Balancing Rain Resistance and Open Time

with Diffusing Wave Spectroscopy and Conventional Application Tests

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Sufficient open time is essential for achieving painting efficiency and delivering aesthetically pleasing results in architectural coatings. The open time can vary widely for an exterior coating because the wet coat may experience extreme weather conditions from humidity and temperature changes to varying wind speeds. Additionally, the open time of the coating can be influenced by solids, pigment volume concentration, polymer composition, rheology modifiers, additives like humectants, and solvents.

The open time and early rain resistance are seemingly diametrically opposed properties, and it is difficult to improve the early rain resistance without negatively influencing open time. Through the use of statistical design of experiments, this study identified polymer structure factors that can influence the open time and early rain resistance of the paints. The rain resistance was tested using the shower head test method, while the open time was tested using conventional methods such as ASTM

D 7488 and Gardco Quadracycle drying time.

Further insight on open time was gained by a novel test method using diffusing wave spectroscopy which provides information on critical steps of the film formation process such as water evaporation-concentration, particle packing, particle deformation, and film dry through. Combining this data with polymer structure study allowed for the elucidation of structure-property relationships, specifically regarding open time. The resulting novel insights helped in the development of new polymer prototypes that positively influence both early rain resistance and open time.

Introduction

Weather, especially rain, has a severe impact on the film formation of freshly applied paint on an exterior wall. A fast-drying paint will provide early resistance to rain. However, developing[1,2] a fast-drying paint with sufficient open time is challenging. The open time[3] of paints has been defined as the period of time during which a painter can make corrections to the freshly applied wet paint film without leaving brush marks. Sufficient open time is essential for achieving painting efficiency and delivering aesthetically pleasing results in architectural coatings. The open time of the coating can be influenced[4,5] by solids, pigment volume concentration, polymer composition, rheology modifiers, additives like humectants, and solvents.

Through the use of statistical design of experiments, this study identified polymer structure factors that can influence the open time and early rain resistance of the paints.

Film formation[6,7] from polymer dispersions is schematically depicted in **Figure 1**. It is expected that water-based paints undergo similar stages, such as water evaporation-concentration, particle packing, particle deformation, and particle coalescence-interdiffusion, to form a coating. The water evaporation stage strongly influences the open time of the paint. The drying conditions of the paint, including temperature, humidity, and air flow, have a significant impact on the water evaporation rate and open time. Low temperature, high humidity, and stagnant air will slow down water evaporation and increase open time. Conversely, high temperature, low humidity, and high-velocity air flow will speed up water evaporation and reduce open time.

In this research, we studied the polymer composition to improve the open time without compromising early rain resistance. Statistical design of experiments was used to identify polymer structure factors that can influence the open time and early rain resistance of the paints. Multi-speckle diffusing wave spectroscopy[8,9] was used to gain understanding on the critical steps of the film formation process such as water evaporation-concentration, particle packing, particle deformation, and film dry through. Diffusing wave spectroscopy is an extension[8] of classical dynamic light scattering to concentrated and opaque media. The diffusing wave spectroscopy and polymer structure factor data were analyzed to develop new polymers with improved open time without compromising early rain resistance.

FIGURE 1
Film formation in polymer dispersions.[6,7]

