Runnability and flow-induced aggregation of paper coating suspensions

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Keywords: Runnability, Ring-slit device, Elongational viscosity, Converging flow, Paper coating colour, Styrene butadiene dispersion, Styrene acrylic ester dispersion, Blade coating defects

SUMMARY: Besides high shear rheology and water retention, colloidal stability seems to be a key parameter controlling the runnability of paper coating colours. A clear correlation between the formation of stalagmites in pilot coater trials and the flow-induced aggregation of paper coating suspensions has been found.

A ring-slit device has been developed capturing the essential features of the strongly converging flow field at the blade entrance of standard paper coating machines. The new device is mounted to a controlled flow-rate capillary rheometer. When aggregation takes place the slit is gradually clogged resulting in a strong pressure increase. Thus aggregates are simultaneously formed and "detected". This device allows an investigation of flow-induced aggregation phenomena even on a laboratory scale.

The effect of pigment type, polymer dispersion, thickener and dispersing agent on the stability of paper coating colours has been studied systematically. The size and type of pigment as the main ingredient, the choice of the dispersant and the kind of colloidal stabilisation of the polymer dispersion play a crucial role for the stability of the complete formulation.

Examples are presented where the stability of coating colours could be optimised by appropriate modifications of the binder composition.

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Among all other paper grades coated printing paper enjoys the highest growth rates in recent years. In order to keep this leading position there is still a need for enhancing the productivity by maintaining a high quality level.

Runnability is becoming more and more the key issue, due to the improvements in technology made in the last 20 years and the direct link to cost as a key concern for every entrepreneur. Modern machines run at 1800 m/min, pilot coaters even as fast as 3000 m/min. In addition, the new coaters have a width of up to 10 m. Therefore, it is not surprising that, in a recent survey, runnability was addressed as the most important feature to be improved in the future, even ranked before other properties like brightness, gloss, opacity, printability, higher bulk and uniformity in cross direction and machine direction (Ryan 1999).

Good runnability usually means coating without visual defects on the coated surface and a uniform coat weight. It also means the ability to obtain a certain coat weight at a sufficiently low blade loading in order to avoid web breaks. This aspect becomes more and more important as the machine speed increases and coat weight decreases.

Runnability problems manifest themselves in different ways depending on the coating technique. In blade coating it includes scratches, skips, streaks, spits and "beards", also called stalagmites, growing at the exit of the blade (Eklund, Fors 1988; Engström, Rigdahl 1989).

Scratches usually appear in the form of fine indentations in the coating layer running in the machine direction. Skips are associated with a patterned surface appearance because of areas devoid of coating layer. Stalagmite formation at the blade tip, an easily visible phenomenon, does not necessarily impose a poor coating performance but it questions the long-term reliability of the coating formulation.

In high-speed metered film coating which is becoming a popular alternative to conventional blade coating two other runnability problems occur: misting and orange peel formation (Roper et al. 1999; Reglat, Tanguy 1998). The term misting is used for the phenomenon of the spitting of small colour droplets, and orange peel formation describes the appearance of nonuniformities in the coating layer after film splitting.

A great deal of work has been done in order to understand the different factors influencing the runnability of coating colours, which is in generally balanced by the interplay between base paper properties, application parameters and coating colour features.

By applying an aqueous suspension of pigment and binder onto the base paper, a porous and absorbing material, several physical changes like surface roughening, fibre debonding and weakening of the whole cellulose network immediately take place (Gane et al. 1992). The influence of the application technique like blade geometry or short dwell applicator vs. roll applicator is widely investigated and thoroughly reviewed elsewhere (Triantafillopoulos, Aidun 1997).

A coating colour is a very complex colloidal system composed of a variety of ingredients. Its rheology as well as its water retention properties have a strong effect on runnability. Consequently, numerous investigations are reported trying to characterise these parameters in laboratory experiments. Various test methods characterising dewatering and immobilisation of paper coating colours like the AA-GWR test (Sandås et al. 1989) and the immobilisation cell of BASF (Willenbacher et al. 1999) are now commercially available. The complex rheology of paper coating colors has been studied utilising high shear capillary rheo-

