

APE Alternatives for Universal Pigment Concentrates

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1 Introduction

More than 450 000 tonnes/year of alkylphenol ethoxylates (APE's) are manufactured world-wide. This type of surfactant is used in a variety of applications, e. g. in the cleaning and detergent industry, agricultural applications, plastics, for use in domestic appliances and in the paper and pulp industry [1]. In the paint and coatings industry there are two application fields where they are used: as emulsifiers for the emulsion polymerisation process, and as dispersing additive for water-based pigment pastes. Usually these water-based pigment concentrates are manufactured for tinting a range of water-based decorative paints (acrylics, PVAc, low and high PVC paints, etc). Despite the fact that such pigment pastes often contain a significant percentage of glycols to improve performance, their universal usage is difficult, as explained in figure 1. Alkylphenol ethoxylates in principal enable the coatings industry to produce water-based pigment concentrates allowing tinting of water-based and solvent-based decorative paints. The use of so-called universal colorants is state of the art in the decorative paint industry [2].

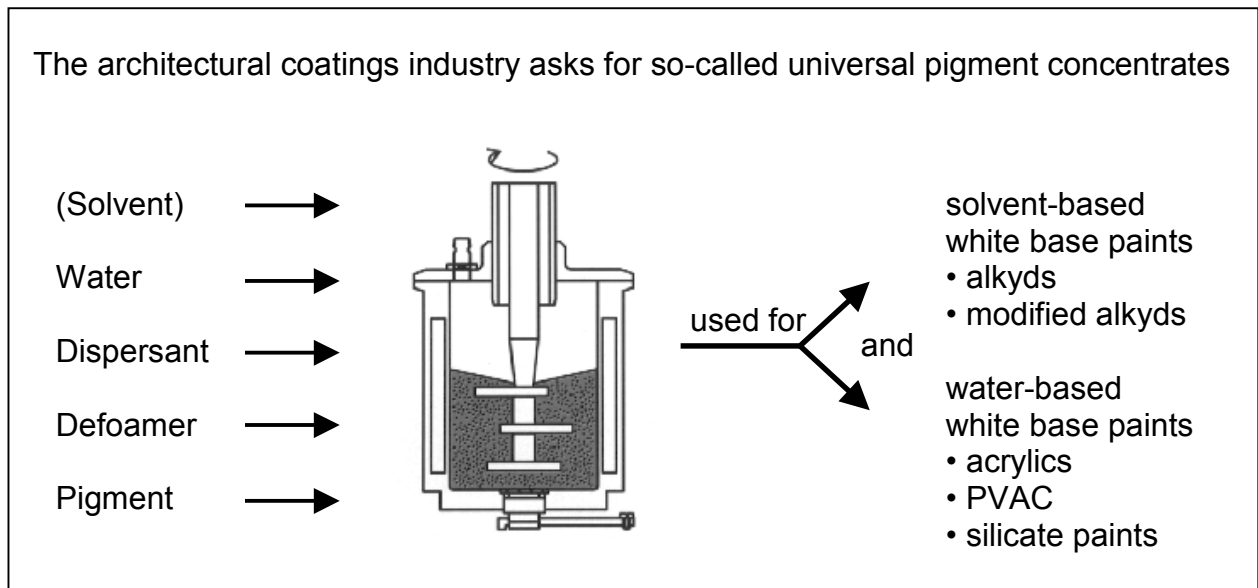


Figure 1: Manufacture of universal pigment concentrates

This paper will discuss a new class of dispersing additives which enables the coatings industry to formulate water-based pigment concentrates for universal tinting fulfilling the requirements of the coatings industry. Therefore they can be seen as an answer on legal requirements which will be imposed on the paint and coatings industry in order to regulate the use of APE's. It seems very likely that legislation will prohibit or limit the use of APE's in the future. The APE's used in the coatings industry are often nonylphenol ethoxylates (NPE's) with a degree of ethoxylation between 5 and 10 [4]. The main degradation products are the corresponding nonylphenol and ethylene glycol. Due to their persistence (further biochemical degradation to methane, carbon dioxide and water proceeds very slowly) nonylphenols will be stored up in sediments of polluted water [5].

Nonylphenols even at very low concentrations are toxic to aquatic organisms. Moreover, they are discussed because of their estrogen-like structure; in figure 2 they are compared with 17, β -estradiol, the most effective female hormone [1, 6-11].

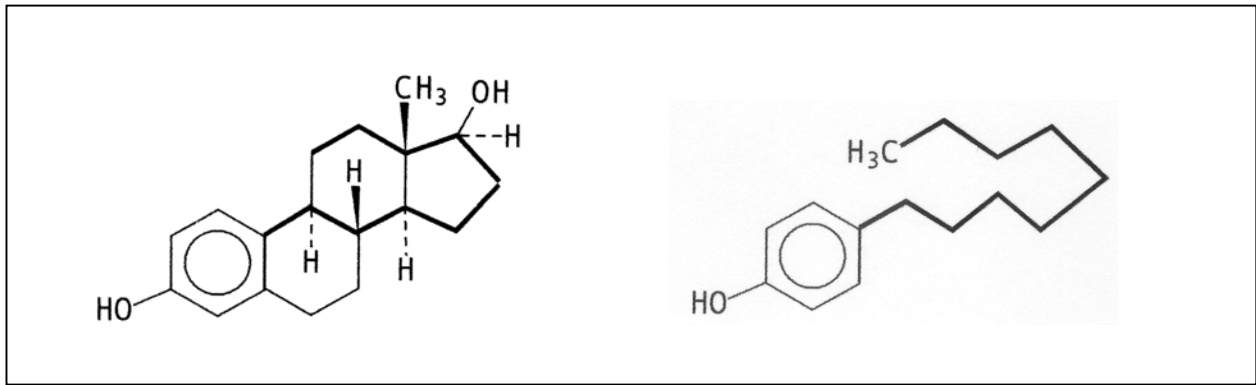


Figure 2: Comparison of 17,β-estradiol with nonylphenol

Therefore nonylphenols – the degradation products of NPE's – intervene in the fertility cycles of organisms, as proved for fish and mammals. The hypothetical impairment of human reproduction is not yet proved [12].

