

# Studies on Rheological Properties of High Solids Coating Colors (I)

## – Effect of Rheology Modifiers on Viscoelastic Properties –

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### ABSTRACT

For a fundamental study for high concentration pigment coating, the effects of alkali swellable emulsion (ASE) type rheology modifier and surface adsorption emulsion (SAE) type rheology modifier on both the stability and the viscoelastic behavior of a coating color were elucidated. The coating color prepared with SAE type rheology modifier showed superior thermal and mechanical stability than that with ASE type. In the high concentration and high speed coating process, the mechanical stability of a coating color was a key parameter since both impact force and shear force were increased with the increase of coating color concentration and coating speed, respectively.

**Keywords:** *High concentration coating, rheology modifier, alkali swellable emulsion, surface adsorption emulsion*

## 1. Introduction

It is quite obvious that the high concentration coating has several advantages such as improved quality of the coated paper, increased productivity and reduced production costs. Papermakers have tried to increase the speed of a coating machine by increasing the coating color concentration. However, rheological properties (bleeding and streak), penetration behavior

and stability of coating color might be deteriorated when the coating color concentration is increased.<sup>1-3)</sup>

In 1970', starch had been generally used as a thickening agent or a water retention agent as well as a traditional usage, binder.<sup>4)</sup> However, there has been a limitation in increasing coating color concentration because the cooking concentration of starch is low. Recently, starch has been modified for coating. But problems such as deterioration in paper gloss and smoothness still remained unsolved because of the inherent thermosetting properties of starch and thus the

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poor calenderability of coating layer. In addition, the print mottle due to the irreversible shrinkage of film during drying is one of the reasons of the limited usage of starch. Thus, starch has been mainly used only for under-coating or MSP (metering size press) coating.<sup>5)</sup>

In 1980<sup>7)</sup>, SBL (styrene-butadiene latex) was introduced on the market. Coating technology was upgraded with the usage of latex, which made the high concentration coating possible. In addition, the coated paper with latex shows excellent smoothness improvement after calendering due to good thermoplastic characteristics of latex. However, a new synthetic thickening agent has been needed in order to overcome the limitations of SB latex (water retention and thickening) and to substitute starch. Alkali swellable synthetic thickening agent was developed and has been utilized up to recently.<sup>6)</sup> However, the synthetic thickening agent could not perfectly overcome the fundamental limitation. Water retention and thickening behavior of the alkali swellable synthetic thickening agent still depend on the swelling of the chemicals, the same with starch. The maximum coating color concentration with a synthetic thickening agent is about 64% in case of double coating and about 67% in case of single coating. Moreover, a decrease in carrier-ability of dyes has been showed due to the decreased amount of SB latex addition compared with starch which serves both as binder and as thickening agent.

Recently, in order to improve the shortcomings of the synthetic thickening agents, a surface adsorption type rheology modifier has been developed, which has amphoteric charges, low molecular weight, and high glass transition temperature (Tg).<sup>7)</sup> The surface adsorption type rheology modifier can redisperse the charged pigments with improving the dynamic penetration to base paper and the rheological behavior of coating color.

The objective of this paper was to elucidate the effect of SAE (surface adsorption emulsion) type rheology modifier on properties of coating color. High concentration coating colors were prepared with ASE (alkali swellable emulsion) type thickening agent and SAE type rheology modifier, and then the stability and the viscoelasticity of coating colors were evaluated.

## 2. Experimental

### 2.1 Materials

GCC (ground calcium carbonate, KFMT-95H) and clay (Ultra Gloss LV) were used as coating pigments. Table 1 shows the physical properties of the pigments. SB latex was used as binder. The properties of SB latex used are shown in Table 2. ASE type and SAE type rheology modifiers were used and their properties are shown in Table 3.