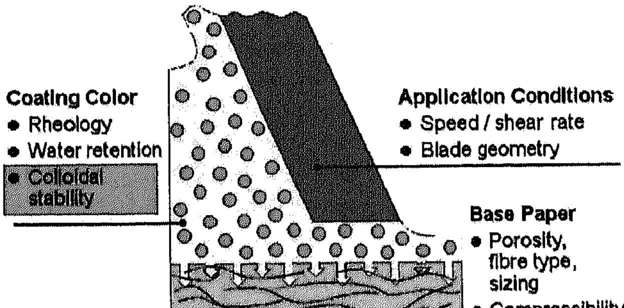

Fig. 1. Factors influencing the runnability.

metry (Laun, Hirsch 1989; Willenbacher et al. 1997), low shear rotational rheometry, small amplitude oscillatory shear (Lavoie et al. 1997) as well as transient shear flow experiments (Ghosh et al. 1997). Elongational flow properties (Lavoie et al. 1998; Isaksson et al. 1998) and apparent wall slip effects (Willenbacher et al. 1997) have also been studied. A modified high pressure homogeniser has been used in order to obtain the viscosity at shear rates even higher than 10^6 s^{-1} (Ramthun et al. 1988). Special slit-shaped capillaries have been developed in order to characterise flow properties under conditions as close to the blade coating process as possible (Weigl et al. 1996).

In this paper we focus on another flow phenomenon which seems to be of great significance especially in converging or elongational flow fields, namely the phenomenon of colloidal stability and flow-induced aggregation. Due to the increased contact time between colliding particles, colloidal suspensions are much less stable in converging flow fields than in shear fields as realised e.g. in viscometric flows (Greene et al. 1994). In order to study this phenomenon we use a capillary viscometer equipped with a slit die resembling essential features of the flow field at the entrance of the blade (*Fig. 2*) in a sense that there is a strongly converging flow field with an entrance angle of 45° into a slit-shaped gap. Of course, the walls of this gap are at rest and they are smooth in contrast to the rough porous web that is in motion during the coating process. Nevertheless, the experiment enables us to study the stability of colloidal suspensions in converging flow-fields. A ring-slit geometry is chosen since it offers the advantage of maintaining a small gap height and a sufficiently large cross-sectional area at the same time. In the first part of the paper the instrument and the operating principle are briefly described. Then it is shown how the results from the ring-slit device correlate to the runnability of paper coating colours as observed on a pilot coater. Finally, the effect of different coating colour ingredients on the stability is discussed systematically and examples are presented where formulations have been optimised based on the results of our laboratory tests.

Experimental

Materials

Hydrocarb 90 and Setacarb GU were supplied by Omya Plüss Staufer, Switzerland; Carbilux and Amazon 88 by Imerys, Netherlands. The carbonates (Hydrocarb 90, Setacarb GU and Carbilux) were received as slurries. Amazon 88 was dispersed in water under addition of a sodium polyacrylate salt (Polysalz S, BASF, Germany) resulting in a slurry with a solids content of 72%.

Styrene acrylic ester dispersions (Acronal, BASF, Germany) and styrene butadiene dispersions (Styronal, BASF, Germany) were used as polymeric binder dispersions. The dispersions were synthesised by radical emulsion in a semi-batch process in a 150 kg vessel polymerisation using persulfate as initiator, according to standard recipes. All binders are derived from commercially available products and modified for purposes of interest: The difference between SB latexes A–E is given by their specific colloidal stability.

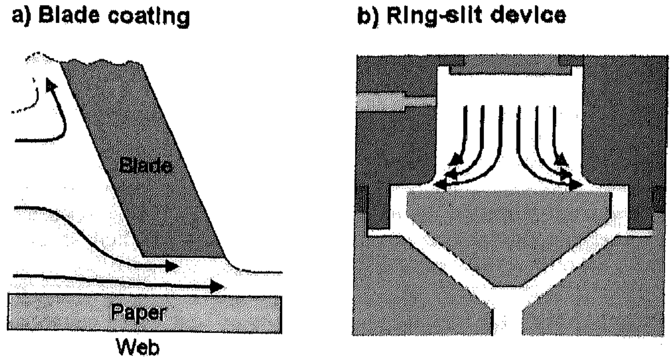

Fig. 2. Analogy between the flow field under the blade and in the ring-slit device.

All dispersions were stabilized by anionic surfactants and acrylic acid was used in all recipes for additional stabilization. After polymerization, the materials were adjusted to pH=7. The average particle size was about 0.15 µm in all cases; Tg of the polymers was in the range 5–15°C.

