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Improvement of Dye Properties of the Azo Pigment Yellow 12 Using a Micromixer-Based Process

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Abstract:

The properties of coloured pigments are primarily affected by the particle size as well as the size distribution. As both are influenced by the production process, the pigment synthesis of Yellow 12 was investigated using a micromixer apparatus. The micromixer ensures fast mixing by multilamination of thin lamellae and thereby a faster complete mixing of the reactants compared to batch processes. It was found that the micromixer-based process leads to a smaller pigment size distribution. This results in an improvement of the pigment properties. Compared to a commercially available Yellow 12 standard the glossiness was increased by 73% and the transparency by 66% with unchanged tinctorial power.

Introduction

Due to the growing use of colour printing in the field of wrapping paper and print media the demand for organic coloured pigments continues to grow. Amongst organic coloured pigments the azo pigments comprise the most well-known class. One example is Yellow 12 which is used as yellow pigment for multicolour printing. The yellow pigment is the last component of the printing process and therefore, it has to have special colour properties. On one hand a high transparency is needed to avoid concealment of the former printed colours; on the other hand a high strength of colour and a high tinctorial power are required. The colour properties of pigments are primarily connected with the particle size and the particle size distribution. Both are affected by the production process.

In an industrial-scale azo pigments are typically synthesised in discontinuous batch processes using stirred tanks with volumes in the range of 20−80 m^3. Thereby, the coupling component is added to a stirred solution or suspension of the diazo component or the other way around. By using such batch procedures, particles with a relatively broad size distribution can be achieved. This is often connected with disadvantages concerning the further processing and the colour properties of the pigments. Frequently, the batch processes necessitate a homogenisation of the product to break up agglomerated and aggregated particles.

Because a broad particle size distribution is a direct drawback of the batch process, advanced processes must be used on alternative production methodologies, which for example, can be based on microreaction technology. During the recent decade microreactors have become a more and more important tool in the field of process development.[1,2] Recently, they have already been used for carrying out azo coupling reactions. Salimi-Mososavi et al. and Wootton et al. report on azo coupling reactions in microchip reactors under an electro-osmotic flow regime.[3,4] In comparison, Hisamoto et al. realised the azo chemistry as a phase-transfer synthesis using a glass microchip.[5] The first published microreactor-based coupling reaction resulting in azo pigments was described by Wille et al.[6,7] Using microreactors composed of microstructured platelets, they studied the azo pigment process on pilot-plant and laboratory scales.

Since the azo coupling is a fast reaction, the process conditions have to be adjusted in a way that a blocking of the microstructured device by the precipitated product is prevented. That a fast precipitation of hardly soluble products can be handled in micromixers has already been demonstrated by Schenk et al.[8] They used various specially designed micromixers to synthesise inorganic powders, e.g., $CaCO_3$ or $BaTiO_3$, with a notably smaller size distribution compared to that of the commercially available material.

The content of this contribution describes the synthesis of the azo pigment Yellow 12 in a semi-continuous process using an interdigital micromixer. Thereby, the microdevice was used for the azo coupling (Scheme 1) — the key step of the pigment synthesis. The azo pigments achieved by applying different experimental conditions were characterised by their size distribution and dye properties.[9]

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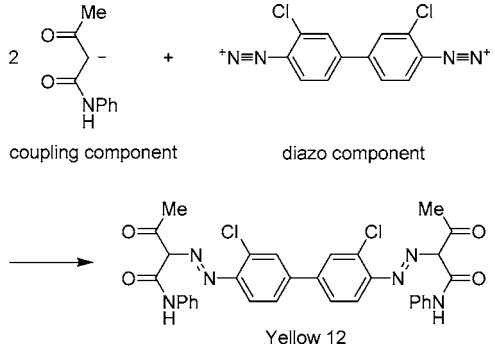
Scheme 1. **Azo coupling resulting in Yellow 12**



Experimental Setup and Processing

The experimental setup consisted of an interdigital micromixer[10,11] (width of the microchannels of the mixing unit, 25 or 40 μm; Figure 1) fed by two HPLC pumps (Gilson-

