

High Shear Rheological Properties of Dispersions – Influence of Polymer Additives

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ABSTRACT

Extremely high shear rates are applied to pigment dispersions at various technical processes. As reported here, one has to know the rheological properties of dispersions under high shear, which cannot be estimated but have to be measured under similar conditions. Carbonate and clay slurries exhibit a maximum of viscosity with increasing shear rate, responsible for failures in coating processes. Several additives under investigation shift the maximum towards higher shear rates and reduce its height. Water-soluble polymers might even level it off, depending on their molecular weight and molecular weight distribution. It is concluded that they stabilize the liquid layer around the particles. Hence, shear forces may disaggregate flocs, but will not increase the interparticle repulsion.

1. INTRODUCTION

Pigment slurries of high solid content very often cause severe problems with handling and application, especially due to dilatancy phenomena. China Clay and CaCO₃ slurries containing surfactants, lattices, water soluble polymers and other additives are handled at fairly high concentrations (solid contents about 55% to 70% weight by weight) as paper coatings. Their rheological properties are crucial for the runnability on high speed paper coating machines where shear rates between 10⁵ to 10⁶ 1/s are common^{1,2,3}. A proper coating formula prevents these problems. It is therefore necessary to

understand the influence of additives on the rheological behavior of the suspensions especially at high shear rates. This applies not only for paper coating colors but also for other pigment slurries at similar production processes. In all these cases it is impossible to predict the high-shear processing properties of these pigment dispersions from rheological data collected at low to medium shear rates. Inevitably, one needs experimental results under high shear conditions similar to those of application. We report viscosity measurements on inorganic pigment dispersions together with various additives extended to the high shear range. Further, zeta potential measurements characterize the state of the dispersion.

2. MATERIAL AND METHODS

The following pigments were investigated:

CaCO₃: HC 60 – Hydrocarb 60, particle size 60% smaller than 2 μm

HC 90 – Hydrocarb 90, particles size 90% smaller than 2 μm,

Kaolinite: US Clay Nr. 1, Amazon and KKN

Polymers: Carboxymethyl cellulose CMC with following molecular weight (MW) and molecular weight distribution (MWD):

MW = 210.000 MWD = narrow

MW = 210.000 MWD = broad

MW = 370.000 MWD = broad

The pigment dispersions in water were prepared using a high speed stirrer (700 RPM). Unless otherwise mentioned all

dispersions were stabilized with 0.3% anionic surfactant (polysalt). Each sample was stirred for 2 hours at uniform speed (500 RPM) immediately before the rheological experiments were performed.

The rheological measurements were performed with a high shear capillary viscometer (HVA-6, A.Paar KG, Graz, Austria ⁴). This instrument uses nitrogen as driving pressure (1 to 160 bar). The sample is suited in a pressure chamber and separated from the surrounding thermostat fluid by a rubber bag. The driving pressure forces the sample through an attached capillary, the pressure at the capillary entrance and the flow rate are recorded. The instrument offers the possibility to change the test fixture, capillaries as well as rectangular slit devices can be used. The slit geometry used was: 1 mm length, 0.1 mm height, 5 mm width.

With slit dies the shear rate range is increased towards higher shear rates. This device simulates the conditions of blade coaters as used in paper coating, textile and polymer coating and many other processes. Due to the small channel length compared to the height a well defined flow is not develop, however this is advantageous because it models the process conditions. This means that the important end effects which cannot be avoided are now made manifest. They may be calculated but remain to be a considerable part of the flow process. The end effects increase the viscosity level.

Rotational rheometer: MC 100/UM, Fa. Paar-Physica, Stuttgart, BRD

Zetapotential values were measured at constant ionic strength (0.001 m KCl) by means of microelectrophoresis as a function of pH. Instrument: Zetaplus, Fa. Brookhaven Instruments, USA

3. VISCOSITY BEHAVIOR OF PIGMENT DISPERSION WITHOUT ADDITIVES

The flow curves obtained by viscosity measurements enable us to discuss the behavior of the dispersion as it changes under various shear rates. It is influenced by the

concentration and the nature of the pigment, its particle size and particle size distribution.

