The Rate of Solvent Action on Modern Oil Paint

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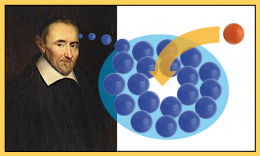

Process of dissolution

In the early 17th century the frech philosopher and scientist Pierre Gassendi (1592-1655) developed a concept to describe the process of dissolution based on the atomic theory by Epicurus. He formulated the idea, that dissolution of a material depends on the cavity formation within the solvent to distribute the material particle (solute molecule) into the liquid. Until today, this a fundamental concept in modern dissolution theories. The energy required to separate the solvent molecules is called cavitation energy and corresponds to the cohesive energy of the solvent.

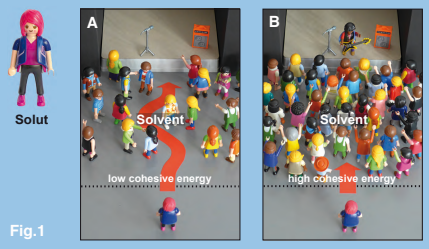

Fig.1

The rate of swelling and dissolution

The thermodynamics are the basis of modern dissolutionfon concepts where the process of dissolution is described by the change in enthalpie and entropy. The enthalpy describes the intermolecular interaction between the polymer molecules and the solvent. The solvation properties defines the range of polarity wherein a specific material can be dissolved (solvent groups in the figures). Over this the rate of dissolution depends on the entropy change what discribes the distribution of the material molecule (solut) into the liquid. This process is influenced by the cohesive energy of the solvent. This can be visualised with a simple analogy **(Fig.1)**. Möchte man als Konzertbesucher an die Bühne gelangen, geht dies einfacher, wenn nur wenige Leute im Raum sind (**Fig 1A**). Mit zunehmender Besucherzahl nimmt die Kohäsionsenergie der Menschenmenge stetig zu. Nun muss man sehr viel mehr Energie aufwenden, um die Leute zur Seite zu drängen, damit man Platz für sich selbst schaffen kann (Abb. 1B). Das Gleiche gilt für Polymermoleküle, die sich in das Lösemittel verteilen wollen. In consequence the rate of swelling and dissolution dependant on the cohesive energy of the solvent. Thus it is given by the vapour pressure of the liquid.

Solvent action on modern oil paint

Modern oil paints have a paint formulation that is distinctly different to classical oil paint systems. One aspect relates to the use of synthetic organic pigments (SOP) in most contemporary artists- and house paint products. Oil paint showing a complex ageing process. Of particular relevance are oxidative cross-linking reactions, oxidative fragmentations, hydrolysis, and carboxylate formation. It is well known that the soap formation process ant the ionic cross-linking of acidic molecules is essential to stabilise aged oil paints. The lack of multivalent ions in modern oil paints (containing organic colorants only), however, leads to a different ageing behaviour.

The swelling and leaching rate within the first few seconds of solvent immersion was investigated. The solvent sensitivity of a nine year old oil paint with different organic pigments (PV19:PR189) was compared to the behaviour of a saponified zinc white paint (PW4). The kinetic of swelling is essentially driven by the cohesive energy of solvent [1]. Within each solvent group the swelling rate increases with increasing solvent vapour pressure (hPa/25°C; x-axys in the diagrams) (**Fig.2**). But in particular the data show, that modern oil paint containing non-soluble synthetic organic pigments exhibits a very fast swelling rate (**Fig.2A**) that is not comparable to classical oil paint or saponified zinc white paint (**Fig.2B**). Within the fist 10 seconds an enormeous increase in volume was observed (**Fig.2C**). Parallel to the swelling behaviour the leaching rate is high. Since low molecular weight degradation products can not be stabilised by soap formations the extraction proscess is very fast (**Fig 3**). Generally modern oil paint are not comparable to classical oil paint. The high swelling rate explains the particular sensitivity of these paints to solvent interaction, as well as other effects observed during the cleaning with solvent soaked cotton swabs [2].