2 Chemistry of NPE's and their alternatives

Because of the problems discussed above there has been effort to reduce the volume of NPE's used in industry, e. g. the German cleaning and detergent industry has been working without NPE's voluntarily since 1986 [13]. However, with the exception of Scandinavia, the European coatings industry still works with significant quantities of NPE's. It can be expected that legislation will be established for the coatings industry in the next two to five years, reducing the amount of NPE's in Europe, North America and Canada significantly. Consequently, raw material suppliers have tried to develop alternatives to nonylphenol ethoxylates as dispersing additives in paste systems.

Apart from common fatty alcohol alkylene oxides [4, 14, 15] special GUERBET derivatives [16] have been promoted as suitable NPE alternatives. However, looking at the performance of the GUERBET's they are not able to be an equivalent dispersing and wetting additive compared with NPE's. Figure 3 shows the structure of a branched fatty alcohol derivative the so-called GUERBET:

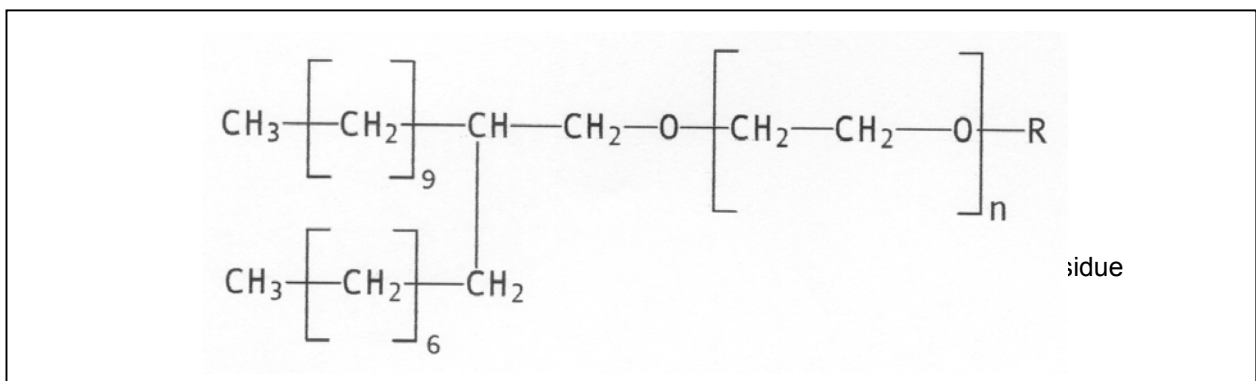


Figure 3: GUERBET derivatives

In the literature “intelligent” polymeric structures such as polyurethanes and polyacrylates are also mentioned as NPE replacements for water-based pigment concentrates [15,17]. Such polymeric chemistry is without doubt able to stabilize a

variety of pigments in a water-based phase [18]. However, when using these water-based concentrates in solvent-based paints (air-drying enamels etc) polymeric structures cannot fulfil the requirements such as:

- preventing pigment flocculation
- easy incorporation of the paste in the paint by hand-mixing
- fast colour strength development

Obviously, these polymers are solubilized from the pigment surface by the solvents used in the solvent-based decorative coatings. That means, in accordance with the definition of universal pigment concentrates (figure 1), that this polymeric chemistry cannot meet the demanded requirements of an universal dispersing additive.

The structure of nonylphenol ethoxylates and their anionic derivatives is given in figure 4.

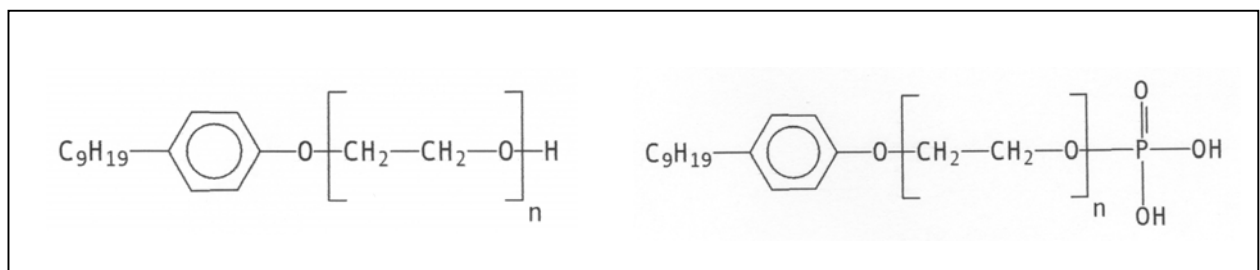


Figure 4: Non-ionic nonylphenol ethoxylate and corresponding phosphoric monoester

Comparing common fatty acid derivatives with NPE structures the additional aromatic structure of the NPE is thought to be the reason for the better overall performance of the NPE, as it gives the high pigment affinity particularly needed for organic pigments.