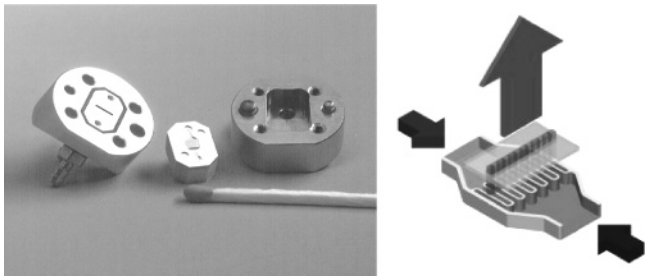


Figure 1. **Interdigital micromixer from IMM (left: upper housing with in- and outlet section, mixing unit, and bottom part of the housing); mixing principle: fast mixing is realised by multilamination[12] of thin fluid lamellae (right).**

Abimed 303 with a preparative pump head SC100), a manometric module (Gilson 803C), and suction hoses with frits.

The starting compounds were introduced as homogeneous liquid solutions (diazo component: 0.12 mol L^{-1} diazotised 3,3′-dichlorobenzidine in hydrochloric acid and coupling component: 0.24 mol L^{-1} acetoacetanilide in an aqueous sodium hydroxide solution). After start-up of the pumps (flow rates: 10, 30, and 50 mL min^{-1}) the first 10 mL of reaction mixture was discarded. The subsequent azo pigment suspension was collected in a stirred beaker (2 L) filled with distilled water (300 mL). After the collection was completed and the reaction mixture was further stirred for 5 min, a resin (CAS No. 8050-09-7) solution was added to stop the crystallisation process. The resinating step was finished after 15 min with stirring. For the after-treatment procedure the reaction mixture was heated to 80 °C to break up a small amount of aggregated pigments and then cooled to room temperature. After 16 h the reaction product was filtered with suction, washed with water (2 × 100 mL), and dried for 24 h.

For the characterisation experiments the azo pigments were dispersed using the adhesive agent Varnish 85 (CIBA, Basel, Switzerland). Both the pigment (0.5 g) and the adhesive agent (2 g) were placed together in a disk mill (PM 240-2, 5100 rpm) and milled four times for 1 min.

The azo pigments were characterised by their particle size distribution investigated by laser diffraction (Mastersizer 2000, Malvern Instruments Ltd., Malvern, UK), by their rheological properties using the rotational rheometer CP-50-1 (Physika Messtechnik GmbH, Stuttgart, Germany), and by their colour properties, namely the glossiness using a reflectometer micro-gloss 60° (Byk-Gardner GmbH, Geretsried, Germany) and the transparency and the tinctorial power based on the CIELab colour difference using a spectral photometer (ColorEye 3100, GretagMacbeth, New Windsor, NY) in connection with the CIELab Software OptiView (Prism Instruments, Pickering, Ontario, Canada).

As reference for the colour properties the commercially available pigment Yellow 12 from the company SICPA (Shanghai, China) was used.[13] For benchmarking, the micromixer-based process for Yellow 12 was compared with a simple batch process. For this purpose, the coupling component was placed in a 2 L beaker, and the diazo component was added slowly with stirring. After complete addition the reaction mixture was stirred further for 3 min, and the resinating step was carried out.

Results

Particle Size Distribution. To check the reproducibility of the micromixer-based procedure for the azo pigment Yellow 12, one experiment was repeated four times. The resulting pigments are evaluated by means of their size distribution.[14] In this context, the volume distribution is more instrumental than the number distribution because the first specifies how fine a certain portion of the total sample is dispersed. In the case of the here-used laser diffraction, the volume distribution is obtained by comparing the detected scattering pattern of a sample with a calculated scattering pattern of an appropriate optical model. The respective diameters gained for the experiments with a mixing unit having 25 μm wide microchannels and a flow rate of 10 mL h^{-1} are listed in Table 1. Due to the small standard deviation of 0.21 μm in the case of the median diameter $D_{50,3}$, a satisfactory reproducibility is given. In contrast, the size distributions within the area of the smaller particle diameters, in particular described by $D_{5,3}$ values, show comparably large deviations.

The particle size distribution was also investigated with regard to its effect on optical and rheological properties of the pigments. Therefore, azo pigments were synthesised with

(9) The content of this publication is based on the diploma thesis of Stephan Forster: Herstellung von Azo-Pigment-Farbstoffen mittels Mikrotechnologie, Nürnberg, Germany, 2001.

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(13) Lot number of the Yellow 12 standard: 20000309(221)RABY.

