Use of Cellulose Esters as Rheology Additives for Automotive OEM Clearcoats

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Automotive coatings have witnessed a definite transition to greener technologies over the past decade. Paint lines are being built or retrofitted for consolidated paint processes, with the intent to reduce energy consumption and operating cost. Specific to automotive clearcoats, there is a move to a one-pass application and a continuing shift to higher solids clearcoats. Consolidated paint processes require a clearcoat with improved strike-in resistance, better flow/leveling, and "filling" power to cope with telegraphing from imperfect substrates. One-pass application requires a clearcoat with an improved sag/flow balance. This article illustrates the improved appearance achieved by the use of cellulose ester rheology additives, alone or in combination with other rheology modifiers, in automotive OEM 1K clearcoats. Electrostatic rotary bell application was utilized to assess clearcoat appearance. Flow and leveling were characterized by a BYK Wavescan Dual, the viscoelastic behavior of clearcoats during the film drying process was investigated using a novel rheological technique, and the speed of solvent release was monitored using thermogravimetric analysis (TGA).

BACKGROUND

Automotive OEM and refinish clearcoats are applied over a pigmented color coat or basecoat to provide protection to the color coat and improve the appearance of the overall finish, particularly gloss and distinctness of image (DOI). To obtain good appearance

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State-of-the-art coatings application development lab at Eastman Chemical Company in Kingsport, TN. Photo courtesy of Eastman Chemical Company.

over horizontal and vertical surfaces with the same spray application, an optimized balance of sag resistance and flow/leveling is needed. Environmental compliance across the globe has resulted in the paint industry attempting to move towards greener and more "eco-friendly" products with similar performance attributes. Increases in the total solids content or replacement of certain organic solvents with water are two alternatives available to limit the amount of volatile organic compounds (VOC) in the paint formulation. A typical automotive OEM high solids clearcoat has a VOC less than 3.5 lb/gal (420 g/l), with the goal to reduce VOC further. Low-VOC, high solids clearcoats are usually formulated with relatively low molecular weight polymers. These clearcoats may have poor rheology control and sag after spray application, particularly when applied to vertical surfaces such as door panels and body panels.

Automotive paint lines are being built or retrofitted for consolidated paint processes (CPP), with the intent to reduce energy consumption and operating cost. CPP concepts vary depending on the supplier, and may also be referred to as the compact paint process, three-wet process, three coat one bake process (3C1B), or B1 B2 system. A conventional system uses a primer surfacer → bake → base and clearcoat wet on wet → bake process. Consolidated paint processes require application of a modified primer surfacer, basecoat, and clearcoat wet on wet on wet. The primer surfacer can be removed and replaced with a basecoat 1, which normally has a similar binder system as the B2 basecoat but does not contain special effect pigments such as aluminum flakes. In this case, a representative paint process becomes basecoat 1 → basecoat 2 → clearcoat → bake, requiring a clearcoat with improved strike-in resistance. Furthermore, consolidated paint processes tend to be thinner in total dry film thickness (DFT). As such, these processes can result in significant telegraphing of the topography of imperfect substrates through to final finishes. To cope with telegraphing, a clearcoat has to have better flow/leveling and "filling" power.

USE OF CELLULOSE ESTERS AS RHEOLOGY ADDITIVES FOR AUTOMOTIVE OEM CLEARCOATS

Cellulose esters that are commonly used in coatings applications include cellulose acetate (CA), cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB), and nitrocellulose. Among those, CABs are most commonly used due to broad solubility and excellent compatibility with a variety of coating resins.[1] Some key attributes provided by cellulose esters in coating formulations include improved surface wetting, better flow and leveling, short dry-to-touch time, quick early hardness development, and improved flake orientation.[2,3] Based on these benefits, cellulose esters, especially CABs, are widely used in wood coatings and automotive basecoats. Traditional cellulose esters are high molecular weight polymers and their use as additives in high solids formulations could lead to reduced formulation solids and increased VOC.

Commonly used rheology modifiers in automotive OEM clearcoats are fumed silicas, microgels, polyamide waxes, and sag control modified resins (SCAs). SCAs have obtained wide acceptance due to their relatively balanced sag/flow properties. SCAs may negatively impact shear stability and storage stability. A majority of SCAs are made by reacting isocyanates with amines to form crystalline particles or needle-like structures suspended in the resin in which they are prepared. As such, they tend to be opaque and clearcoats containing SCAs may also appear opaque. A clearcoat containing SCA typically has to be baked above a certain temperature (in most cases, above 100^{o}C) to form a clear transparent film.

