

**Principles and Benefits of Binder-free Pigment
Grinds for Water-based Printing Inks**

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Introduction

Pigment grinding is the vital step in printing ink production for all the ink manufacturers who do not buy ready-made pigment concentrates. During grinding the pigments have to be dispersed, wetted and stabilised properly in order to achieve the desired colour strength.

The traditional and most common concept for the manufacture of water-based flexo and gravure inks appears to be the grinding in a resin-solution. In most cases these solutions contain water and carboxyfunctional acrylic respectively styrene-acrylic resin - neutralised by the addition of ammonia, organic amine or alkaline hydroxide. These resin solutions provide good pigment wetting, pigment stabilisation and also convey some desirable properties to the finished ink, such as resolubility.

The continuous cost and performance optimisation has forced the ink manufacturers to streamline their production processes. It is possible to save manufacturing costs by increasing the pigment content in the grinding stage. But doing this, negative side effects such as viscosity increase of the grind, even thixotropy or reduced transparency, gloss and colour strength can occur. To avoid all these, special pigment wetting and dispersing additives were developed that allow a significant increase of pigment loading without sacrificing the above mentioned properties.

It may be interesting to note that such an additive can be used at relative low dosages (1 to 3 percent) to display impressive effects as shown in the picture below.

The additive used in this resin-containing carbon-black grind was optimized with regards to its pigment wetting properties to have a positive impact on viscosity. It also contributes to pigment stabilisation, but most of this can be attributed to the high molecular weight resin solution. So the combination of a resin solution and a small amount of this rather low molecular weight pigment wetting additive achieves high pigment contents in the grind and excellent gloss, transparency and colour strength in the ink.



Figure 1: Resin containing carbon black grinds without and with additional use of a wetting and dispersing additive

But even a good concept has its limitations. When it comes to applications where very high resistance properties and/or extremely broad compatibility are required the carboxyfunctional resins tend to create adverse effects. The ultimate rationalisation step in the manufacture of water-based flexo and gravure inks is to have only one pigment grind, respectively concentrate, suitable for all inks. This requires utmost compatibility of the pigment concentrate with all possible let-down binders which can hardly be achieved by the use of the conventional resin solutions. An interesting way to approach these issues is the formulation of aqueous, resin-free pigment grinds.

How to formulate an aqueous, resin-free pigment concentrate

An idealised aqueous, resin-free pigment concentrate (III) consists of water, wetting and dispersing additive and pigment only. Whereas classic resin-containing pigment concentrates are shown by the pictures (I) and (II) illustrated in figure 2. Of course, these formulations are simplified regarding the necessary auxiliaries, such as preservatives, defoamers etc, however, this will not be discussed in this paper.

Wetting and dispersing additives for resin-free pigment concentrates clearly differ from those used in combination with resin solution. The reason for this is that they have to provide excellent wetting **plus** long-term pigment stabilisation. Consequently, resin-free pigment grinds will need significantly more wetting and dispersing additive than resin containing ones.

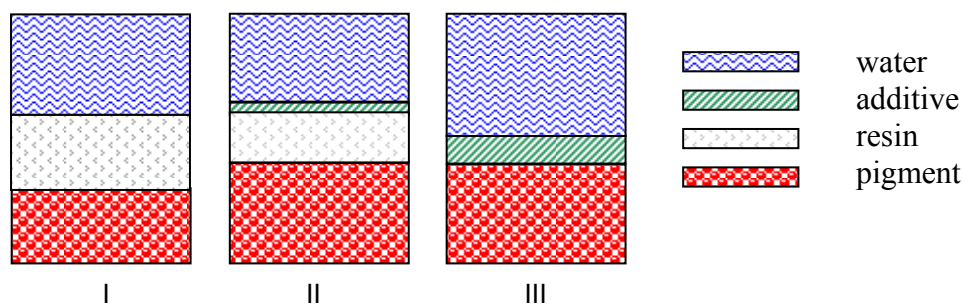


Figure 2: How to formulate an aqueous, resin-free pigment concentrate

Requirements for an aqueous, resin-free pigment concentrate

Such a simplified pigment concentrate (III) has to fulfil the following requirements:

- high pigment loading
- low viscosity for easy incorporation during the let-down
- no thixotropy
- high colour strength development
- good storage stability without pigment sedimentation or viscosity increase
- excellent compatibility with most binders used, that means no reflocculation during or after let-down
- good viscosity stability of resulting printing inks.



Some of the above mentioned criteria can be fulfilled by certain additives. But the most important and critical point is the final stabilisation of the pigment quite independently from the different let-down resins used. Otherwise pigment flocculation as illustrated in figure 3 will occur which results in reduced colour strength and/or gloss. Indisputably, to maintain pigment stabilisation in the final inks had to be understood as the biggest challenge in the successful development of a wetting and dispersing additive.