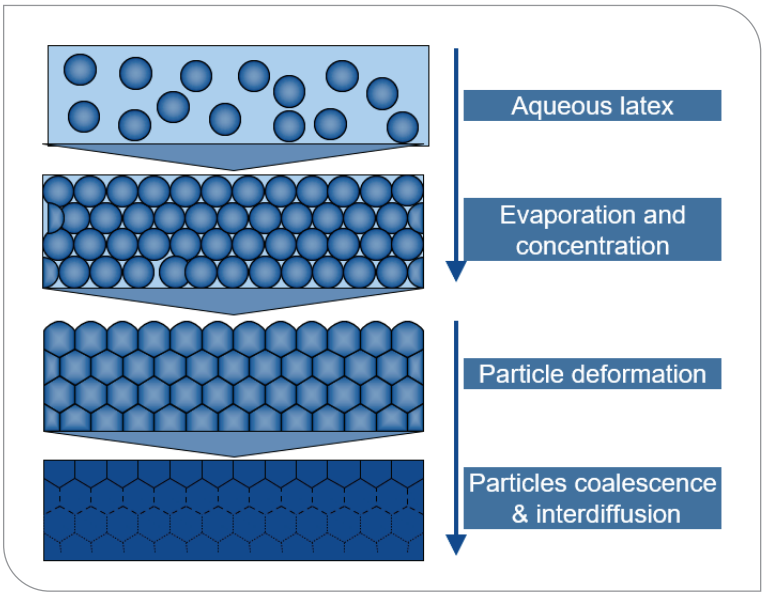


TABLE 1
Polymer Structure Factors Used in the Custom Design of Experiment

Polymer T_g	Hydrophobic monomer	Crosslinker1	Crosslinker2	Acid monomer	Adhesion promoter	Particle stabilizer	Neutralizing agent
Low or High	HMonomer1 or HMonomer2	None or Present	Low or High	AMonomer1 or AMonomer2	None or Present	Stabilizer1 or Stabilizer2	Low or High

TABLE 2
Design of Experiment Polymer Composition Variations

No.	T_g**	Hydrophobic monomer	Crosslinker1	Crosslinker2	Acid monomer	Adhesion promoter	Particle stabilizer	Neutralizing agent
1*	20	BA	0	0.35	AMonomer1	4	Stabilizer1	0.15
2	20	EHA	0.3	0.7	AMonomer2	4	Stabilizer1	0.15
3	11	EHA	0	0.7	AMonomer1	0	Stabilizer1	0.05
4	20	BA	0	0.35	AMonomer1	0	Stabilizer1	0.05
5	11	EHA	0	0.7	AMonomer1	4	Stabilizer1	0.15
6	11	EHA	0.3	0.35	AMonomer2	0	Stabilizer1	0.15
7	20	BA	0.3	0.7	AMonomer2	4	Stabilizer1	0.05
8	11	BA	0.3	0.35	AMonomer2	0	Stabilizer1	0.05
9	11	BA	0.3	0.7	AMonomer1	4	Stabilizer2	0.05
10	11	EHA	0	0.35	AMonomer2	4	Stabilizer2	0.05
11	20	EHA	0.3	0.7	AMonomer1	0	Stabilizer2	0.05
12	20	EHA	0	0.35	AMonomer2	4	Stabilizer2	0.05
13	11	BA	0	0.7	AMonomer2	0	Stabilizer2	0.15
14*	20	EHA	0.3	0.35	AMonomer1	0	Stabilizer2	0.15
15	11	BA	0	0.7	AMonomer2	0	Stabilizer2	0.15
16	20	BA	0.3	0.35	AMonomer1	4	Stabilizer2	0.15

* These dispersions had stability issues and were eliminated from the study; Minimum number of runs needed for studying the main effects in this JMP® custom design of experiment is only 9.
** Calculated T_g (Flory-Fox equation).
BA = n-Butyl acrylate; EHA = 2-Ethylhexyl acrylate
Note: The numbers in the table are percentages of the raw materials in the polymer composition.

Experiments

To study the effect of polymer composition on the open time and early rain resistance, a custom design of experiment using JMP® was carried out. The design consisted of eight structure factors of a control polymer dispersion and the details of the design are given in **Table 1**. Paint formulated using this control polymer provided better early rain resistance and equal open time compared to a leading national brand commercial paint. The goal is to improve the open time of this paint by changing the control polymer structure without reducing the early rain resistance of the paint.

Sixteen different polymer dispersions were synthesized using this design strategy and the composition differences of these polymer dispersions are given in **Table 2**. These polymer dispersions were synthesized by conventional emulsion polymerization using unsaturated monomers, emulsifiers, and initiators. These polymer dispersions have approximately 53% solids content. Two polymer dispersions, Nos. 1 and 14, were not stable and so they were eliminated from the study. For studying the main effects using this JMP® custom design, the minimum number of runs required is only 9.

Flat paints were formulated using the design of experiment polymer dispersions according to the paint formulation in **Table 3**.

TABLE 3
Flat Paint Formulation

Flat Formulation	
Raw Material	**Grams**
Kronos® 4311	275.0
Water	238.2
Dispex® CX 4320	11.0
FoamStar® ST 2420	2.0
Hyrdopalat® WE 3320	3.0
Ammonium hydroxide 28%	0.5
Proxel™ BD 20	3.0
Potassium tripolyphosphate	0.5
Rheovis® PE 1331	15.0
Minex™ 4	225.0
Zoco 101	25.0
Attagel® 50	5.0
Polyphase® 663	7.0
FoamStar® ST 2420	2.0
Texanol™	5.1
Rheovis® PE 1331	15.0
Rheovis® PU 1191	5.0
Polymer dispersion (~53% solids)	317.9
Total	**1155.1**