Sodium polyacrylate salt (Polysalz S, BASF, Germany) was used for the experiments with additional dispersing agent. Carboxy methyl cellulose (CMC; Finnfix 30) was generally used as a cobinder and water retention aid. However, in the machine trial a polyacrylic based polymer as a synthetic thickener (Sterocoll FD, BASF, Germany) was used. Moreover, the effect of the thickener on the flow-induced aggregation was studied by using a polyacrylic based polymer (Sterocoll SL, BASF, Germany).

The coating colours containing pigments, binder, CMC and in one case additional dispersing agent were prepared in a conventional manner and the pH was adjusted to 8.5. The amounts of binder, CMC and Polysalz S are given as the number of parts by weight added to 100 parts of pigments. The solids content was 65% unless stated otherwise.

Coating trials

Machine coating trials were performed on BASF's pilot coater in Ludwigshafen. A woodfree paper with grammage 70 g/m² was coated with 7 g/m² on each side with a formulation containing 50 parts of carbonate (Hydrocarb), 50 parts of clay (Amazon), 6 parts of starch (supplied by Cerestar), 8 parts of a polymer dispersion binder and 0,4 parts of an acrylate polymer dispersion (Sterocoll FD) as a thickener. Three different binders based on styrene-butadiene polymer dispersions were compared in this trial. The machine speed was set to 1600 m/min. The coating colour was applied by a roll applicator with a stiff blade (modular combi-blade JETCOAT 3).

Rheological measurements

For the set of samples where the amount of Polysalz S was varied viscosity was determined in a wide shear rate range. At shear rates <1000 s^{-1} a rotational rheometer (Rheometrics RFS II) equipped with a cylindrical geometry (inner radius R_i=16 mm; outer radius R_a=17 mm; length L=36 mm) was used. The shear rate range from 1000 s^{-1} to 300000 s^{-1} was covered using a home-made piston driven capillary viscometer. The length (L=50 mm) and radius (R=0.3 mm) of the capillary result in L/R=150. For such a capillary the entrance pressure losses for typical paper coating colors are less than 10% and apparent wall slip effects can be neglected for the solids contents as used in this investigation (Laun, Hirsch 1989; Willenbacher et al. 1997). Shear rate as well as viscosity were calculated directly from the piston speed v and the pressure reading p (after performing the Hagenbach-Couette correction), respectively, using the geometric specifications of the capillary given above. All measurements were performed at 23°C.

Description of the ring-slit device

The ring-slit device is mounted to a home-made piston driven capillary viscometer as shown in *Fig. 3a*. A piston drives the sample (dispersion or coating formulation) to flow through the ring-shaped slit at the bottom end of the wall of a cylindrical sample chamber at a pre-selected speed (=constant volumetric flow rate). A pressure transducer mounted above the die records the corresponding pressure as a function of extruded sample volume or time. By repeating the experiment at different piston velocities the effect of flow rate on the stability of a sample can be investigated. The technical specifications are:

Piston speed v:	**1 mm/min – 990 mm/min**
Radius R of cylindrical sample chamber:	**12.5 mm**
Gap height H:	**25 μm**
Mean gap width B=2πR:	**78.5 mm**
Gap length L:	**1 mm**
Entrance length L':	**1 mm**
Entrance angle α:	**45°**

If the sample is stable the pressure adjusts itself to a comparably low constant value determined by the viscosity of the particular sample (*Fig. 3b*). In this case the instrument operates as a high shear capillary viscometer and apparent shear rates $\dot{\gamma}_{app}$ of more than 10^6 s^{-1} can be reached according to

$$\dot{\gamma}_{app} = \frac{6\,\dot{V}}{B\,H^2} \quad \text{with } \dot{V} = \pi\, R^2\, v \qquad [1]$$

$$\tau = \frac{p}{2\,L/H} \qquad [2]$$

If the sample is not stable a strong increase of the extrusion pressure with time is observed due to a clogging of the slit cross-section by the agglomerate created in the converging

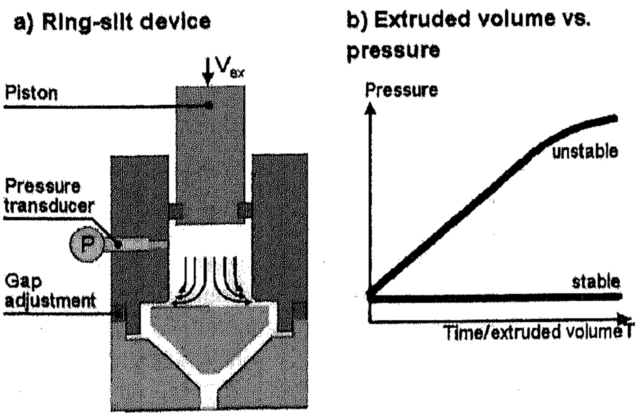

Fig. 3. Ring-slit device (a) and pressure development for stable and unstable samples (b).