U.S. patents 7,585,905; 8,003,715; and 8,039,531 describe the preparation of low molecular weight cellulose mixed esters that are useful in coatings and ink compositions as low viscosity binder resins and rheology modifiers. U.S. patent applications 2008/0069963A1, 2010/0152336A1, and 2011/0020559A1 describe use of low molecular weight cellulose mixed esters to formulate high solids, low-VOC automotive refinish clearcoats, and automotive OEM and refinish basecoats. Recently, Eastman Chemical Company has commercialized two new products, *Solus*^{TM} 2100 and *Solus*^{TM} 2300, for use in high solids systems. Incorporation of a high T_g additive, such as Solus 2100, in high solids automotive refinish clearcoats reduces dry-to-touch time very effectively.[4]

Application Example: Impact of Cellulose Esters on the Appearance of OEM Clearcoats

Experimental

Three automotive OEM 1K clearcoats were prepared according to *Table* 1.

The steel panels used for appearance testing were 12x12 in. E-coated cold rolled steel from ACT Test Panels. These panels were base coated with a commercial waterborne black basecoat to achieve a 15 to 20 micron DFT and dehydrated for 10 min prior to clearcoat application. The clearcoats prepared in *Table* 1 were reduced to 30 sec on a Ford cup #4 (FC#4) using the solvent blend listed in *Table* 2, then applied to steel panels using electrostatic bell application. The clearcoats were applied to vertical panels in two passes to achieve a 40 to 45 micron target DFT. A one-minute flash time was inserted between the two passes. After the second pass, the panels were flashed for 10 min in the spray booth and then baked at 140 °C for 30 min. Four panels were sprayed over two spray events. Two panels were flashed and baked vertically and another two were flashed and baked horizontally. The relevant bell application conditions are shown in *Table* 3.

Table 1—Clearcoat Formulations Used in This Experiment (weight parts per 1000)

Ingredients	Clear No. 1	Clear No. 2	Clear No. 3
	22.5% SCA[a]	9.5% DPA #1[a,b]	9.5% DPA #2 [a,b]
Acrylic polyol (74% solids)	377.0	448.2	448.2
SCA modified acrylic polyol (60% solids)	164.2	0.0	0.0
Melamine resin (70% solids)	230.4	228.7	228.7
Butanol	15.1	15.5	15.5
Solvent blend	197.7	198.5	198.5
Tinuvin 292 (BASF)	4.6	4.6	4.6
Tinuvin 1130 (BASF)	6.4	6.4	6.4
50% DPA #1 in n-butyl acetate		93.6	
50% DPA #2 in n-butyl acetate			93.6
10% BYK 331 in xylene	4.6	4.6	4.6
Total	**1000.0**	**1000.0**	**1000.0**
Solids at FC #4 30 in. (%)	48.13	48.79	48.84
Calculated VOC at spray viscosity (g/l)	462	456	455

(a) Based on resin solids.
(b) DPA #1 and 2 (Developmental Performance Additive) are novel cellulose esters designed for high solids automotive OEM clearcoats.

Table 2—Solvent Blend Composition Used in *Table* 1

	Weight (%)
EB acetate	10
Xylene	40
Aromatic-100	50
Total	**100**

The appearance of clear coated panels was evaluated using a BYK Wavescan Dual. Three Wavescan measurements were taken from each panel. The data presented represents an average of six sets of readings from two panels.

Electrostatic Rotary Bell Application Results

Figures 1 and 2 show the Wavescan results at different wavelengths on panels baked horizontally and vertically, respectively. The dullness number (Du) and the numbers in the short wave region (Wa, Wb) are indicators of surface haziness and DOI. The numbers in the long wave range (Wd, We) are indicators of surface smoothness and/or orange peel. Across all the wavelengths, a lower number indicates better surface appearance.

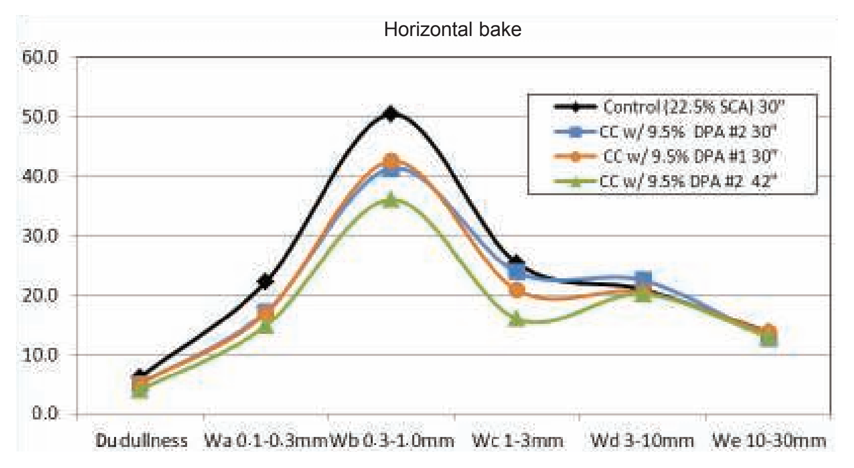

Figure 1—Wavescan data on horizontally baked panels applied by electrostatic rotary bell.