3.1. CaCO₃ dispersions

Suspensions of Hydrocarb 60 don't show rheological abnormalities, they are insignificantly shear thinning at shear rates below 1000 1/s, exhibit constant viscosity between 1000 and 10.000 1/s and only a slight viscosity increase at high shear rates if the solid content exceeds 65%. Below this concentration almost newtonian behavior is observed.

Hydrocarb 90 slurries are somewhat different (fig. 1). They exhibit a viscosity maximum at concentrations above 65% and shear rates higher then 100 1/s. This viscosity maximum increases with increasing concentration, for example the viscosity of a 75% slurry at a shear rate of 70.000 1/s is the threefold of that at 4000 1/s.

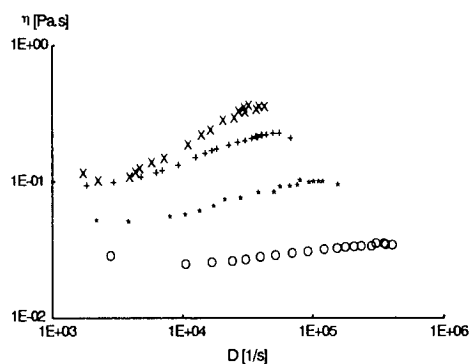


Figure 1: Viscosity curves of HC 90 slurries x 77% solid, + 75,6% solid, . 70% solid, o 65% solid

3.2. Clay dispersions

Suspensions of China Clay (fig. 2) show a rheological behavior very much depending on concentration and shear rate. The low shear behavior is dominated by the increasing yield stress and exhibits therefore high apparent viscosity, rapidly decreasing with increasing shear rate. At the high shear region an other effect onsets which becomes

remarkable at concentrations above 50%. At shear rates above 10^4 1/s a viscosity increase and a viscosity maximum around 10^5 1/s is observed. This maximum is shifted towards lower shear rates around 10^4 1/s with increasing solid contents and the maximum viscosity increases.

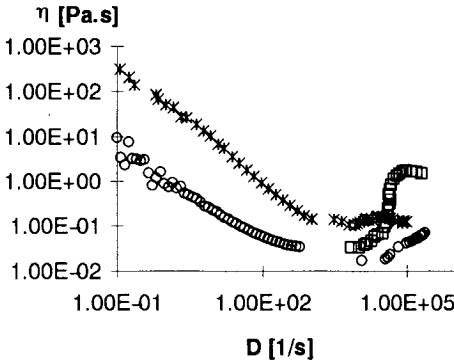


Figure 2: Viscosity curves of Amazon in water

- x 70% solid, capillary: $l = 40$ mm, $d = 0.4$ mm
- o 67% solid, capillary: $l = 40$ mm, $d = 0.4$ mm
- 67% solid, slit geometry

With slit geometries or extremely short capillaries a shift of the flow curve towards higher viscosity is observed. The rheological properties obtained by the slit geometry may simulate the process conditions very well.

The possible reasons of the viscosity increase can be discussed as a change of the particles structure and effective volume. Indeed, the rheological data maintain further information about the hydrodynamically effective volume and structure of the particles. One possible way to obtain information about the interaction between the solid and the solvent is the procedure described by Mooney⁵.

$$\frac{1}{\ln \eta_i} = -\frac{1}{[\eta] \cdot \Phi_i} + \frac{1}{[\eta] \cdot \Phi} \quad (1)$$

- $[\eta]$ = Volume limiting viscosity number
- Φ_i = Immobilization concentration

The relative viscosity values at different concentrations and constant shear rates are correlated to the volume fraction of the solid content. Following Mooney the results should be straight lines at any given shear rate. From the slope we calculate the limiting viscosity number, which describes the hydrodynamically effective volume of the particles. From the intercept we obtain the immobilization concentration, which describes the state of maximum package of the dispersed particles.

The Mooney plot in fig. 3 shows two straight lines describing the typical flow situation at the low shear rate and high shear rate region, respectively.

