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Some aspects of the rheological properties of paper coating suspension and its application: 2. Influence of pigment composition, binder level, co-binder and simple electrolytes on flow properties

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The effect of pigment composition on the rheological properties of coating suspensions, containing 5 to 15 wt% of synthetic binder, was studied by using a low-shear rheometer, 0.5 to 100 rpm, at 22°C. The pigments used differed in shape from plate-like (China clay) to spherical-like ($CaCO_3$) particles and were used either individually or in blends. The effects of five types of co-binders and three types of simple electrolytes on the flow parameters of clay-based coating suspension were also presented. The results showed that the flow properties (τ_0, η_{pl}, $\Delta\eta$ and η_i) of the coating suspension formed from pigment blends decreased with $CaCO_3$ content. Individual pigments have a higher degree of pseudoplasticity and lower thixotropic coefficient compared with pigment blends. Coatings containing synthetic binder have lower flow parameters compared with binder-free suspensions. Synthetic binder in combination with hydrocolloid additives, namely three grades of CMC, HEC, HMC (carboxymethyl, hydroxyethyl and hydroxymethyl celluloses), oxidized starch and casein (as synthetic/synthetic or synthetic/natural dual binder) produced higher flow parameters compared with single binder coating formulation. Also, it was found that addition of monovalent electrolyte (NaCl) has a smaller effect on flow parameters than divalent electrolytes ($CaCl_2$ and $MgCl_2$).

(Keywords: rheological properties; coating suspensions; pigment and binder)

INTRODUCTION

An inorganic pigment is a finely divided inorganic substance, usually a stable solid, which is added to the vehicle to produce a stable coating. The purpose of the pigment is to obtain opacity, colour and control of flow during application, and to influence the course of weathering after exposure to various environments. These properties are related to particle-size distribution, particle shape, colour and refractive index at all wavelengths.

The geometry of the shape of a particle is of importance for two reasons. The surface area of any shape approaching that of a sphere is a maximum; the edges of an acicular shape often offer areas of high surface activity and by their alignment in the surface relieve and reduce strain. At this time, the shape, particle size and interchemical nature of pigments are some of the most studied and documented subjects in the coating industries.

Most of the literature is concerned with studying the mechanical and optical properties of pigmented coating films including plate-like clay and/or spherical $CaCO_3$ particles as a pigment component and styrene–butadiene latex as a binder[1–10]. However, a few investigators have examined the rheology of coating suspensions including a pigment blend of clay and $CaCO_3$ (refs 11, 12). The literature on coating formulations usually has contained one binder (styrene–butadiene latex occupies the dominant position for paper coatings), despite the fact that a dual binder, e.g. synthetic/natural binder system, provides flexibility, i.e. introduces significant quality enforcement. The rheological properties of coating suspensions including either single or dual synthetic binder have been evaluated at higher shear rates[13–18].

From the above survey, it is of interest to study the flow properties of coating suspensions, measured at low shear rates (0.5–100 rpm), and to consider the effects of pigment composition, binder level, type of co-binder (synthetic or natural) and simple electrolytes. The latter two factors are investigated in comparable conditions with those mentioned in previous work[19]. All formulations under investigation include Acronal/Acrosol (anionic acrylic copolymer) as a binder.

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Table 1 Viscometer speeds

Speed (rpm)	Shear rate (s^{-1})
100	122.36
50	61.81
20	24.47
10	12.24
5	6.12
2.5	3.05
1.0	1.22
0.5	0.61

EXPERIMENTAL

Two types of coating suspensions have been used in this work. The first, delivered from Paper Mill, Alexandria, Egypt, possessed a solid content of 25 wt% and included clay (Amazon 88) as a pigment. The other was prepared in our laboratory with the same formulation as above, except for using clay or $CaCO_3$ (Hydrocarb), either individually or in a blend, as a pigment component.

The two coating formulations used in this study were based on 100 parts of mineral pigment (clay and/or $CaCO_3$) to which 0.29 pph sodium polycarboxylic acid (as a dispersing agent), 54 pph Acronal/Acrosol (in ratio 7/1 as a binder), 3.075 pph Urecol (as a smoother) and 0.123 pph optical brightener (Blancophor) were added. The solid content was held constant at 25 wt%, and pH was adjusted with NaOH to 8.6.

For the rheological measurements, a low-shear rheometer (0.5–100 rpm), model ERV-8, was used, at 22°C. The viscometer speeds are shown in *Table 1*.