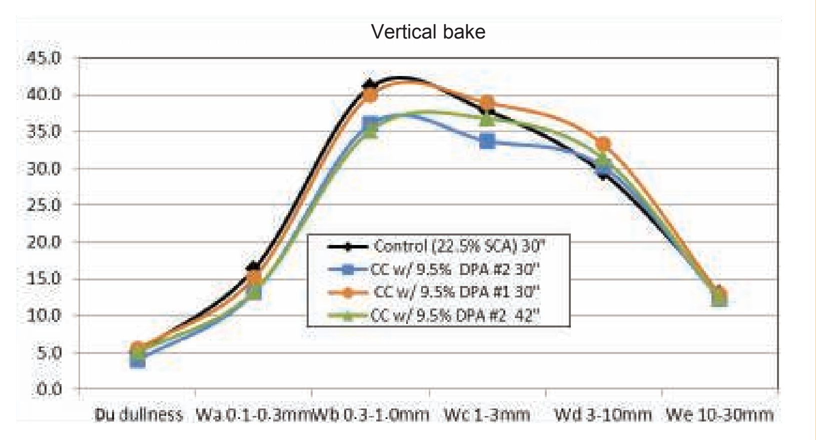

Figure 2—Wavescan data on vertically baked panels applied by electrostatic rotary bell.

In *Figures* 1 and 2, the results for a clearcoat with 9.5% DPA #2 that was sprayed at FC#4 42 sec is also shown for comparison to other clearcoats sprayed at FC#4 30 sec. During an earlier application study of clearcoats using pneumatic hand spray guns, it was noted that the clearcoats containing cellulose esters as rheology modifiers instead of SCA tended to atomize better and could be applied at higher viscosity.

From this study, clearcoats containing DPA #1 or DPA #2 showed improved smoothness across almost all wavelengths when panels were flashed and baked horizontally. With vertically baked panels, the data was mixed. Wavescan numbers at Wd (3–10 mm wavelength) were reversed, but at other wavelengths, clearcoats containing DPA #1 or DPA #2 showed improved smoothness. It was also evident that the clearcoat containing DPA #2 can be applied at higher viscosity and still be atomized properly to result in equivalent appearance.

Assessments using BYK Wavescan Dual also provide long wave, short wave, DOI, and combined Ford (CF) readings. DOI is a function of Du, Wa, and Wb while CF is calculated from DOI and Wa through Wd. Higher DOI and CF numbers indicate better appearance. *Figures* 3 and 4 show the long wave, short wave, DOI, and CF results for panels baked horizontally and vertically, respectively.

Clearcoats containing cellulose esters showed significant improvement in short wave and marginal improvements in long wave, DOI, and CF for the horizontally baked panels. The results from vertically baked panels showed mixed results, as there were no clear differences between the control clearcoat and the clearcoats containing cellulose esters.

Sag Resistance Test Results for the Clearcoats

The panels used for sag limit testing were 4x12 in. (10x30 cm) steel panels with 10 to 12 holes. These panels were specially designed for sag testing and were purchased from ACT Test Panels. A sag panel was positioned at about a 60° angle from horizontal on a rack in the spray booth. Clearcoats were spray applied using a Devilbiss JGA 502 gun to achieve a dry film thickness of around 20 microns at the top and 60 to 80 microns at the bottom of the panel. This was done by spraying five passes: the first pass was from top to bottom, the second pass started 6 cm below the top edge and continued down to the bottom edge, and so on. Between each pass, a one-minute flash time was inserted. At the end of the application, the panel was allowed to flash for 5 min in the same position, and then baked vertically for 30 min at 140°C. The sag limit was determined by measuring the clear film thickness from the point where the sag trail was 5 mm long from a hole.

Table 4 shows the spray solids and sag resistance results for each of the clearcoats.

As expected, the clearcoat containing 9.5% DPA #2 at 42 sec showed the highest sag resistance. The three clearcoats at 30 sec showed similar sag resistance. It is understood in the industry that ideally an OEM clearcoat would have a sag limit 5 microns above the targeted film thickness with good flow and leveling. In this experiment, E-coated sag testing panels were used without primer and basecoat. The results obtained in this experiment provide a relative comparison.