Slope and intercept of these graphs indicate, that the volume limiting viscosity number decreases with increasing shear rate; the following values were obtained:

low shear rates: $[\eta]$ from 9 to 5 (g/g)

high shear rates: $[\eta]$ from 3.95 to 3.5 (g/g)

The immobilization concentration also decreases from:

low shear rates: $\Phi_i = 0.85$

high shear rates: $\Phi_i = 0.59$

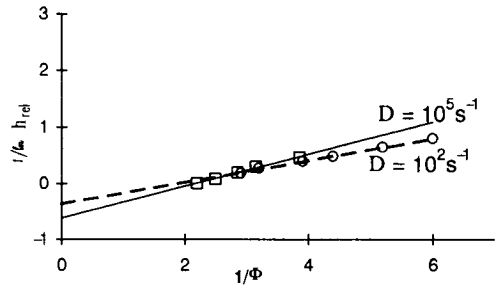


Figure 3: Mooney plot – Amazon in in water at different shear rates

These rheological properties may be explained in the following way⁶: Suspensions of China Clay exhibit at low shear rates weakly agglomerated (flocculated) particles causing the high yield stress. The adhering dispersant contains the counterions balancing the particles charge.

Increasing solid content causes closer packing of the agglomerates and therefore demands higher shear stresses for flow onset.

At high shear rates the aggregates are mainly unflocculated leading to a suspension of a rather high number of small particles as indicated by the reduced limiting viscosity number. Moreover, the particles lose a part of the adhering dispersant including a part of the counterions. This causes strong repulsive forces and an increase of viscosity.

In this way two different states of the same system are supposed⁷, one with agglomerates and balanced particle charge and the other one of particles which considerably have lost the contact to their counterions. Both may be described by continuously decreasing viscosity functions. One state exists under low shear rates, the other one with great viscosity contribution at high shear rates. The transition from one to the other causes the maximum in viscosity and may be called a transient dilatancy. This intermediate increase of the viscosity is the reason of instabilities and the well known production problems.

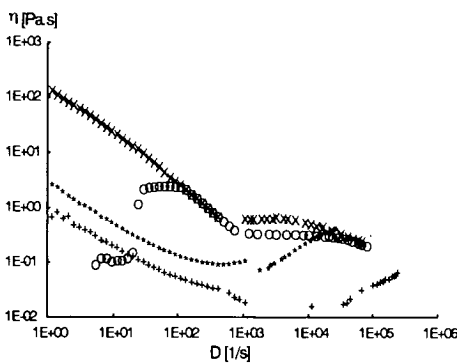


Figure 4: Flow curves of several clay dispersions

- x Amazon 88 68% without dispersant
- + Amazon 88 67% with dispersant
- . US Clay Nr.1 68%
- o KKN 65%

A very similar flow behavior is found with US Clay Nr.1, it shows almost the same

rheological properties as Amazon. The clay KKN which causes even more problems during coating shows a more pronounced shear thickening. Immobilization is reached at a concentration of 68 % and shear rates above 10^5 1/s (fig. 4).

4. THE INFLUENCE OF POLYMER ADDITIVES

4.1. The influence of polymer additives on rheological properties

Water-soluble polymers (carboxymethyl-cellulose CMC) influence the rheological properties of pigment dispersions depending on the molecular weight (MW) and the molecular weight distribution (MWD) of the polymer.

The addition of CMC to clay dispersions increases the viscosity up to medium shear rates and then reduces the dilatancy. This depends on the applied concentration (fig. 5). 0.25% CMC reduces the dilatancy effect, the addition of 0.5% CMC causes the dilatancy phenomenon to vanish, resulting in a suspension showing shear thinning at low to moderate shear rates. Above 10^4 1/s the viscosity remains constant.

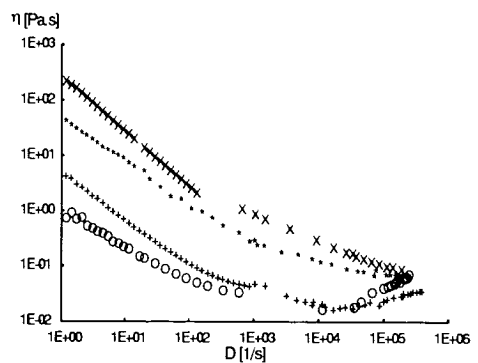


Figure 5: Rheological properties of clay dispersions as a function of CMC concentration

