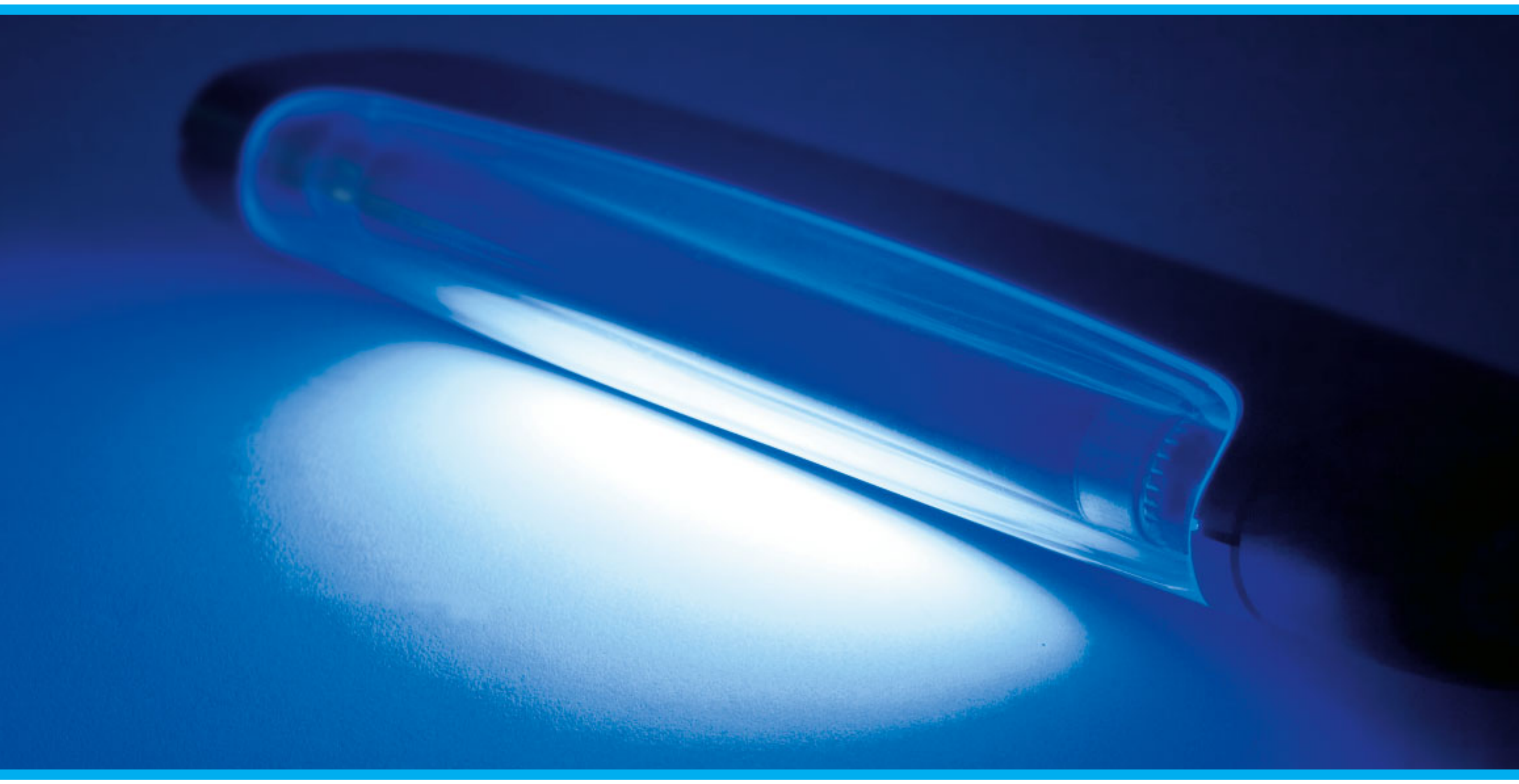
Specialty carbon black for UV curing printing inks

Technical Information 1257



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Contents

1 Introduction

UV-curing printing inks currently represent the fastest growing market segment in the printing industry. The rapidly growing demand for low-emission products and the high processing capabilities of UV inks are contributing to the steady growth of UV-curing printing inks in the market.

In this segment, the formulation of black UV-curing printing inks, above all, poses a great challenge. On the one hand, specialty carbon blacks absorb a portion of the UV radiation which is needed to crosslink the binders and so affects the curing of the ink. On the other hand the customer expects a deep-colored black, which, as a rule can be accomplished by adding fine specialty carbon black. The finer the specialty carbon black the higher the absorption of UV radiation.