Natural Weathering of OEM Clearcoats

Clearcoats for Weathering Testing

Four clearcoats were prepared based on *Table* 5.

Preparation of Exposure Panels

Substrates used were 4x12 in. (10x30 cm) phosphate treated, E-coated steel panels from Q-Panel. A commercial waterborne metallic basecoat was applied to achieve a 15–20 micron dry film thickness and dehydrated for 10 min at 80°C prior to the clearcoat application. Each clearcoat was spray applied to base

Table 3—Bell Application Conditions for Clearcoat

Item		Value
Bell	Type	Sames 607
	Diameter	65 mm
	Serration	Serrated
Target distance		300 mm (12 in.)
Pattern diameter		380–450 mm
Tip speed (robot)		500–600 mm/sec
Bell speed		45K rpm
Voltage		90 kV
Down draft		60 ft/min
Booth temp./humidity		75/65 (°F/%RH)
Target DFT		37–45 microns

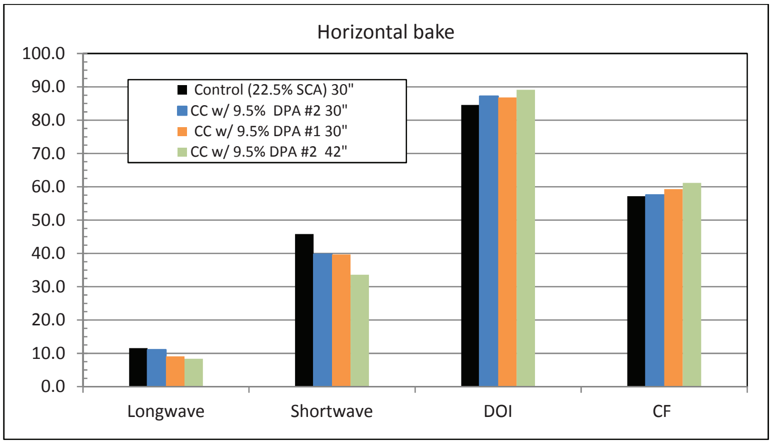

Figure 3—Long/short wave, DOI, and combined Ford number (CF)—Horizontal panels.

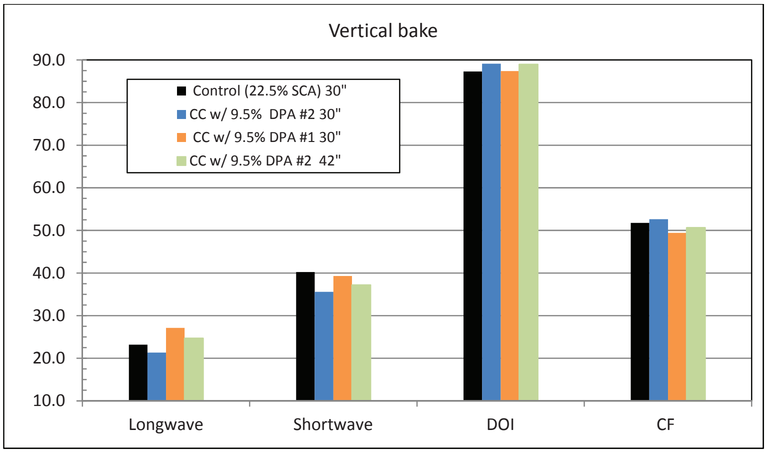

Figure 4—Long/short wave, DOI, and combined Ford number (CF)—Vertical panels.

Table 4—Spray Solids and Sag Resistance for the Clearcoats Used in the Bell Application Testing

	Solids (%)	Sag Limit (μm)
Control clear (22.5% SCA) 30 in.	48.1	35
CC w/ 9.5% DPA #2 30 in.	48.8	35
CC w/ 9.5% DPA #1 30 in.	48.8	34
CC w/ 9.5% DPA #2 42 in.	53.2	42

coated panels targeting 38 to 45 microns DFT using a pneumatic hand spray gun. Panels were flashed for 5 min at ambient temperature and then baked at 140°C for 30 min.

Florida Exposure Results

Florida exposure was carried out in Miami. Panels were positioned at 45° South. *Figures* 5 and 6 illustrate the 20° and 60° gloss retentions, respectively, over 22 months of exposure.

After 22 months of Florida exposure, the two clearcoats containing DPA #1 and CAB 551-0.01 demonstrated superior 20° gloss retention as compared to the controls. Gloss retention of 60° was comparable for all OEM clearcoats, with most values in the 95–96% range for 60° gloss retention.