(14) In practice, the definition of size distribution assumes the definition of sizes into a number of subsets. Subsequently, the number of particles, the size of which is found within these subsets, is determined. Results may be shown in the form of tables, histograms, curves, or equations. On the basis of the cumulative percentage of such a distribution various diameters can be defined. For example $D_{50,3}$ is a volume-based diameter at a cumulative percentage of 50% and in this case is equivalent to the median diameter.

Table 1. **Reproducibility of the particle size distribution using a mixing unit with 25 μm wide microchannels and a flow rate of 10 mL min^{-1}**

no.	$D_{5,3}/\mu$m	$D_{10,3}/\mu$m	$D_{50,3}/\mu$m	$D_{90,3}/\mu$m	$D_{95,3}/\mu$m
1	2.1	3.0	7.3	14.7	17.4
2	1.3	2.8	6.9	15.8	18.6
3	2.0	3.1	7.5	14.4	18.3
4	0.3	1.2	7.4	16.2	19.3
5	0.4	1.8	7.2	15.1	18.0
$\bar{D}$	1.2	2.4	7.3	15.3	18.3
σ	0.8	0.8	0.2	0.8	0.7

the micromixer using both mixing units. Furthermore, the volume flow was varied to study the effect of the flow rate on the pigment quality. The results in Figure 2 and Figure 3 illustrate that the particle size in general can be decreased if a mixing unit with smaller microchannels is used. In particular the amount of bigger particles which are represented by volume-based diameters $D_{90,3}$ and $D_{95,3}$ can be reduced.

For benchmarking the here-described micromixer-based process for Yellow 12, a simple batch process was carried out in accordance to the lab procedure of Trust Chem, Hangzhou, China. The results of the best micromixer-based experiments and the batch experiment are listed in Table 2.

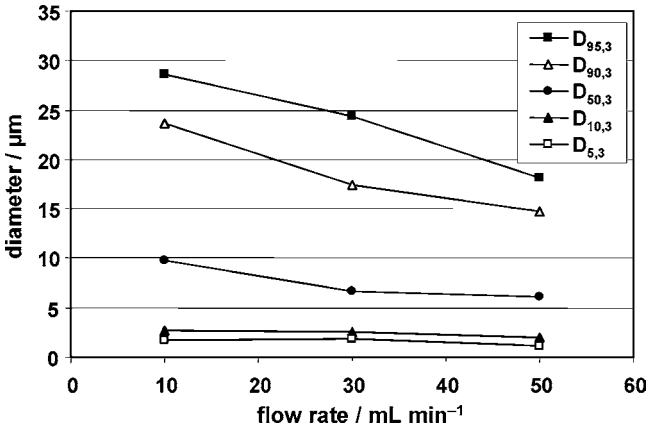

Figure 2. **Various percentiles of the volume-based particle diameter using a channel width of 40 μm (mixing unit) and various flow rates.**

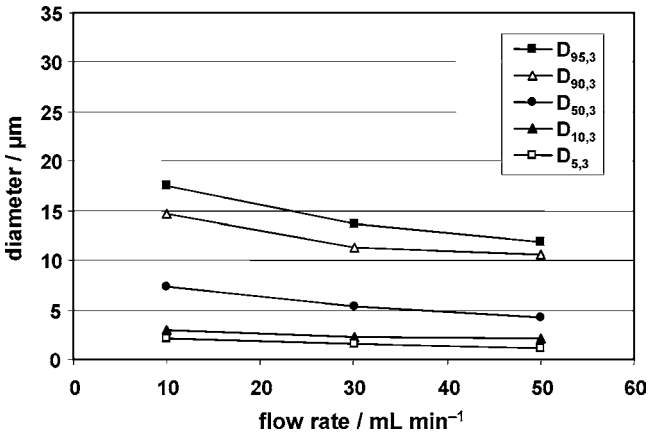

Figure 3. **Various percentiles of the volume-based particle diameter using a channel width of 25 μm (mixing unit) and various flow rates.**

Table 2. **Comparison of the volume-based particle diameters of Yellow 12 prepared by the micromixer-based process (mixing units: 25 μm or 40 μm, flow rate: 50 mL min^{-1}) and the batch process**

equipment	$D_{5,3}/\mu$m	$D_{10,3}/\mu$m	$D_{50,3}/\mu$m	$D_{90,3}/\mu$m	$D_{95,3}/\mu$m
micromixer (25 μm)	1.1	2.1	4.2	10.1	11.9
micromixer (40 μm)	1.1	1.9	6.1	14.8	18.2
batch	1.0	2.2	18.1	48.4	59.0