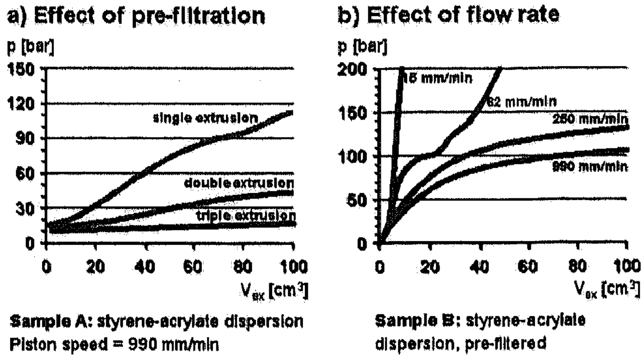

Fig. 4. Effect of pre-filtration (a) and flow rate (b) on the pressure in the ring-slit device for two different styrene acrylate polymer dispersions; gap h=25 μm.

flow field at the entrance of the slit (*Fig. 3b*). In this case the apparatus simultaneously creates and detects the agglomeration.

Aggregates created in previous processing steps are collected at the slit entrance, too. Such aggregates can be removed by pre-filtration through a standard 5 μm or 20 μm filter or by repeated extrusion of the sample through the ring-slit device itself. This is shown in *Fig. 4a* for a pure polymer dispersion. The strong pressure increase observed in the first extrusion of the fluid vanishes completely after triple extrusion of the same sample volume. This dispersion is considered stable in the flow field of the ring-slit device and the agglomerates collected at the entrance of the slit which cause the pressure increase in the first extrusion stem from previous manufacturing or processing steps. On the other hand, the polymer dispersion presented in *Fig. 4b* shows a strong pressure increase with time (or total extruded volume) despite a 5 μm pre-filtration and a large amount of coagulum is found at the slit-entrance after the extrusion experiment. Moreover, the pressure increase strongly depends on the flow rate further confirming that this is due to flow-induced aggregation.

The examples in *Fig. 4* are just shown to demonstrate the performance of the ring-slit device. A discussion about the colloid-chemical reasons for the different behavior of these dispersions is without the scope of this paper.

The characteristic features of the flow field in the ring-slit device have been visualised by simulations using the commercial CFD code COMET. As can be seen from *Figs. 5* and *6* elongation is pre-dominant in the entrance region and the highest elongation rates $\dot{\varepsilon}$ are achieved at the centreline right in front of the slit entrance. In this area where $\dot{\varepsilon}$ is much larger than the shear rate $\dot{\gamma}$ aggregates are formed. On

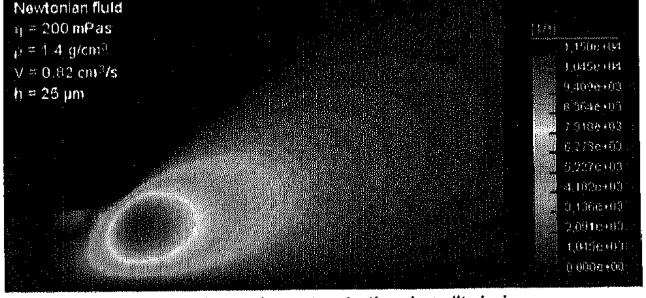

Fig. 5. Simulation of elongation rates in the ring-slit device.

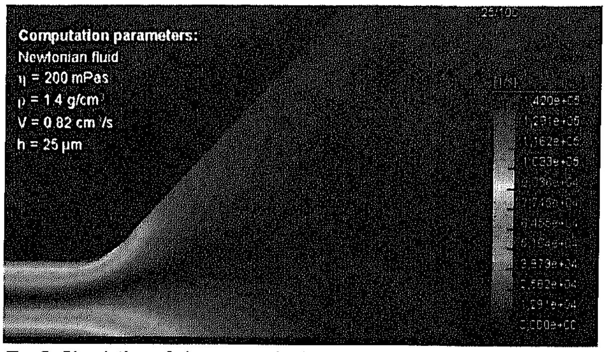

Fig. 6. Simulation of shear rates in the ring-slit device.