Approaching from this angle a new class of dispersing additives for pigment concentrates with universal use has been developed at Tego Chemie Service. One of the core technologies is the manufacture of polyethers which allow the block-wise synthesis of structures. Depending on the monomers and different chain lengths used for the polyether, different HLB values and chemical modifications can be realized. Normal polyethers are made using only ethylene oxide and propylene oxide, whereas Tego also makes use of other monomers such as styrene oxide. A non-ionic polyether structure as given in figure 5 has been synthesized.

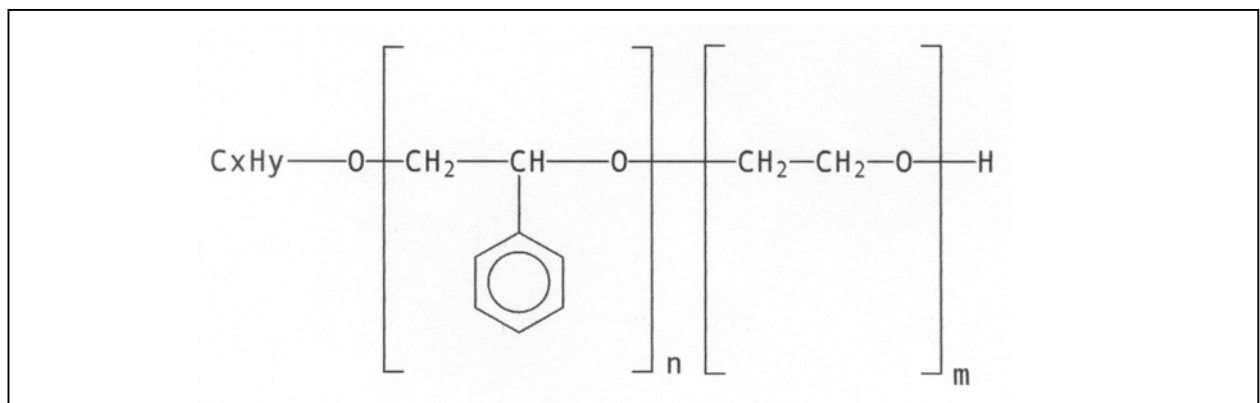


Figure 5: Non-ionic unique polyether structure

The hydrophilic-lipophilic balance of the molecule can be adjusted easily by modifying the hydrophobic block made from the aliphatic starting alcohol and styrene oxide in relation to the hydrophilic block made from the ethylene oxide chain.

The terminal OH group of the unique polyether (figure 5) can be functionalized easily, e. g. by aminosulphonic acid or by a phosphorylation reaction. By adding a phosphoric ester structure to the polyether, as shown in figure 6 for example, the molecule is given an additional option to work not only with the help of steric stabilisation but also by electrostatic repulsion when it is adsorbed on a pigment surface.

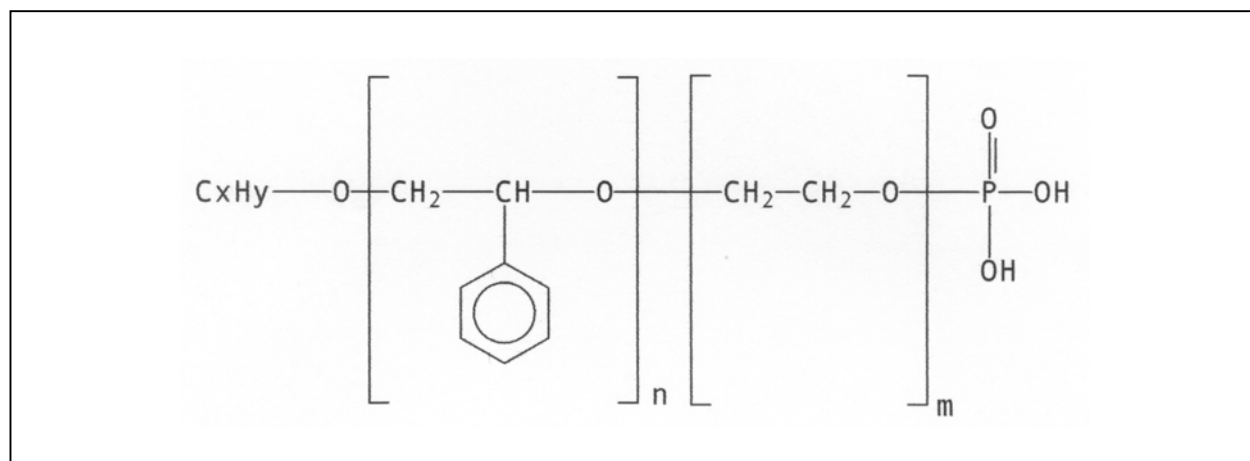


Figure 6: Phosphoric monoester of the unique polyether

Depending on the phosphating agent, the temperature and other reaction conditions used, the phosphorylation reaction gives a complex but defined mixture of monoester, diester, triester, free phosphoric acid and non-ionic polyether [19-21]. The ratio of these components plays a decisive role in the final performance of the anionic surfactant. For easy use the product has been neutralized and is available with a solid content of 35 %.

3. Tests results

3.1 Products and test systems

As mentioned in the introduction, non-ionic and anionic nonylphenoethoxylates (NPE's) still play an important role in the paint market. For this reason they were tested against the corresponding new wetting and dispersing additives. In the following charts the products will be named as shown in table 1.

For the evaluation of gloss, colour strength and viscosity four different pigment types were tested: iron oxide yellow (PY 42), iron oxide red (PR 101), phthalocyanine blue (PB 15:4) and carbon black (PBk 7).