Although the small volume-based diameters $D_{5,3}$ and $D_{10,3}$ for all configurations are similar, the achieved size distributions differ significantly overall. If the batch process is compared with the micromixer-based process using a mixing unit with 40 μm wide channels, it can be seen that the percentiles of the volume-based particle diameter which are equal or larger than the median $D_{50,3}$ can be reduced by a factor of 3. An even larger reduction ratio is obtained in the case of the mixing unit with 25 μm wide channels. In particular the amount of large particles represented by the $D_{95,3}$ value is decreased. The factor of reduction amounts to 5 in the latter case.

A further difference between the micromixer-based and the batch processes is the number of modes of the particle size distribution. In Figure 4 it is illustrated that the batch process leads to a bimodal distribution, whereas the micromixer-based process results in a monomodal distribution having a light tailing in the diameter range of 0.1−1 μm.

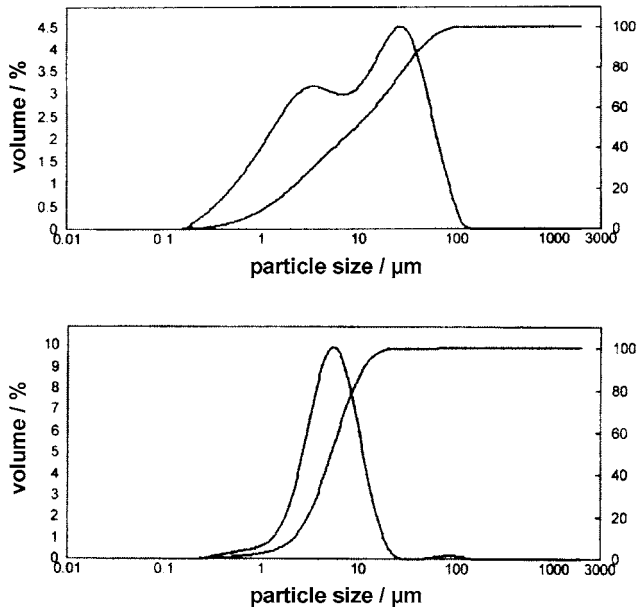

Figure 4. **Particle size distribution of the batch process (top) and the micromixer-based process (bottom: mixing unit with 25 μm wide channels, flow rate 30 mL min^{-1}).**

Furthermore, the batch process results in a comparatively broad particle size distribution having a maximum at approximately 40 μm (Figure 4, top). This illustrates the high values of the volume-based diameters $D_{90,3}$ and $D_{95,3}$ of the batch process listed in Table 2 and their large difference from the median diameter. In comparison, in the case of the micromixer-based processes the differences between various

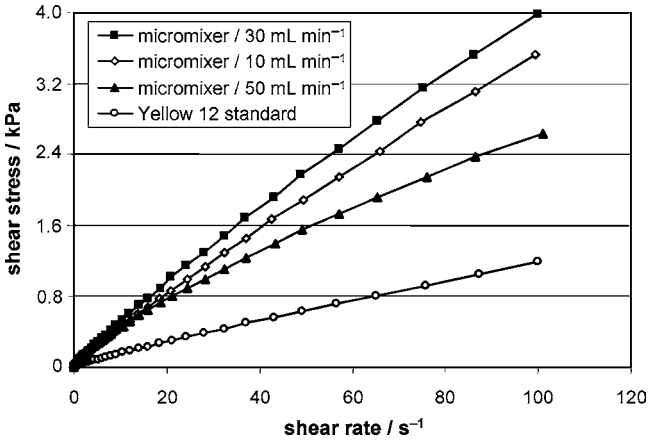

Figure 5. **Flow curves of the pigment dispersions. Relationship between shear rate and shear stress (mixing unit with 25 μm wide channels).**