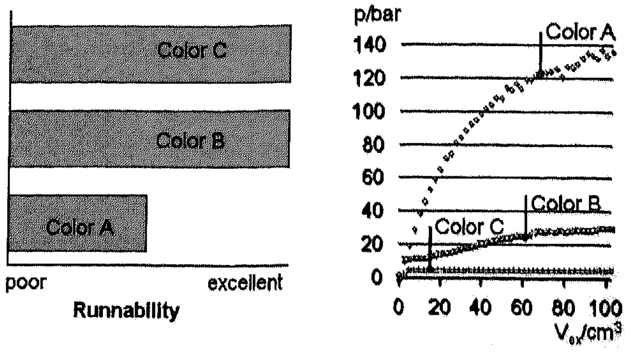

Fig. 7. Correlation between machine trials on BASF's pilot coater (woodfree paper 70 g/m²; coat weight 7 g/m²; 1 600 m/min; stiff blade) and ring-slit experiment (gap h=25 µm; piston speed=990 mm/min).

the other hand, shear flow dominates in the slit itself ($\dot{\gamma} > \dot{\varepsilon}$) with the highest shear rates directly at the wall.

Results and discussion

Correlation between machine trials and ring-slit test

The correlation between the results from the ring-slit test and the runnability of the coating colour is illustrated here using a series of coating formulations, based on carbonate and clay as pigments, with three different synthetic binders, starch as a natural binder and a synthetic thickener. The results are shown in *Fig. 7.*

The formulation A exhibited severe runnability problems when tested on BASF's pilot coater in Ludwigshafen. Much stalagmite formed at the exit of the blade and the blade load increased rapidly. Finally, the trial was stopped because the desired coat weight could no longer be reached. Correspondingly, this colour shows a strong pressure increase in the ring-slit test (*Fig. 6*), indicating that the runnability problems observed on the pilot coater are due to a flow-induced aggregation. On the other hand, the two other formulations B and C with excellent runnability are also stable in the ring-slit test.

Paper coating colours are complex heterogeneous systems and their stability largely depends on the balance of the colloidal interactions among the various ingredients. In the subsequent part of the paper we will present various examples demonstrating the effect of the most important components on the stability of paper coating formulations in converging flow fields.

Effect of pigment type on flow-induced aggregation

Pigments are by far the main part by weight in a coating formulation, and the pigment industry has developed a huge variety of pigment types showing a characteristic chemical composition, particle size distribution, brightness and other properties. Here we focus on carbonate rich formulations. Therefore, we chose three types of pigments: Hydrocarb 90, a fine carbonate, Setacarb and Carbilux, both carbonates with a narrow particle size distribution compared to Hydrocarb 90, but from different suppliers. The coating colours were made up with 10 parts of the styrene-butadiene binder A (dispersion A) and 0.4 parts of CMC as thickener. All three formulations were tested in the ring-slit device; the results are shown in *Fig. 8.*

A constant pressure signal is observed for the Setacarb formulation, showing that this formulation is perfectly stable. The moderate pressure increase observed in the case of Hydrocarb 90 indicates the onset of flow-induced aggrega-

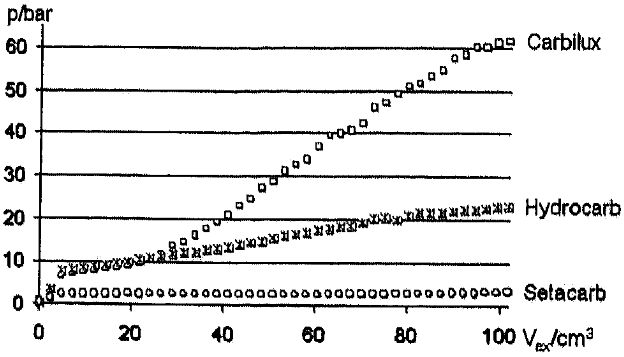

Fig. 8. Effect of pigment type on the stability of a coating formulation (100 pts. pigment; 10 pts. SB-Latex A, 0.4 pts. CMC, s.c. 65%; gap h= 25 µm; piston speed=990 mm/min).

tion. A strong increase of the pressure signal is observed for the Carbilux formulation. Obviously, fast aggregation takes place when this colour is exposed to the strongly converging flow field at the entrance of the ring-slit. In a next step we investigated whether it is possible to improve the stability of the Carbilux formulation by an appropriate choice of binder.

