Rheology - An Important Issue For Paper Coating Industry : A Review

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ABSTRACT

The mechanism of rheology control during coating application is well linked with the advancement in paper coating technology. The speed of paper coating machine has been increased to a great extent and the trend seems endless, which creates runnability issues because of inefficient knowledge of rheology. The applied shear, the interaction of the ingredients and composition are mainly responsible for the change in rheology as well as coated paper quality. The present article is the review of the work and experience carried out earlier in the field of rheology of coating color, which directly affects the runnability of machine and end paper properties.

Keywords: *High shear viscosity, immobilization, rheology modifier, water retention*

Introduction

Paper coating color, a concentrated colloidal suspension in aqueous phase, consists of pigments such as ground calcium carbonate, binder such as polymer emulsion or starch for adhesive properties, and rheology modifiers to control the flow properties, water retention and other ingredients. Coating colors are generally formulated at high solid content to improve the quality and minimize drying requirement. The typical range of solid content varies from 50-70% by weight. However, the high solid content makes the rheology more complicated. As the coating solid increases, the coating speed decreases for the smooth running of machine. There are also other parameters which create complicity to the rheology during application and metering. The runnability problems are also observed while metering of coating color. The common problems are the scratches, streaks, or skips in the coating layer due to the build-up of coating on the blade. The blade build-ups are often called "whiskers", "stalagmites", "weeps", or "spits". Therefore, metering of coating color is critical to give defect free and targeted coated layer thickness to the base paper. The web roughness, porosity, compressibility, and the nature of coating color ingredients like particle charge, particle size, compatibility, shear induced behavior, stability etc. attribute high complexity in the operation of paper coating [1].

The components of the suspension or coating color interact with each other. This affects the structure and properties of the system. These interactions influence the rheological properties of the coating color which, in turn, have consequences on the runnability of the coating machine [2-3].

The aqueous phase of the coating color acts as a vehicle. If this water penetration is not controlled, there will be excessive material shift from the coating color to the base, before immobilization of the coating color. The migration rate, towards the surface, of primary pigment particles, polymer emulsion and optical brightening agents (OBA), will have a significant impact on coated paper quality and machine runnability. Pressure has a fundamentally more important influence on liquid penetration than contact time, so it's important in relation to continuing increases of coater speed. [4]

Rheology

Rheology is the study of how matter flows and deforms in response to an applied stress. The yield stress or yield point is the minimum stress necessary to cause a fluid to flow. These fluids behave like solids and do not flow if the applied stress is below the yield point. A fluid in which structure rebuilds slowly after stress stops is thixotropic. This is the decrease in viscosity at the same shear rate over time. It usually originates from the strength of the interaction between particles, polymers adsorbed on the pigment surface, dissolved polymers in the liquid phase, etc. Besides being viscous, pigment slurries, coating colors, and most concentrated suspensions have a degree of elasticity. Therefore a more appropriate term for them is viscoelastic fluids. In behaving as an elastic fluid, coating colors deform under stress and then regain their original form after stress removal [5].The response of polymers and coatings to deformation can be characterized by their viscoelastic behavior [6].

In particular, after the leveling, the rate of the recovery is controlled by both viscoelasticity and processing speed. Poor runnability due to dewatering of the color during the coating process and surface defects can also be correlated with viscoelasticity [3].

Effect Of Pigment On Rheology

Pigment represents 80-90% by weight of the coating color and their main function is to improve the paper surface quality. So the role of pigment in a coating color has pronounced effect on rheology. The main factor affecting the water retention ability, rheological properties, runnability and final properties of coatings, is the packing ability of the pigment particles. This property is, in turn, affected by, e.g., particle size, size distribution, particle shape, shape distribution, and various colloidal forces including interactions with other components in the coating color. Most pigment particles for the coating of paper and board are either flaky, like kaolin and talc, or more or less "round", like ground calcium carbonate (GCC), silica, polystyrene,