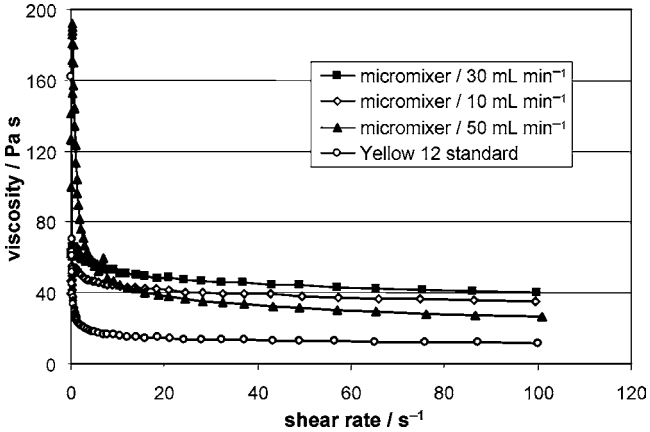

Figure 6. **Dependence of the dynamic viscosity on the shear rate (mixing unit with 25 μm wide channels).**

percentiles are small in particular when the mixing device with 25 μm wide microchannels is applied (Table 2). In accordance, a narrow size distribution is obtained at a flow rate of 30 mL min^{-1} (Figure 4, bottom). As illustrated by Figures 2 and 3, narrower size distributions can be obtained when higher flow rates are applied since the share of bigger particles is then significantly reduced.

Rheological Properties. The flow characteristics of the pigment dispersions are important parameters for the further processing of the dyes. Therefore, the rheological properties of the synthesised pigment dispersions were investigated by determining the relationship between the shear rate and the shear stress as well as the dependence of the dynamic viscosity on the shear rate. The results of the rheological investigations are illustrated in Figures 5 and 6.

The first figure indicates that the azo pigment dispersions synthesised with the micromixer show a stronger dependence of the shear stress on the shear rate than the Yellow 12 standard. A clear trend in terms of the effect of the flow rate on the rheological properties cannot be derived. In general, all dispersions show a more or less linear relationship between shear rate and the resulting shear stress, which is typical for Newtonian fluids. The sole exception is the pigment dispersion resulting from the experiment with a flow rate of 50 mL min^{-1}. The latter pigment exhibits rather a shear thinning behaviour.

Table 3. **CIELab-based colorimetric evaluation of the azo pigments (mixing unit with 25 μm wide channels)**

CIELab coordinate	micromixer flow rate (mL min^{-1})			Yellow 12 standard
	10	30	50	
L^*	84.1	84.2	84.5	84.3
a^*	−6.8	−6.9	−7.3	−3.7
b^*	77.2	72.0	70.8	83.2
ΔE_{ab}^*	6.8	11.7	13.0	

The effect on the dynamic viscosities is shown in Figure 6. Compared with the standard the micromixer synthesised azo pigment dispersions have higher viscosities. Observably different is the dynamic viscosity of the pigment synthesised with the highest flow rate of 50 mL min^{-1}. The large increase of the viscosity at lower shear rates is typical for fluids with shear-thinning properties.

Colourant Properties. A visual comparison using the draw-down method[15] indicates roughly that the transparencies of the pigments synthesised with the help of the micromixer are larger than that of the Yellow 12 standard. This is mainly based on the smaller particle size of the first-mentioned pigments. Furthermore, no difference was observed concerning the hue and the tinctorial power.

To obtain more reliable data for the hue, reflection spectra were recorded. On the basis of these experimental data the coordinates of CIELab colour space (L^*, a^*, and b^*) were evaluated for all azo pigments (Table 3). The differences of these coordinates with respect to the Yellow 12 standard were calculated which led to the colour difference ΔE_{ab}^* as a measure of the Euclidean distance between two colours which are expressed by the Lab coordinates.

While the coordinates for the lightness L^* are similar for all azo pigments, divergences can be found for the redness/greenness a^* and the yellowness/blueness b^*. In the case of the azo pigments synthesised with the micromixer only minor differences between the redness/greenness are obtained. Compared with that of Yellow 12 standard, the green hue of these pigments is slightly larger. Divergences between both pigments can also be found on the b^* coordinate. In general the values of the micromixer-based pigments are smaller, which means that the yellow hue is slightly diminished. The best accordance with the Yellow 12 standard is achieved with the lowest flow rate (10 mL min^{-1}). Since smaller particles should increase the b^* value, the obtained divergences indicate that not the particle size itself but rather the interaction between the smaller pigments and the used adhesive agent Varnish 85 causes the resultant colour shift. Such shifts can be compensated by modification of the pigment dispersion formulation. Nevertheless, the experiments were carried out with an unchanged formulation to allow a direct comparison with the Yellow 12 standard. The overall divergence of the pigments is characterised by the colour differences ΔE_{ab}^* listed in Table 3. With respect to the hue of the Yellow 12 standard the largest conformity of the azo pigments is achieved with the lowest flow rate.

