Organic polymer treatment - the way to modern pigments

A characteristic of “modern” pigments is that they exhibit either novel properties or a much improved performance as compared to conventional products. These special features may be associated with special colour effects, but are more often related to superior handling and processing properties of the pigment as well as long-term performance. This includes improvements in low tendency of dusting, ease of dispersing in combination with reduced flocculation, compatibility with organic and aqueous media, consistency of colour, stability against chemical and environmental exposure. To attain these properties, one approach is an organic polymer surface treatment of the pigments.

There are a number of ways of polymer deposition on the pigment surface, as summarised in Figure 1.

Polymer adsorption

Adsorptive pigment treatment is commonly used for most of the stabilisers which are available on the market [1, 2]. This surface treatment may be done directly during the pigment manufacture, or subsequently in a separate processing step. When the polymeric additive comes into contact with the pigment surface in a pigment dispersion or in a finished coating formulation, these macromolecules can be adsorbed at the pigment surface; the resulting adsorption layer is bonded to the pigment surface either physically (reversibly) or chemically (irreversibly).

Chemisorption - stable, but often too thin

In chemisorption, the polymer is attached to the pigment surface by a covalent bond; typically, this produces only a thin, monomolecular polymer layer which is usually not thick enough or too loosely packed in order to ensure proper screening of the pigment surface and efficient resistance to flocculation. Different possibilities for the anchorage and conformation of polymer molecules on the pigment surface are illustrated schematically in Figure 2.

Physisorbed substances may be displaced

A polymer layer which is adsorbed physically, by means of electrostatic or van der Waals forces, can be obtained much thicker and may be composed of several “layers” of molecules; however, a physisorbed layer is less firmly bonded to the pigment surface and can be displaced by the binder polymer or other components of the coating formulation as a result of competing adsorption. Physically bonded polymer layers are not particularly resistant to shear either, which means that this can impair the quality of the polymer layer.

Simple treatment, broad application

However, the simplicity and relatively low cost of adsorptive polymer treatment of pigments are undisputed, and in many cases it is beneficial in dispersing and stabilising pigments. The broad range of commercially available polymer stabilisers often allows to select this additive specifically in such a way as to give the pigment surface a desired charge or produce a particular type of stabilising effect (electrostatic, steric or electrosteric). To achieve further effects, different and special methods of pigment surface treatment have to be applied.

Polymer grafting

Modifying pigments by polymer grafting is a relatively complex matter and can in principle be performed by various techniques (“grafting from” and “grafting onto”) and polymerisation methods [3, 4].

Complete dispersion is necessary

A precondition for the applicability of the grafting is that the pigment particles must be in a completely dispersed state which is free of flocculation during the treatment. The grafting-from method requires an initiator which is attached to the pigment surface or indeed an immobilised catalyst. Because an immobilised initiator/catalyst, and, of course, a monomer are required, there are a number of ways of conducting the polymerisation reaction at the pigment surface:

Atom transfer radical polymerisation (ATRP [5]) is one example of a surface treatment of this kind. The polymerisation may last for minutes or hours, and the surface treatment ends in the usual steps of separation and clean-up. The grafting-onto method appears less suitable, for practical reasons.

The same requirement of completely dispersing the pigment beforehand applies to (micro)emulsion polymerisations [3]; this is usually realized by means of low-molecular wetting agents and stabilisers which may also be incorporated later by polymerisation. The monomer is dispersed with the aid of an emulsifier and applied in the disperse state to the pigment surface, where free-radical polymerisation is initiated and proceeds.

Customised pigments

The relatively high efforts and costs of polymer grafting, as compared with chemisorption or physisorption, are only justified if a substantially better quality of product is attained in the end. Completely encapsulating the pigment particles and hence providing an efficient barrier to external influences, a protection against mechanical damage, or tailored hydrophobicity or hydrophilicity in the pigment surface may justify this expense in individual cases.

Polymer precipitation

Another option for organically modifying pigments is that of precipitating the polymers onto the pigment surface. Polymer precipitation may be achieved by thermodynamic, chemical or physical means. Polymer precipitation which is controlled thermodynamically, by varying the temperature, is regarded as an innovation with great potential, because of its simple application and versatility. The principles can be seen from the diagram in Figure 3, showing the phase behaviour of polymers in solution as a function of concentration and temperature; the encapsulating of a pigment dispersed in a polymer solution as achieved by use of the lower critical solution temperature (LCST), is schematically illustrated in Figure 4.

Thermodynamics rule

The concentration and temperature ranges of complete solubility of a polymer in a solvent and demixing of a polymer solution are determined by the molecular polymer/polymer and polymer/solvent interactions; the ratio of entropic and enthalpic contributions to the free energy of mixing determines the phase behaviour, i.e., if the polymer is soluble over the entire range of concentrations, or if there
is a miscibility gap.

**Making use of cloud points**

If a polymer solution demixes when the temperature is raised (cloud point or lower critical solution temperature, LCST), this behaviour can be exploited to encapsulate the pigment particles [6-8]. The homogeneous polymer solution, shown at temperature T1 in Figure 4 (polymers are dissolved as individual coils at lower polymer concentration, or in entangled form at higher concentration) demixes if the temperature is raised to T2; theoretically two polymer phases are formed, with polymer volume fractions φ1 and φ2, are formed. However, the large surface area of the pigment dispersed in the system causes the polymer to be precipitated onto the pigment at the same time as the phase separation occurs, with the result that the polymer solution is severely depleted of polymer if the LCST is exceeded. Accordingly, if a polymer demixes when the temperature is lowered (upper critical solution temperature or UCST behaviour, cf. Figure 3), this can also be used for the surface treatment of pigment particles [7, 9].