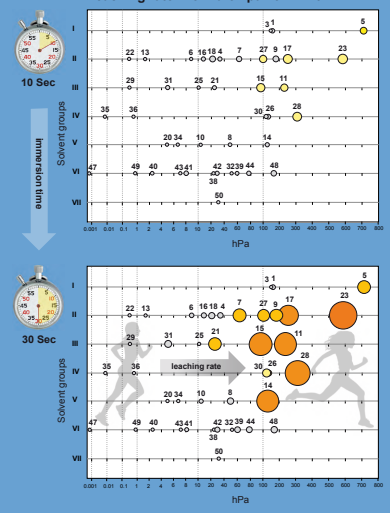

Figure 3: Leaching plot of aged oil paint [1]. Rate of extraction normalised to the solvent with the highest action (after 30 sec).

[1] Stefan Zumbühl, Nadim C. Scherrer, Nina L. Engel, Wolfgang Müller, The Kinetics of Dissolution of Varnishes – The Influence of Vapour Pressure on the Rate of Solvent Action, ICOM-CC 17th Triennial Conference Preprints, Melbourne 15-19 September, J. Bridgland (Ed.), Art. 1611, 11pages (2014).

[2] Diana Blumenroth, Stefan Zumbühl, Nadim C. Scherrer, Wolfgang Müller, Sensitivity of Modern Oil Paints to Solvents. Effects on Synthetic Organic Pigments, In: Issues in Contemporary Oil Paint, Van den Berg, K.J., Burnstock, A., de Keijzer, M., Krueger, J., Learner, T., de Tagle, A., Heydenreich, G. (Eds.), Springer Verlag (2014), 351-362.

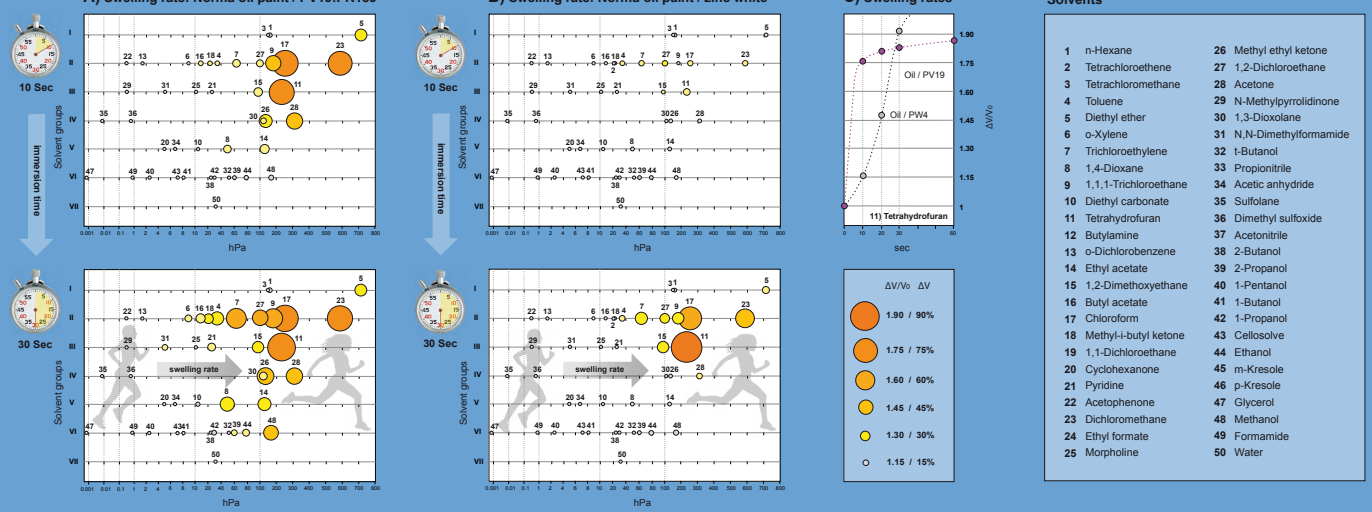

Figure 2: Swelling plot of two different 9 years old oil paint. The variably sized circles represent the volume change after 10 sec (upper) and 30 sec (lower) immersion time.

Publication to the general principle of solvent action: Stefan Zumbühl, „***Wie geht das?***" - Die Löslichkeit von Materialien: Teil II: Physikalische Grundlagen von Lösungsprozessen und Materiallöslichkeiten, Zeitschrift für Kunsttechnologie und Konservierung 31-2 (2017).

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