(15) Test for visual comparison of dyes which is also known as "tap-out". It is carried out by drawing the dye solution or suspension out along a sheet of paper using a palette knife, showing variations in intensity from full body to light tints.

Table 4. **Glossiness of the imprinted colour (GU = glossiness units; mixing unit with 25 μm wide channels)**

	GU: micromixer flow rate (mL min^{-1})			GU: Yellow
no.	10	30	50	12 standard
1	38.5	49.1	51.9	31.7
2	41.3	47.9	51.1	27.6
3	39.8	45.3	51.0	30.4
4	42.3	46.5	52.0	29.8
5	42.7	46.7	48.8	27.7
mean	40.9	47.1	51.0	29.4
σ	1.8	1.4	1.3	1.8

Table 5. **Transparency numbers based on the CIELab colour difference using a sheet of black paper (mixing unit with 25 μm wide channels)**

	g·m^{-2}: micromixer flow rate (mL min^{-1})			g·m^{-2} Yellow
no.	10	30	50	12 standard
1	1.60	1.71	2.31	1.37
2	1.52	1.59	2.41	1.48
3	1.57	1.82	2.52	1.51
mean	1.56	1.71	2.41	1.45

In addition to the hue based on the CIELab colour space the glossiness was also investigated. Thereby, the azo pigments were used for a colour print, and the glossiness of the imprinted colour was determined at five positions. The results are listed in Table 4.

Compared to that of the Yellow 12 standard the glossiness is significantly increased at the lowest flow rate by 39% and by 73% if a flow rate of 50 mL min^{-1} is used. Further investigations refer to the transparency and the tinctorial power. The transparency number[16] was determined with the help of the CIELab-based colour difference ΔE_{ab}* between an imprinted and nonimprinted standardised sheet of black paper. Every measurement was repeated three times, and the detected colour difference was related to the weight of pigments on the paper. The results listed in Table 5 point out that the micromixer-based setup results in pigments with much higher transparency. The latter can be increased up to 66% in the case of the flow rate of 50 mL min^{-1}.

The tinctorial power[17] was determined in a procedure analgous to that of transparency except that the azo pigments were imprinted on a standardised sheet of white paper. Compared with the standard sample of the Yellow 12 pigment (0.39 m^2 g^{-1}) the micromixer-based azo pigments show only minor differences regardless of the flow rate used (10 mL min^{-1}: 0.37 m^2 g^{-1}, 30 mL min^{-1}: 0.36 m^2 g^{-1}, and 50 mL min^{-1}: 0.40 m^2 g^{-1}). The largest tinctorial power is obtained for the azo pigments synthesised with the largest flow rate of 50 mL min^{-1}.

(16) The transparency number defines the amount of pigment dispersion which has to be painted on an area of 1 m^2 black paper to achieve a CIELab colour difference of one unit.

(17) The tinctorial power defines the size of a standardised white paper which can be painted with 1 g of pigment dispersion to achieve a CIELab colour difference of one unit.

Summary and Conclusions

The synthesis of azo pigments as a typical batch process was successfully transferred into a semi-continuous process using an interdigital micromixer. Due to the generation of alternating thin lamellae by the interdigital channel structure of the mixing unit a fast mixing of the diazo and the coupling component is achieved. The described experiments demonstrate that the latter leads to a significantly smaller median diameter of the particles as well as a narrower particle size distribution (Figures 2 and 3).

Furthermore, it was shown that, in connection with the particle size reduction, the colour properties of the pigments were affected positively. In comparison to the glossiness of the Yellow 12 standard, the glossiness was increased by 73% (Table 4) and the transparency by 66% (Table 5) in connection with an unchanged tinctorial power.

Overall, the micromixer-based apparatus leads to a significant improvement of the azo pigment process. The colour properties were improved with larger flow rates of the diazo and the coupling component. This is due to a better mixing efficiency of the micromixer at higher flow rates. A blocking of the mixer was not observed at the used concentrations. Concerning the rheological properties, no clear influence of the flow rate was observed, but in general, the viscosity (Figure 6) and the relationship between shear rate and shear stress (Figure 5) were higher than the respective values of the Yellow 12 standard. Nevertheless, the latter parameters are mainly affected by the resin whose improvement was not investigated here.

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