**Table 1. Physical properties of coating pigments**

Pigments	%, <0.23 $\mu\text{m}$	%, <0.55 $\mu\text{m}$	%, <1.09 $\mu\text{m}$	%, <2.15 $\mu\text{m}$	Mean particles diameter ( $\mu\text{m}$ -d50%)	Surface area ( $\text{m}^2/\text{cm}^3$ )
GCC	0.00	4.82	57.16	97.79	1.025	7.378
Clay	23.60	65.18	68.31	79.65	0.366	19.051

**Table 2. Physical properties of SB latex**

Surface tension (dyne/cm)	Viscosity (cPs)	Tg ( $^{\circ}\text{C}$ )	Gel contents (%)	Particle size (nm)
52.5	350	2	83	110

**Table 3. Properties of rheology modifiers**

Series Properties	ASE type rheology modifier	SAE type rheology modifier
Chemical composition	acrylate polymer	modified acrylate oligomer
Solid content (%)	30	30
pH	3.5	8.1
Viscosity (cPs)	10	150
Ionic charge	anionic	amphoteric
Average molecular weight (g/mole)	> 400,000	< 2,000
Glass transition temperature (°C)	15°C	50°C
Mechanism	alkali swellable thickening	adsorption on pigment surface
Function	water immobilization	steric stabilization of pigment

## 2.2 Methods

### 2.2.1 Preparation of coating color

For the preparation of coating color, only types of rheology modifier were varied while the coating color formulation and solids content were unchanged. The added amounts of each rheology modifiers were varied

**Table 4. Coating formulation for evaluating the effects of rheology modifier on the coating color properties (unit = part)**

Series Components	ASE type rheology modifier	SAE type rheology modifier
Clay	20	20
GCC	80	80
ASE type rheology modifier	0.07	-
SAE type rheology modifier	-	0.20
Latex	11	11
OBA	0.5	0.5
Solids content (%)	70	70
LSV (cPs)	1350	1280
HSV (cPs)	40.6	34.4
Hysteresis area (cm <sup>2</sup> )	13.247	7.962

to adjust the low shear viscosity (LSV) of the two prepared coating colors at a similar value. Details of the formulation and the basic properties of the coating colors are shown in Table 4.

### 2.2.2 Evaluation of rheological properties

Basic physical properties and rheological properties of coating color were tested as follows:

- Water retention value : Water retention value tester (ÅA-GWR, Kaltec, USA), 10 cc, 60 sec, 2 bar.
- Low shear viscosity: Brookfield viscosity (LV-DV1+, USA), Spindle No. 4, 60 rpm.
- High shear rheology: Bob E (DV-10, Kaltec, USA), 4400 rpm.
- Viscoelastic behavior : Cone & Plate (Stresstech HR, Rheologica, Germany), Gap 0.20 mm, interval 2.000E+1s, Frequency 1.0E+0 Hz, Delay time 1.00E+0 sec.

### 2.2.3 Evaluation of coating color stability

Mechanical stability of coating color was evaluated with Maron tester (AB-802, Tester sangyo, Japan). A given amount of coating color sample (50 g) was stirred for a given time at a given speed (rpm) and then filtered on 325 mesh wire. The stirring time and speed were adjusted in order to better assess the experimental

results, depending on coating color conditions. The weight of the remained was measured. Experimental results were expressed as follows, (the solids weight remained on 325 mesh x 100 / total solids weight). The lower value indicated superior mechanical stability.

Chemical stability was evaluated as follows. Calcium chloride solutions with various concentrations were prepared. 0.05 g of coating color sample was introduced into 5 mL of calcium chloride solutions. After 1 minute, it was checked if aggregation of solids was formed. Higher concentration of the calcium chloride solution at which aggregation was formed means that the chemical stability of the coating color was superior.

Thermal stability was evaluated as follows. A sample of coating color was stirred (speed: 1000 rpm, temperature: 60°C) and filtered on 325 mesh wire. The weight of the remained on the wire was measured. Thermal stability was calculated by the same method with the mechanical stability. The lower value indicated superior thermal stability.

Viscosity stability was evaluated by letting a given sample of coating color stand at 25°C for 24 hours and by measuring viscosity of the coating color without stirring. The difference between the measured viscosity and the initial viscosity of the coating color was calculated. The lower the difference is, the better the viscosity stability is.

Unlike other experiments, dispersion stability was measured after filtration of the prepared coating color on 325 mesh wire. The filtrate was let stand for 24 hours at 25°C, stirred for a given time at a given speed and re-filtered on 325 mesh wire. The weight of the remained solids on the wire was measured. Calculation is the same as the mechanical stability. A lower value represents superior dispersion stability.

### 3. Results and discussion

#### 3.1 Stability of coating color

In case of high concentration and high speed coating, the coating color is exposed to severe physical and chemical environments and thus has a high chance of stability deterioration. Since the deterioration in stability of a coating color will profoundly influence the runnability of a coating process and the quality of coated paper, the system stability of a coating color is considered to be very important.