The flow curves were analysed as a Bingham fluid[20]. The coefficient of thixotropy, Bingham parameters (τ_0 and η_{pl}), pseudoplasticity ($d \log \tau / d \log D$; S) and structural viscosity ($-d \log \eta / d \log D$; $\Delta\eta$) were measured from the equations in our previous work using linear regression analysis[19].

RESULTS AND DISCUSSION

Influence of pigment composition

To obtain coating suspensions of different structures, mineral pigments of different compositions and shapes are included, e.g. China clay and $CaCO_3$. In this trial, the following formulations are examined:

Pigment	100
$CaCO_3$/clay (%)	0, 25, 50, 75 and 100
Sodium polycarboxylic acid	0.29 pph of pigment
Acronal/Acrosol (7/1)	54 pph of pigment
Urecol	3.075 pph of pigment
Optical brightener	0.123 pph of pigment

The individual suspensions were adjusted to 25 wt% solid content. Coating suspensions were prepared in a kneader at 1000 rpm, and the rheological measurements were carried out at 22°C after storage for 24 h from the time of preparation.

Figures 1 and *2* and *Table 2* show the flow behaviour of coating suspensions based on clay, $CaCO_3$ or their blends.

Figure 1 and *Table 2a* show that the formulations with pigment blends and with 100% $CaCO_3$ have a thixotropic behaviour. The coefficient of thixotropy increased gradually on increasing the $CaCO_3$ percentage from 25 to 75% in pigment blends, while a relatively low value was obtained from the formulation containing 100% $CaCO_3$.

The formulations containing individual pigments have a higher degree of pseudoplasticity as compared with that containing a pigment blend. The degree of pseudoplasticity increased (decrease of S value) on reducing the percentage of clay in the pigment blend from 75 to 25% (*Table 2a*).

For the individual pigments, the initial viscosity (η_i), structural viscosity ($\Delta\eta$) and Bingham parameters (τ_0 and η_{pl}) in the case of clay-based coating suspension are higher than those for $CaCO_3$-based suspension (*Figure 2*

Table 2 Influence of pigment composition

$CaCO_3$/clay (%)	Coeff. of thixo. ($g s^{-1}$)	Bingham parameters			$-d \log \eta/d \log D$		$d \log \tau/d \log D$			
		τ_0 (Pa)	η_{pl} (mPa s)	$+r$	$\Delta\eta$	$-r$	S	$+r$	η_i[a] (Pa s)	R[b]
(a) In presence of binder										
0	–	0.711	22.045	0.998	0.705	0.992	0.295	0.958	1.180	–
25	0.023	0.485	17.219	0.999	0.561	0.988	0.415	0.966	0.750	–
50	0.023	0.312	13.666	0.994	0.578	0.991	0.422	0.984	0.494	–
70	0.063	0.384	13.306	0.993	0.605	0.997	0.395	0.993	0.520	–
75	0.074	0.455	14.418	0.971	0.617	0.999	0.383	0.997	0.520	–
100	0.019	0.489	11.182	0.995	0.684	0.990	0.274	0.932	0.885	–
(b) In absence of binder										
0	0.041	0.764	8.621	0.997	0.808	0.995	0.205	0.917	1.350	0.874
25	–	0.729	9.289	0.989	0.798	0.972	0.212	0.919	1.250	0.600
50	–	0.411	11.605	0.992	0.705	0.984	0.295	0.919	0.720	0.686
75	–	0.797	13.965	0.998	0.724	0.995	0.276	0.970	1.390	0.374
100	1.160	4.557	60.600	0.965	0.681	0.999	0.317	0.998	6.930	0.128

[a] η_i = apparent viscosity at 0.5 rpm
[b] $R = (\eta_i)_p/(\eta_i)_a$ where $(\eta_i)_p$ = initial apparent viscosity of suspension in presence of binder and $(\eta_i)_a$ = initial apparent viscosity of suspension in absence of binder

