

**A new Dispersant for water-based
Pigment Concentrates
(TEGO[®] Dispers 745 W)**

Authors: **Andreas Stüttgen*, Dipl. - Ing.**
 Wernfried Heilen, Dipl.- Ing.

Company: **Tego Chemie Service GmbH**
 Goldschmidtstrasse 100
 45127 Essen
 Germany

Telephone: **+49(0)201 1 73-22 74**

Fax: **+49(0)201 1 73-18 81**

After a short technical review the authors discuss the dispersion process and the concept of an ideal water-borne pigment concentrate. The pigment pastes, formulated with a new dispersant provide excellent colour strength development, good stabilisation of the pigments (low rub-out values), excellent compatibility in various binder systems and storage stability of more than 6 month. Concluding the authors state, that it is possible to economically produce water-borne paints by the use of pigment concentrats containing the new dispersant.

TABLE OF CONTENTS

1	Introduction
2	Technical review
2.1	Tinting
2.2	Pigment pastes for solvent-based coatings
2.3	Pigment pastes for water-borne coatings
3	The dispersion process
3.1	Wetting of pigment particle surfaces
3.2	Mechanical deagglomeration of pigment particles
3.3	Modes of stabilization
3.4	Methods of evaluation
3.5	Influencing factors
4	Concept of an ideal water-borne pigment concentrate
5	Properties
5.1	Pigment content and viscosity
5.2	Paste viscosity and stability
5.3	Colour strength development and stability
5.4	Compatibility with resins/paints
5.5	Flocculation stability and coating properties
5.6	Other properties
6	Conclusions and recommendations
7	Literature

1 Introduction

There are hardly any coatings manufacturers who do not have to supply relatively small quantities of product in custom colours. Production and labour costs can be the same, independent of the quantity of custom colour to be mixed. This directly affects profit. In most cases, it is not possible to assign a price for small batches of custom colours which is reflective of the actual costs ensued in their production.

The recent recession has affected the European coatings industry (like many others) to the extent that coatings producers have considered re-thinking production processes, to minimize the costs of predicting custom colours in small quantities. Many coatings producers have sought alternatives to the co-grinding or direct grinding processes, whereby pigment in the desired colour combination is dispersed in a resin of choice.

Another concept which has been tried is the intermixing of finished paints to achieve a desired colour. Although this does not always produce the desired colour match, the practice is used in the automotive refinishing industry.

Two economical approaches to achieving effective colour matches have found favour in the United States and in Scandinavia. One practice is known as tinting and the other is the use of resin-containing pigment pastes. Both methods allow a solution to cost problems in producing small as well as large quantities of custom colours, because only mixing is required in the final stage of paint production.

2 Technical review

2.1 Tinting

Production of a base colour (be it transparent or white) is essential for tinting. Bases can be economically produced in large quantities. Tinting also requires standardized universal pigment pastes. Tinting systems require that the pre-dispersed colorants contain the same resin as the base. Ideally these tinting pastes would be compatible with water-borne as well as solvent-based base colours. With tinting pastes, small quantities can be added "in can" and the desired colour can be obtained through volumetric or gravimetric addition of the universal paste through simple mixing.

2.2 Pigment pastes for solvent-based coatings

In these pastes, organic as well as inorganic pigments can be dispersed using a pigment wetting and dispersing additive and an appropriate wetting resin (ideally having universal compatibility with bases). The organic resin is essential for preventing drying out of the paste and also for helping to maintain the stability of the pigment preparation. In the event of an outside influence to the paste, for example by mixing with a minimally compatible resin system, it can happen that the pigment mixture "kicks out", causing the paste to lose its original properties. The loss of properties can result in loss of colour strength, loss of gloss or pigment flocculation. Despite this drawback, these pastes are used for solvent-borne coatings in some countries, due to the flexibility of the system. Currently work is underway to develop this principle in water-borne coating systems.

2.3 Pigment pastes for water-borne coatings

In the building protection sector, pigment preparations have been in use for more than 25 years. Organic pigments are dispersed by non-ionic and anionic pigment wetting and dispersing additives in water and a low-volatile organic solvent having high water solubility. The properties of this type of dispersion, including its long-term stability, is dependent on the physical and chemical characteristics of the pigments used.

Pigment preparations made with ethylene glycol and alkylphenoethoxylates, for example, have not found wide use in the industrial coatings market due to their limited compatibility with the variety of resins used in many formulations.

The standardization of these pigment preparations is not dependent on the pigment content, but rather the colour intensity and hue. Colour pastes are made for the main use, which is in emulsion paints.

Producers of industrial coatings are constantly seeking ways to reduce the solvent content, both for ecological reasons as well as a response to environmental legislation. This technological challenge opens the way to develop water-borne systems.

Before we look at the concept of an ideal pigment preparation, it is best to understand the theoretical principles of the dispersion process. This gives us a basis for discussion of the development of new wetting and pigment-stabilizing additives.

3 The dispersion process

By regarding colour development as a function of time, the quality of the dispersion process is measurable. Exactly what kind of process is dispersion? It may be viewed as pursuing three different objectives simultaneously.

3.1 Wetting of pigment particle surfaces

During *wetting* air is displaced from the pigment surface through the liquid of the grinding mixture. Especially when pigments or extenders and/or fillers have non-polar surfaces in water-borne systems, a wetting agent must be used [1, 2].