Figure 3: Flocculation during the let-down ^[1]

Theoretical discussion of different wetting and dispersing additive technologies

Effective pigment wetting in water can be achieved by a number of different technologies.^[2] From the principle point of view wetting and dispersing additives can be described either by their molecular weight or by their electric charges. Therefore, wetting and dispersing additives are called surfactant-like if they are low molecular. Both non-ionic or anionic ones are available. Moreover, there are higher molecular structures available as wetting and dispersing additives which can be called oligomeric or even polymeric.

It is always advisable to start an evaluation by paying special attention to the relationship between amount of wetting and dispersing additive used and viscosity of the resulting pigment concentrate which is dependent on the pigment grade and its loading, too. Figure 4 illustrates this aspect in dependence on the so-called additive on pigment content following called AoP.

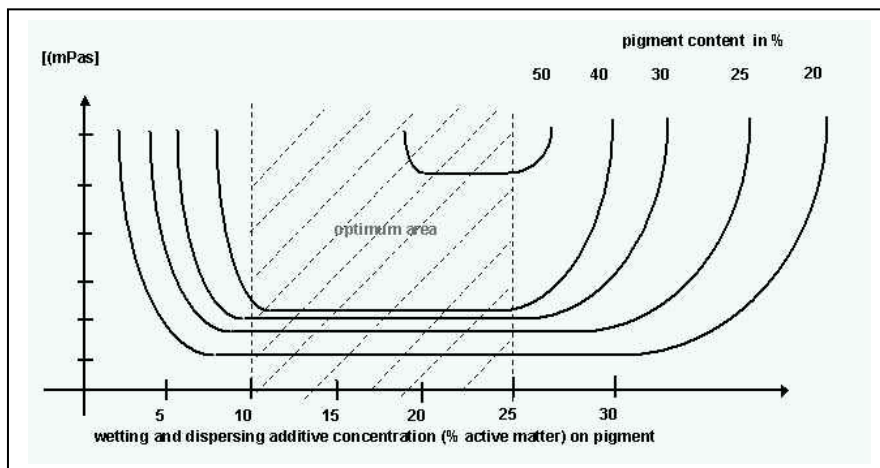
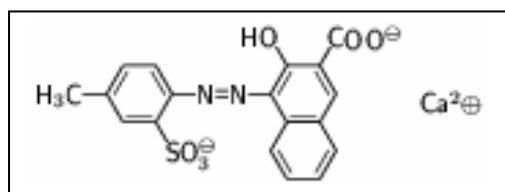


Figure 4: Relationship between viscosity, pigment content and AoP

Especially ionic dispersing additives tend to result in thixotropic systems or in a significant increase of viscosity when too high wetting and dispersing additive dosages are used. One of the most critical ink pigments is in that connection Magenta P.R. 57:1. Its principal structure is given in figure 5 below.



The Ca^{++} ions in the structure are responsible for quite a lot of interactions with certain wetting and dispersing additive technologies and for curious viscosity developments in the pigment pastes. On the other hand tremendous flocculation problems occur during the let-down with certain resin solution or dispersions.

Figure 5: Magenta P.R. 57:1 [3]

The evaluated wetting and dispersing additives can be described as given in table 1.

Table 1: Wetting and dispersing additive technologies used [4, 5]

- A non-ionic, styrene oxide/ethylene oxide-based surfactant
- B anionic, phosphorylated species of A, neutralised
- C non-ionic oligomeric surfactant, more hydrophilic than A
- D high-quality polymeric wetting and dispersing additive based on SMA
- E polymeric wetting and dispersing additive with flocculation resistance during let-down

Practical findings - viscosity of aqueous, resin-free pigment grinds

Yellow 13 is a very common pigment for printing inks and often used as a process colour. Figure 6 illustrates the problems which may occur with different technologies.