- o 67%, + 0,25% CMC, . 0,5% CMC, x 0,7% CMC

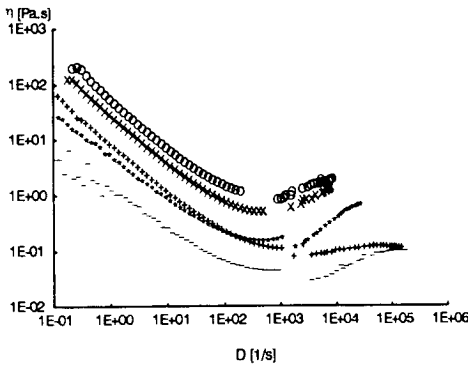


Figure 6: Flow properties of CaCO₃ slurries as a function of solid content and CMC concentration

- 65% without polymer
- + 65% + 0,5% CMC
- . 70% without polymer
- o 70% + 0,5% CMC
- x 70% + 0,25% CMC

This is also observed with different clay types and CaCO₃ (fig. 6). KKN needs more CMC than Amazon to reduce the dilatancy and to shift it towards higher shear rates, although it never vanishes.

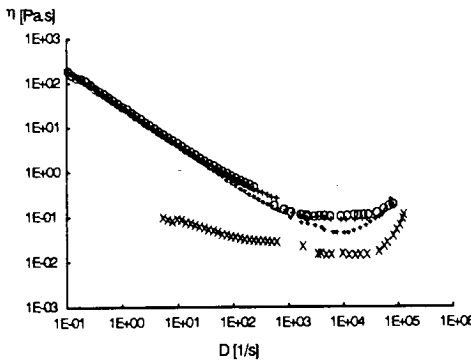


Figure 7: Flow curves of 70% Amazon with 0.5% CMC of different molecular weight

- x without CMC
- o 0,5% CMC medium MW narrow MWD
- + 0,5% CMC medium MW broad MWD
- + 0,5% CMC high MW broad MWD

The varying effect of different polymer MW and MWD is shown in fig. 7. A 70%

Amazon slurry is combined with three different qualities of CMC all at 0.5%. Adding CMC of medium MW with narrow MWD does not alter the flow curve but increases the viscosity level. The addition of CMC with broad MWD causes a reduction of the dilatancy and a shift towards higher shear rates. A wide range of constant viscosity from 10³ to 5*10⁴ 1/s is observed. A very similar effect is found with CMC of high MW and broad MWD.

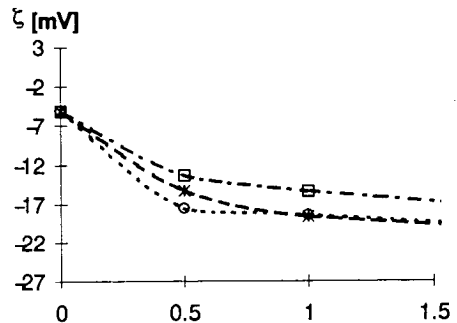


Figure 8 : Zetapotential of Amazon as a function of CMC concentration and quality

- medium MW narrow MWD
- * medium MW broad MWD
- o high MW broad MWD

4.2. The influence of polymer additives on the zetapotential of pigments

The rheological observations can be explained by the interaction of CMC with pigment particles. Fig. 8 shows the zetapotential of Amazon particles as a function of CMC concentration and quality. CMC is weakly anionic, it is adsorbed on the particle surface and increases the zetapotential depending on MW and MWD. Polymers of higher MW will adsorb better and extend the adhering layer. The counterions shielded in the hairy polymer layer cannot be removed by shear forces. This prevents dilatancy the more as long chained polymers build up a thicker dispersant layer on the particle surface.

4.3. The influence of polymers on particle friction

There should be a similarity between the friction effects when particles are passing one another and the wall slip effect^{3,8}. From the rheological data we can calculate a 'slip - coefficient' describing the strength of the interaction between particle and dispersant. This property is also supposed to express the dynamic water retention.

