Novel Rheology Control Agents

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The automotive coatings industry continues to search for technologies that will provide the optimum balance between cost effectiveness and performance. Although various rheology control agents (RCAs) are well known to automotive coatings formulators, achieving the required balance of ease of incorporation, sag resistance, leveling, and stability that the automotive industry demands remains a challenge. This article presents the structure-property relationships of a new class of RCAs that function via a controlled flocculation mechanism. Such physical characteristics of the RCAs as particle size and rheology profile will be related to such performance properties as degree of sag and leveling and ease of incorporation. Using a 1K high-bake coatings system, the proper techniques required to maximize the beneficial contributions of RCAs will be illustrated. The beneficial features of the new RCAs are higher solids, an additive nature, and high efficiency for sag resistance. Their incorporation results in automotive coatings suitable for the global market that possess good robustness, lower VOCs, and ease of both manufacturing and application.

INTRODUCTION

The requirements for automotive clearcoats have changed significantly in the last two decades. The most dramatic change has been in the VOC reduction of clearcoats. For solventborne clearcoats, VOC levels have changed from 5–5.5 lb/gal to as low as 3.5 lb/gal for OEM applications. The number average molecular weight (Mn) of the resins used for clearcoats was around 5,000 a couple of decades ago and now it is around 2,000–2,500 Daltons.

The rheological behavior of clearcoats has also become increasingly important as the molecular weight of resins has decreased over this period of time. Automotive OEM coatings are applied using automatic electrostatic spray equipment. The applied clearcoats are allowed to flash for 10 min and are baked at 250–280°F for about half an hour. At the time of application,

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the viscosity of the paint is low (25–30 sec on Ford #4). However, once applied to the substrate, the viscosity of the coating must increase rapidly to prevent sagging. Lower molecular weight resins (lower VOC) have a greater tendency to sag during flash-off time and during the bake cycle because of an inverse relationship between the molecular weight and viscosity.

To prevent sagging in low-VOC coatings, where there is very little evaporation of solvents, coating formulations must be pseudoplastic.[1] In the automotive industry, three major types of rheology control agents are used to control sagging: fumed silica, microgels, and urea crystals (SCA).[2,3] Each of these three rheology agents has particle morphology. In clearcoat paint under low shear conditions, these particles can flocculate in a controlled manner—forming a three-dimensional network, trapping liquid, and effectively increasing the viscosity.

In this article we study novel rheology control agents (RCA) developed by Nuplex Resins. The bulk and surface characteristics of RCAs are tailored to give controlled flocculation in commonly used automotive resins. These RCAs have a particle size of less than 100 nm. Particle size plays an important role in appearance of the clearcoat, i.e., for haze-free films particle sizes of much lower than the wavelength of the visible light (400–700 nm) are desired.

EXPERIMENTAL

Materials

Rheology Control Agent—Nuplex Resins has developed novel rheology control agents for clearcoats designed for automotive applications. Three variations, RCA-82, RCA-84, and RCA-86, are studied here. The active RCA is 65% based on solids. The remaining 35% is the stabilizing resin. The main compositional difference between these three RCAs is the type of stabilizing resin. RCA-82 and RCA-86 use an acrylic polyol resin based on the proprietary Controlled Molecular Structure Polyol (CMSP) technology developed by Nuplex Resins. RCA-84 is stabilized by hexamethoxymethyl melamine (HMMM). *Table* 1 summarizes the physical properties of the RCA.

Acrylic Resin—High solids acrylic resin was used in this evaluation. The equivalent weight of the resin was 350 and the % NVM was 70%.

Melamine Resin—A commercially available hexamethoxymethyl melamine resin (>98%) was used as a curing agent for the acrylic resin.

Formulations and Application

The ratio of acrylic to amino resin was maintained at 75:25 (on solids) in all the formulations. No flow or wetting additives were added to the clearcoat formulation so as to focus on the effect of rheology control agents. Typically, in a clearcoat a formulation up to 4% RCA was used based on the total resin solids. The formulas were adjusted to a sprayable viscosity of 30 sec (#4 Ford cup) using 1:1 xylene:PM Acetate solvent.