**Precipitation in water or organic solvents**

The respective LCST and UCST values are dependent on the polymer (structure and molecular weight) and solvent used, and can be varied further by altering the polymer concentration and, as far as aqueous systems are concerned, by the ionic strength of the solution. Depending on the type of polymer and its molecular weight, precipitation in water can be realized in a temperature range from 1°C to 80/90°C under standard atmospheric conditions; generally speaking and as to organic solvents, the limitations are set by the freezing and boiling temperatures of the respective solvent system. The film thickness of the polymer encapsulating the pigment particles may be adjusted from a few nm to as much as 0.5 µm or more. To achieve this, it is a simple matter to use shear forces or repeated precipitation steps in addition to altering the polymer concentration.

**Crosslinks fix the polymer coating**

If no additional measures are taken, the precipitated polymer layer is only bonded to the pigment surface to a limited extent and for a limited time period, as in the case of a solubilisation. The polymer layer can be permanently fixed by way of active groups or by crosslinking the polymer molecules using a condensation or addition reaction.

The AFM images in Figures 5 and 6 show a polymer layer which has been precipitated from a single pigment particle: water by exceeding the LCST: Figure 5 shows the non-crosslinked and Figure 6 the crosslinked polymer film. Both pictures have been taken before (a) and after (b) the non-crosslinked and crosslinked polymer films have been exposed to (rinsed with) water.

The images clearly exhibit that on precipitation, in addition to a continuous polymer base layer, the LCST polymers feature island-like relief structures; the shape and frequency of these structures and the topology of the layer surface, among other parameters, depend on the crosslinking of the precipitated polymer as well as on other parameters (compare Figure 5a with Figure 6a). In the case of polymers which have not undergone crosslinking, rinsing them with water resulted in the pigment islands being gradually removed, first leading to a smooth surface (Figure 5b) and finally wearing away of the base layer. In the case of the crosslinked layer, the polymer islands and surface roughness are maintained despite the exposure to water.

**Chemical precipitation for unstructured pigment coatings**

The polymers can also be made to precipitate onto the pigment surface chemically, e.g., by solvolysis [10] or the use of poor solvents [11]. If a polymer contains derivatised hydroxy and/or carboxy groups, these can be solvolysed and the polymer thus converted to a form with reduced solubility. Adding a poor solvent to a polymer solution causes the polymer to precipitate out of the solution, as a result of the reduction in the solvent quality. Both methods can be used to encapsulate the pigment surface with a polymer: contrary to the LCST or UCST method, no or only negligible surface structures are formed. This is because no special phase separation initially resulting in two phases of lower and higher concentrated polymer solution occurs, followed by the collapse of the entangled polymer coils of the concentrated solution and the polymer adsorbed on the pigment surface, as it is assumed to be the case with the LCST and UCST treatment.

Pigments can also be coated by precipitation using polymers in an aerosol, melt or solution. There are numerous variants, described in the patent literature, for performing this procedure. A pigment may for example be encapsulated by the polymer directly in a molten polymer, or by way of extrusion or in a polymer slurry in which the temperature is raised above the melting point of the polymer [12]. These methods of precipitation of polymers on particle surfaces have already been known for a considerable time for organic pigment treatment, but they only allow a limited adjustment of the film thickness of the polymeric pigment coating, and no immobilisation. They do not generate the surface structures which are important in the stabilising action.

**Easy processing**

The precipitative procedures are easy to perform and are user-friendly. The profiles and improvements to the properties of the pigments that can be obtained by this type of polymer coating are numerous: they can be used to come up with pigments which are dust-free, suitable for making pastes, easily dispersed and resistant to flocculation. As a result of creating an efficient polymer barrier, the pigment can be protected against external influences and mechanical stress. The pigment surface can be given a desired degree of hydrophility or hydrophobicity, and so provide compatibility with a particular matrix. The precipitated polymer is also suitable as a medium for precipitating other substances onto the pigment surface, so that the pigment can be given a particular functionality or property. The examples given above illustrate how controlled surface modification with polymers is suited to turn a conventional pigment into a modern pigment.

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**References**


LIFELINES

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Figure 1: Methods of surface treatment of pigments with organic polymer coatings:
LCST: lower critical solution temperature; UCST: upper critical solution temperature

Figure 2: Possible conformation and attachment of macromolecules on the pigment surface
Figure 3: Schematic phase diagram of a polymer solution showing lower and upper critical solution temperature (LCST and UCST).

Figure 4: Encapsulating a pigment by polymer precipitation, using the principle of the lower critical solution temperature (LCST): When the temperature is raised from T1 to T2, demixing into two phases with polymer volume fractions Phi1 and Phi2 occurs; this leads to deposition of the polymer onto the pigment surface (optionally with subsequent crosslinking).
Figure 5: AFM image of a poly(oxyethylene) based LCST polymer as precipitated to a SiO2 wafer by exceeding the LCST; a) before and b) after treatment with water at a temperature 10°C above the LCST value.

Figure 6: AFM image of an LCST polymer as precipitated to a SiO2 wafer by exceeding the LCST and subsequently crosslinked; a) before and b) after treatment with water at a temperature 10°C above the LCST value.