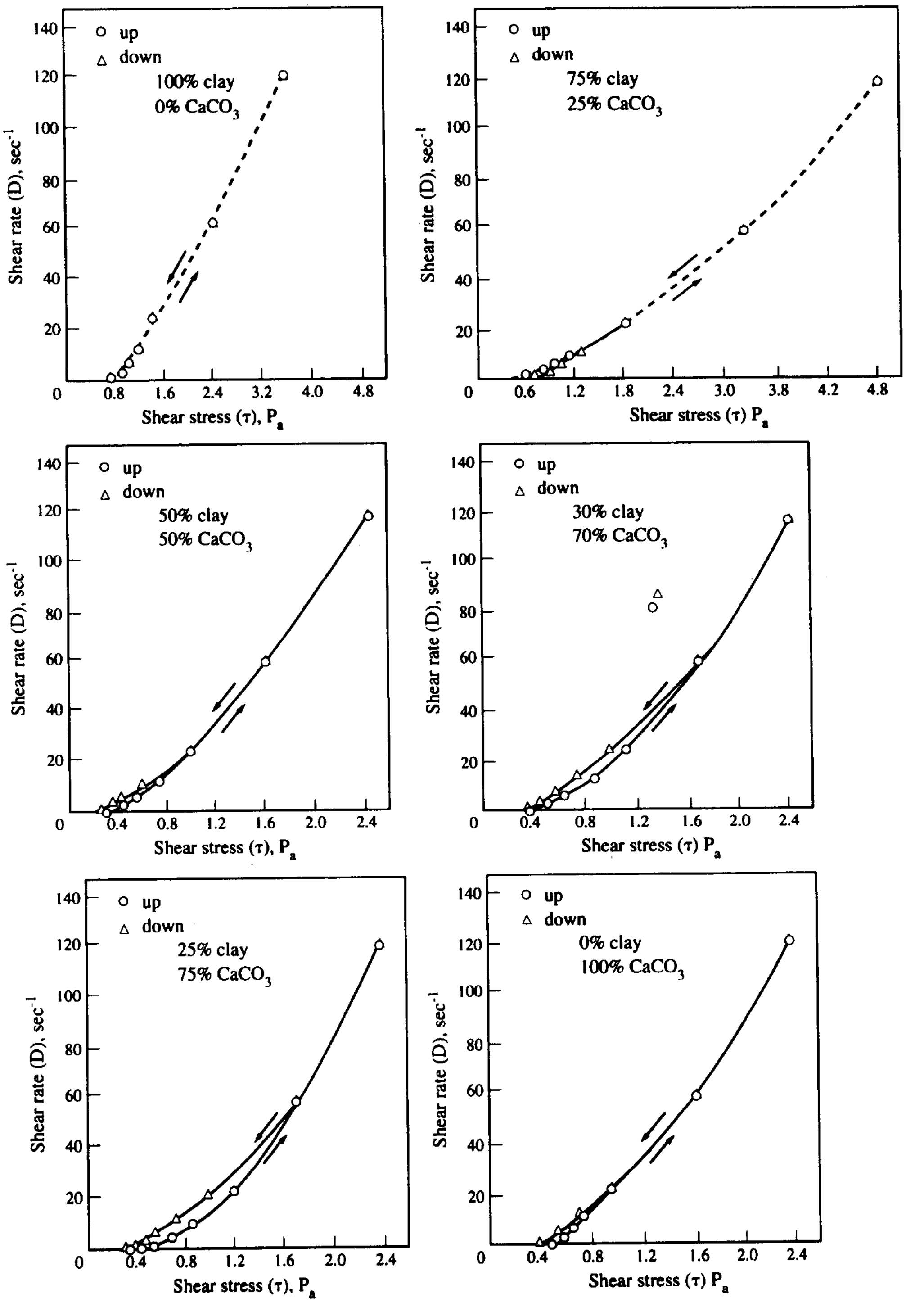

Figure 1 Influence of $CaCO_3$ content in pigment blend on flow curve of coating suspension including binder

and *Table 2a*). Again, the flow parameters decreased when the percentage of $CaCO_3$ increased from 0 to 50% in the pigment blend. Further increase in $CaCO_3$ led to an increase in the flow parameters, while these values are still low compared with the values of the formulations containing 100% clay.

To verify the discussion on the above results, the suspensions were examined in the absence of binder. The results are illustrated in *Table 2b* and *Figure 2*.

The greatest effect shown in *Figure 2* and *Table 2b* is for the initial viscosity data for suspensions in the presence or absence of binder. Obviously, the binder-free pigment suspensions possess higher initial viscosity as compared with binder pigment suspensions. This difference in η_i increases to reach a maximum when the formula contains 100% $CaCO_3$. This behaviour suggests that clay and $CaCO_3$ particles do not interact with the binder in the same manner.