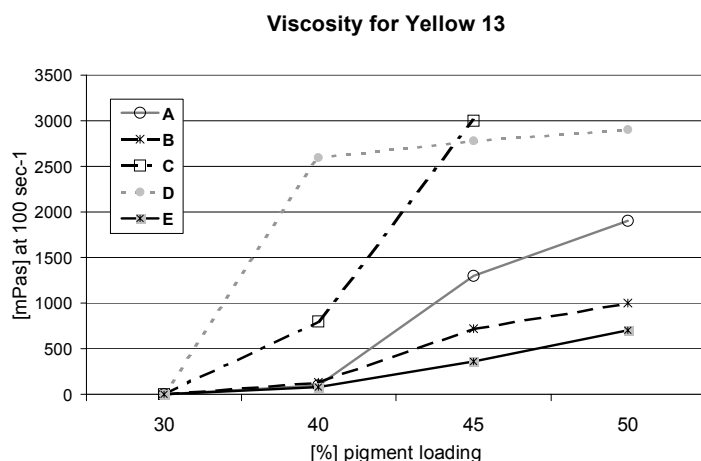


Figure 6: Viscosity of Yellow 13 pastes with 12% AoP one day after preparation

Polymeric structures as D are limited in terms of wetting efficiency. Consequently, a quite high viscosity can occur using a cost-wise attractive, limited amount of wetting and dispersing additive (12% AoP). Surfactant-like structures as A or B allow to receive low viscose grinds. But as soon as their structures get higher molecular and too hydrophilic (structure C), they will fail. That means the paste with 50% Yellow 13 is not even possible to manufacture. Moreover, taking into consideration that too low viscosities (at 20 and 30% pigment loading) display weaknesses during the storage, the aim is to use at least 40% pigment in the grind formulation. Structure E does not have any problems to be used for Yellow 13 and results in the lowest viscosity at all.

Completing the picture for a Magenta grade, e.g. Irgalith 4 BV or Solintor WF 57, the importance of selecting the right wetting and dispersing additive technology is getting even more obvious.

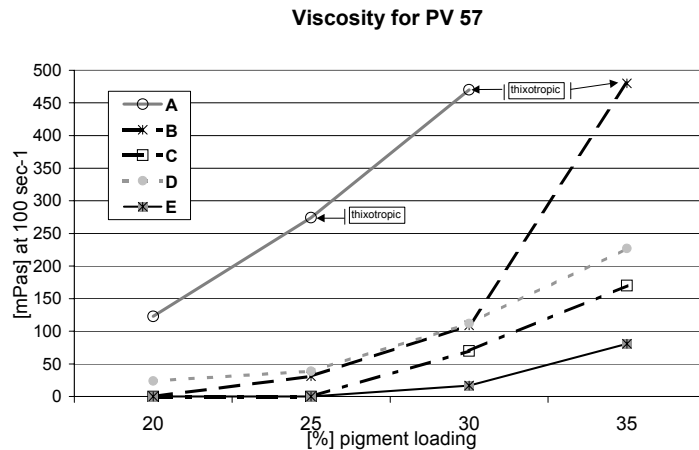


Figure 7: Viscosity of Irgalith 4 BV pastes with 15% AoP one day after preparation

Structure A does not allow to manufacture fluid, non-thixotropic pastes with higher pigment loads. The anionic surfactant B shows limitations for the pigment loading by significant increase of viscosity. Oligomeric or polymeric structures as C or D seem to be beneficial in connection with such pigment grades. The polymeric structure E is the only one which shows a moderate rise in viscosity with increased pigment loading. No thixotropy can be observed neither for Yellow 13 nor for Magenta nor for any other grade evaluated with this technology of structure E. This wetting and dispersing additive allows even the manufacture of a 40% Irgalith 4 BV paste.

However, as mentioned before pigment wetting and stabilisation in the pigment grinds is just one point whereas the situation in the let-down may differ considerably.

Practical findings – colour strength and viscosity of the final inks

The diagram below illustrates the resulting colour strength of Yellow 13 pastes which have been used for a let-down with a common flexo ink binder. 1 part of paste was stirred into 2 parts of let-down mix to receive the final ink.

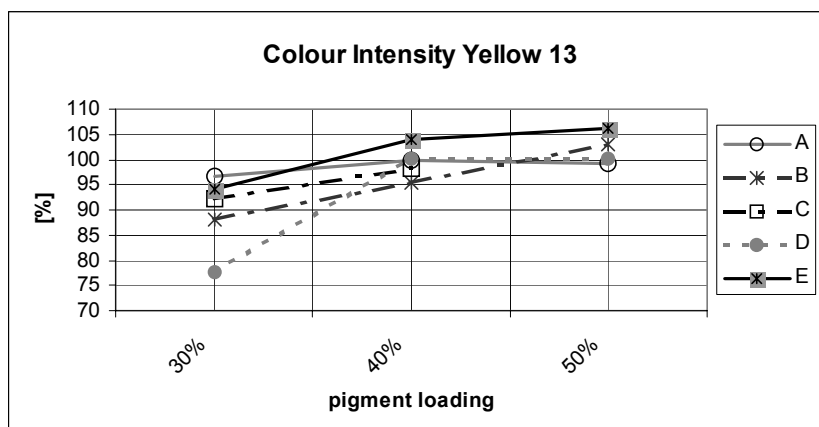


Figure 8: Colour strength of Yellow 13 pastes

Usually one would expect that higher pigment loading results in higher colour strength. But as the diagram in figure 8 shows in contrast to the expectation: At any point the optimum filling is reached for every wetting and dispersing additive technology. That means further increase of pigment loading is cost-wise prohibited because it does not go along with an adequate increase of colour strength.