3.2 Mechanical deagglomeration of pigment particles

Agglomerates are broken down in mechanical *separation* through the use of energy. Dissolvers or pearl mills supply the shear force necessary to allow for reduction of pigment particle size. Additives have relatively little influence during the deagglomeration process, which is more dependent on the amount of energy input and time duration [3]. It can be noted that a complete breakdown of aggregates to primary particles is very rarely achieved in practice.

3.3 Modes of stabilization

The aim of stabilization is to keep the pigment particles separated as achieved in the last step, and to control that degree of pigment particle size through the let-down and filling phase, storage and application, so it is a somewhat complex matter. Stabilization is achieved through adsorbing of polymer on the pigment surface, so that repulsive forces prevent other particles from approaching close enough for the attractive van der Waals forces to cause agglomeration.

Electrostatic stabilization occurs whereby equally-charged local sites on the pigment surface come into contact with one another. Two particles having the same charges give a repelling effect. The resulting Coulomb-repulsion of the charged particles allows the system to remain stable. The surface potential cannot, unfortunately, be measured directly. It is possible to calculate the surface charge by way of determining the Zeta-Potential (electrical potential in the shear phase of the electrical double layer) [4].

A pigment is said to be *sterically* stabilized when the surface of the solid particles are completely covered by polymers, making particle-to-particle contact impossible. Strong interactions between polymers and solvents (organic solvent or water) prevent the polymers from coming too close into contact with one another (flocculation).

3.4 Methods of evaluation

While sophisticated methods of evaluating the degree of stability achieved and maintained have to do in general with the rheological profile of the pigment concentrate, more practical (though indirect) methods such as gloss and colour strength development or the Rub-Out-Test on mixed pigments are most often used.

3.5 Influencing factors

On what factors is the dispersibility of a pigment dependent?

Generally, dispersibility of a pigment is dependent on the pigment's characteristics. Some important characteristics are density, chemical structure, crystalline structure and size, shape, surface geometry, production process and surface treatment [5, 6].

Special consideration needs to be given to surface treatment of polar, inorganic pigments as well as non-polar, smaller-sized organics. Unfortunately, there is no easy way to "see" the surface of a pigment particle, although this may be of high interest to understand specific interactions of pigments and polymers.

4 Concept of an ideal water-borne pigment concentrate

After our theoretical excursion, we would like to return to the question of what an ideal pigment paste looks like.

The most important ingredient of the paste is of course the pigment, be it either organic or inorganic. The liquid medium required to carry the pigment should be composed mainly of water. During grinding, the pigment must be as completely wetted as possible, to ensure maximum colour development. This requires the help of a pigment surface wetting agent. As foam can develop with the use of certain pigment wetting agents, a defoamer may be required.

The pigment paste must not only be storage stable, but must remain stable when

added to coatings having different resin systems, and must not cause problems when mixed with coatings containing different pigments. For stabilizing the pigment particles in the paste, a dispersing additive is required.

Some pigments, though finely dispersed, tend to settle hard, due to their high densities. This sediment may not be easily re-mixed to a paste. For these pigments, a thixotropic thickening agent is necessary.

These are the basic requirements for an ideal pigment paste. It should be emphasized that a special vehicle, which has often been a part of paste formulation, is not necessary, provided carefully selected combinations of raw materials are used.

As a result of the above-mentioned requirements, we have developed pigment wetting and dispersing agents which go a long way in the direction of producing ideal pigment concentrates. A special modified polyacrylate forms its basis, following our experience with our work with polyacrylates cited above. It should not be overlooked that for the preparation of the dispersing agent component, less than 9 % solvent content in the finished additive was required. In terms of practical formulation, the solvent content is expected to be below regulated amounts in the finished coating, however.

For the elimination of foam during the early grinding phase, organo-modified siloxane defoamers have proved most effective. We recommend the use of a 100 % defoamer, to ensure maximum shear stability during grinding. A thickener, if needed, such as a modified bentonite-type or fumed silica, gives excellent thixotropy in small amounts, and is compatible with a wide variety of resins.

We shall now look at examples of the efficiency of this concept.

5 Properties

The properties of an additive for the production of pigment preparations were critically researched under the following experimental areas:

1. pigment content and viscosity
2. paste viscosity and storage stability
3. colour strength development and stability
4. compatibility with resins
5. flocculation stability and coating properties

During the development of this class of dispersing and stabilizing additives we evaluated two competitive products from Europe and the United States (indicated as Additive B and Additive C below).

5.1 Pigment content and viscosity

From the standpoint of productivity and formulation flexibility, not least on economic reasons, we set a goal of developing pastes having high pigment concentrations.