It is calculated according equation 2 known as Buckingham - Reiner equation⁹. Fig. 9 presents this data for the same CMC qualities as described above.

$$\frac{Q}{R^3 \cdot \pi} = \frac{\tau}{4 \cdot \eta} + \frac{v_s}{R} \quad (2)$$

Q = volume flow
R = radius of capillary
v_s = slipping velocity

The clay dispersion without polymer shows the highest slipping coefficient, indicating the weakest interaction between the pigment and the dispersant. The CMC sample with medium MW and narrow MWD reduces the slip coefficient but it is still the

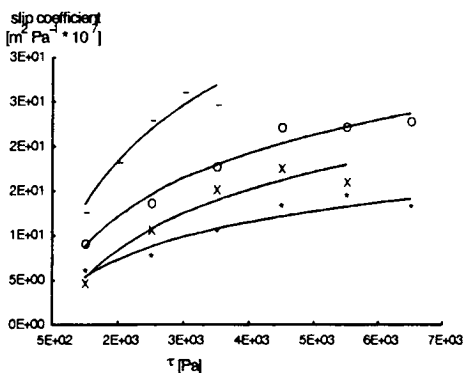


Figure 9: Slip coefficient as a function of shear stress for clay slurries with different CMC types

- without CMC
- high MW broad MWD
- x medium MW broad MWD
- o medium MW narrow MWD

highest one of all CMC samples. The sample with broad MWD containing more of high molecular species - has a smaller slip coefficient. The high MW CMC does not render much slip. This data indicate an increase of pigment - dispersant interaction with increasing amount of high molecular weight CMC.

5. HIGH SHEAR VISCOSITY OF PAPER COATING COLORS

Paper coatings are widely used at high shear rates. Their rheological properties are responsible for the runnability in coating devices. This rheological properties are influenced by the type of pigment, the applied polymer binder and the latex added. Some examples are shown on fig. 10.

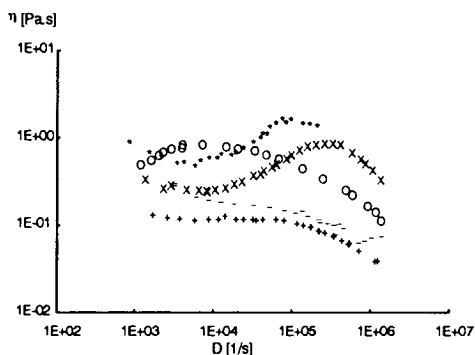


Figure 10: Rheological properties of different paper coating colors

- + Coating A / 67% solide
- x Coating B / latex B
- Coating C / latex C
- CaCO₃ / US Nr.1 67% solide
- o CaCO₃ / US Nr.1 67% solide surfactant

Coating A and the CaCO₃/US Clay Nr.1 slurry with different polymer additives don't exhibit rheological instabilities and perform satisfactory in high shear coating machines. Paper coatings with good processing characteristics show this type of viscosity functions with viscosity values at high shear rates between 0.05 to 0.25 Pa.s. The CaCO₃/Clay slurries may be handled under processing conditions with higher viscosity.

Coating colors B and C cause poor coating quality. Both colors show an increase of viscosity of approximately the 3 fold in the shear rate range of high speed machine conditions. It is generally experienced, that all coatings showing dilatancy phenomena cause problems during processing.

6. DISCUSSION

The flow properties of pigment slurries are mainly determined by the particle-particle and particle-dispersant interaction. These can be modified by means of surface active polymer additives. The systems are very sensitive to shear forces. Moderate shear rates, as coming along with maintaining the stock slurries, may deflocculate weakly aggregated particles. Strong forces due to the coating process may alter the surface and neighborhood of the particles and influence in this way the interaction between particles and dispersant. As the liquid adjacent to the particle surface is sheared off more charges are separated. This gains interparticle repulsion and enhances the viscosity of the slurries. The results presented here show the viscosity increase under high shear forces and the possibility of additives in order to control the crucial viscosity maximum.

The presence of water-soluble polymers which are adsorbed on the particle surface enforces the attraction of dispersant to the particle surface. This layer is not so easy to be sheared off and therefor prevents the viscosity increase with higher shear rates. This effect depends on the polymer molecular weight. The higher the amount of long chained molecules, the more pronounced is the depression of the viscosity increase. This is reasonable because the higher the molecular weight the stronger is the polymer adsorption on the pigment particles. The adsorbed hydrophilic polymers stabilize a layer of immobilized water and counterions around the particle.

The better understanding of the colloidal mechanism under high shear conditions may help to optimize the coating formulas i.e. to

increase the solid content and to improve the processability of pigment dispersions.

7. REFERENCES

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