image of an array of lines screen printed with graphene paste, scale bar is $500 \mu\text{m}$; SEM images of large-area prints at e) $500\times$ magnification; f) $5000\times$ magnification. In Figure 4d, the wavy features between the graphene (black) lines originate from charging of the polymer substrate.

for gel formation, and it is shown that the graphene concentration plays a crucial role in this process. By a solvent exchange procedure, we utilized the gelled dispersion to prepare highly concentrated, environmentally friendly^[62] and colloiddally stable graphene pastes (52 mg mL^{-1} in DPM) that show excellent performance in screen printing. We demonstrated that the paste has excellent screen printability down to lines of $40 \mu\text{m}$ in width as well as for more complex structures. Most importantly, printed patterns dried at 100°C for only 5 min exhibit sheet resistances of $30 \Omega \square^{-1}$ at $25 \mu\text{m}$ thus removing the need for long-time high temperature annealing, doping, and other treatments. Such a low drying temperature, in combination with the low solvent evaporation rate at printing temperatures ($20\text{--}25^\circ\text{C}$), makes printing and drying feasible by high-volume roll-to-roll applications. The formulation is fully compatible with industrially relevant substrates, such as PET foil and paper, thus extending the possible application range even further.

4. Experimental Section

Preparation of Graphene Dispersion by High-Shear Mixing: 6 g of EG (13 mg mL^{-1} dispersion) was added to a 1 l glass cylinder with a diameter of 80 mm containing 450 mL of isopropanol and 18 g of a 60:40 copolymer of *N*-vinyl-2-pyrrolidone and vinyl acetate (Plasdone S-630, Ashland Inc., USA) to constitute graphene:binder weight ratio of 1:3.^[13] The thick slurry was subjected to high-shear mixing^[35] by means of a Ystral T2001 (2000 W) apparatus (Ystral GmbH, Germany) using a 35 mm diameter internal stator and a 25 mm diameter internal rotor at 2000–7000 rpm for 1 h. The high-shear mixing was carried out under constant cooling with iced water. Within a few minutes of mixing at 2000 rpm the slurry converts into a homogeneous dispersion, which is

then subjected to treatment at 7000 rpm. The obtained dispersions were used without any further treatments.

Gelation and Solvent Exchange of Graphene Dispersion: The gelation and in situ solvent exchange was performed using Heidolph Hei-VAP Precision rotary evaporator (Heidolph Instruments GmbH, Germany). In a typical experiment 100 mL of graphene dispersion were transferred into 250 mL round-bottom flask followed by addition of 25 mL of methyl ether of dipropylene glycol (Dowanol DPM, Sigma Aldrich, USA). The dispersion was then evaporated at 73°C and 400 mbar until no distillate was pouring into the receiver flask. The residue, thick homogeneous paste was transferred to a container by a spatula and used without any further treatment.

Screen Printing of Graphene Paste: Screen printing was performed using DEK Horizon 03i (DEK International, UK) semiautomatic screen printer with a 45° angle polyurethane squeegee, at a printing speed of 50 mm s^{-1} . We used woven 40/25 mesh emulsion screens with patterned areas of $160 \times 160 \text{ mm}$ and smallest features of $20 \mu\text{m}$. As printing substrates special application paper LumiForte (Stora Enso, Finland) and PET foil (Agfa, Belgium) were employed.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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- [62] By this statement, we, to the best of our knowledge, refer to the conformity of Plasdene S630 (copolymer of *N*-vinyl-2-pyrrolidone and vinyl acetate) to U.S. Pharmacopeia (USP) and The European Pharmacopoeia (Ph.Eur.) standards. Methyl ether of dipropylene glycol used as a solvent is classified as "Not a hazardous substance or mixture according to Regulation (EC) No. 1272/2008" as well as "this substance is not classified as dangerous according to Directive 67/548/EEC".