The paint film was applied using automated spray equipment to ensure controlled film thickness and consistent application. After spray application, panels were flashed off for 10 min and then baked at 280°F for 20 min.

Testing and Measurements

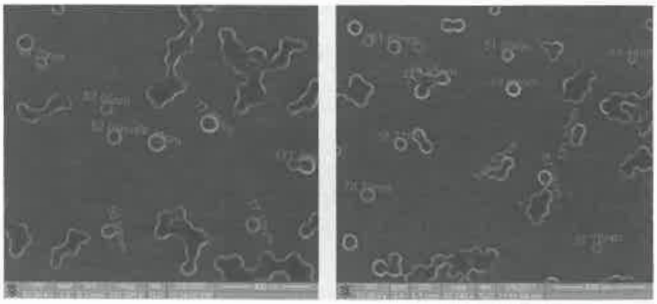
Scanning Electron Microscopy—A drop of RCA suspension was put on a TEM copper grid with a holey carbon film and the remaining solvent was immediately absorbed by filter paper. Secondary electron imaging was performed with a Nova 600 FEG SEM at 10 kV.

Measurement of Sag Limit—Paint tends to sag when applied at higher film thicknesses. The resulting sag is more pronounced when there are indentations or protrusions on the substrate. Sag measurements were run on 4 × 18 in. electrocoated panels (ACT Lab., APR36321) with 17 holes drilled 1 in. apart along the length of the panel. The panels were sprayed vertically at progressively higher film thickness from top to bottom. Typical film thickness varied from 0.5 mil at the

Table 1—Physical Characteristics of the Rheology Control Agents

RCA	RCA-82	RCA-84	RCA-86
% NVM	46.3	50.0	42.8
% Active RCA on NVM	65.0	65.0	65.0
Stabilizing resin	CMSP-61A	HMMM	CMSP-61B
Mn (stabilizing resin)	1250		1520
Mw (stabilizing resin)	2050		2640
Particle size (nm)	35-80	35-80	35-80
Solvent	MAK, Hexyl acetate	MAK, Hexyl acetate	MAK, Hexyl acetate
Viscosity (mPa.s) @ $1 s^{-1}$	2030	3860	16,900
(as supplied) @ $100 s^{-1}$	420	850	1500
Viscosity (mPa.s) @ $1 s^{-1}$	190	55	1290
(at 40% NVM) @ $100 s^{-1}$	35	55	315

Figure 1—SEM micrographs of RCA-86 at magnification of X101.4K (left) and X85.2K (right).



top to about 2.0 mils at the bottom of the panel. When paint starts sagging, it forms "tears" underneath the holes. The length of the tear was measured from the bottom of its respective hole. The film thickness corresponding to a 5 mm sag was reported as the Sag Limit in mils (1 mil = 25.4 micron).

Appearance Measurements—Appearance was measured using the BYK Gardner wave-scan DOI instrument. Short-wave, long-wave, orange peel, and Combined Ford appearance measurements were made on the panels using standard procedures.

Rheology Measurements

All the rheology measurements were performed on an Anton Paar UDS200 controlled stress rheometer, using cone and plate geometry at 23°C. A cone of 1° angle and 50 mm diameter was used for all measurements. A closed cover set-up was used to prevent evaporation of solvents during the measurements.

Sample Preparation—Three levels of RCA, 2%, 3% and 4%, based on total resin solids, were used. The acrylic to melamine ratio was maintained at 3:1 for all the samples. For all rheology measurements, the solids content of the clearcoats was adjusted to about 65% NVM by evaporating the solvent. This solids content was close to that of the paint on the panel directly after spraying.

Viscometry Test—This test is carried out to determine the viscosity, η, as a function of the applied shear stress, σ:

$$\eta(\dot{\gamma})=\frac{\sigma}{\dot{\gamma}}$$

Where $\dot{\gamma}$ is the measured shear rate. In this test, the shear stress is varied in logarithmic steps from 50 Pa down to 0.1 Pa.