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and some grades of precipitated calcium carbonate (PCC). However, other shapes also exist, and amongst the most interesting is the needle-shaped (acicular) aragonite (PCC), which often has a complicated flow behavior but sometimes yields a high quality coated paper. Kaolin slurries like other concentrated colloidal suspensions are viscoelastic and exhibit a wide range of rheological behavior shear thinning to Newtonian to shear thickening that depends on shear and shear rate. At lower shear rates, viscosity of the slurry decreases with increasing shear rate shear thinning. Pigment surface area is another important factor that controls viscosity at low shear rates. At the same weight percent solids, particles with higher surface area have higher Brookfield viscosities. Dispersant level and type, such as anionic dispersants like sodium polyacrylate, sodium hexametaphosphate, or sodium metasilicate are also important in controlling viscosity in this shear rate regime. Suspensions with smoother particles have a lower viscosity. This is because friction is lower as water moves around the particles and as they move past each other [5, 7-8]. All the narrow particle size pigments perform the same with regard to maximum runnable solids, whether PCC or GCC, calcite or aragonite. GCC, having broad particle size distribution (PSD) is the only pigment with higher maximum coating color solids [9]. Coating kaolin with good runnability can be achieved when an optimal percentage of fine particles is present which promotes more efficient particle packing (Fig.1). Thus, a kaolin coating clay can be engineered to have good runnability. Delaminated kaolins with a high aspect ratio and a low percentage of ultrafine particles are the most efficient coating pigments for lightweight paper coatings (LWC) [10]. From the rheological point of view, kaolin coating colors usually exhibit higher viscosity in comparison to those of ground calcium carbonate (GCC), for a given pigment concentration. The differences are mainly due to morphology of the particles, platelet like morphology of kaolinite confers them poorer packing ability, but at the same time, offer better coverage properties of the base paper, especially for light coating weights. During the coating process, lamellar particles have a natural tendency to orientate in the coating layer, therefore covering the base paper more efficiently than non-lamellar particles [11].

PCC particles have a great difficulty to hide the irregularities of base paper. Contrarily, the fine and rhombohedral GCC particles are very suited for paper coating, imparting smoother paper surfaces, which are improved with increasing solids content [12]. Close packing of blocky pigment particles, such as fine calcium carbonate, creates a network of fine capillaries, tends to slow capillary dewatering of colors into absorbent base papers. However, under the external applied pressures at the blade, narrow capillaries alone are likely to be insufficient to resist water loss. Closely packed platey particles introduce an added tortuosity which tends to resist the passage of fluid under pressure [13].

Most talc products currently used for paper coating applications exhibit high aspect ratio and steep PSD. These characteristics have proven beneficial for coverage, runnability and printability in light weight coated rotogravure applications. Judging from the effect of PSD on slurry rheology, a broader PSD should encourage shear thinning behavior [14].

Effect Of Binder On Rheology

It is well known that the addition of binder and in particular, natural binder like starch affects the rheology of coating suspensions. Starch shows weak interaction with the pigment. In some coating suspensions, association between the pigment particles and some components may occur to create a network in the aqueous suspension. This association is the attraction between coating pigments and polymer emulsion caused by some colloidal force such as bridging. If the network has sufficient integrity, one may assume it will withstand some stresses imparted to the coating during drying. The addition of a polymer emulsion that interacts with clay in a clay suspension forms a bulkier structure and enhances void fraction, light scattering, oil absorption, and lower gloss [15]. Different interactions between the polymer emulsion and pigment can occur along with possibly a redistribution of adsorbed material on the pigment or polymer particle surfaces. PVOH (Poly vinyl alcohol) also shows a high interaction with the pigment, but it does not lead to formation of a three dimensional structure at low shear rates. However, strong individual aggregates are formed with enough strength to keep the colors aggregated up to very high shear rates. Coating colors containing