Impact of Cellulose Esters on the Drying Behavior of Automotive OEM Clearcoats

The drying behavior of a clearcoat, which contains polymers, additives, and solvents, is a complex phenomenon involving a number of simultaneous processes including evaporation and diffusion. Evaporation and diffusion are inter-dependent. Solvents in an applied wet clearcoat film tend to diffuse from the bulk of the wet film to the surface and are then lost by evaporation. At a given temperature, diffusion speed is governed by the concentration of solvent and polymer–solvent mutual diffusion coefficient. The polymer–solvent mutual diffusion coefficient not only depends on each individual polymer and solvent, but also on the polymer–solvent interaction.

Table 6—Clearcoats Solids for Drying Study

	Solids (%)
Control clear (22.5% SCA)	48.1
CC w/ 9.5% DPA #2	48.8
CC w/ 9.5% DPA #1	48.8

Thermogravimetric analysis (TGA) has been used in drying studies of automotive solventborne coatings.[5,6] In this work, the impact of cellulose esters on the drying behavior of automotive OEM clearcoats is investigated using in-situ drying rheology measurements and TGA.

Experimental

Clearcoats

Clearcoats 2 and 3 listed in *Table* 1 were used in this study. It should be noted that the control clearcoat 1 contains a slightly higher proportion of aromatic 100 and xylene compared to clearcoats 2 and 3. This is not a concern in the bell application testing for appearance as it may provide an advantage to the control clearcoat in flow and leveling. For the drying study, the control clearcoat was prepared again with an adjusted solvent composition to ensure it matches that of clearcoats 2 and 3.

The three clearcoats were adjusted to FC#4 30 sec before testing using the solvent blend described in *Table* 2. These samples were run at the same viscosity and their measured solids content for these formulations were very similar, as indicated in *Table* 6.

TGA Analysis

For the purpose of this study, the TGA instrument functions as a fine microbalance with excellent temperature control. The TGA output consists of a series of sample weights (in mg) as a function of time when the sample is subjected to constant temperature. For this set of experimentation, the TA Instruments Model 2980 TGA was used. An initial liquid coating sample weighing

Table 5—Clearcoats Formulations for Durability Testing (weight parts per 1000)

Description	No RM	22.5% SCA	9.5% CAB 551-0.01	9.5% DPA #1
Acrylic polyol (74% solids)	518.6	383.6	454.2	454.2
SCA modified acrylic polyol (60% solids)		167.1		
Melamine resin (70% solids)	231.9	230.2	231.7	231.7
Solvent blend[a]	233.8	204.6	140.0	140.0
Tinuvin 292 (BASF)	4.6	4.3	4.6	4.6
Tinuvin 1130 (BASF)	6.5	6.0	6.5	6.5
30% CAB 551-0.01 in MEK	0.0	0.0	158.3	0.0
30% DPA #1 in MEK				158.3
10% BYK 331 in xylene	4.6	4.3	4.6	4.6
Total	**1000.0**	**1000.0**	**1000.0**	**1000.0**
Solids at FC #4 20 in.	**51.1**	**49.2**	**47.7**	**53.5**
Calculated VOC (g/l)	435	452	465	414

(a) The solvent blend contains 45% n-butyl acetate, 35% MAK, 15% MEK, and 5% butyl glycol. Clearcoats were reduced to 20 sec on a Ford cup #4 with solvent blend before spray.

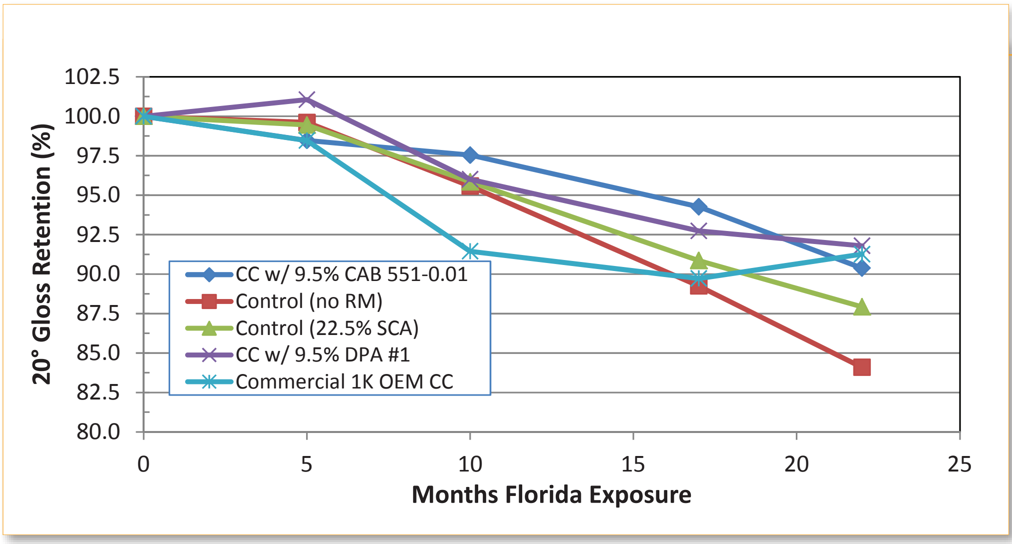

Figure 5—20° Gloss retention: 22 months in Miami at South 45° angle.