Besides the primary particle size, the structure and the surface chemistry of the pigments used have a strong effect on the rheology of the printing ink. As a rule, the finer the pigment, the higher the viscosity of the printing ink. Specialty carbon blacks that have been surface treated and those with low structures, on the other hand, give lower viscosity.

For these reasons, the choice of pigments, the amount of photo-initiators, wetting agents, the composition of the binder, and the intensity of the UV-radiation must be adjusted to give the optimum properties.

The furnace process*, the Degussa gas black process* and Orion Engineered Carbons expertise in the post treatment of specialty carbon blacks provides the technical capability for the production of different specialty carbon blacks suitable for UV-curing printing inks.

*The furnace process and Degussa gas black process are two different production processes for manufacturing specialty carbon blacks. For further information on this topic, see our Technical Bulletin series „What is carbon black?"

1.1 Specialty carbon black recommendations

The selection of the most suitable specialty carbon black to meet the particular customer requirements could be challenging. The below described relationships should assist to differentiate the various products.

Under the prerequisite of good pigment wetting and sufficient dispersion, the use of low-structured, post treated furnace specialty carbon blacks like SPECIAL BLACK 250, SPECIAL BLACK 275, SPECIAL BLACK 350, NEROX® 2500 and NEROX® 3500 makes it possible to formulate UV-curing printing inks with outstanding flow properties, very good gloss, and a distinctive blue hue. Having a somewhat smaller than average primary particle size and a resulting higher specific nitrogen surface area, SPECIAL BLACK 350 and NEROX® 3500 possesses some special advantages with respect to jetness, whereas SPECIAL BLACK 250 and NEROX® 2500 produces printing inks with the lowest viscosity and a very strong bluish undertone. Our most recently developed product SPECIAL BLACK 275 is combining the fast curing and blue undertone of the SPECIAL BLACK 250 with slightly higher jetness.

The SPECIAL BLACK 550 and NEROX® 305 can provide highest optical density, due to their finer primary particles. However, the pigments containing the higher surface areas will require increased amounts of wetting agent to avoid disadvantages in rheology, especially in low-viscosity flexographic inks.

Besides the above mentioned specialty carbon black characteristics, tailored variations in surface chemistry are also possible. For instance the corresponding SPECIAL BLACK and NEROX® grades differ by the utilized post treatment technology. Both technologies result in slightly deviating compositions of the acidic groups on the specialty carbon black surface and these could influence the interaction with wetting agents and binder components.

In addition to the above described furnace grades, Orion Engineered Carbons does additionally offer specialty carbon blacks that are manufactured according to the Degussa Gas Black Process. The specialty carbon black SPECIAL BLACK 4 has a comparatively high structure and a large surface area. Due to the additional post treatment SPECIAL BLACK 4 possesses a very large number of acidic surface groups. The excellent wetting behavior of this product leads to UV-curing printing inks with high jetness, very good gloss, special flow properties and characteristic high transparency.

Furthermore to this general differentiation of the recommended products regarding their main physico-chemical data, regulatory issues e. g. compliance status for food packaging is gaining importance. For UV curing food packaging applications SPECIAL BLACK 275, SPECIAL BLACK 350 and NEROX® 3500 should be utilized. This recommendation is based on their compliance status with the relevant European Union regulations (No. 10/2011) and additional international classifications. More details can be found in our product safety information sheets that are available for each particular product.

Table 1

Recommended products and application characteristics:

SPECIAL BLACK 250/NEROX® 2500	Lowest viscosity, very blue hue, fastest curing, high gloss
SPECIAL BLACK 275	Low viscosity, very blue hue, fastest curing, high gloss, food packaging approval
SPECIAL BLACK 350/NEROX® 3500	Low viscosity, blue hue, fast curing, high gloss, food packaging approval
SPECIAL BLACK 550	Moderate viscosity, highest jetness, high gloss, high specific surface area requires increased amounts of wetting agent content
NEROX® 305	High jetness, low viscosity, moderate gloss, low wetting agent demand
SPECIAL BLACK 4	High jetness, highest gloss, high transparency, possible utilization of reduced pigmentation levels