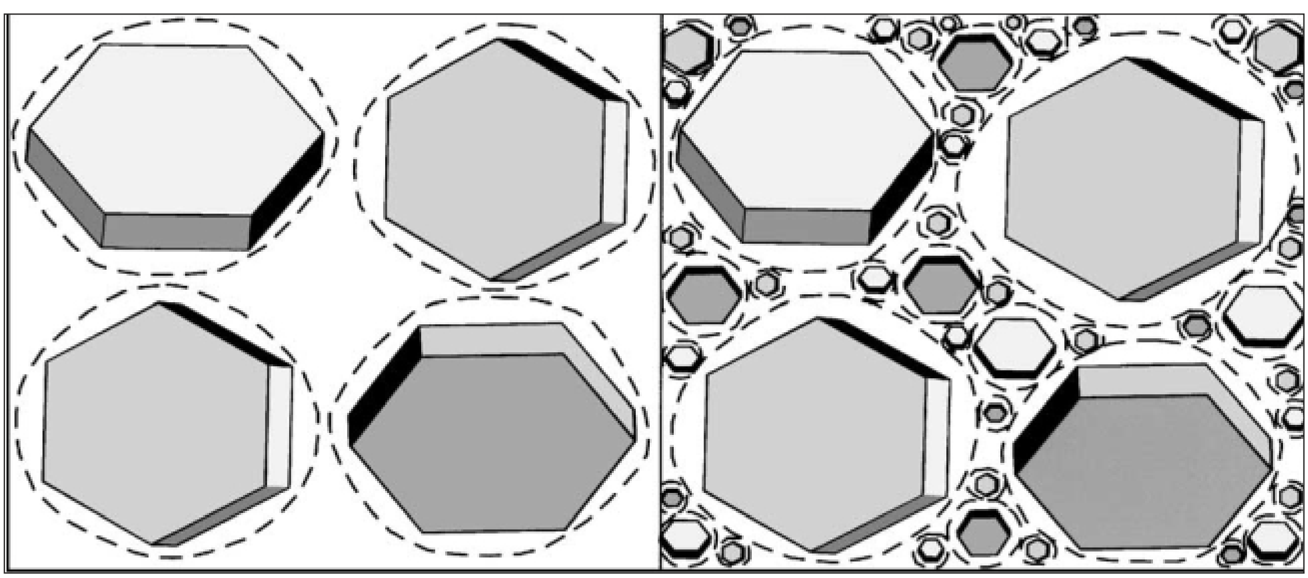

Fig. 1: Particle packing in kaolinite water system

this type of cobinder have a less-pronounced shear thinning nature. The rheology is thus mainly that of the pigment dispersion and the cobinder solution [16].

Role Of Rheology Modifier

Runnability of paper coating colors and the properties of final coated paper depend strongly on dewatering of the color into the base paper during application which is maintained by addition of rheology modifier. Production data demonstrate that over time, coating solids increase, quantity of binder in the coating decreases, and the particle size distribution becomes coarser**.** Considerable effort is put on adjustment of the water retention properties of paper coating colors by proper selection of their ingredients especially the co-binders, thickeners, like CMC (Carboxy Methyl Cellulose), HEC (Hydroxy Ethyl Cellulose) etc. [17- 19].

Both the polymers CMC and HEC have an interaction with the pigment in the color. HEC shows greater affinity than CMC. This greater affinity may be due to the nonionic nature of HEC that allows strong hydrogen bonding with clay. In contrast, the anionic nature of CMC may suppress bonding particularly in the presence of polyacrylate dispersant resulting in a lower affinity. This lower affinity may mean that more CMC is present in the aqueous phase to increase the viscosity and therefore decreases the rate of drainage into the sheet. Due to low clay adsorption, CMCs give desirable high-shear rheology under conditions of high solid content and high speed, and a more continuous coating structure. The poor water-retaining characteristics of the HEC containing colors probably come from strong interaction with the clay resulting in formation of structure within the color [20-21].