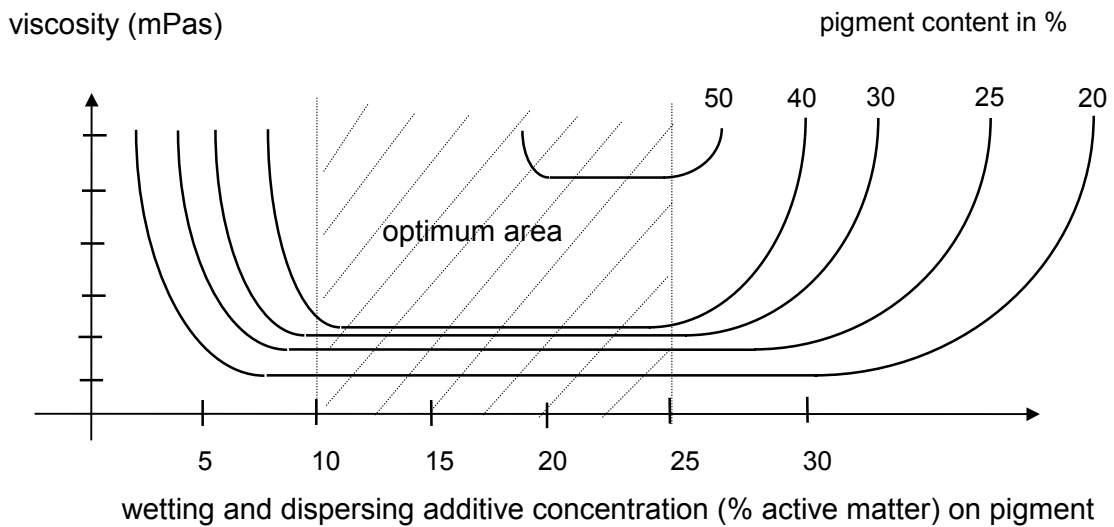
Various tools used to predict maximum pigment content in pastes are cited in the literature, including BET-surface (m^2/g pigment), oil absorption and DOP number (similar to oil absorption). However, it must be taken into consideration that water does not behave like other liquids. Therefore no general statement can be made regarding

the pigment content of a water-borne pigment paste.
The most practical and reliable way is to produce pigment concentrates directly with various pigment and additive levels (see graph 1).

It is recommended to check at least 3 different additive concentrations. After the grinding procedure (e. g. 1 - 2 hours on a Scandex shaker) the pastes with low viscosity can be regarded as optimized. The area of low viscosity is an indication of maximum treatment of the pigment surface with additive and thereby the maximum stabilization of the paste. In the next steps other properties such as storage stability, colour strength have to be taken into account.

graph 1: Paste viscosity depending on pigment content and additive concentration

(pigment: phthalocyanine blue, Pb 15 : 4)

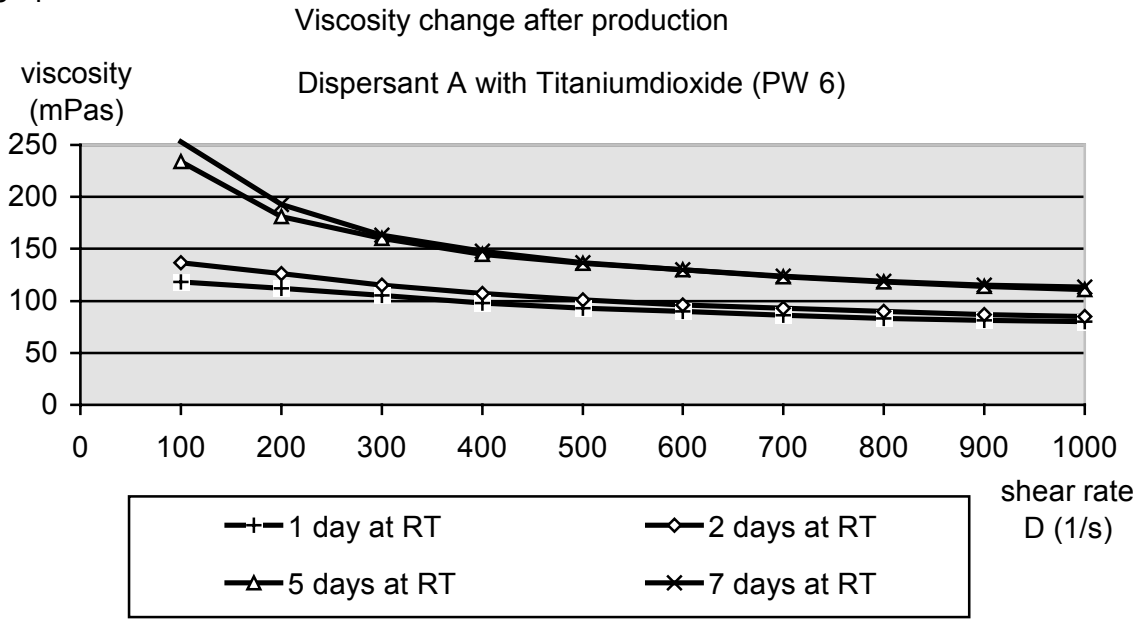


If a certain (minimum or maximum) pigment content is required the amount of trials can be reduced by only varying the dispersant concentration. It has to be noted, that this optimization has to be carried out for each individual pigment. Pigments having the same chemical composition (and Colour Index) can show totally different rheological behaviour due to their surface area and surface treatment. Practical experience with the individual pigments is always required.