The tinting was carried out in five different white bases:

Alkyd 1 = long oil alkyd, solvent-based,
 Alkyd 2 = PU-modified long oil alkyd, solvent-based
 Acrylic high gloss, water-based
 PVAc terpolymer, water-based
 PU modified acrylic, water-based

Table 1 Products tested

Product	Active matter content	Remarks
NPE non-ionic	100 %	Nonylphenol ethoxylate, 9 EO
Tego non-ionic	100 %	Modified polyether
NPE anionic	35 % in water	Nonylphenol ethoxylate ester
Tego anionic	35 % in water	Ester of a modified polyether

3.2 Test formulations

First of all the products were tested with a standard formulation as shown in table 2. For the iron oxide pigments both non-ionic wetting and dispersing additives were combined with an additional wetting and dispersing additive (dispersant 2) to reduce the mill base viscosity (see viscosity charts).

Table 2 Formulations for the pigment concentrates used

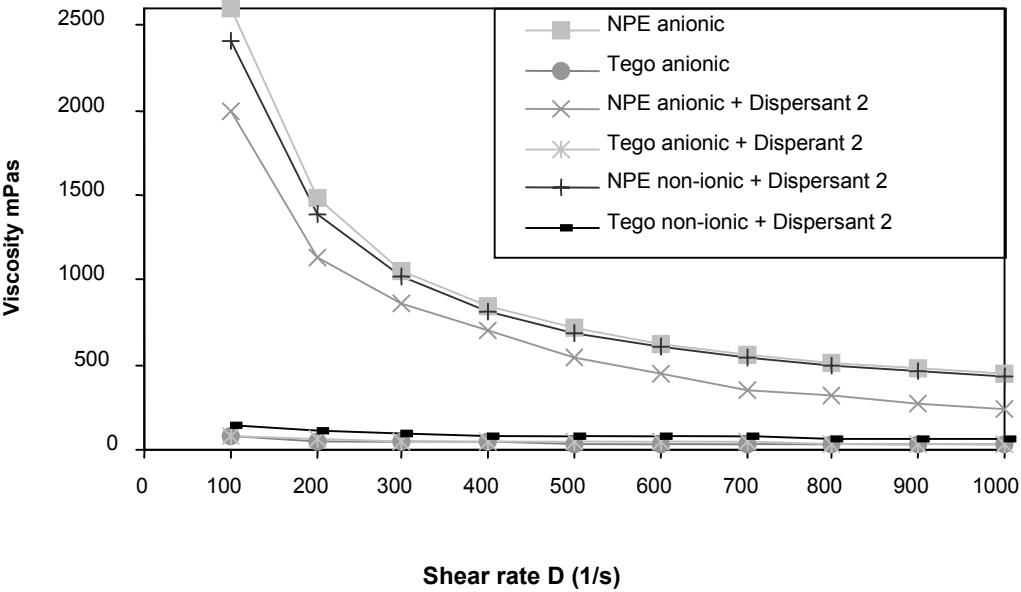
Product	Iron oxide red PR 101		Iron oxide yellow PY 42		Phthalocyanine blue PB 15:4		Carbon black PBk 7	
Water, demin.	32.5	20.0	38.0	26.5	55.3	39.4	71.0	56.1
Dispersant non-ionic	6.0	-	5.5	-	8.7	-	8.0	-
Dispersant anionic	-	17.0	-	15.5	-	24.6	-	22.9
Dispersant 2	-	1.5	-	1.5	-	-	-	-
Defoamer, silicone-free	1.5	1.5	1.5	1.5	1.0	1.0	1.0	1.0
Pigment	60.0	60.0	55.0	55.0	35.0	35.0	20.0	20.0

The pigment concentrates were ground in a bead mill or paint shaker (red devil) with 2.5 mm glass beads (inorganic pigments = 1 hour, organic pigments = 2 hours).

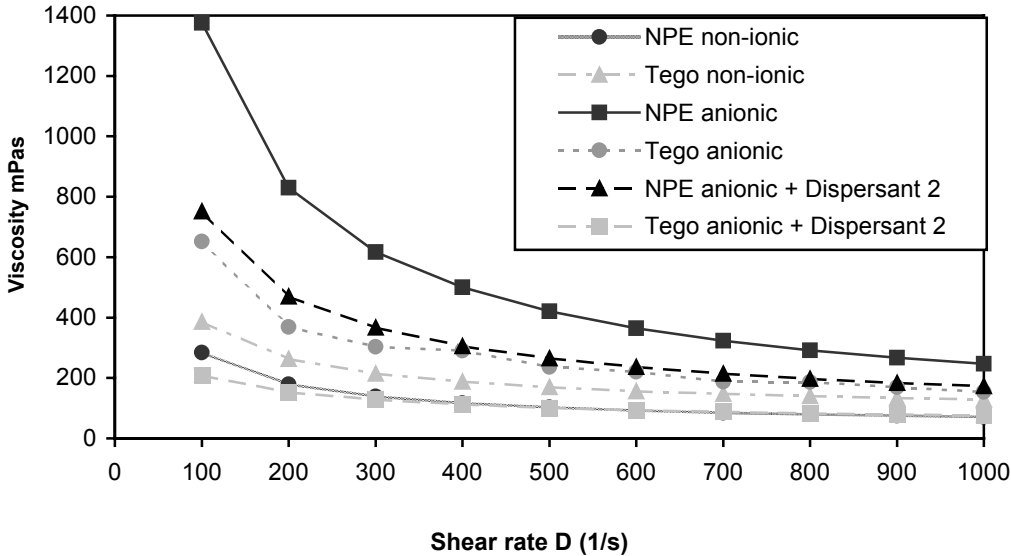
3.3 Rheological profiles

The viscosity of the pigment concentrates was measured by cone and plate apparatus. The desired pigment loading for iron oxide yellow was achieved with only the Tego dispersants (both non-ionic and anionic). However, the addition of dispersant 2 is beneficial for the reduction of the mill base viscosity. For the iron oxide red pigment the non-ionic dispersants provided a very low mill base viscosity, whereas the anionic types gave a significantly higher viscosity. The combination of these latter with dispersant 2 gave optimal grinding conditions.