Acrylic thickeners have a high affinity for pigments because the polar functional groups of the thickener molecule are attracted by the polar surface of the pigment. The polymer chains adsorb onto the surface of the pigment particles and bind them together by means of a bridging mechanism, which leads to a higher degree of crosslinking within the entire system. The thickening effect, i.e. the increase in viscosity at low shear, is principally the result of the thickener forming bridges by means of adsorption. As the shear rate increases, the structure is broken down into individual aggregates or flocs. The strength of these flocs is not, however, sufficient to withstand the shear forces at high shear rates, giving the colors a pronounced shear-thinning behavior. It is seen that an increase in the addition level led to a substantial decrease in coated paper roughness. Higher viscosity created at a higher addition level, results in poor runnability under the blade leading to uneven surface structure. Coating mixtures having higher viscosity are less susceptible to binder migration than coating mixtures having low viscosity. The thickener that produces an increase in the viscosity of the coating mixture controls the rate of water retention and results in improving the flow property [16, 22-23].

Addition of HASE (Hydrophobic alkali-swellable emulsion) increases the strength of a network to withstand stress during consolidation. Increasing HASE, therefore, gives a bulkier dry coating. Elastic modulus increases with HASE and solids levels [15].

So far as PVOH is concerned, it either stabilizes or destabilizes a colloidal suspension. PVOH containing suspension possesses the highest critical strain as compared to CMC. The CMC and ASE (Alkali-swellable emulsion) containing suspensions give dry layers of higher porosity than the PVOH containing suspension [24]. It has also been found that changing either the amount or the kind of thickener often leads to changes in the porosity of the immobilized layer**.** The thickness of the immobilized layer is proportional to the amount dewatered [25].

Shear Response On Rheology

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 with increase in machine speed and decrease in coat weight [8]. High-shear rheology is one of the key parameters controlling high-speed runnability [26].

As the machine speed increases, a point is reached at which the particle packing of clay platelets may become disordered and the first signs of spitting and dilatancy become apparent under the nonslip condition. However as speed increases; the aspects of pulse dewatering and coat-weight control are likely to become ever more important. It is necessary, however, for blocky pigments to be coated at high solids to gain maximum coverage at the lowest coat weights [13].

Compared to traditional methods such as metered size press (MSP) or blade coating, curtain coating gives superior coating coverage in LWC. Reaching high speeds during coating application is possible. Requirements for forming and maintaining a uniform curtain and defect free coating include control of the boundary air layer and air bubbles in the color. With curtain coating, 85% coverage was achieved with a coat weight of 5.8 g/m^2, while the MSP technique required 8.5 g/m^2 to reach 87% coverage. At the same coat weight of 5-6 g/m^2, there was almost a 40% difference in coverage in favour of the curtain coating method. Because there is no pressure penetration in a curtain coater, low solids coatings give a bulky coating structure and better coverage [27-28].

Effect Of Solids Level On Rheology

In a time of energy conservation, the paper industry has been looking into the possibilities of reducing the demand of energy during the production process. This, of course, also pertains to the field of coating of paper and board where major energy is consumed for evaporation of water from the coated web. It is obvious that by reducing the amount of water in the coating colors, i.e. increasing the solid content, considerable energy savings are possible. The calcium carbonate coating colors show a tendency towards dilatancy only at very high solids content (76%); the clay coating colors show this phenomenon at a solid content of 63%. Working with clay at high solids is much more problematic because the area of dilatant flow behavior is reached at a much earlier stage. This holds true particularly for primary clays (English clays) because of their high shape factor. Secondary clays (US clays) with lower shape factors and especially the globular calcium carbonate show considerably less pronounced change- over from pseudoplastic to dilatant flow behavior. This is the reason why calcium carbonate coating colors have excellent runnability at a solids level only about 8% below the solidification point (SP), while with primary clays a difference of about 10-12% is needed. Electron micrograph shows that with increasing solids a much more closed coating surface is obtained, this leads to a smoother sheet with better hiding power and a higher ink holdout. For LWC rotogravure paper, an increase in coating solids normally improves printability [29].

Defects At Application End

As discussed earlier the control of rheology is very essential for good runnability. The most serious problems arising from poor rheology at high production speed are streaking, skip coating, and most importantly, stalagmite formation and bleeding.

Streaking

Streaking is defined as shadow mark, i.e., areas with greater translucence. The shadow mark occurs only when stiff blades are used which are most common during application of medium coat weight (1015 g/m^2/side). Specifically, this phenomenon is observed in zones of thicker coating, where it appears as a streaky pattern in the machine direction. If optical brighteners are present in the base stock or the coating color, the streak can be recognized easily under ultraviolet light [6, 21].