Creep Measurements—Creep measurements were performed to determine the increase in viscosity as a function of time at a constant applied shear stress. The sag/leveling balance of paints depends on the time-integrated film fluidity, Ψ_∞, which in turn (strongly) depends on the applied wet layer thickness and on the time-integrated paint fluidity.[4,5] The time-integrated paint fluidity is equal to:

$$\int_0^\infty \eta(t)^{-1}dt$$

In a creep test, this time-integrated paint fluidity is equal to the measured compliance J(t). For a Newtonian, non-thixotropic paint, J(t) is equal to t/η (and thus independent of the applied shear stress); for non-Newtonian, thixotropic paints, the time-integrated paint fluidity generally depends on the applied shear stress.

We can mimic, by varying the level of the applied shear stress in a creep test, the influence of variations of the applied wet paint layer thickness on the time-integrated paint fluidity. For non-horizontal wet paints, the shear stress in the paint layer is linearly proportional to the thickness of the applied wet layer. As an example, a wet paint layer of 100 microns, applied on a vertically mounted plate, experiences a shear stress of 1 Pa (assuming a density of 1 g/cm^3).

Prior to the creep measurement, all paints were subjected to prolonged preshearing (1000 Pa) to erase any previously built up structure in the sample. The influence of the constant creep shear stress was evaluated at 0.5 and 1.0 Pa (that is, about 2 mil and 4 mil wet paint layer thickness for vertically mounted substrates).

RESULTS AND DISCUSSION

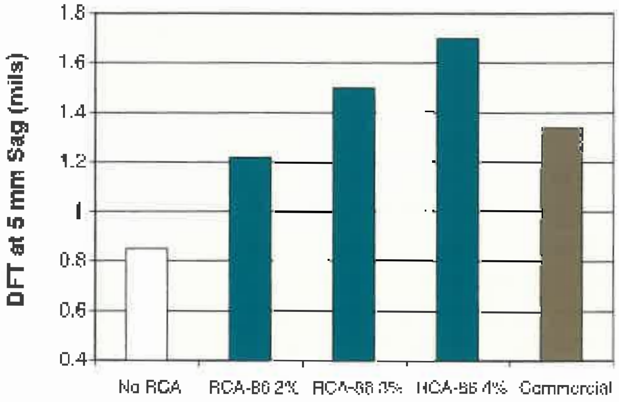
Scanning Electron Microscopy

SEM micrographs reveal that the particle size of the RCA particles was in the range of 35–80 nm. Based on the visual observation it was seen that the majority of the particles were between 50 and 70 nm. Some of the particles were seen to be flocculated in the agglomerates. The particle sizes of all the RCAs were approximately the same. These particles were much smaller than the wavelength of visible light (400–700 nm). When the particle size is much smaller than the wavelength of light, it helps reduce any Mie scattering effect, resulting in a film with no or negligible haze.

Sag Measurement

The level of RCA was varied from 0 to 4%, thereby placing special emphasis on the sag properties of the coatings. *Figure* 2 describes the results of sag limit tests when varying the RCA level from 0 to 4%. A commercial clearcoat formulation was used for comparison. The sag limit, i.e., the dry film thickness (DFT) at which

Figure 2—Comparison of sag limit for increasing level of % RCA.



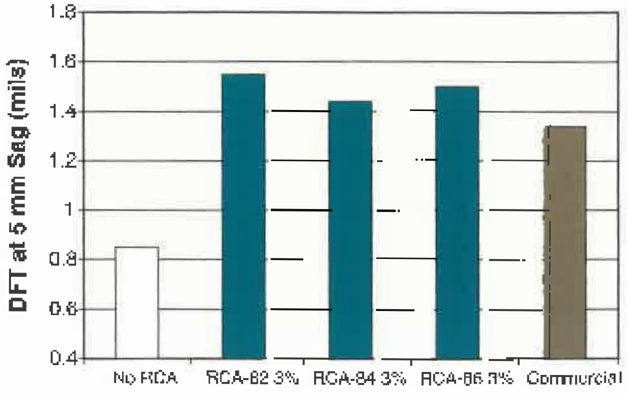
the sag tear was 5 mm, was determined. The higher the DFT at 5 mm sag, the better the sag resistance of the coating. As the RCA content was increased, the DFT increased progressively. *Figure* 2 indicates that about 2.5–3% RCA would be sufficient to obtain the sag resistance comparable to that of the commercial sample.