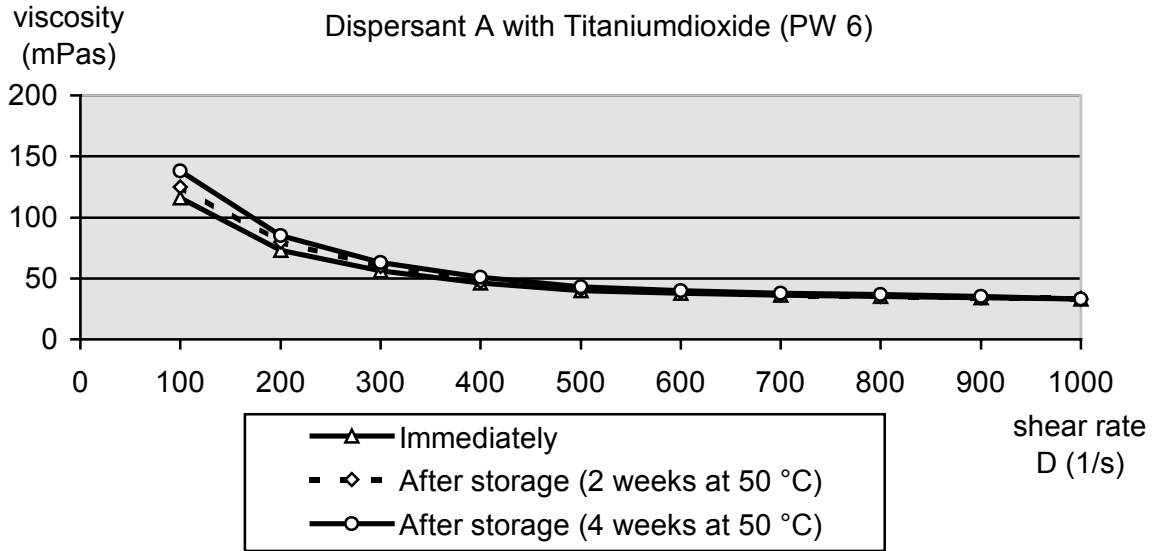
5.2 Paste viscosity and stability

It has to be pointed out, that the viscosity of the pigment concentrate should not be evaluated during the first days, if reliable results for the viscosity change are required. In fact pigment concentrates need some days after production to "ripen" until a final state is reached (in case of Titaniumdioxide e.g. 5 days, graph2). From this starting point storage tests can be carried out at e. g. 50 °C. This effect might be caused by rebuilding of interaction forces of the pigments and the complete wetting of the pigments.