Skip coating

In blade coaters equipped with conventional roll applicator, the frequency of skip coating increases at high coater speed. The scanning electron micrograph (Fig. 2) illustrates the skip coating phenomenon [6].

Bleeding

The biggest problem in high speed coating, particularly by a blade coater is a loss of color runnability because of bleeding on the blade edge. Bleeding occurs at high speeds, causing streaks or mottle on the coated paper surface. The factors that cause or contribute to bleeding are (Table 1):

- Coating conditions (coating speed, blade angle geometry, coat weight, and other mechanical factors)
- Coating color properties (high shear viscosity, water retention)
- Base paper properties (sizing, pore structure, smoothness, modulus of elasticity, formation etc.)

Many studies indicate that low high-shear viscosity and high water retention are desirable color properties for good coating runnability. In practical operations, however, coating colors with both of these properties do not always exhibit a high runnability, and several of these studies indicate that the viscoelasticity of the color is also a determining factor. It is generally recognized that bleeding decreases with decreasing high shear viscosity and with increasing water retention within the color. Poor particle packing in the region immediately upstream of a blade tip is also a contributing factor to blade bleeding and stalagmite formation (Fig 3), [6, 30].

Table 1: Parameters Influencing bleeding

Parameter	More bleeding	Less bleeding
Slow dewatering	-	
High Solids		-
High coating color temperature		-
Low water retention		-
High viscosity		-
Dilatancy		-
Presence of fibres		-

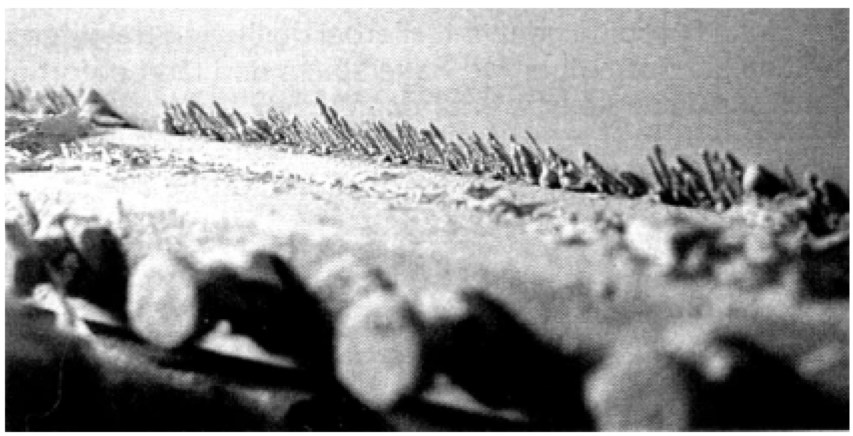

Fig 3: Stalagmites at blade tip

The worst conditions for blade bleeding are high solids in conjunction with low blade angle (stiff blade mode) and high speed. Furthermore the faster a machine runs, the greater will be the influence of the impulse pressure and the greater the likelihood of color dewatering and solids rise at the blade [13].

Scratching

Scratching during metering is also a major defect, which is observed frequently in paper coating application. The following factors are responsible for scratching during paper coating application [21];