The explanation of the results in *Table 2a* depended on the differences that exist between clay and $CaCO_3$ coatings[12,21]. According to Hunter[21], clay coating suspension has a degree of agglomeration or flocs structure. This agglomeration or flocs structure provides

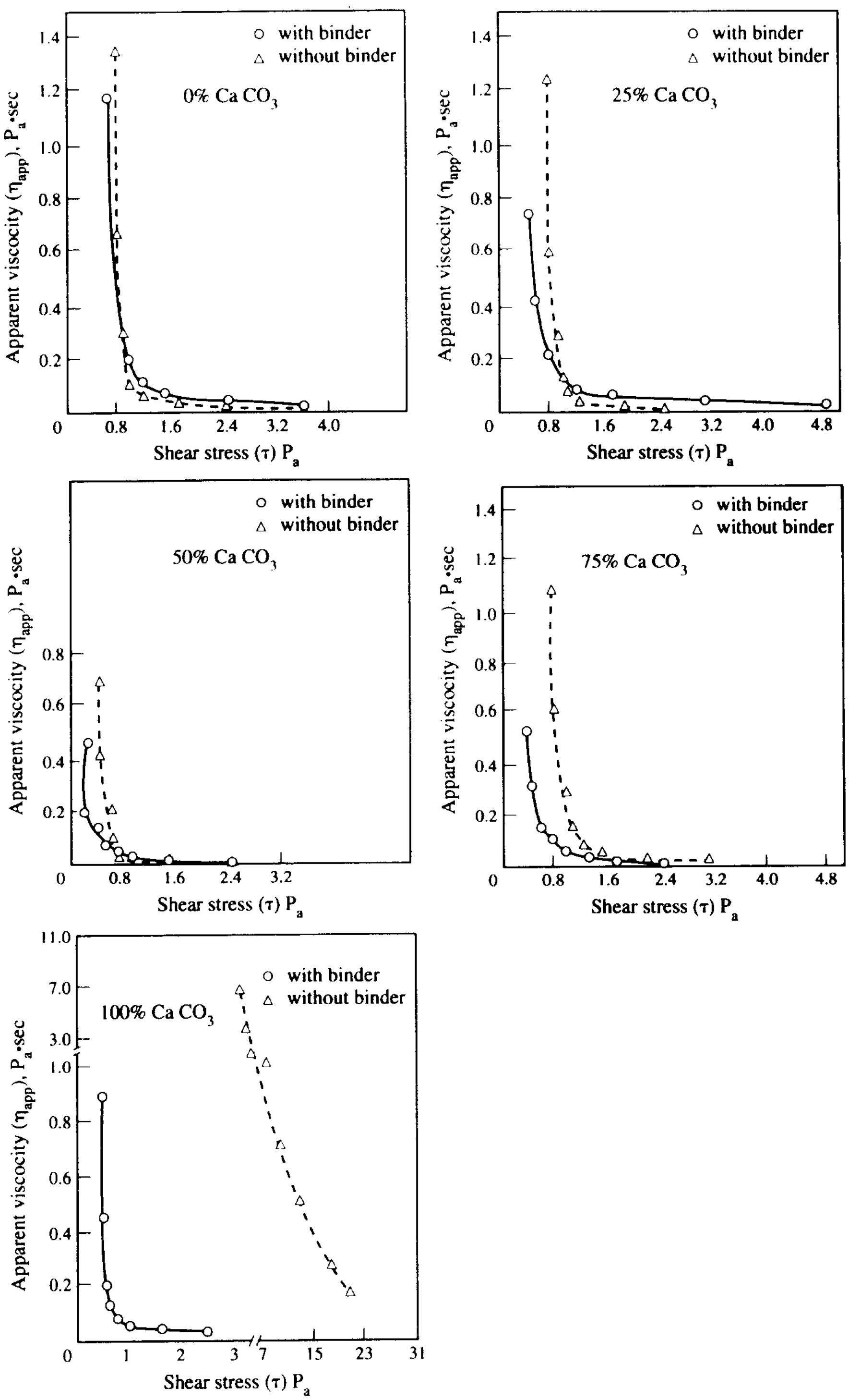

Figure 2 Influence of $CaCO_3$ content on viscosity curve

interparticle capillaries that increase the number of trapped or immobilized water molecules in the coating system. As a result, more stress (τ_0) is required to commence flow of the clay suspension compared with $CaCO_3$-based coating suspension. The same comment can be applied to decreasing η_i, τ_0, η_{pl} and $\Delta\eta$ in formulations containing pigment blends on increasing the percentage of $CaCO_3$ from 0 to 50%.

The unexpected result of increasing flow parameters as the percentage of $CaCO_3$ increases to 75% can be attributed to a restriction in the movement of particles in the flowing medium[12]. This restriction may result from physicochemical interaction between particles of different surface properties. This view is emphasized by the values of τ_0, η_{pl} and $\Delta\eta$ of the binder-free coating system (*Table 2b*).