Iron oxide yellow



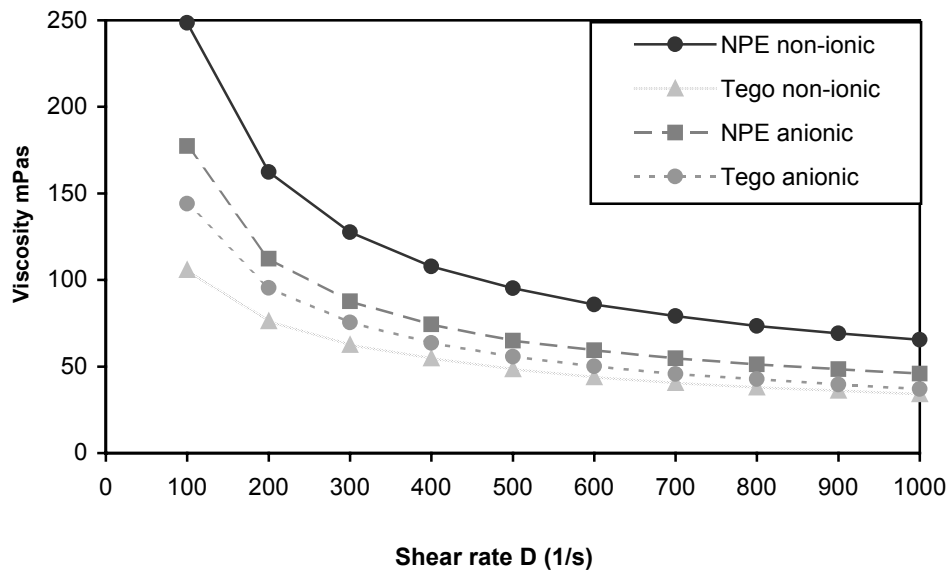
Iron oxide red



Carbon black

All pigment concentrates based on carbon black showed very low viscosity. Therefore, they were ground in a paint shaker. There are no graphs for these pigment concentrates in this paper since no differentiation occurred.

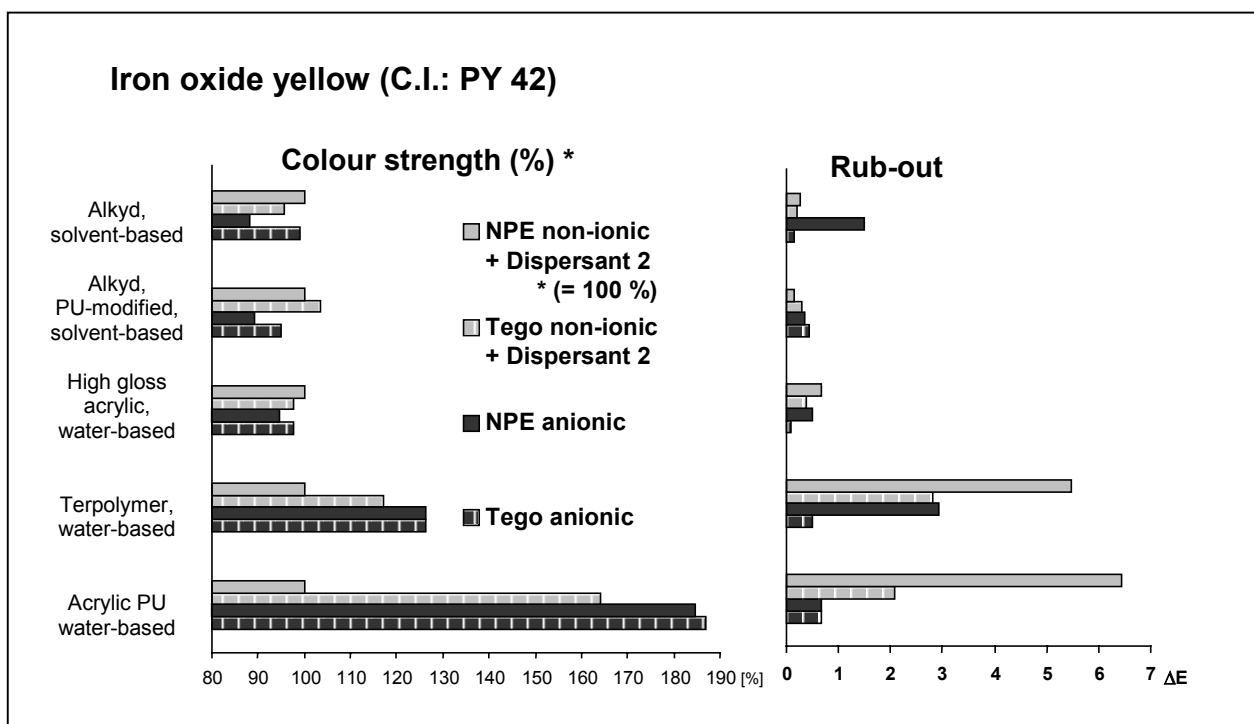
Phthalocyanine blue



3.4 Colour strength and rub-out (ΔE)

To measure the rub-out value and the colour strength the individual white base paints were tinted (5 % by volume) with the pigment concentrates and hand-mixed. The paints were drawn down at 100 μm and during drying one part of the film was rubbed with a finger.