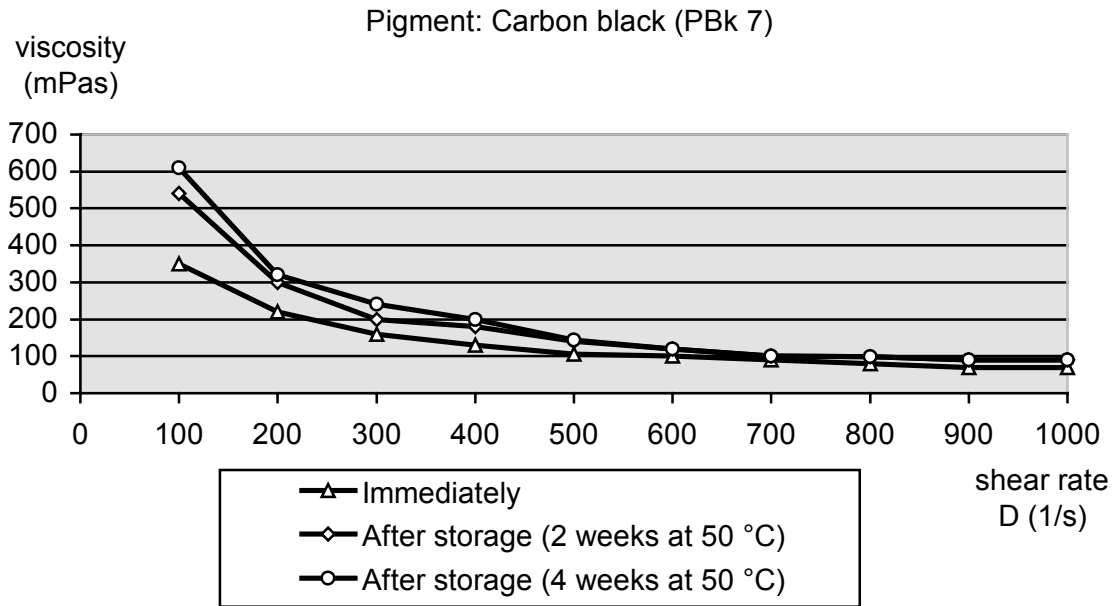
graph 2



graph 3



graph 4

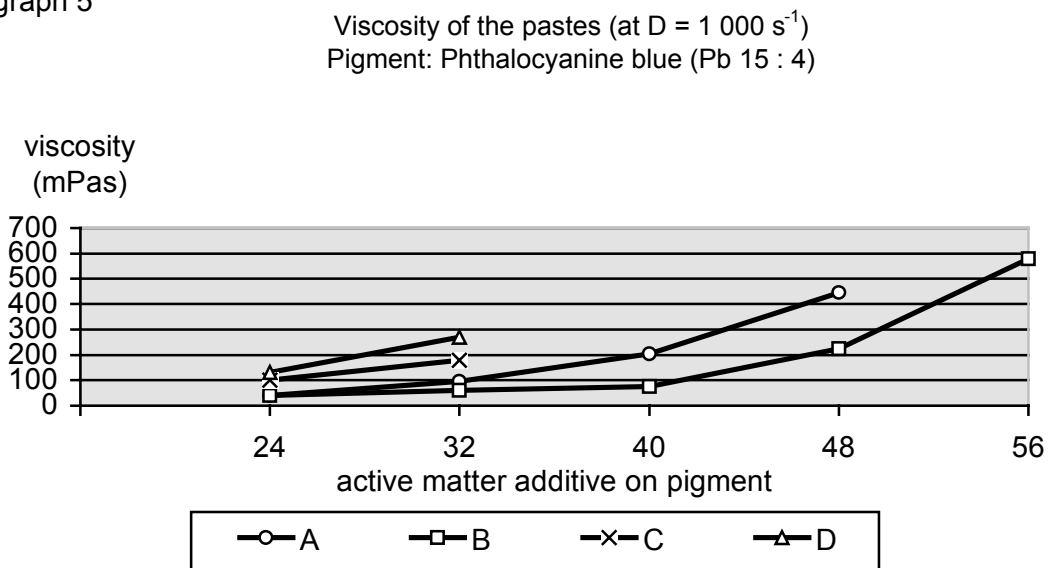


Graph 3 and 4 show the viscosity change of an ideal pigment concentrate during storage. The viscosity was measured using the cone and plate method. As can be seen from the chart the viscosity was nearly constant.

It is significant that reliable results were achieved at shear rates higher than approx. $D = 500 \text{ s}^{-1}$.

Paste viscosity can also depend on the dispersant concentration and chemical structure of the additives used. The higher the concentration, the higher the viscosity (graph 5).

graph 5



Pigment pastes having a high yield point have been cited in the literature as being unsuitable for use in automatic tinting machines. It should be noted that this is only partially true. If it can be demonstrated that pastes having a high yield point show reduced settling tendencies, as well as excellent system compatibility, then there should be no barrier to its use in such applications.

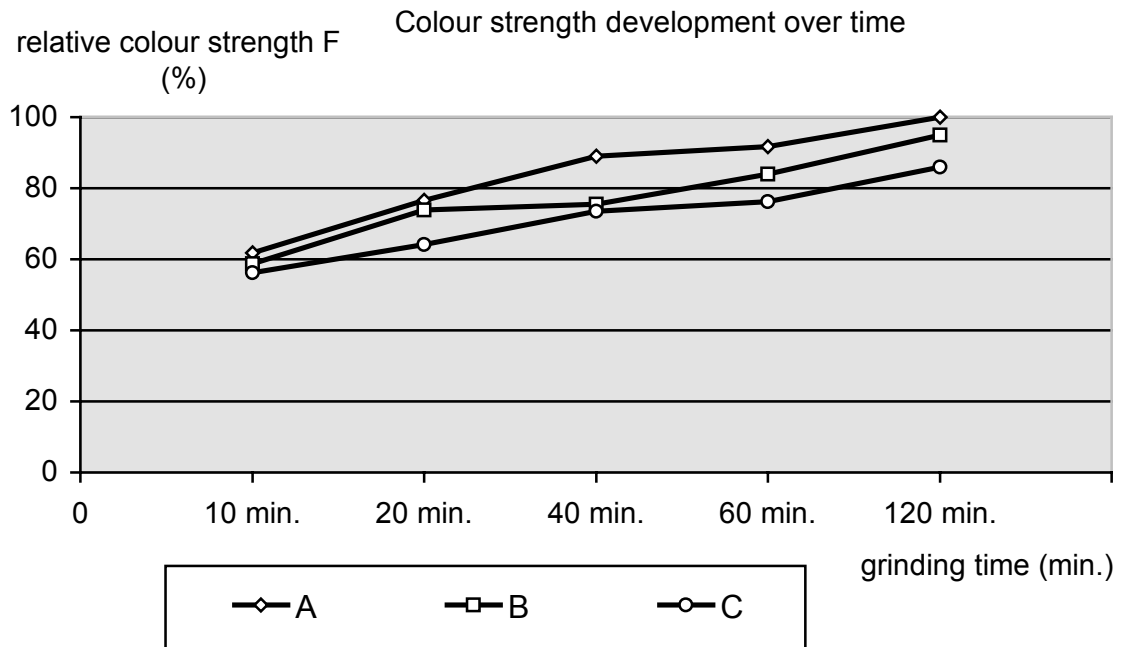
5.3 Colour strength development and stability

Not only is the optimal pigment content and viscosity stability a determining factor in a pigment preparation, but also out of cost considerations a distinct colour strength development as a function of dispersion time [7]. In the following example, 3 different additives were used to make identical pastes made with Heliogen®* Blue L 6920 (pigment Blue 15 : 1) and titanium dioxide (pigment White 6) in a ratio of 1 : 25. After being dispersed in a pearl mill for 120 minutes, colour development was compared. The colour strength was calculated according to the equation of Kubelka/Munk:

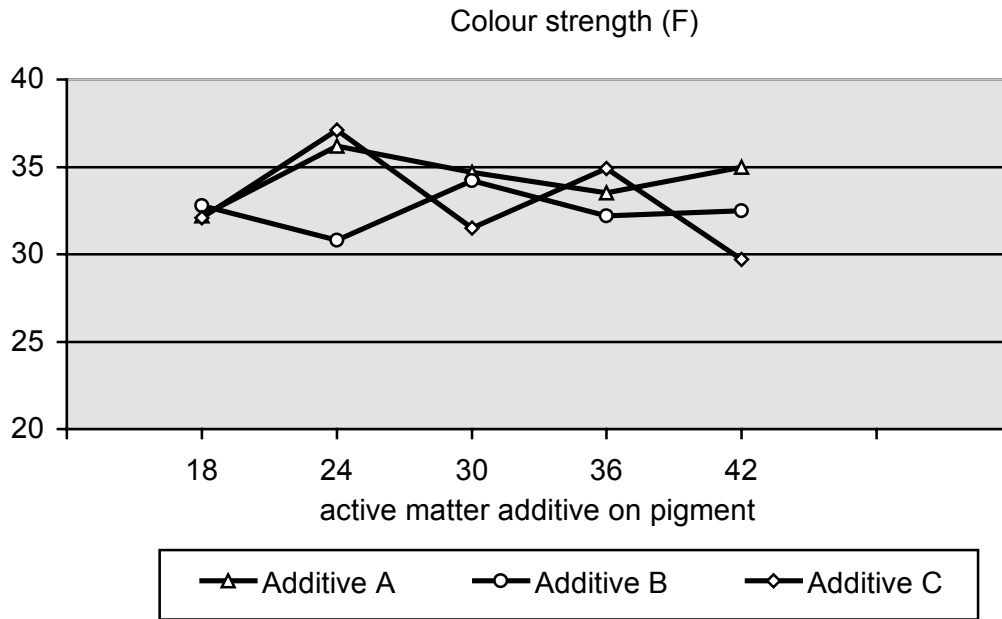
$$\text{Colour strength } F = \frac{K}{S} = \frac{(100 - Y)^2}{2 \cdot Y}$$

where K is the absorption coefficient and S is the scattering coefficient. Additive C yielded only 86 % relative colour strength when compared with Additive A. Additive B gave only 82 % colour strength. This can translate directly to cost considerations, when proportionately more of an additive and/or grinding time is needed to achieve the same results.

graph 6



graph 7



Pigments used: Pigment blue (C.I. 15 : 1)
Pigment white (C.I. PW 6)

Mixing ratio: 1 : 25 p.b.w.

It is a common practice to compare/substitute wetting and dispersing additives one by one when comparing them. The graph 7 shows, that this can cause misreadings and leads to wrong conclusions!

In any case it is recommended to test at least 2 - 3 different concentrations of additive to make sure, that the optimized colour strength is achieved.

5.4 Compatibility with resins/paints

For practical considerations it is impossible to evaluate the compatibility of wetting and dispersing additives with all of the water-borne resins on the market. The results are dependent on how the pigment concentrate acts in the resin. A typical test is to thin the additive 1 : 1 with water and mix it into the selected resin, looking for signs of flocculation or turbidity. No gellation or hazing indicates that the additive is appropriate for use with the given resin.

The pigment concentrates based on an organic pigment (phthalocyanine green) have been let down under stirring in different paint systems (via full mixing= let down of the paste in "clear coat"). In Table 1 the results concerning achieved transparency and possible flocculation have been determined visually.

Table 1:

Let down of the phthalocyanine green pastes in the clear coat (pigment content 4 %)

	acrylic emulsion	PU emulsion	2-pack PU	2-pack epoxy	acrylic melamine	polyester melamine
A	+	+	+	±	+	+
B	-	+	-	±	+	-
C	+	+	-	±	+	+

+ = no flocculation
good transparency

± = slight flocculation
slight turbidity

- = strong flocculation

5.5 Flocculation stability and coating properties

The stability of a pigment preparation is easily determined using the Rub-Out-Test, is performed by most paint producers. Using this method, two pastes (titanium dioxide and Heliogen® Blue) were mixed in the ratio 25 : 1 (white/coloured) and stirred into a selected binder under agitation. The mixed colour was spray-applied (100 µm wet film thickness). The rubbing was done on the sprayed area.

Additive	Rub-out value initially [ΔE]	Rub-out value after storage [ΔE]
A	0.3	0.35
B	0.8	1.1
C	0.9	1.5

The table indicates that the ΔE^* with the paste made with Additive A shows no difference in colour value after storage of the paste. This means that the pigment paste has excellent stability. This also indicates that the pigment paste is stable against flocculation.

Colour stability

Once a paste has been produced the desired colour shade has to be stable. To check the colour stability, different pigment concentrates have been let down into a white acrylic emulsion paint (white/coloured pigment mix = 25 : 1). After storage of the paste this procedure has been repeated and the difference in colour determined as ΔE value. In the next table, we see the results of the colour stability (ΔE).