The sag performances of all the RCAs were tested at 3% (*Figure* 3). At this loading level the sag resistance of the RCA was significantly better than the "No RCA" clearcoat and was slightly higher than the commercial clearcoat. The sag resistance of RCA-82 and RCA 86 was slightly higher than RCA-84. This indicates that the CMSP-stabilized RCA gives slightly better sag resistance than the melamine stabilized RCA. The sag resistance of RCA-86 was marginally lower than that of RCA-82, which implies that the increase in the molecular weight of the stabilizer did not affect the sag performance significantly.

Appearance Measurements

Typically, when a rheology control is used in a clearcoat, some appearance is sacrificed to obtain the improvement in the sag control. *Figure* 4 illustrates the appearance of different RCAs at 3% loading. For comparison, a clearcoat without any RCA and a commercial clearcoat were included in the study.

Figure 3—Comparison of sag limit for various RCAs.



Orange peel is a measure of the leveling of a clearcoat. The higher the number of the orange peel rating, the smoother is the film. After incorporation of the RCA, although the sag resistance was improved considerably, the smoothness was also decreased to some extent as is evident from *Figure* 4. Among the three RCAs investigated, RCA-86 contributes the best appearance. This indicates that the stabilizing resin plays an important role and that the higher molecular weight CMSP resin contributes a relatively better balance of sag and leveling. It can also be observed that the smoothness is better than the commercial sample.

Distinctness-of-image (DOI) is the reflective characteristic of a coating. It is a quantification of the spread of light reflected at a specular angle. It gives an indication of how sharp the image reflected by an object is likely to be. DOI increases with increasing surface smoothness. A higher number is desired for the clearcoat. *Figure* 4 shows that the DOI of the RCA-containing samples is slightly lower than for the samples without the RCA. Among the three RCA studied, RCA-86 gives a DOI that is comparable or slightly better than the commercial clearcoat.

An additional measure of appearance is Combined Ford (CF). It is a combination of various surface appearance measurements. About 15% weightage is given to luster, 35% to sharpness of image, and 50% to the orange peel. The Combined Ford appearance of RCA-86 was observed to be very close to that of the clearcoat without RCA and better than that of the commercial control.

Rheology Measurements

Viscometry is a very useful tool for initial screening of an RCA. In many cases the degree of pseudoplasticity is a very good measure of the effectiveness of an

Figure 4—Comparison of various appearance indicators using different RCAs.

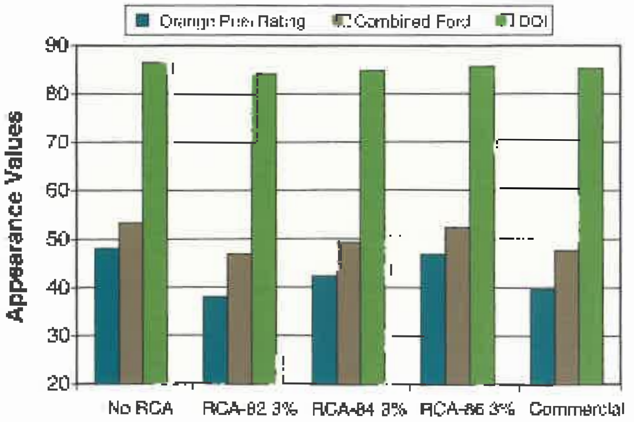


Figure 5—Measured viscosity as a function of applied shear stress of different RCA-containing clearcoats. For comparison purposes, a clearcoat without any RCA and one commercial clearcoat are included. All the samples are measured at the ready-to-spray viscosity of 30 sec (#4 Ford Cup).