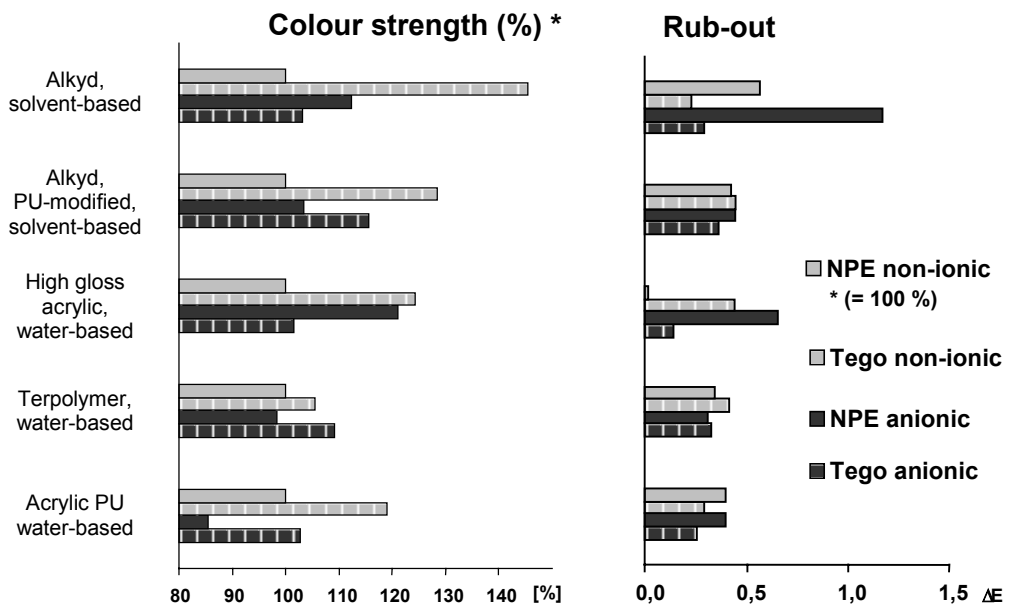
For the evaluation of colour strength, the test results for the non-ionic NPE dispersant were set as the standard = i.e. 100 % colour strength. The results for the individual products were calculated in relation to this standard. The following charts show the colour strength and rub-out values (ΔE) obtained.



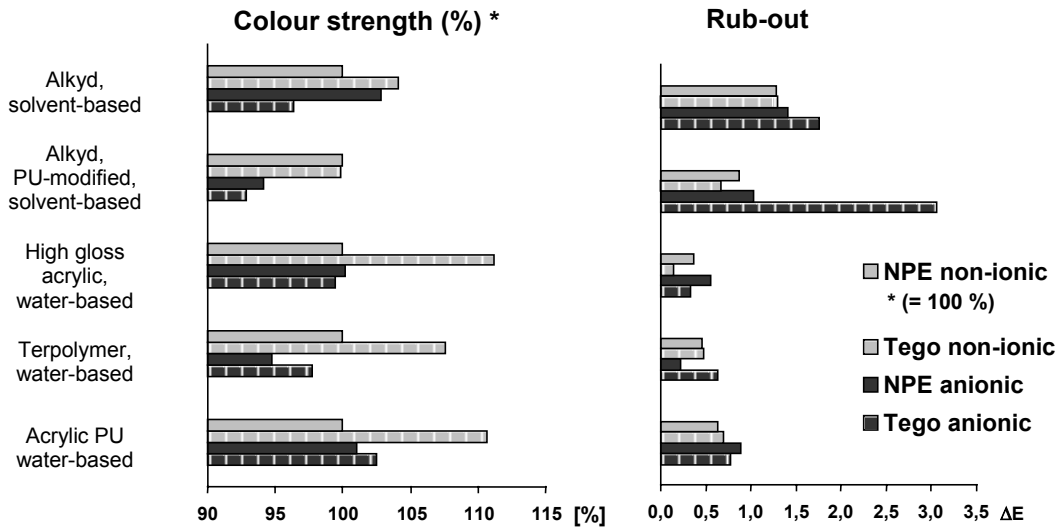
Iron oxide red (C.I.: PR 101)



Carbon black (C.I.: PBk 7)