Influence of binder level

Figure 2 confirms that there exists a significant difference in pigment–binder interaction in clay and $CaCO_3$ coatings. This result persuaded us to perform a further study on the effect of binder level on the flow behaviour and parameters of coating suspensions including clay or $CaCO_3$ as a pigment (*Figure 3* and *Table 3*).

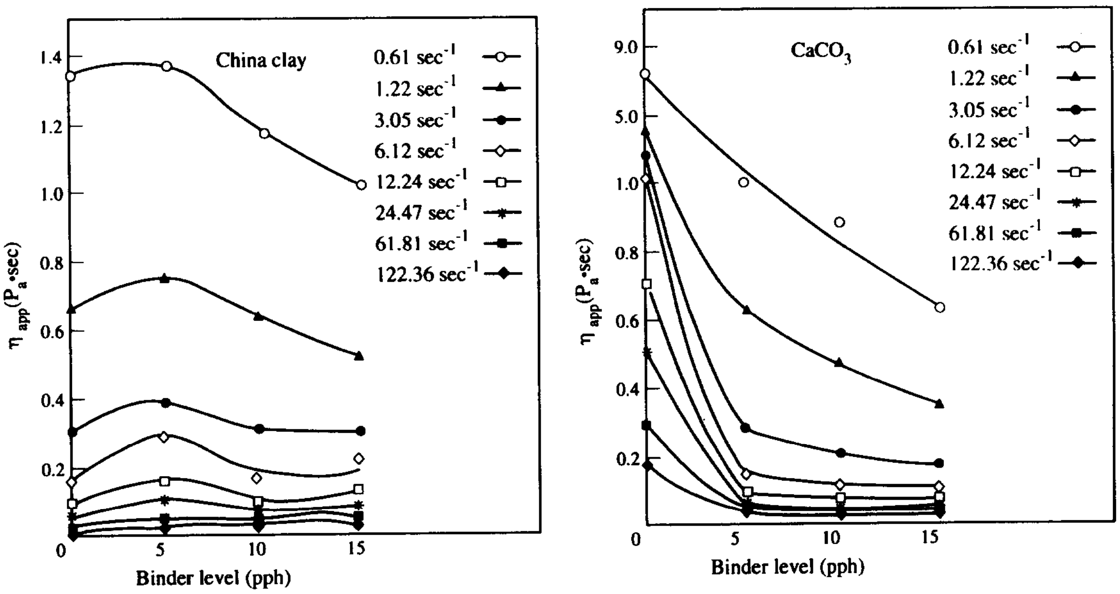

Figure 3 Influence of binder level on apparent viscosity at different shear rates

In a series of experiments three amounts of binder, namely 5, 10 and 15 pph (based on coating suspension), were used in preparation of the coating suspensions. The method of preparation was the same as that used in considering the influence of pigment composition.

Tables 3a and *3b* show that, at a binder concentration of 10%, the flow curves (shear stress *versus* shear rate D, as in *Figure 1*) of clay-based suspensions changed their behaviour from thixotropic to pseudoplastic, i.e. coefficient of thixotropy equal to zero. However, all $CaCO_3$-based suspensions behaved thixotropically. The coefficient of thixotropy decreased on increasing the amount of added binder.

Again, increasing the amount of binder led to gradual decrease in the degree of pseudoplasticity in clay-based suspensions, while the reverse trend was obtained with $CaCO_3$-based suspensions. The flow parameters, especially τ_0 and $\Delta\eta$, for both coatings decreased with increasing binder level; this is clearly discernible at 15 pph binder content.

Figure 3 shows the variation in η_{app} as a function of binder concentration at different shear rates. The decrease in η_{app} was negligible in the case of increasing the binder content from 5 to 15%, when the measurement was carried out at relatively high shear rates (24.47 to 122.36 s^{-1}).

In general, the initial viscosity, η_{app} at 0.61 s^{-1}, decreased when the percentage of binder in coating formulations increased. The rate of decrease in the initial viscosity (R) was more pronounced in the case of $CaCO_3$ than in the clay-based suspensions.

The degree of interaction between pigment and binder seemed higher in the case of $CaCO_3$ than for clay[22]. Changing the binder content led to change in the solid volume content and consequently in the flow parameters.