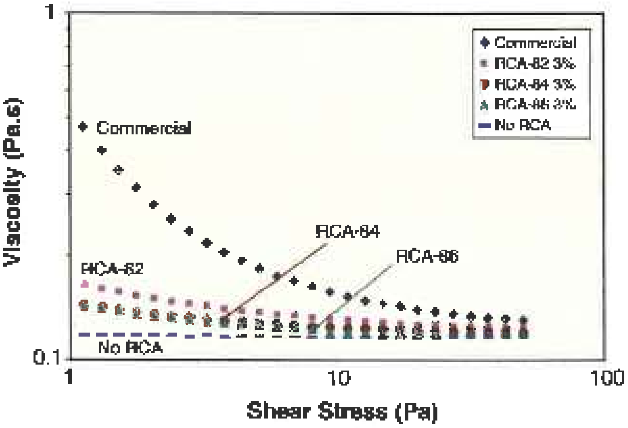


Figure 6—Viscosity of clearcoat paint measured in a creep test at 0.5 Pa shear stress. All the samples were made with 3% RCA. Control sample does not contain any RCA.

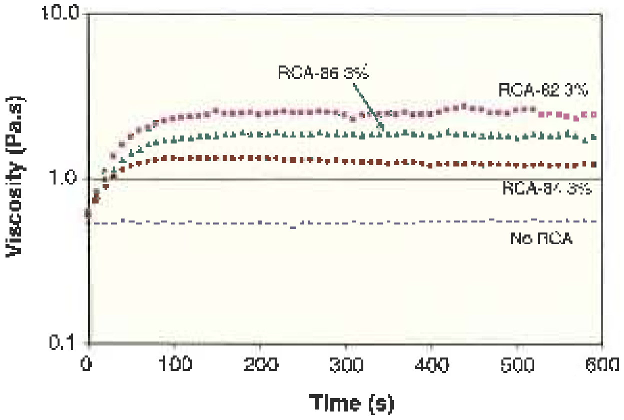
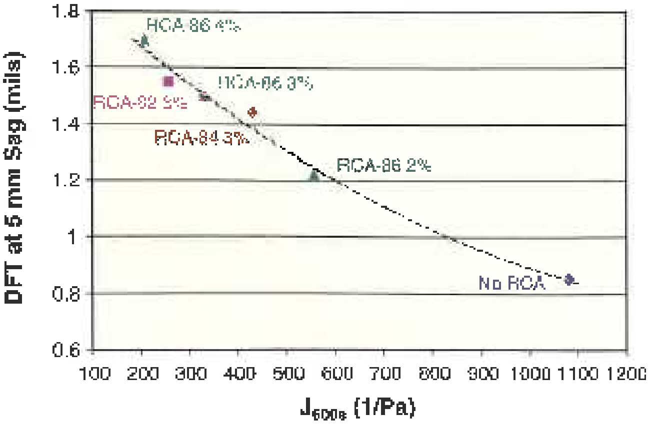


Figure 7—Correlation between integrated paint fluidity (J_{600s}) at 0.5Pa and sag limit for RCA-containing clearcoat system.



RCA in a particular resin system. *Figure* 5 shows that without the RCA, the clearcoat is more or less Newtonian as there is almost no effect of shear on the viscosity of the paint. On the other hand, all three RCAs exhibited some pseudoplasticity even at 3-wt% level. Among the clearcoats studied, the commercial sample exhibited the highest amount of pseudoplasticity in the ready-to-spray clearcoat.

It is interesting to note that the degree of pseudoplasticity may not be the most conclusive way of judging the sag performance of a clearcoat. In *Figure* 5, the commercial sample exhibits the most pseudoplasticity, and, thus, could be expected to give excellent sag resistance as compared to the other RCAs. However, *Figure* 3 shows that all the RCAs give better sag resistance than the commercial clearcoat.