	Phthalocyanine blue (Pb 15 : 4)	Phthalocyanine green (PG 36)	Quinacridone (PV 19)	Carbon black (PBk 7)
Additive	ΔE	ΔE	ΔE	ΔE
A	0.25	0.5	0.3	0.45
B	0.9	0.6	0.6	1.4
C	0.6	0.5	0.8	2.0

5.6 Other properties

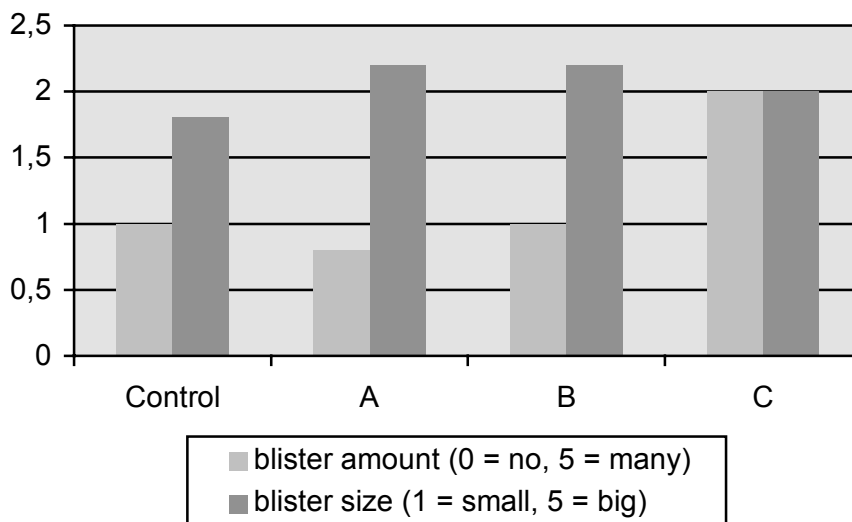
In the last step, the water-sensitivity and the UV-light resistance were checked. Therefore, a white acrylic paint was tinted with pigment concentrates and sprayed on aluminium panels. After drying some panels were exposed to UV-light (1 000 hours), and others 100 % relative humidity (240 hours). Summarizing we can say that Additive A in comparison to Additive B and C (at the same addition level) had no negative influence on water-sensitivity and light resistance (see following graphs).

Water sensitivity

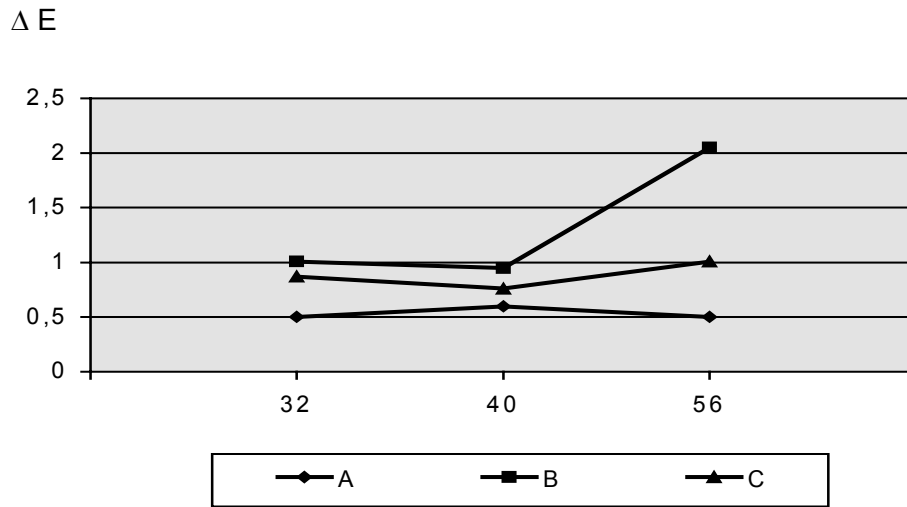
White emulsion paint tinted with Hostapermred E3B

Pigment mixing ration white/red = 25/1 p.b.w.

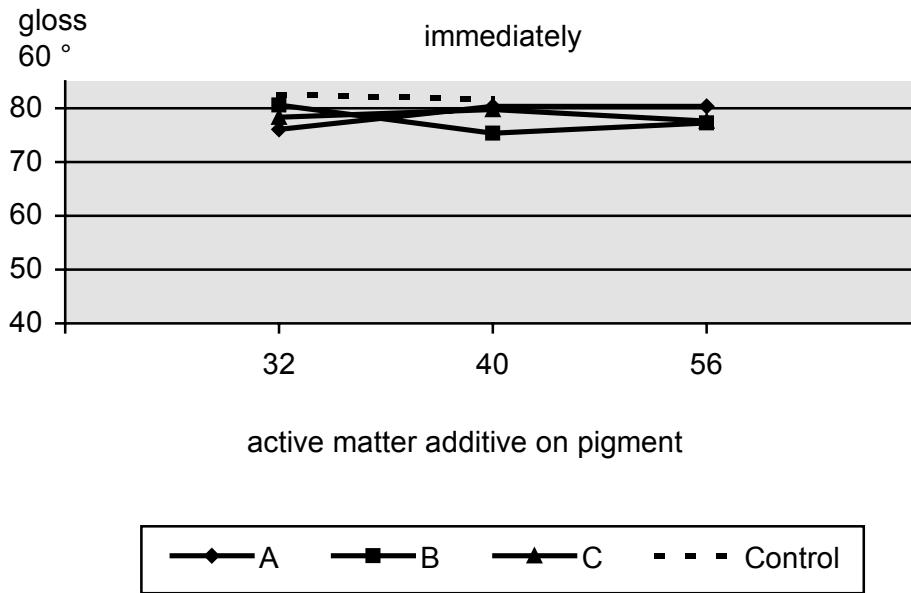
Results after 14 days at 100 % rel. humidity and 40 °C