2 Pigment properties and their effect on printing inks

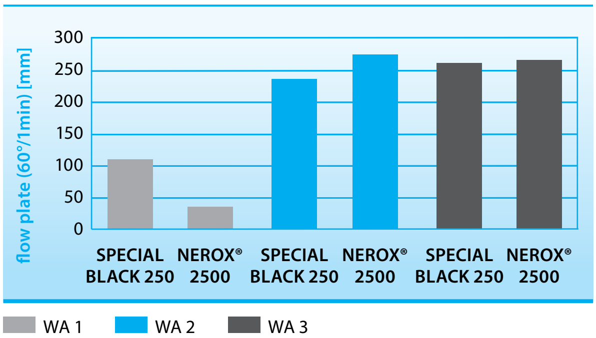
2.1 Post treated specialty carbon blacks for optimum pigment wetting

Optimum pigment wetting is extremely important for achieving an UV-curing printing ink with sufficient storage stability, a good flow and excellent color properties. Post treated specialty carbon blacks are well suited for achieving a balance between colorimetric properties, dispersibility and flow properties in black UV-curing printing inks. When these pigments are used with common binders having sub-optimal wetting properties, their acidic, polar surface groups yield to UV-curing printing inks with outstanding rheological properties and very good storage stability.

Nevertheless, the additional use of wetting and dispersing agents in these formulations is still recommended to achieve maximum performance. The choice of the most suitable wetting agent as well as a sufficient loading is of substantial importance. If all the components are optimally adjusted, good flowing and stable UV-curing printing inks could be achieved with all recommended specialty carbon blacks. The following can help to explain general relationships between specialty carbon blacks and wetting additives:

- Post treated grades show significant compatibility, flow and stability advantages over non post treated specialty carbon blacks.
- The higher the surface area of the specialty carbon black, the higher the wetting agent demand.
- Different wetting agents are partially leading to significant deviations in the achievable jetness and gloss levels of the resulting UV curing printing inks.
- The particular surface chemistry of the specialty carbon black, predominantly as a result of the post treatment technology, could lead to differing interactions in combination with certain commercially available wetting agents. (see below figure 1)

Figure 1



Graph to show the effect of different post treatments in combination with wetting agents. The SPECIAL BLACK surface treatment is showing a significant advantage in combination with wetting agent (WA) 1, a slightly shorter flow with WA 2 and almost similar behavior with WA 3.

More application test results that reinforce the relevance of the above statements could be found in chapter 3.

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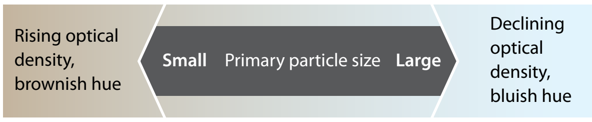
2.2 Optical density and hue

Excellent pigment dispersion and stabilization is mandatory to achieve an optimum colorimetric performance. Under these conditions the primary particle size of the specialty carbon black impacts strongly on the optical density and the color shade of the printing ink. The finer the specialty carbon black, the higher the optical density that can be achieved. On the other hand, fine specialty carbon blacks always cause the hue of printing inks to shift slightly towards a brownish color, whereas coarser specialty carbon blacks make it possible to achieve printing inks with more bluish hue. Deviations from this rule are mainly based on insufficient pigment wetting and dispersion.

Figure 2

Influence of primary particle size on colorimetric properties of the printing ink

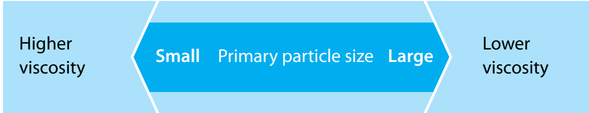


2.3 Rheology

In addition to the surface chemistry of the specialty carbon black, the primary particle size and the corresponding surface area affect the rheology of printing inks. Fine specialty carbon blacks have a high surface and consequently a higher binder demand to achieve good pigment wetting and this in turn results in a higher viscosity.

Figure 3

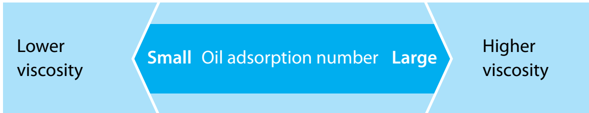
Influence of primary particle size on rheology



Another aspect to be considered in the rheology of printing inks is the structure of the specialty carbon blacks. Structure, here describes the branching of primary particles into aggregates. Oil Adsorption Number (OAN) values provide a good measure for the structure of specialty carbon blacks.

Figure 4

Influence of structure on rheology



The furnace process provides the possibility to vary the structure of specialty carbon blacks within a wide range. The Degussa gas black process, on the other hand, generally produces high structured specialty carbon blacks.