Effect of polymer dispersion on flow-induced aggregation

In these experiments styrene butadiene dispersions A to E were used, differing in the nature of colloidal stability. Carbilux was used as the only pigment in all formulations, and CMC as thickener. The coating colour was made according to the standard recipe with 10 parts of binder, 0.4 parts of thickener and a solids content of 65%. The results of the ring-slit measurements are shown in *Fig. 9.*

The formulations with binders A and B again show a strong tendency to agglomeration. However, modifications introduced with binder C to E reduce the aggregation significantly and with binder C an almost stable formulation is achieved.

Effect of dispersing agent on flow induced aggregation in coating colors

A series of samples with different amounts of added sodium polyacrylate salt as dispersing agent was investigated. This series was based on a coating colour made up by mixing 10 parts of a standard styrene-butadiene polymer dispersion (Styronal, dispersion A) with 0.4 parts of CMC and 100 parts $CaCO_3$ (Setacarb slurry, used as received). All samples were tested in our ring-slit device. The results are presented in *Fig. 10.* The basic sample does not show a

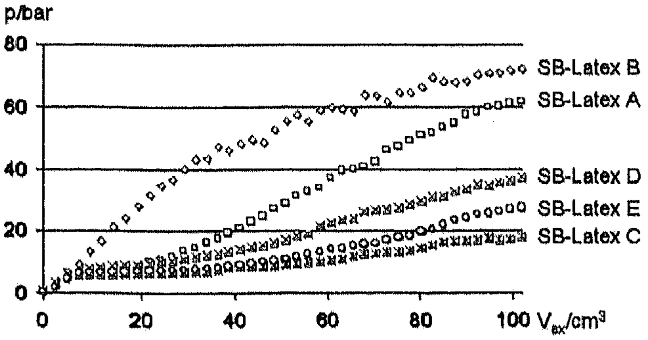

Fig. 9. Effect of latex modification on the stability of a coating formulation (100 pts. Carbilux; 10 pts. latex; 0.4 pts. CMC; s.c. 65%; gap h= 25 μm; piston speed=990 mm/min).

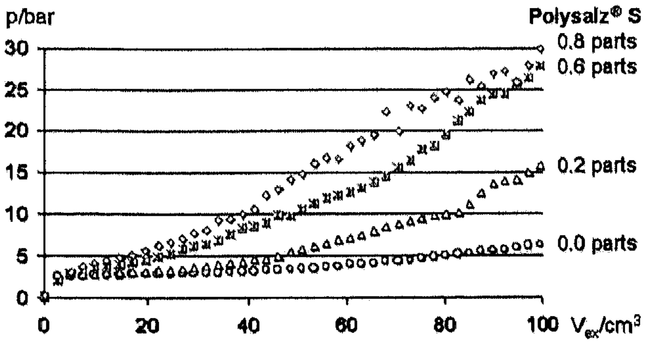

Fig. 10. Effect of added dispersing agent on the stability of a paper coating formulation (100 pts. Setacarb (slurry); 10 pts. SB-Latex A; 0.4 pts. CMC; gap h=25 μm; piston speed=990 mm/min).

significant increase of pressure with time and can be considered stable. But as the amount of salt added increases, the pressure rises more and more steeply, indicating that the slit is clogged faster. Obviously, the formulation is getting more and more destabilised.

Shear viscosity measurements were performed for this set of samples in a wide shear rate range (*Fig. 11*). At high shear rates of around 100 000 s^{-1}, no effect of added dispersing agent on viscosity is observed (no aggregates are formed since the streamlines in this flow field are parallel and hence the contact time between two colliding particles is very short). At low shear rates the viscosity increases with an increasing amount of added dispersing agent. This is typical for weakly aggregated colloidal systems with a gel-like structure (Potanin et al. 1995). This flocculation is presumably caused by a screening of the electrostatic repulsion due to the added salt resulting in van der Waals forces prevailing and hence a net attraction among the particles (van Olphen 1977).