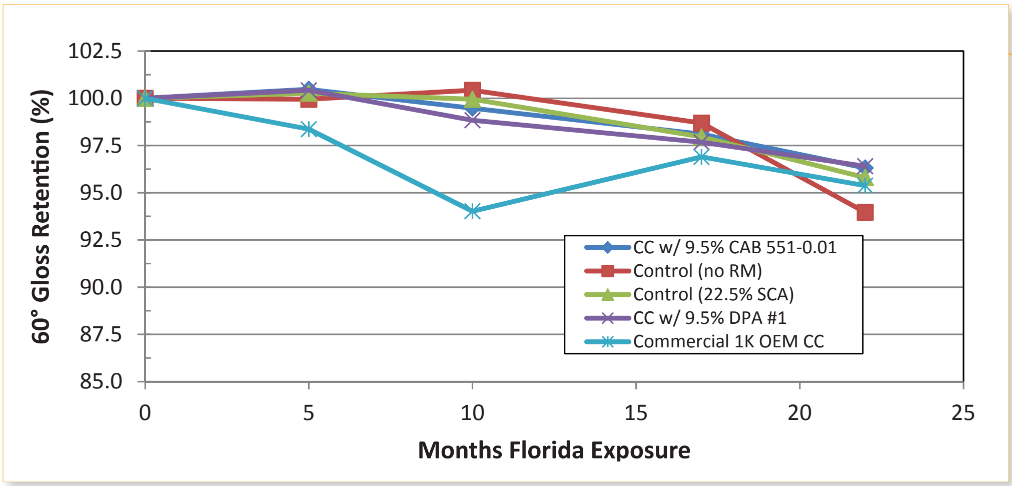

Figure 6—60° Gloss retention: 22 months in Miami at South 45° angle.

approximately 15 mg was placed in an open differential scanning calorimetry (DSC) pan which was in turn placed on the TGA pan. To ensure identical initial volumes, a micropipette was used to introduce the sample to the DSC pan. The weight loss of the coating was measured as the solvent was evaporated under a 50 cm^3/min nitrogen purge at a temperature of 30°C for a period of two hours. The fraction of solids in the remaining coating film at prescribed time intervals was then calculated.

In-Situ Drying Rheology Measurements and Steady State Shear-Viscosity Profile

To mimic the drying process of a thin film in an open air environment, a dynamic time sweep was conducted on a stress-controlled rheometer at 25 rad/sec frequency and 100% strain. An AR2000 rheometer from TA Instruments with an internally modified probe was used for the testing.[7] Environmental conditions, including air flow, have been found previously to have a profound impact on the measurement results. These experiments were done at 25°C and 65% relative humidity with carefully controlled air flow. Steady state shear-viscosity profiles of each clearcoat were measured over 0.1 to 100 sec^{-1} shear range using an AR2000 rheometer at 25°C.

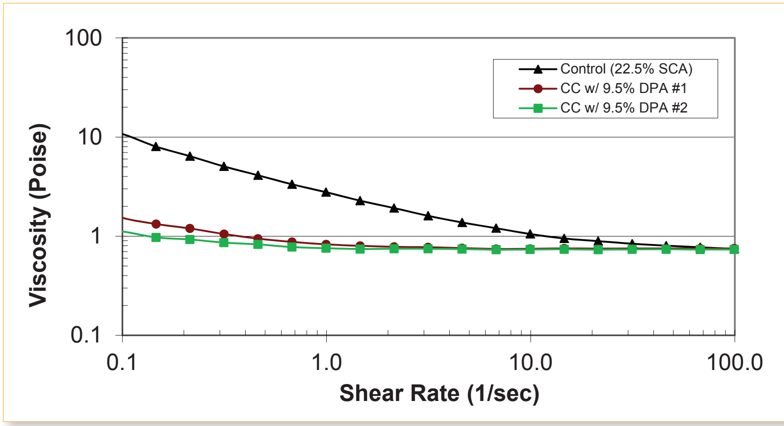

Figure 7—Steady state shear-viscosity profiles of three clearcoats.