In principle, it can be stated that specialty carbon blacks with higher structures lead to printing inks with shorter flow.

3 Application test results of specialty carbon blacks

To illustrate the different effects described in chapters 1 and 2, extensive investigations with a variety of specialty carbon blacks and different wetting agents were carried out. All tests were based on the following UV flexographic ink formulation:

3.1 Guide Formulation

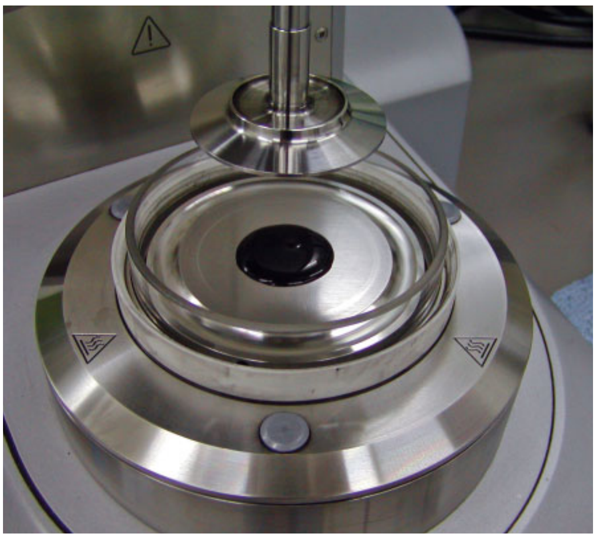
Table 2

Amount	Component
23.7 %	UV Base (91.5 % Ebecryl 3420 + 8.5 % TPGDA both Cytec)
16.1 %	Specialty carbon black
60.2 %	Let down varnish (91.0 % Ebecryl 40 + 3.6 % Irgacure 184 + 5.4 % Irgacure 369)
Variable	Wetting agent (the particular wetting agent addition has been calculated with 12.5 %, 25.0 % and 37.5 % active matter based on the amount of specialty carbon black)

All formulation components were weighed into 250 ml glass bottles. After premixing with a spatula, the blend was ground for 60 minutes in a LAU Disperser using 150 g of zirconium silicate beads as grinding media.

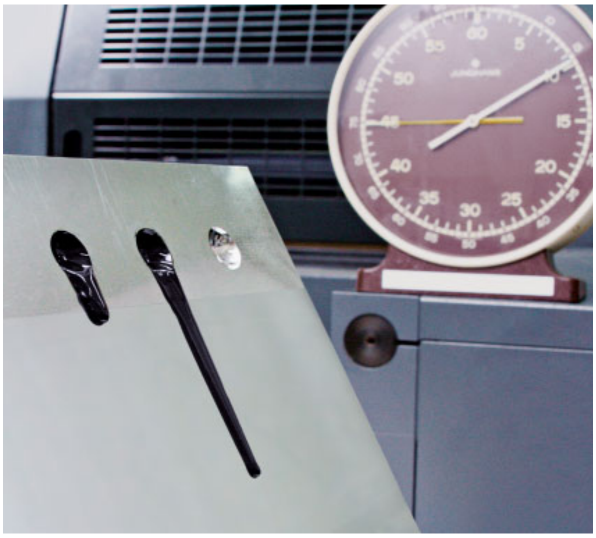
3.2 Rheology

Rheology plays a very decisive role, especially in low viscosity flexographic inks, in determining the most suitable specialty carbon black to use. In this application, the goals are low viscosity and nearly Newtonian flow behavior. This could be measured in the state of the art rotation rheometers like the MCR 301 from Anton Paar (picture 1).



Picture 1 – cone/plate measurement system of MCR 301 rheometer

An additional test showing the low shear behavior is the so called flow-plate method (picture 2). The flow behavior is assessed by determining the flow distance the printing ink covers on a flow-plate in one minute at room temperature at an angle of 60°.



Picture 2 – flow-plate method

The flow properties of UV curing printing inks depend on the specialty carbon black characteristics such as surface area, structure and the wetting properties. Figure 5 and 6 represents a comparison of the flow properties of different specialty carbon blacks at similar wetting agent loadings of 12.5 % calculated on the amount of specialty carbon black. Figure 5 is showing the rheometer measurements and figure 6 the flow-plate determination.

The coarsest pigments, SPECIAL BLACK 250 and NEROX® 2500, display the best flow behavior, whereas the fine sized pigments, SPECIAL BLACK 550 and SPECIAL BLACK 4 are showing significantly shorter flow.