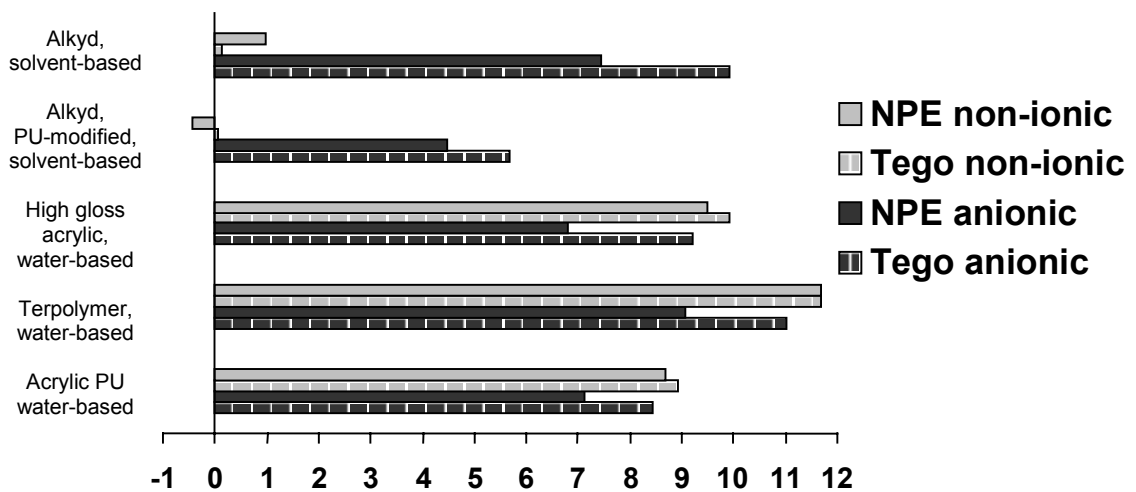


Phthalocyanine blue (C.I.: PB 15 : 4)



b* value of the Cielab system

Iron oxide red (C.I.: PR 101)



For the iron oxide yellow only the Tego structures (non-ionic and anionic) had paste viscosities low enough for use in manufacturing. Both NPE structures would not be manageable in an industrial production unit. Together with the above colour strength and ΔE values it can be summarized that the anionic Tego structure, especially in water-based systems, provides significant benefits compared to the non-ionic Tego structure.

Non-ionic structures (NPE and Tego) are not capable of stabilizing iron oxide red pigments in solvent-based systems, as can be seen from the high ΔE values. From the colour strength and rub-out values, both anionic structures seem to be suitable.

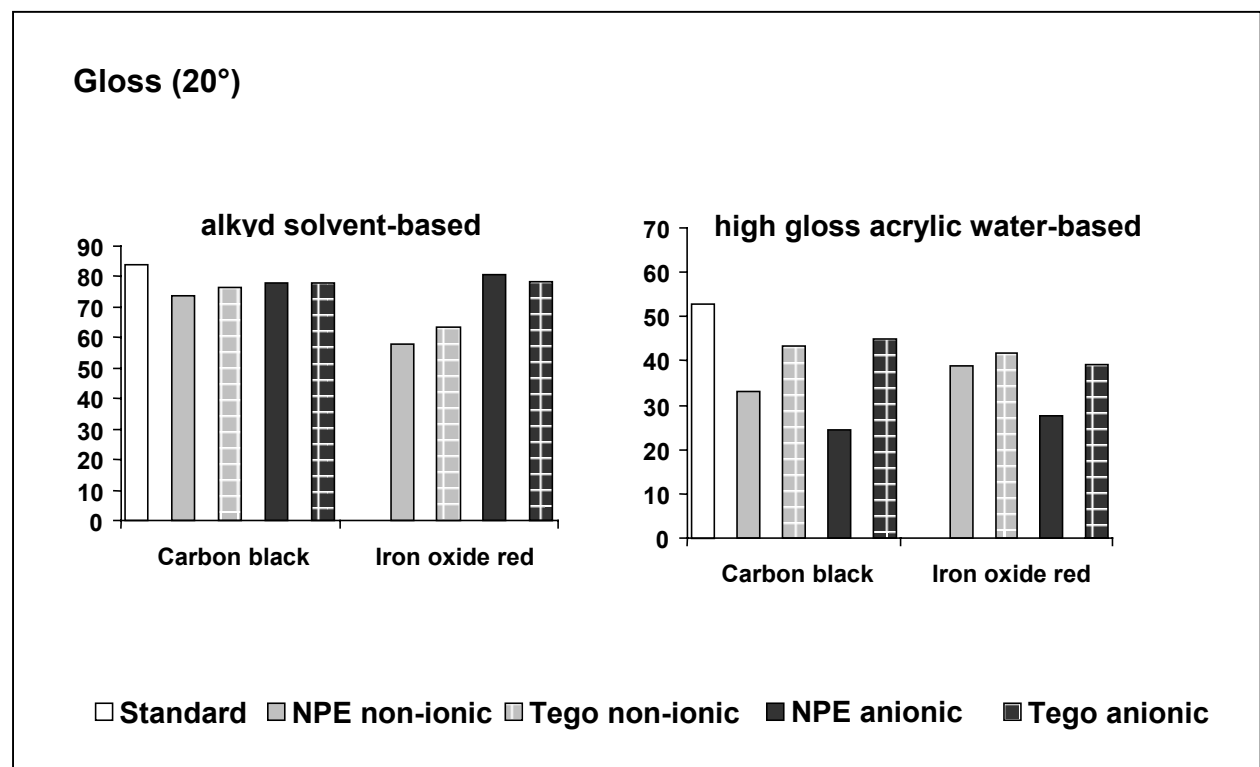
The visual appearance of the draw downs made it necessary to further evaluate the yellow shade of the iron oxide red. Looking at the b-values, the higher efficacy in preventing flocculation (smaller pigment particles are more yellow) can easily be seen for the anionic Tego structure.

For both organic pigments (phthalocyanine blue and carbon black) non-ionic structures perform far better than anionic structures.

In comparison with the NPE non-ionic structure the Tego non-ionic structure provides better colour strength - particularly in water-based systems - combined with acceptable ΔE values.