The amount of sagging and leveling in a drying paint is strongly related to the time-integrated film fluidity (or total film flow). The higher the total film flow, the higher the amount of sagging in non-horizontal wet paints. The total film flow depends strongly on the wet layer thickness and on the paint flow. Creep tests are highly useful to determine the total paint flow (time-integrated paint fluidity) as a function of the applied shear stress. The total paint flow is equal to the measured compliance J. The increase of the viscosity η (t) of the paint during the creep test is also determined and is equal to:

$$\eta(t)^{-1} = \frac{dJ(t)}{dt}$$

For non-horizontal wet paints, gravitational forces cause a shear stress in the paint layer, which is linearly proportional to the thickness of the applied wet layer. As an example, a wet paint layer of 100 microns, applied on a vertically mounted plate, experiences a shear stress of 1 Pa (assuming a density of 1 g/cm^3). Thus, the creep curves in *Figure* 6, which are under 0.5 Pa shear stress, represent the shear stress corresponding to about 2 mils (50 microns) thick wet, vertical film. This test mimics the actual spraying of the paint where the shear rate at the spray gun is very high, in the range of 2000–3000 Pa, and, when the paint hits the panel, the shear rate is very low, on the order of 0.5 Pa.

Figure 6 shows the results of creep tests carried out at 0.5 Pa mimicking the behavior in a vertical wet paint layer of 50 microns. The NVM of the clearcoat was adjusted to 65% to mimic the NVM of the paint film immediately after application. Thus, 50 microns of wet film correspond to about 33 microns (1.3 mils) of dry film, which is relatively close to the sag limits observed in *Figure* 3.

In the first 60–70 sec there is a rapid increase in viscosity due to the formation of RCA network in the

Table 2—Effect of wt% of RCA, Types of RCA, and Applied Shear Stress on the Total Paint Fluidity Integrated Over Time from t = 0 to t = 600s (J_{600s})

RCA	J_{600s} (1/Pa)
	0.5 Pa
No RCA	1082
RCA-82 3%	258
RCA-84 3%	432
RCA-86 2%	559
RCA-86 3%	332
RCA-86 4%	212

paint film. This network is formed as a result of the controlled flocculation of the RCA particles in the resinous media. This viscosity increase is an important step in restricting the sag of the paint during flash-off stage. *Figure* 6 shows that all three RCAs are effective in restricting sag during flash-off time. Among the three, RCA-82 appears to be the most effective. The viscosity of RCA-82 and RCA-86 plateau after about 120 sec. In the case of RCA-84, the viscosity decreases slightly after 120 sec. This is probably due to some over-flocculation (partly collapsing) of the RCA network.

Table 2 summarizes the effect of shear stress on the total paint fluidity (J_{600s}) integrated from time t=0 to t=600s. This represents the flow of the paint during the flash-off stage. The lower the total fluidity, the lower will be the sag of the paint film. When the wt% content of the RCA-86 was increased from 2 to 4%, the total paint fluidity decreased considerably. This indicates that the effectiveness of increasing the % RCA is significant in decreasing paint fluidity, and, hence, the sag of the paint film in vertical position. Among the three RCAs investigated, RCA-82 has the lowest total film fluidity (J_{600s}), indicating the least sag among the three RCAs.

The creep measurements carried out represent only the flash off time during the total cure cycle. During the bake, the viscosity of the paint initially decreases, then, as it cures and as solvent evaporates, the viscosity increases again. RCA plays an important role during the heating stage of the clearcoat. It is very complicated to study the rheology during the cure stage. However, a correlation between the total paint fluidity (J_{600s}) and the sag limit of a clearcoat is observed in the RCAs studied. *Figure* 7 shows that in the RCAs studied, as the total paint fluidity decreases, the sag resistance increases. Thus, the creep measurements, which are less time consuming, can be used to screen the RCA or clearcoat formulas to optimize the sag resistance of a clearcoat.

CONCLUSIONS

It was demonstrated that novel RCA significantly improves the sag resistance of clearcoats. Normally, the appearance of a clearcoat deteriorates noticeably when the sag resistance is improved. However, in this evaluation, RCA-86 exhibited the best appearance in an RCA-containing clearcoat—an appearance which was not significantly different from that of a clearcoat without any RCA. Creep measurement is an important tool to screen the clearcoat for the sag-resistant performance. Using creep experiments, the total paint fluidity can be calculated. It was demonstrated that there is a direct correlation between the total paint fluidity (J_{600s}) and the sag resistance of a clearcoat.

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