Surfactant-like structures as A and B are totally limited in terms of colour strength because of their insufficient prevention of flocculation during the let-down or during the storage if used as the only wetting and dispersing additive. Together with their limitations discussed in connection with the resulting viscosities of the pigment grinds they are not recommended for aqueous, resin-free pigment grinds based on Magenta grades.

The wetting and dispersing additive E can achieve the highest colour strength (see figure 8).

The tremendous problems which can occur during the let-down are demonstrated by using a white ink based on the same resin formulation. Reduced tinting strength in connection with the observation of real coloured agglomerates in the white tint made the understanding of flocculation more obvious. Even a simple black and white picture of the resulting tintings with the Magenta pastes based on structure A in comparison to structure E gives an understanding of the importance of the prevention against flocculation (white tint of Magenta pastes Figure 9). The resulting ink of structure E looks much darker and no agglomerates can be seen in comparison to the much paler of the draw-down of structure A with a lot of agglomerates inside. Figure 10 illustrates that not only colour strength is influenced by insufficient pigment stabilisation but also the gloss in the final ink.

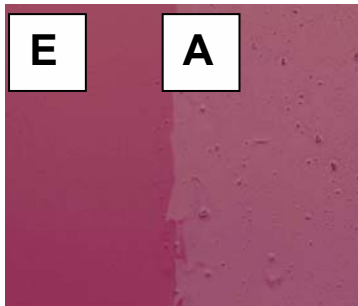


Figure 9: White tint of Magenta pastes

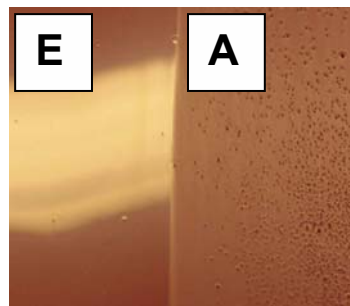


Figure 10: Gloss development

However, colour strength was just one point when discussing the requirements of a wetting and dispersing additive for an aqueous, resin-free pigment grind. Constant viscosity of the final inks has to be guaranteed as well. Therefore, the diagram below shows the viscosity of the pigment pastes for a Magenta grade in mPas at 100 1/s and 1000 1/s one day and 30 days after manufacture as well as the resulting efflux times of the inks given in seconds measured with the DIN 4 cup.

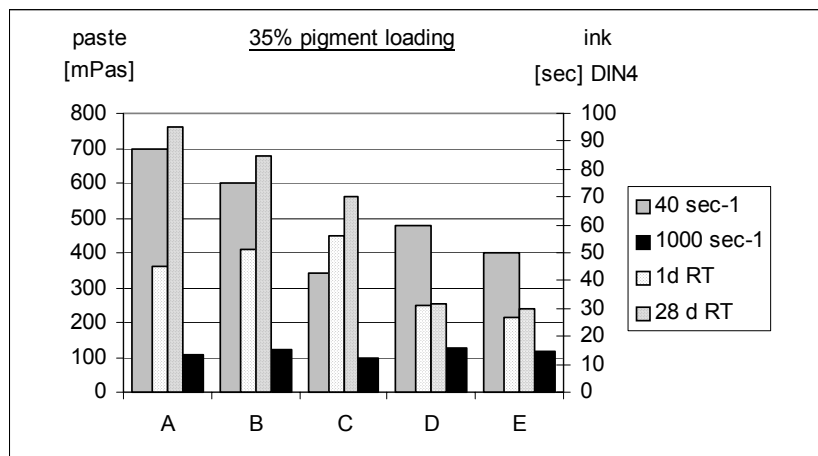


Figure 11: Viscosity of Magenta pastes and those of corresponding printing inks

Surfactant-like structures A and B have shown limitations in terms of reducing the viscosity of pigment pastes with higher loading from the very beginning. Bearing in mind that structure A led to a thixotropic

paste it is not very surprising that these pastes show such a strong increase of viscosity after 30 days. This made the use in an ink senseless. All three surfactant-like structures A, B and C have obviously problems to stabilise the pigment in the let-down. This can be seen by the significantly higher efflux times of those inks in comparison to the much lower viscosities of the polymeric structures D and E.

Conclusion

Our studies indicate that the most suitable wetting and dispersing additive for water-based flexo and gravure inks is of polymeric nature and contains groups of high pigment affinity. Developing the right structure results in an additive that provides excellent pigment wetting and stabilisation for all common ink pigments. The resulting pigment concentrates are compatible with all tested let-down binders. On individual pigments it may be beneficial to combine this polymeric additive with a lower molecular weight pigment wetting additive to achieve optimum results.

Literature:

[1] T. C. Patton, Paint Flow and Pigment Dispersion, John Wiley & Sons Verlag, 378

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[4] A. Stüttgen, K. Lehmann, Farbe & Lack, 3 (2002), 56

[5] S. Silber et. al., Bauchemie - Tagung, Kassel, 11/2001