Evaluations were also carried out where the wetting agent loadings were adjusted to achieve an optimum wetting in regards to the surface area of the particular specialty carbon black. Please refer to table 3 which shows the detailed loadings per grade.

Figure 5

Flow curves with logarithmic scale showing viscosity values from 0.1 to 1000 Pa*s

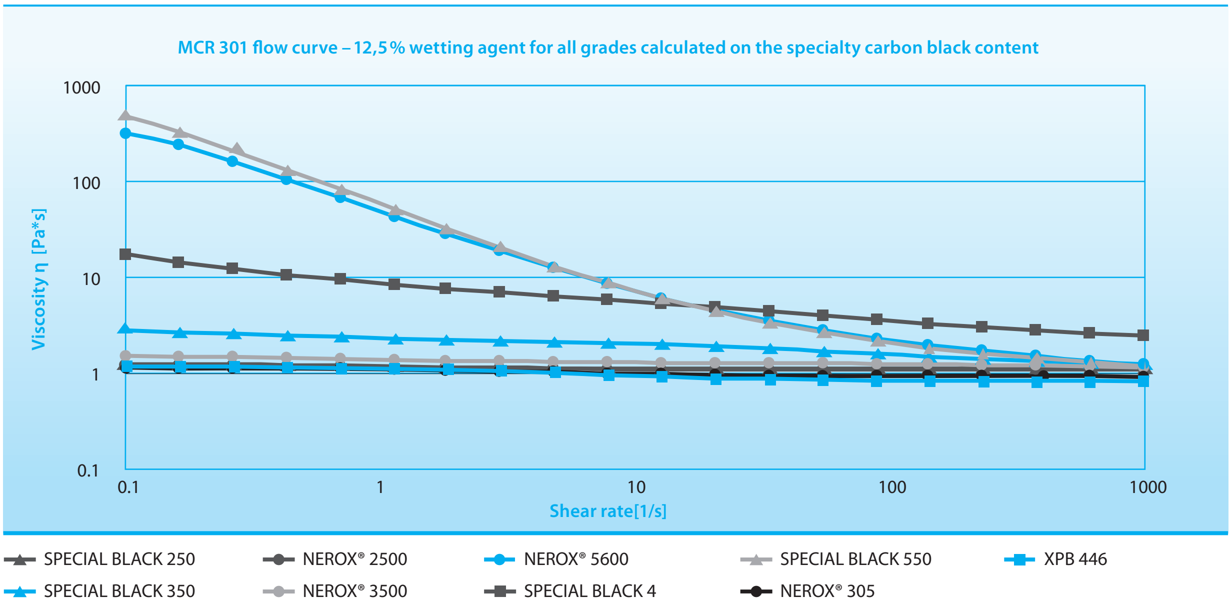


Figure 6

Flow-plate method readings

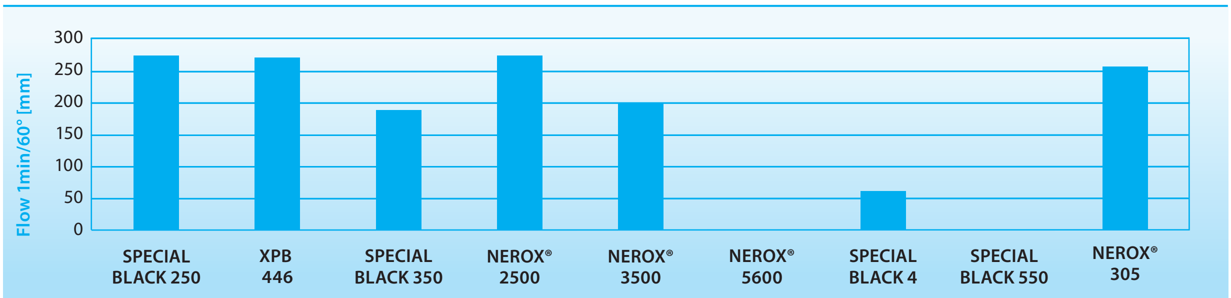


Table 3

Specialty Carbon Black	**Wetting Agent Loading** (calculated on Specialty Carbon Black content)
SPECIAL BLACK 250	12.5%
SPECIAL BLACK 275	12.5%
SPECIAL BLACK 350	25.0%
NEROX® 2500	12.5%
NEROX® 3500	25.0%
SPECIAL BLACK 4	37.5%
SPECIAL BLACK 550	37.5%
NEROX® 305	25.0%