Influence of co-binder

The effect of various types of co-binder on the flow measurements of clay-based coating suspension was studied, using five types of synthetic and natural co-binders, namely three grades of carboxymethyl

Table 3 Influence of amount of binder

Binder level (pph/susp.)	Coeff. of thixo. ($g\,s^{-1}$)	Bingham parameters τ_0 (Pa)	η_{pl} (mPa s)	$+r$	$\Delta\eta$ Value	$-r$	S Value	$+r$	η_i	R^a
(a) For clay-based suspension										
0	0.041	0.764	8.621	0.997	0.808	0.995	0.205	0.917	1.350	1.0
5	0.021	0.737	14.539	0.949	0.715	0.999	0.285	0.991	1.375	1.0
10	–	0.711	22.045	0.998	0.705	0.992	0.295	0.958	1.180	0.8
15	–	0.594	20.320	0.980	0.628	0.998	0.370	0.994	1.024	0.7
(b) For $CaCO_3$-based suspension										
0	1.160	0.456	60.600	0.966	0.681	0.999	0.317	0.998	6.930	1.0
5	0.048	0.582	14.414	0.989	0.742	0.997	0.240	0.964	1.014	0.1
10	0.019	0.489	11.182	0.995	0.684	0.990	0.274	0.932	0.885	0.1
15	0.005	0.395	7.110	0.997	0.690	0.996	0.275	0.973	0.623	0.0

^{a} R = relative change of initial viscosity of suspension at different binder contents with respect to initial viscosity in absence of binder

Table 4 Influence of co-binder

Co-binder[a]	Coeff. of thixo. ($g s^{-1}$)	Bingham parameters τ_0 (Pa)	η_{pl} (mPa s)	$+r$	$\Delta\eta$ Value	$-r$	S Value	$+r$	Clay-based suspension[b] η_i	R	$CaCO_3$/clay-based suspension[c] η_i	R
–	0.068	0.274	10.112	0.989	0.594	0.995	0.407	0.993	0.460	1.000	0.325	1.00
CMC-L	0.070	0.257	10.543	0.988	0.580	0.998	0.404	0.979	0.470	1.022	0.597	1.837
CMC-M	0.037	0.470	12.785	0.997	0.641	0.996	0.357	0.989	0.830	1.804	0.908	2.794
CMC-H	0.021	0.631	35.270	0.997	0.586	0.988	0.414	0.977	1.420	3.087	1.408	4.332
HEC	–	0.621	14.151	0.992	0.788	0.993	0.212	0.916	1.290	2.804	–	–
HMC	–	1.246	55.720	0.994	0.572	0.998	0.428	0.997	2.160	4.696	–	–
Oxid. starch	–	0.380	7.546	0.998	0.690	0.992	0.306	0.960	0.780	1.696	–	–
Casein	0.116	0.326	8.087	0.998	0.666	0.990	0.328	0.963	0.670	1.457	–	–

[a] One part per hundred parts of pigment
[b] Suspension under investigation
[c] Suspension investigated in previous paper[19]

cellulose (CMC) ($DS = 0.46-1.31$), one grade of hydroxyethyl cellulose (HEC) ($MS = 1.58$), hydroxymethyl cellulose (HMC), oxidized starch and casein. The obtained results are recorded in *Table 4*.

The single binder coating formulation used in this study was delivered from Paper Mill, Alexandria. All the tested suspensions had a total solid content of 25 wt% and a pH level of about 8.6. The amount of co-binder added was calculated as one part per hundred parts of clay (pph).

Table 4 shows the pseudoplastic behaviour (i.e. coefficient of thixotropy equal to zero) for clay coatings