When coating color concentration is increased, the specific gravity is increased and therefore the impact force which is proportional to mass is increased. Such phenomenon is aggravated when coating speed is raised at high concentration coating. Thus it is very important to check the mechanical stability of a coating color and the shear fatigue caused by being exposed to

**Table 5. The stability of coating color depending on the type of rheology modifiers**

Series	Stability items	ASE type rheology modifier	SAE type rheology modifier
Viscosity (cPs)	initial	1,350	1,280
	without agitation after 20 hr	3,980	1,810
	Re-agitation after 20 hr	1,630	1,250
	Dispersion stability (%)	0.05	0.03
	Thermal stability (%)	0.21	0.02
	Mechanical stability (%)	0.23	0.03
	Chemical stability (%)	above 0.05	above 0.05

repetitive shear forces.

Table 5 shows the effects of the type of rheology modifier on stabilities of coating color. Coating color with ASE type rheology modifier showed a little bit lower thermal and mechanical stabilities than that with SAE type rheology modifier. This might be due to the swelling effect of ASE type rheology modifier and the aggregation of pigments. Other alkali swellable type rheology modifiers such as CMC and starch would be expected to show similar behavior. In addition, due to its molecular structure, natural rheology modifiers would increase the deterioration rate of coating color stability by retrogradation when it is exposed to heat and shear.

### 3.2 Viscoelastic behavior of coating color

In high concentration coating, it is very important to consider viscoelastic characteristics of coating color since coating speed will be raised due to faster immobilization of coating color and easier drying. Physical meaning of viscoelastic parameters of coating

color is illustrated in Fig. 1.  $G'$  (storage modulus) represents the elastic component and  $G''$  (loss modulus) the viscous component.  $\delta$  (phase angle) means phase difference between shear strain and shear stress. If the phase angle of a material is  $0^\circ$ , the material is a perfect elastic body in which there is no phase difference at a given shear strain. If the phase angle of a material is  $90^\circ$ , the material is a perfect viscous body in which there exists a phase difference at a given shear strain.

Figs. 2 and 3 show the effect of type of rheology modifiers on rheological properties. The coating color with ASE type rheology modifier showed a bit slower increase rate in phase angle ( $\delta$ ) with increasing shear stress than that with SAE type rheology modifier, which implies the slow decrease of elasticity of the coating color (Fig. 2). In addition,  $G'/G''$  (storage modulus/loss modulus) value of the coating color with ASE type rheology modifier showed slower decrease with increasing shear stress than that with SAE type rheology modifier (Fig. 3). This result indicates that elastic component was more dominant than viscous component in all ranges of the tested shear stress. On the other hand, the coating color prepared with the SAE type rheology modifier showed a bit faster increase in phase degree and a faster decrease in  $G'/G''$  value with increasing shear stress, which is the behavior of viscous material.

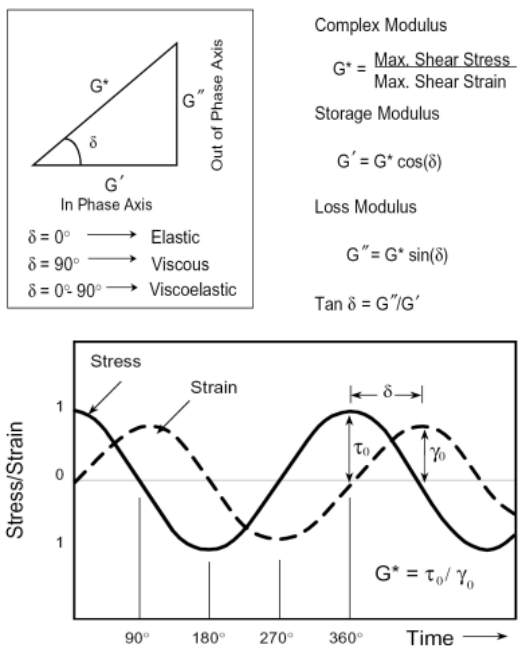


Fig. 1. Definition of viscoelastic parameters.<sup>8-11)</sup>

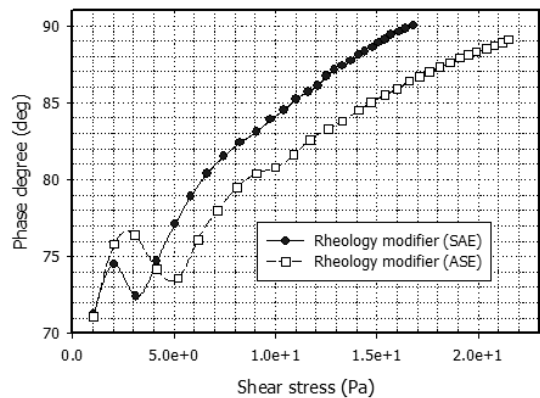


Fig. 2. Effect of rheology modifiers on the relation between phase degree and shear stress.