Figure 7

Flow curves with logarithmic viscosity scale showing values from 0.1 to 10 Pa*s for better differentiation

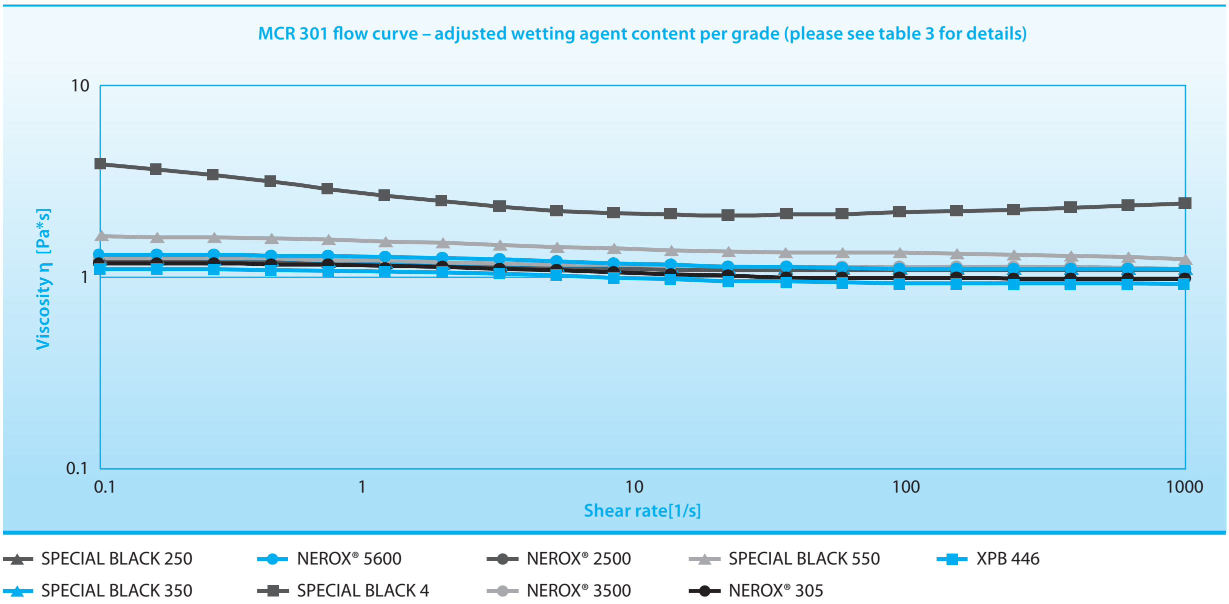
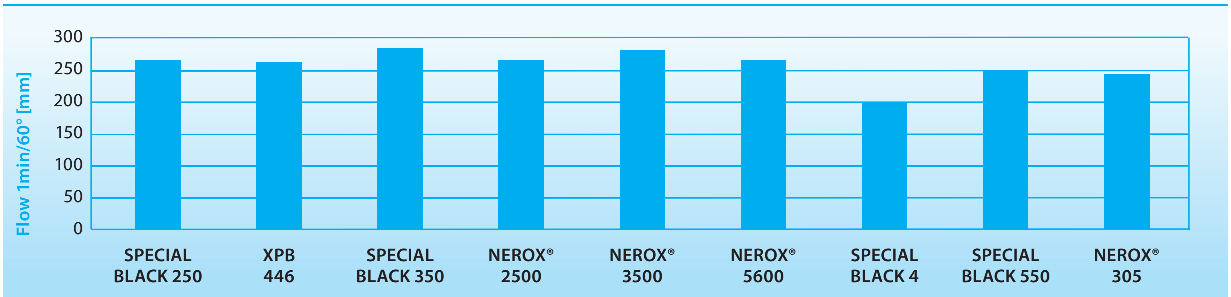


Figure 8

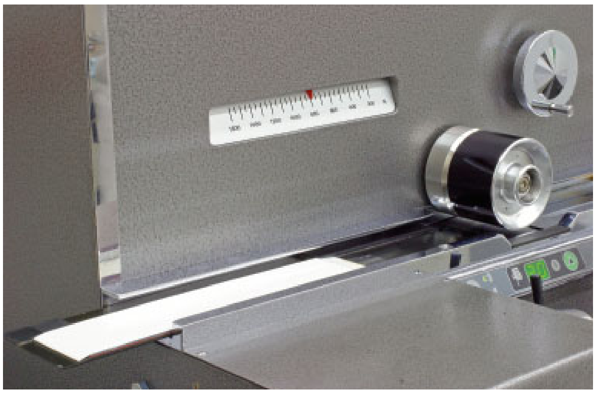
Flow-plate results with adjusted wetting agent content