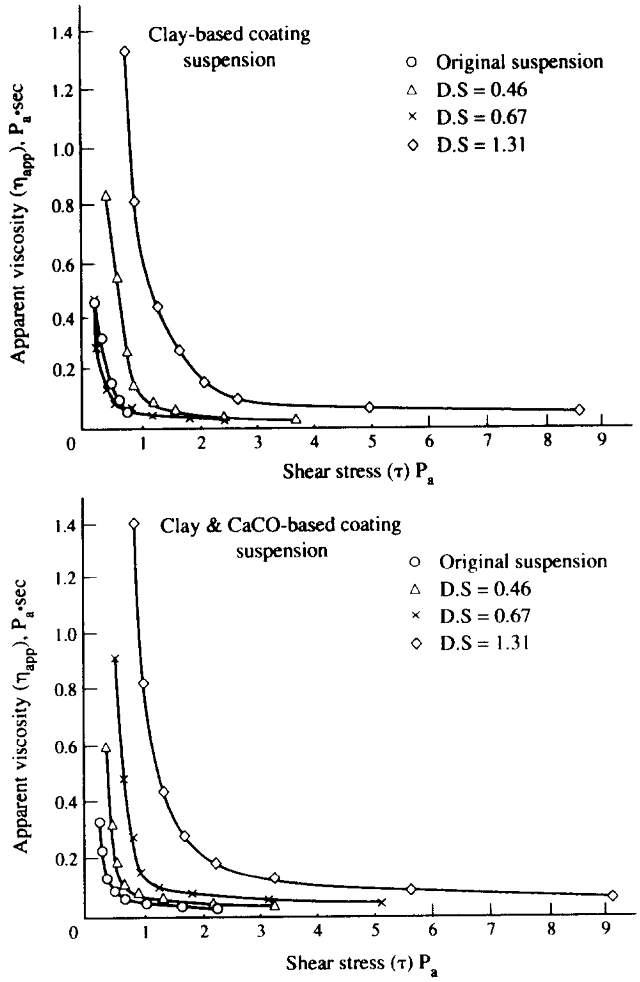

Figure 4(a) Influence of DS of CMC on viscosity curves of two coating formulations

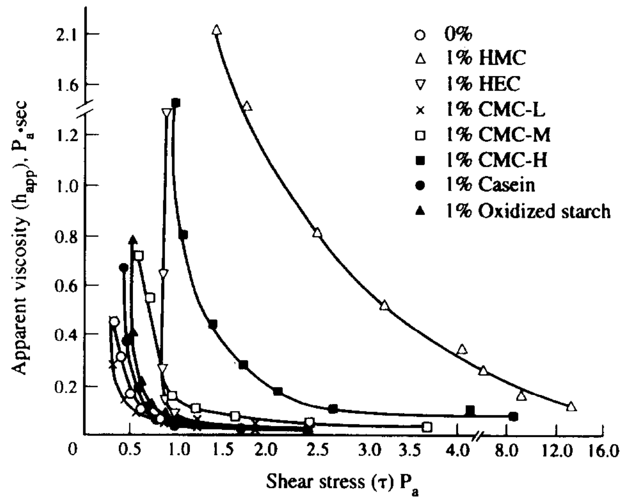

Figure 4(b) Influence of cobinder on viscosity curve of clay-based coating suspension

Table 5 Influence of simple electrolyte

Electrolyte[a]	Coeff. of thixo. ($g s^{-1}$)	Bingham parameters τ_0 (Pa)	η_{pl} (mPa s)	$+r$	$\Delta\eta$ Value	$-r$	S Value	$+r$	Clay-based suspension[b] η_i	R	$CaCO_3$/clay-based suspension[c] η_i	R
–	0.068	0.274	10.112	0.989	0.594	0.995	0.407	0.993	0.460	1.000	0.325	1.000
NaCl	0.015	0.154	10.803	0.990	0.502	0.997	0.506	0.994	0.506	1.100	0.492	1.514
$MgCl_2$	0.056	0.448	7.095	0.996	0.753	0.975	0.303	0.986	0.810	1.761	0.875	2.692
$CaCl_2$	–	0.561	6.601	0.995	0.717	0.995	0.278	0.962	0.870	1.891	1.010	3.108

[a] At level of 0.78 parts of electrolyte with respect to 100 parts of pigment
[b] Suspension under investigation
[c] Suspension investigated in previous paper[19]

containing HEC, HMC and oxidized starch. However, coatings containing the other co-binders, e.g. CMC and casein, have a thixotropic behaviour. In the case of CMC, the increase in its *DS* led to gradual decrease in the coefficient of thixotropy, while the reverse trend was observed in the case of Bingham parameters (η_0 and η_{pl}).

Figure 4(a) shows the influence of shear stress on the apparent viscosity. At low shear rate ($0.61\ s^{-1}$), the addition of CMC with $DS = 0.67$ and 1.31 produced a higher apparent viscosity compared with the original suspension, indicating a strong interaction between CMC and the clay particles[16,17].

Table 4 reveals that the Bingham parameters of a coating including non-ionic cellulosic polymer, e.g. HEC and HMC, are greater than those in anionic polymer, e.g. CMC. This is attributed to the assumption that all cellulosic polymers contain a substantial amount of hydroxyl groups that can undergo hydrogen bonding with hydrated surface species on clay[23]. At pH $\simeq 8.6$, the edges of the clay particles are negatively charged and will tend to repel the anionic CMCs, while the non-ionic HEC and HMC can readily bond with clay. For the same reason, the $\Delta\eta$ value of CMC with $DS = 1.312$ is decreased compared with that for $DS = 0.67$.