Results and Discussion

Figure 7 shows the steady state flow shear sweep results for the three clearcoats. The control clearcoat showed thixotropic behavior and had higher low-shear viscosity. In comparison, two clearcoats containing celluloses esters exhibited more Newtonian behavior in this shear rate range.

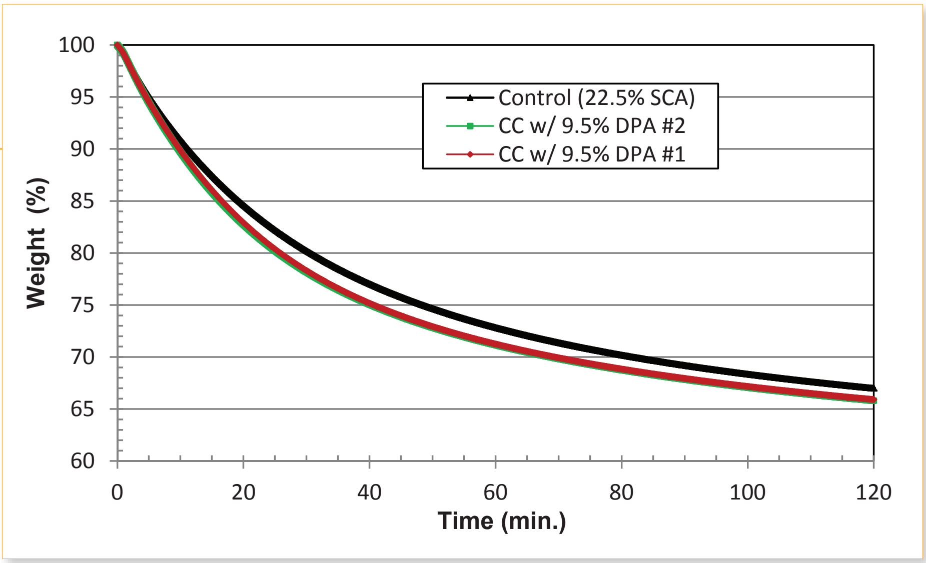

Figure 8—TGA traces of clearcoats.

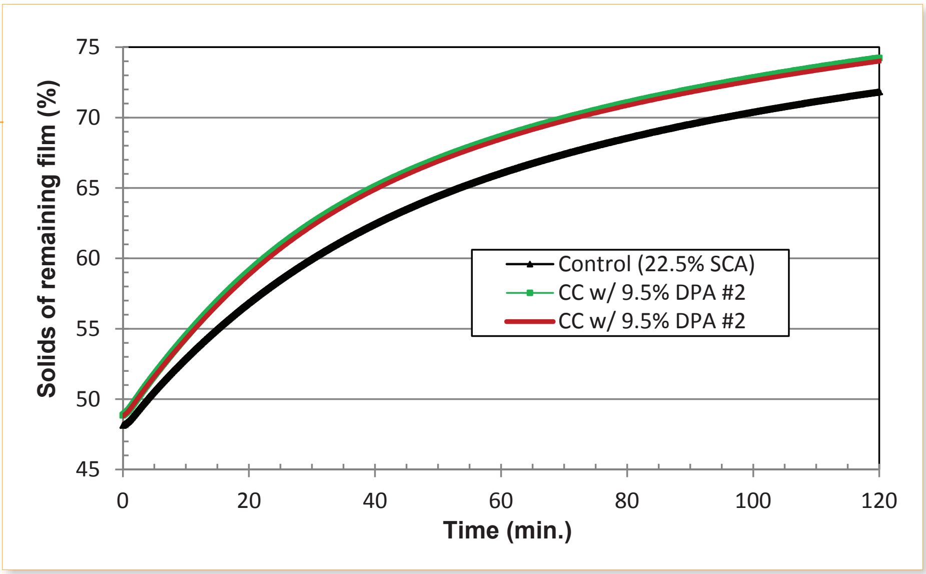

Figure 9—Increase in solids fraction as a function of drying time.

Figure 8 illustrates that the two clearcoats containing cellulose ester lost more weight than the control clearcoat for each given time. This indicates that the solvent loss is greater at a given time in systems containing cellulose esters when compared to systems containing SCA. These results are in agreement with literature reports that describe the drying behavior of automotive refinish basecoats.[5,6] In this experiment, the largest difference appeared in the first 30 to 40 min between the control clearcoat and the two cellulose ester containing clearcoats.

Figure 9 shows the calculated remaining film solids versus time. The remaining film solids of two clearcoats containing celluloses esters were higher at a given moment because of fast solvent release, even though the solids of three clearcoats were identical in the beginning.