It is obvious that the adjusted wetting agent loading leads to significant flow improvements in the range of the high surface area and high structure grades. Even though there are differences in the particle size and structure of the post treated grades, it is possible to achieve sufficient flow properties when adjusting the wetting agent loading according to the specific surface area of the specialty carbon black. The above statement is not true for the range of non post treated furnace grades. These kind of products do not reach the flow properties of SPECIAL BLACK or NEROX® grades – even at the upper end of the tested wetting agent loading.

3.3 Optical density, gloss and hue/undertone

A Prüfbau laboratory proof printing equipment (picture 3) was used to provide proof prints on aluminium-coated paper, with an ink layer of 1.50 g/m². Curing took place in an IST UV Minicure (picture 4) machine at a belt speed of 50 m/min and lamp power of 150 W/cm.



Picture 3

Picture 4

The optical density, gloss, and hue achieved with the different pigments in UV curing flexographic inks are plotted in figures 9 to 11. The prints used to obtain all the results shown below, were made using inks that had good flow properties (after optimizing the wetting agent loading).

Figure 9

Optical density (D_B) comparison

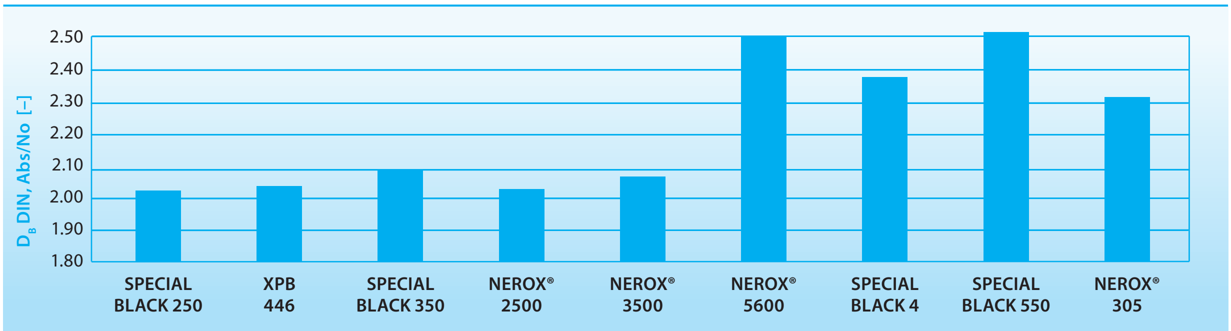


Figure 10

Gloss 60° comparison

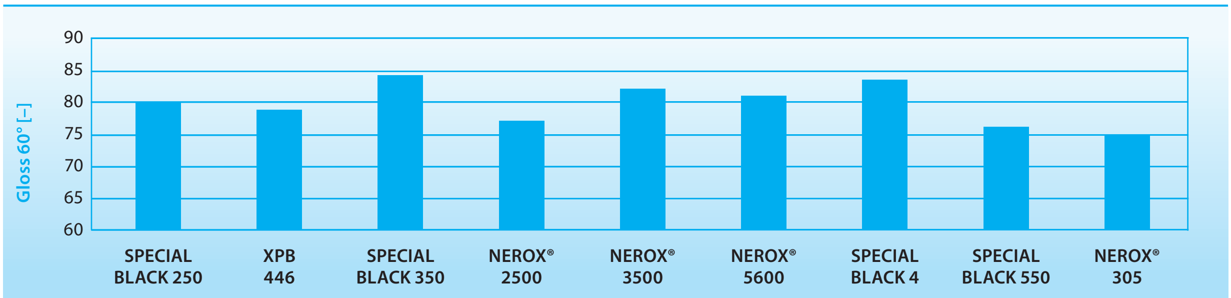
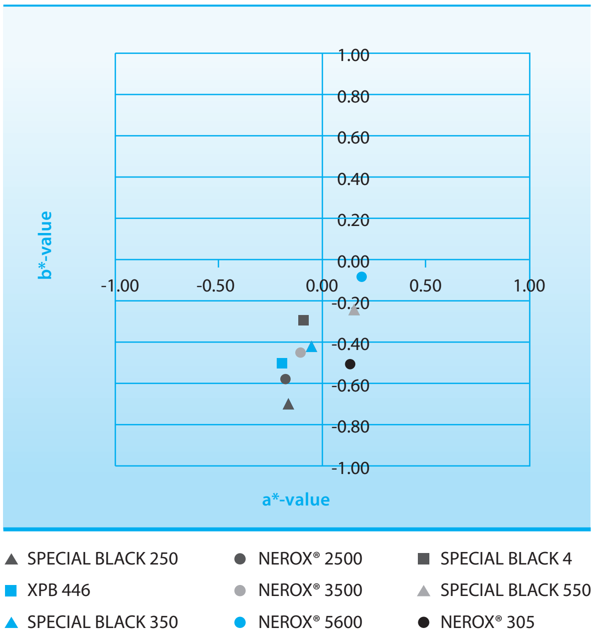