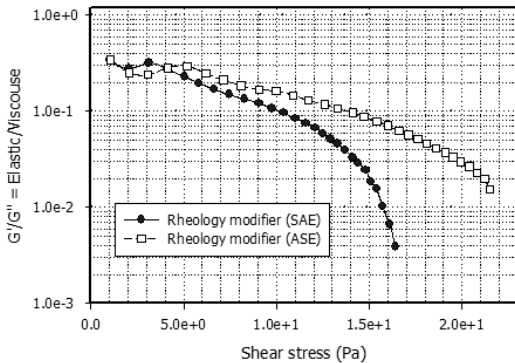


Fig. 3. Effects of rheology modifier on the storage modulus and loss modulus ratio.

These results suggest that the ASE type rheology modifier provided higher elasticity on coating color than the SAE type rheology modifier. One possible explanation for this is that ASE type rheology modifier dominantly absorbed water molecules in coating color and behaved like a swelled sponge. In a high concentration and high speed blade coating process, it has a high possibility of causing troubles in the runnability of the coater and the quality of coated paper when a coating color has high elasticity. Higher elasticity of a coating color means higher resistance to pressure under a metering blade. Thus, if elasticity of a coating color is high, it can increase the possibility of causing an increased coat weight problem in case of a bent blade coating or a runnability problem like bleeding in case of a tip blade coating. In addition, high elasticity of a coating color implies high impact force which is a function of stress absorbing time. In case of coated paper quality, the coating color with high elasticity would cause bleeding and streaks due to the die swelling effect that is the phenomenon in which coating layer applied on paper is compressed under a metering blade and then expanded right after leaving the metering blade (Fig. 4).<sup>12, 13)</sup> Natural binders which interact with water molecules would still have the problem of increased elasticity.

On the other hand, it was observed that SAE type rheology modifier changed the elastic behavior of a

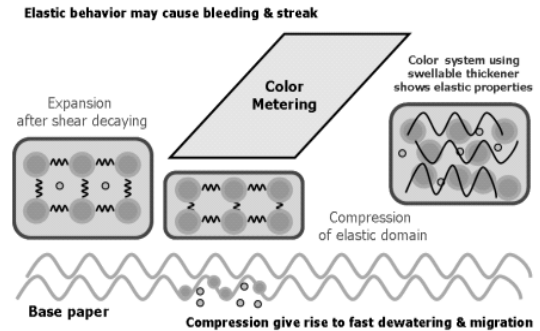


Fig. 4. Effects of the elastic behavior of coating color under blade pressure on the bleeding and streak.

coating color to viscous behavior under shear (Figs. 2 and 3). This may be due to the fact that SAE type rheology modifier did not cause local unevenness of coating color concentration and thus did not form the elastic and swelled structure. Because the elasticity of coating color is low, the smoothness of coated paper surface with SAE type rheology modifier would be superior to that with ASE type rheology modifier due to the reduced swelling of coating layer after metering. In addition, control of coated weight would be easier with SAE type rheology modifier. Effects of type of rheology modifier on properties of coated paper were studied in previous researches.<sup>14-16)</sup>

## 4. Conclusions

Effects of rheology modifier types on stability and visco-elastic behavior of coating color were elucidated. It was found that the coating color with alkali swellable emulsion (ASE) type rheology modifier showed lower thermal and mechanical stability than that with surface adsorption emulsion (SAE) type. In the high concentration coating process, types of rheology modifier significantly influenced on the chemical, mechanical and thermal stabilities of the coating color. Mechanical stability of a coating color shall be a key parameter to be considered in high concentration and high speed coating because the increased concentration of coating

color would increase specific gravity and thus impact force and the increased coating speed would increase shear force. Moreover, it was observed that ASE type showed higher elasticity in high concentration than SAE type while SAE type rheology modifier changed the elastic behavior of a coating color to viscous behavior when shear force was applied.

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