3.5 Gloss

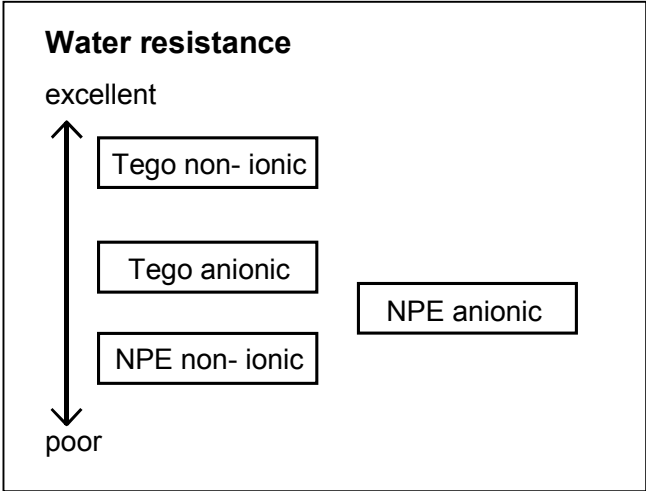
The gloss (20°) values were measured for just two pigments (one inorganic, one organic) in the 'Alkyd 1' and 'High gloss acrylic' paint systems. The results for the low gloss systems are of less interest.



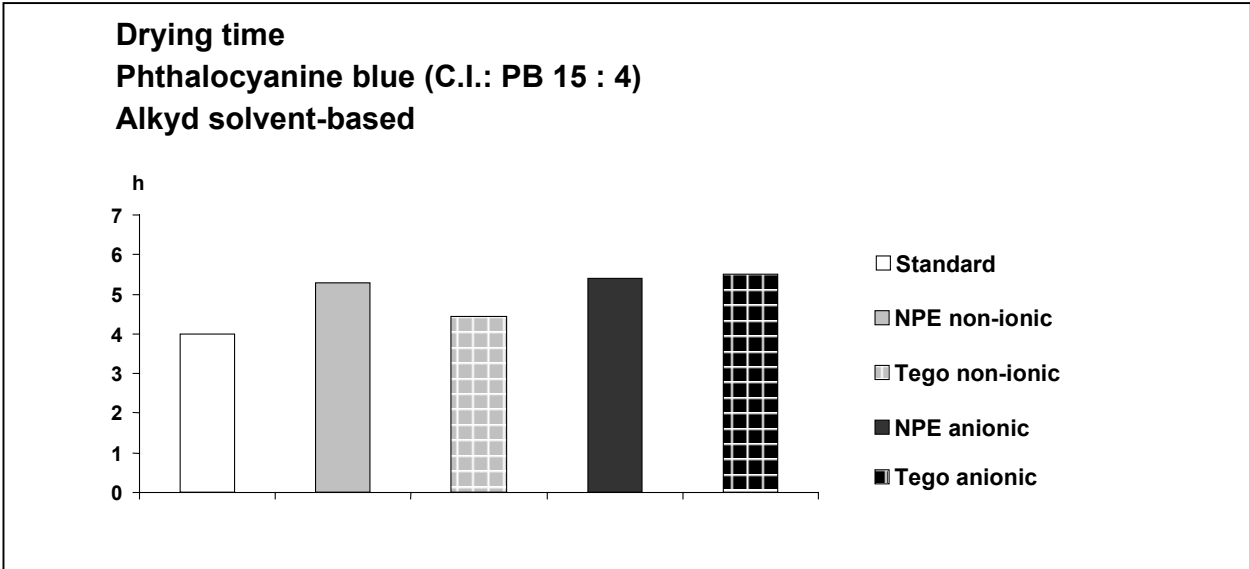
For the carbon black the recommended non-ionic Tego structure gives good gloss values. The recommended anionic Tego structure allows tinting with iron oxide red pastes without significant gloss reduction.

3.6 Influence on coating properties

To have a critical test system, the water resistance was tested in the 'High gloss acrylic base paint' with the phthalocyanine blue concentrate, since this pigment requires a high additive content. The dry paint film was treated with water and the blister formation evaluated visually. The Tego non-ionic structure showed the best resistance to water. Both anionic structures were still acceptable.



The drying time was recorded for the white base paint in comparison to the control (no paste addition) for the 'Alkyd 1' with the phthalocyanine blue.



The diagram confirms that the Tego non-ionic structure has no influence on drying time. The slight retardation in drying time using the anionic products as recommended for inorganic pigments, will not be of importance due to a much lower additive loading.

The values for the scrub resistance are pending and will be presented in the final paper.

4 Conclusion

Thanks to a new synthetic approach Tego offers the coatings industry a new class of wetting and dispersing additives for universal pigment concentrates. It has been demonstrated, that these wetting and dispersing additives provide better performance for universal pigment concentrates than the NPE types.

Regarding the various pigment types, it can be stated, that non-ionic Tego polyether structures stabilize organic pigments very efficiently which is confirmed by high colour strength, excellent pigment stabilisation and high gloss values.

The anionic modified species of this unique technology is beneficial for inorganic pigments. Using a secondary wetting and dispersing additive in combination with the anionic structure prevention against flocculation is given and viscosity adjustment is possible during grinding, so that a higher pigment loading can be achieved.

5 Outlook

There is a significant potential within this product class: Wherever NPE's are used today, there is a good chance of finding better performance with these new products. These materials have been modified particularly for emulsion polymerisation. Using a similar chemistry for both the emulsifier in the emulsion polymerisation and the wetting and dispersing additive in the pigment concentrate it is likely to get optimal performance in the final paint system.

Acknowledgements

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