- Poor water retention of coating color

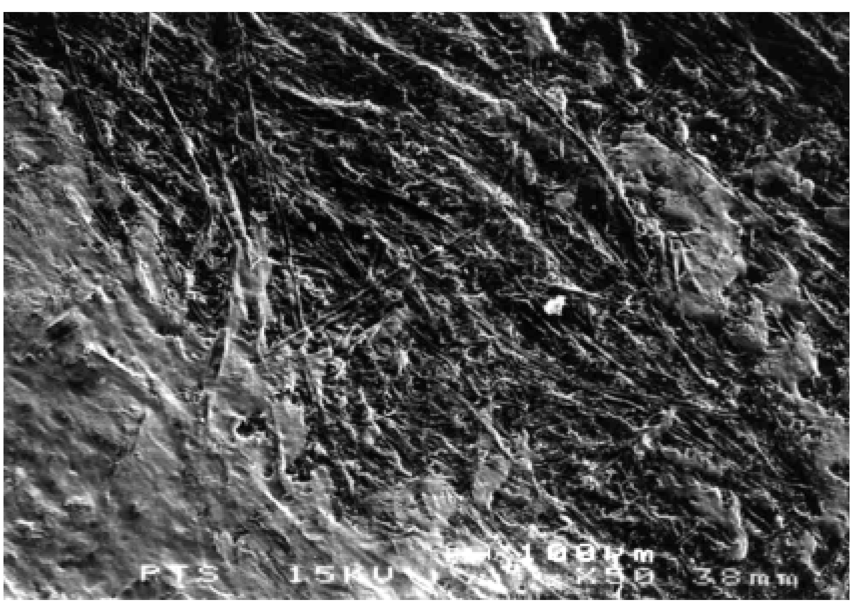

Fig. 2: Skip coating

- Coating filter cake immobilized too soon after application and before metering
- Coating solids too high
- High shear viscosity too high
- Pigment blend forms filter cake with low tortuosity
- Blade geometry

Defects In Coated Paper Generated Due To Poor Rheology

The control on rheology is a key factor for good runnability of coating machine. The different type of defects may generate in the coated paper if the rheology of coating color is not optimized. Some of the defects are described below:

Mottling/ orange peeling

The general opinion is that mottle is caused by an uneven distribution of binder at the coating surface i.e., the result of binder migration from the coating layer during the consolidation process. Another cause of uneven binder distribution is uneven transport of water from the wet coating layer to the base paper. Calendering of a coating with an uneven distribution of mass also can alter the porosity distribution of the coating and thus contribute to mottle in the offset print [31]. Unlike a blade coater, the metered film coater has a film split of the coating color in the exit of the application nip, which may lead to misting and/or orange peel formation. These are the two dominant runnability and quality issues in high-speed film coating that limit its applicability. The relationship between orange peel formation and coating variables is complex. Coating process, base paper, and formulation impact orange peel formation. In most cases, there is a positive correlation between misting and orange peel. In other words, factors that reduce misting at high speed also seem to reduce the degree of orange peel formation. These factors include higher coating solids, higher high-shear viscosity, and smoother base paper. The degree of color flow and leveling after the nip also appears to be important. It has been proven that a coating formulated with a thickener having a slower recovery of viscosity after shearing gives better leveling and lower orange peel formation [32].

Effect on bulk

When applying shear to color under the blade, the shear breaks up particle associations, but these associations recover for the most part within ten seconds after shear force is withdrawn. Study reveals that the coatings that are dried or dewatered rapidly result in lower void fraction. This reduction in void fraction may be due to increased compaction forces but in part can be accounted for by setting a recently sheared coating layer. Although the absorptivity of a substrate has major effect on the dry coating bulk, increasing the elastic modulus of the coating suspension increases the strength of the network and make the dry coating bulkier. The dry coating bulk may become higher with an increasing elastic modulus of a coating suspension [20].

Effect on surface structure

Characterization of surface structure of coating layer is important, since particle orientation and degree of surface order determine gloss and affect the penetration of fluids, such as printing inks. The pore structure in the coating layer is considered one of the most important parameters affecting printing ink behavior on paper surfaces. It is well known that pore diameter and volume fraction can affect adsorption and setting of the ink vehicle. An increase in the amount of thickener could be correlated to an increase in pore volume and gloss. The fact that the CMC coating suspension had the highest modulus may explain why CMC gave the lowest surface roughness if compared with PVOH and ASE [33].

Conclusions

The rheology of coating color is crucial factor, which affects the machine runnability and coated paper properties. The particle size, size distribution, particle shape, shape distribution, and various colloidal forces including inter particle interactions are responsible for the change in rheology. The type of thickener, binder, cobinder, process conditions also affect the rheology of color. So the problems, which occur during metering of color, can be sorted out by proper selection of each ingredient keeping in mind the effect on rheology as well as end paper quality.

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