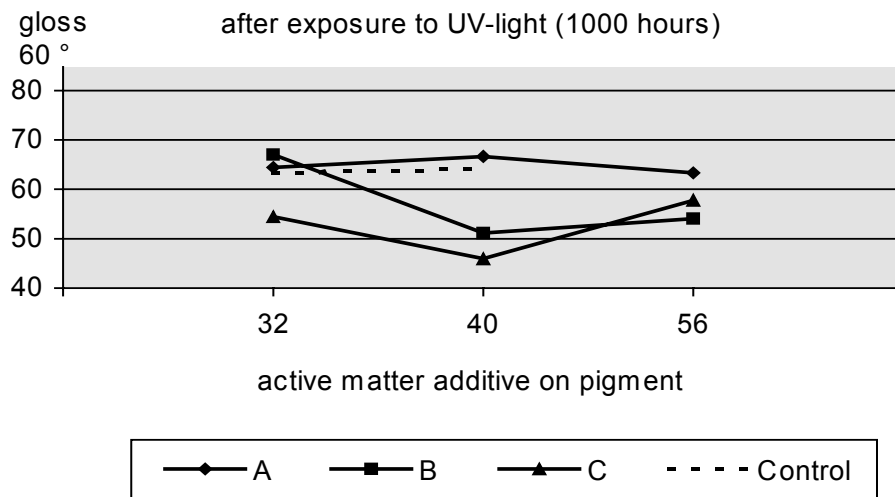


QUV-resistance (1 000 hours)
Colour change (ΔE) during weathering



QUV-resistance
Gloss (60 °) change during weathering





6 Conclusions and recommendations

Economy and ecology are causing coatings producers to re-think their formulations. Small batches must be more cost effective to produce and should be as easy to supply as large ones. Traditional applications for solvent-based coatings are giving to water-borne technology. Pigment preparations, made essentially from pigment and water and a desired additive, can help formulators to produce economically sound coatings as well as environmentally responsible products. Recently developed products allow the formulation of water-borne pigment pastes having high pigment loading, good colour development, long-term storage stability, broad compatibility and excellent rub-out results.

Finally it should be mentioned that these dispersants are also suitable for glycol containing pastes and for the direct grind (grinding the pigment mixture with binder). Enclosed you will find some guiding formulations of our latest development, TEGO[®] Dispers 745 W (Additive A).

*Heliogen[®] is a trademark of BASF. Neocryl[®] is a trademark of ICI (Zeneca).

Authors' thanks

The authors would like to thank their colleague, Mr. Jay Adams, for his assistance in translating and preparing this paper.

7. Literature

1. Calbo, Leonard J., Handbook of coatings additives, Marcel Dekker, New York, 1987, p. 511
2. Herbst, W., Hunger, H., Industrial organic pigments, Verlag Chemie Weinheim, 1993, p. 75
3. Winkler, J., Dulog, L., Farbe + Lack No. 90, p. 244 (1984)
4. Osterhold, M., Farbe + Lack No. 101, p. 683 (1995)
5. Reck, E., European Coating Journal, June 1996, p. 406
6. Brock, T., Farbe + Lack No. 101, p. 757 (1995)
7. Schmitz, J., Kraker, R., Pluhar, P., Farbe + Lack No. 79, p. 733 (1973)

Enclosure

Below are listed some pigments that have been checked with Additive A.

Survey of tested pigments:

Pigment	C. I.	water %	AMP 90 %	Additive A %	Defoamer %	Fumed silica %	Pigment %
Kronos 2160	PW 6	16.4	0.0	12.3	1.0	0.3	70.0
Tioxide TR 92	PW 6	16.4	0.0	12.3	1.0	0.3	70.0
Ti-pure R 900	PW 6	16.4	0.0	12.3	1.0	0.3	70.0
Bayferrox Red 103 FS	PR 101	20.5	0.0	18.0	1.0	0.5	60.0
Bayferrox Yellow 3920	PY 42	18.8	0.2	24.7	1.0	0.3	55.0
Carbon Black FW 200	PBk 7	60.1	1.4	22.5	1.0	0.0	15.0
Carbon Black FW 285	PBk 7	62.7	2.0	20.3	1.0	0.0	14.0
Elftex 435	PBk 7	43.8	0.2	35.0	1.0	0.0	20.0
Hostaperm Red E 3 B	PV 19	46.5	0.0	22.5	1.0	0.0	30.0
Heliogen Blue L 7101 F	PB 15 : 4	36.0	0.0	28.0	1.0	0.0	35.0
Heliogen Green L 8730	PG 7	34.0	0.0	25.0	1.0	0.0	40.0
Hostaperm Violet ER 02	PV 19	46.5	0.0	22.5	1.0	0.0	30.0
Novoperm Red F 3 RK 70	PR 170	34.0	0.0	25.0	1.0	0.0	40.0
Paliogen Red L 3885	PR 179	59.7	0.0	11.3	1.0	0.0	30.0
Hostaperm Pink E	PR 122	46.5	0.0	22.5	1.0	0.0	30.0
Novoperm Orange HL 70 NF	PO 36	46.5	0.0	22.5	1.0	0.0	30.0
Brilliant Yellow 2 GX 70	PY 74	29.0	0.0	30.0	1.0	0.0	40.0
Hostaperm Yellow H 3 G	PY 154	37.7	0.0	26.3	1.0	0.0	35.0