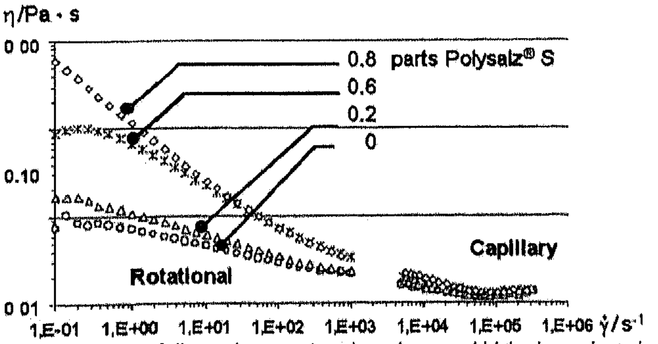

Fig. 11. Effect of dispersing agent on low shear and high shear viscosity (100 pts. Setacarb (slurry); 10 pts. SB-Latex A; 0.4 pts. CMC).

In conclusion, our investigations reveal, that an excess of dispersing agent can impair the runnability of a coating color not by affecting the high shear rheology, but due to its effect on the stability of the formulation.

Effect of thickener on flow-induced aggregation

Water-soluble polymers like CMC or polyacrylic acid based polymers have an important influence on the rheology of coating colours. They are widely used to optimise the flow behaviour from low to high shear rates. Here we have studied the effect of standard synthetic thickeners on the flow-induced aggregation of coating formulations. The coating colours were composed of Hydrocarb 90 and Amazon 88 as pigments, 10 parts of polymer dispersion and a water-soluble, polyacrylic acid based polymer as a synthetic thickener. Two different binder dispersions were used, namely a styrene butadiene dispersion (dispersion A) and a styrene acrylic ester dispersion (dispersion F). Results are presented in *Fig. 12.*

In the case of the coating colour containing the styrene acrylic ester dispersion F the increase of the pressure with time is small and the pressure rise is dominated by viscous contributions, when only 0.3 parts of thickener are used. However, the pressure signal increases dramatically when 0.5 parts of thickener are used. This effect must be due to flow-induced aggregation since it exceeds the viscous contribution by far, as the latter increases only slightly when the amount of thickener is increased. Nevertheless, aggregation is not further promoted when the amount of thickener is further increased.

On the other hand, for the coating colour containing the styrene butadiene dispersion A the reverse effect is observed. Even at a low thickener concentration a strong aggregation effect is observed, which can be reduced by adding more thickener. When 0.5 parts of thickener are used instead of 0.3 parts the extrusion pressure decreases by about 20%, although the viscosity of the coating color rises. In both cases flow-induced aggregation occurs. The colloidal mechanisms controlling these stabilisation/destabilisation phenomena will be the subject of a more detailed forthcoming investigation.

Conclusion

A correlation between the formation of stalagmites in pilot coater trials and the flow-induced aggregation of paper coa-

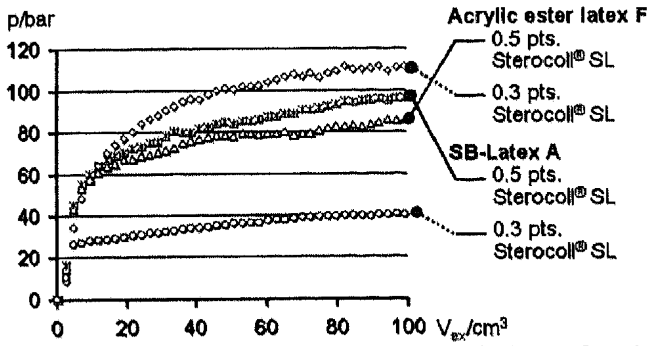

Fig. 12. Effect of thickener Sterocoll(SL in a clay/carbonate formulation (50 pts. Hydrocarb 90; 50 pts. Amazon 88; 10 pts. latex; s.c. 65%; gap h=25 μm; piston speed=990 mm/min).

ting colours has been found.

A ring-slit device has been developed capturing the essential features of the strongly converging flow field at the blade entrance of standard paper coating machines. The device is mounted on a controlled flow-rate capillary rheometer. When aggregation takes place, the slit is gradually clogged, resulting in a strong pressure increase. Thus aggregates are simultaneously formed and "detected". This device allows us to study flow-induced aggregation phenomena even on a laboratory scale.

The effect of pigment type, polymer dispersion, thickener and dispersing agent on the stability of paper coating colours has been studied systematically. Especially, the size and type of pigment as the main ingredient, the choice of the dispersant and the nature of colloidal stabilisation of the polymer dispersion play a crucial role in the stability of the complete formulation.

Examples are presented where the stability of coating colours could be optimised by appropriate modifications of the binder composition.

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