Drying rheology curves for the different clearcoat formulations are shown in *Figure* 10. In the first 15 min, the increasing rates of complex viscosity for the three clearcoats were slow and very similar. After the initial 15 min, it can be seen that the two clearcoats containing cellulose ester showed a much steeper increase in complex viscosity than the control clearcoat.

The clearcoats containing DPA #1 and DPA #2 exhibited relatively Newtonian behavior as shown in *Figure* 7. This likely explains why clearcoats using DPA #1 or DPA #2 as rheology additives provide better flow/leveling properties and give smoother finishes as demonstrated by the application examples. At the same time, DPA #1 and DPA #2 promote more rapid solvent release compared to SCA-containing formulations as illustrated in *Figures* 8 and 9. DPA #1 has a T_g of 75°C and the estimated T_g for DPA #2 is around 80°C; these are much higher than the T_g of typical binder resins used in clearcoat formulations. Faster solvent loss coupled with higher T_g should result in rapid viscosity build. Drying rheology data as shown in *Figure* 10 further demonstrates this point. This explains why cellulose esters can also provide improved sag resistance.

Since the drying rheology measurements were done in an ambient environment without any equipment to promote air flow, it took about 15 min to see differences

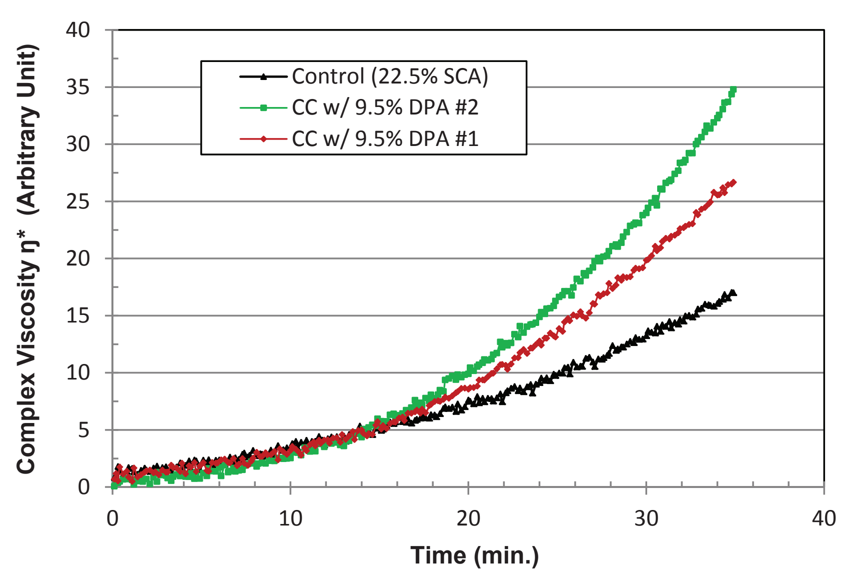

Figure 10—Complex viscosity as a function of drying time for three clearcoats at 25°C.

in viscoelastic response appear for the three different clearcoats. When a clearcoat is spray applied to a target in a spray booth, a high percentage of solvent is lost due to the atomization process. Furthermore, one may expect that high velocity air draft in the spray booth would also result in faster solvent release. It is reasonable to assume that the differences of the three clearcoats in viscoelastic response could occur within the sag formation period, which is within a few minutes after spray.

CONCLUSIONS

The impact of cellulose esters on clearcoat appearance, sag resistance, and spray solids was investigated. The results showed that use of cellulose esters as rheology additives in 1K automotive OEM clearcoats promoted flow and leveling, resulting in a smoother finish and increased DOI over control clearcoats. Improved surface smoothness was achieved while maintaining the same level of sag resistance at equal or increased spray solids.

The impact of cellulose esters on the clearcoat durability was tested by Florida exposure. After 22 months of Florida exposure, two clearcoats containing DPA #1 and CAB 551-0.01 demonstrated superior 20° gloss retention as compared to control clearcoats.

The use of cellulose ester rheology modifiers improved the surface smoothness of clearcoat formulations, and at the same time, provided the benefits of improved sag resistance. To further understand the mechanism behind the attributes of these benefits, the impact of cellulose esters on the drying behavior of automotive OEM clearcoats was investigated using in-situ drying rheology measurements and TGA. Steady state flow shear sweep results illustrated that the two clearcoats containing cellulose esters were more Newtonian while the control clearcoat demonstrated thixotropic characteristics. TGA measurements revealed that the formulations containing cellulose esters exhibited faster solvent release. Drying rheology data illustrated that the clearcoats containing cellulose esters build viscosity faster than control after being applied to a substrate. Newtonian characteristics promote the flow while fast solvent release, high T_g, and viscosity build prevent the clearcoat from sagging after application. CT

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