HMC has a structure similar to that of HEC, except for its small hydrophobicity. The hydrophobic moieties can be associated with one another and a stronger structure is formed in aqueous solution[18]. As a result of this behaviour, the Bingham parameters of coatings containing HMC are higher than for those with HEC.

As shown in *Table 4*, addition of oxidized starch and casein to clay coating formulation decreases the coefficient of thixotropy and Bingham parameters, while the degree of pseudoplasticity, η_i and $\Delta\eta$ are increased.

Influence of simple electrolytes

From the previous work[19] it could be concluded that the flow curves changed from thixotropic to pseudoplastic behaviour, or the reverse, at a critical divalent electrolyte percentage, 0.78 pph of pigment. The effect of adding this amount of NaCl, $MgCl_2$ and $CaCl_2$ on the flow properties of clay-based coating suspension is illustrated in *Table 5* and *Figure 5*.

The results showed that addition of divalent simple electrolytes led to a decrease in the coefficient of thixotropy and η_B, while the degree of pseudoplasticity, τ_0 and $\Delta\eta$ are increased. The reverse took place in the case of NaCl (monovalent electrolyte). Divalent electrolytes have a stronger effect on flow as compared with monovalent ones. Such results can be attributed to the following two reasons[24,25].

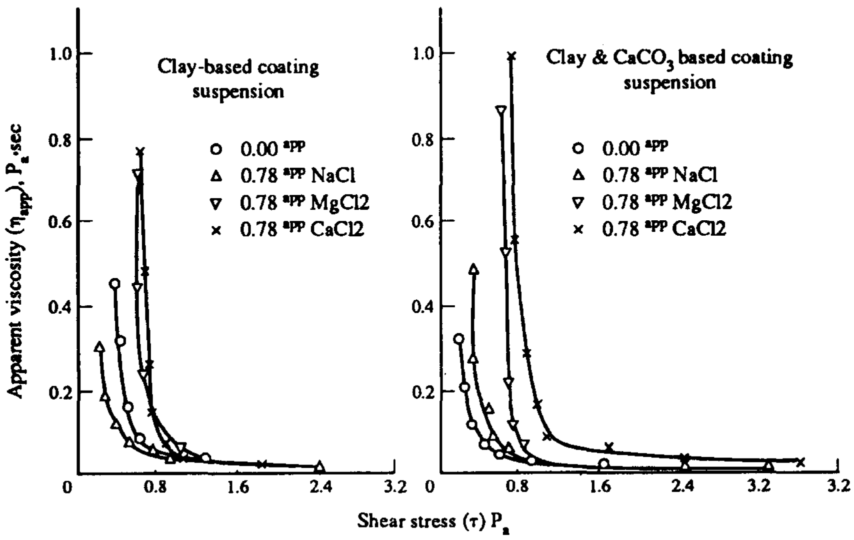

Figure 5 Influence of simple electrolyte on viscosity curves of two coating suspensions

(1) Reduction in the electrostatic repulsion between the pigment particles, especially when divalent cations are present[24], leads to an increase in the degree of adsorption of binder particles on the pigment surface, and yields an increase in viscosity (η_i). Owing to the formation of hydrated shells around the cations of $CaCl_2$, the increase in η_i and τ_0 is more pronounced in the case of $CaCl_2$ than for $MgCl_2$ addition.

(2) Addition of electrolytes led to a greater increase in the volume fraction of the flocs (ϕ_f) than the volume fraction of the clay in the suspension (ϕ), by an amount corresponding to the volume of immobilized water in the flocs[25]. Therefore, the floc void fraction, E_f (bulkiness), calculated from the relation $E_f = 1 - \phi/\phi_f$, increases with electrolyte addition.

A comparison was made between the flow parameters measured on three grades of CMC or three types of simple electrolytes in clay coating suspension, with those obtained in our previous work[19] (*Tables 4* and *5*, *Figures 4b* and *5*). It is clear that the extent of increasing the flow parameters in the former suspensions (under investigation) is lower than for the latter one. This may be attributed to the change in the degree of adsorption of electrolytes and binder deposition on the pigments of the different components in coating suspensions[24].

FINAL REMARKS

The main observations present in this work can be summarized in the following:

Variation in coating composition by using two types of mineral pigments either individually or in blends had a profound effect on the flow parameters.

Coatings containing binder have a lower initial viscosity (η_i) than the binder-free systems. The degree of decrease in η_i increased with increasing carbonate content and amount of binder added.

The presence of non-ionic co-binder affects the properties of suspension compared with an ionic one and synthetic natural dual binder.

Addition of divalent electrolytes had more effect on properties compared with a monovalent electrolyte.

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