Figure 11

CIE a*/b* value comparison for showing deviations in hue



The colorimetric analysis was performed with GretagMacbeth SpectroEye (Ilumination/Viewer: D65/10 °) and Byk Haze-Gloss. The optical density (D_B) was also determined with GretagMacbeth SpectroEye using a DIN Filter, relative to absolute white, measured without polarizing filter.

It can be seen that the earlier described dependence of print parameters like optical density and bluish hue on specialty carbon black characteristics like primary particle size are valid. The finer primary particle sized specialty carbon blacks especially SPECIAL BLACK 550 achieve very high optical densities, whereas the rather coarse primary particle sized products like SPECIAL BLACK 250 and NEROX® 2500 are distinguished by their bluish hue at somewhat lower D_B values.

The high surface area grades like SPECIAL BLACK 4, NEROX® 305 and SPECIAL BLACK 550 give the possibility to achieve outstanding jetness or regular optical density at reduced pigment loadings.

In terms of gloss superior levels can be achieved by SPECIAL BLACK 4 and SPECIAL BLACK 350. This is mainly due to their good balance between wetting behavior and primary particle size related to the color strength.

3.4 Through cure/film stability

Through cure and film stability was tested via the acetone test method. An acetone wetted tissue is pressed on a proof print and removed after a defined residence time. The degree of print surface damage is evaluated according to an internal scale. Most of the specialty carbon blacks follow the general rule of more difficult through cure with increasing optical density. An exception is the gas black SPECIAL BLACK 4, which shows significantly better film stability in comparison to high surface furnace grades like SPECIAL BLACK 550.

3.5 Storage stability

The storage stability of the test inks was evaluated by comparing the viscosity value of the fresh ink with a measurement of the viscosity that was carried out after approximately 6 weeks of storage at room temperature. Any problems in storage stability would be obvious in a significantly increased viscosity after the storage time.

The results did show that the storage stability is not an issue for all post treated specialty carbon blacks as long as they were well dispersed and sufficiently wetted. Problems were only observed for inks with low wetting agent loadings in combination with high surface area grades or non-post treated products.

3.6 Transparency

The transparency of black printing inks was computed from the difference in optical density of a printing ink printed on transparent film, when measured over a white and a black background. It was found that the greater the difference in optical density, the better the transparency of the printing ink.

Whereas post treated furnace grades showed expected transparency values, it is worth pointing out that exceptionally high transparency values were obtained with the gas black SPECIAL BLACK 4.

3.7 Summary

The intention of this technical information is to help make a preliminary selection of suitable specialty carbon blacks for black UV curing printing inks. Since the properties of printing inks still depend on additional parameters like binders, additives, the dispersion process and the printing carrier used, it is possible for small deviations to occur.

However, this does not affect the principle statements made in this Technical Information such as:

- The higher the surface area of the specialty carbon black, the higher is the wetting agent demand.
- Different wetting agents are partially leading to significant deviations in the achievable jetness and gloss levels of the resulting UV curing printing inks.
- In the selection of commercially available wetting agents the particular surface chemistry of the specialty carbon black needs to be considered to achieve optimum results.
- The lower the surface area of the specialty carbon black, the lower is the impact on the viscosity of the resulting printing ink.
- The finer primary particle sized specialty carbon blacks achieve very high optical densities, whereas the rather coarse primary particle sized products are distinguished by their blue undertone at somewhat lower optical density values.
- Gas blacks like SPECIAL BLACK 4 show advantages in terms of transparency and through cure.

For further information, consulting, and in answering manufacturing and application-engineering questions, please contact our Technical Market Managers responsible for printing systems.

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