PVC = 49
% Weight solids = 57.0
% Volume solids = 38.1

Test Methods

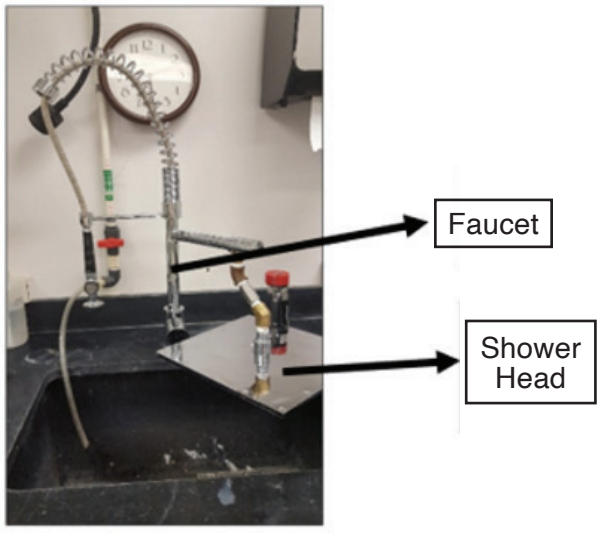
Testing early rain resistance (ERR)

The following test procedure was used to test paints for early rain resistance and was slightly modified from a previously reported procedure.[10] To prepare the test panels, the paints were drawn down using a 7 mil Dow drawdown bar on a Leneta Form P121-10N black scrub test panel. The panels were then cured in an environmental chamber set to 45 °F and 70% relative humidity. The paint films were tested for ERR at 5-minute incremental cure time until it passed the ERR test.

The apparatus used for ERR testing is shown in **Figure 2**. The apparatus consists of a water faucet with a pressure control valve and a shower head. The panel was placed in the panel rack angled at 45 degrees and centered under the showerhead. The water flow rate was adjusted to mimic a 3-inch-per-hour rain rate. Before testing the samples, the water flow rate was measured and adjusted to ensure testing consistency. The experimental paints were tested along with a control paint, as shown in **Figure 3**, to identify any spurious results.

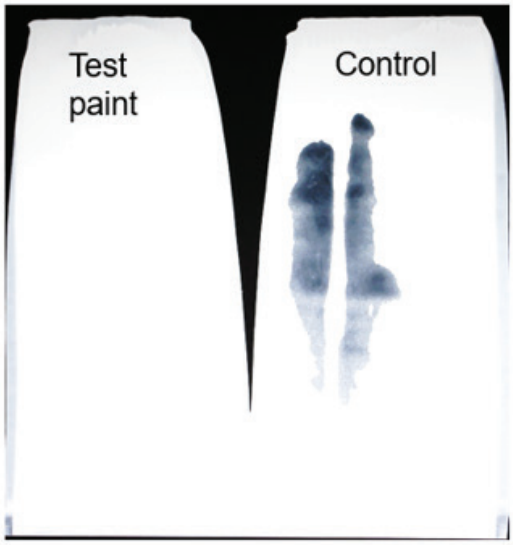
The cure time at which each paint showed no damage after 2 minutes of showering was recorded as the ERR time, and the sample was considered to have passed the test.

FIGURE 2
The shower station.



Note: Water line pressure control valve is hidden.

FIGURE 3
Experimental paint and control.



Testing paint open time by ASTM D 7488-11

The testing was carried out by following the ASTM D 7488-11 test method in a controlled environment with a constant temperature and relative humidity of 75 °F and 50% humidity. The paints were drawn down using a 7 mil Dow drawdown bar on Leneta Form P121-10N black scrub test panel for testing open time.

Studying paint drying by diffusing wave spectroscopy (DWS)

Diffusing wave spectroscopy measurements were made using the Rheolaser® Coatings HT instrument supplied by Formulaction™ scientific instruments to study the paint curing process. Rheolaser®Coatings is based on Multi Speckle Diffusing Wave Spectroscopy (MS-DWS) and detects particle Brownian motion. Light is scattered by the particles (scatterers) present in the sample, creating an interference pattern (Speckle Image). Due to the motion of the scatterers in the product, the speckle image changes as a function of time. During the film formation of a coating, different mechanisms such as solvent evaporation, particle packing, and particle deformation can be determined.

Curinscan™ software provided by Formulaction™ scientific instruments was used for the analysis of the data. A typical scan, **Figure 4**, shows change in micro dynamics mD (Hz) of the particles with time. Micro dynamics is the change in speed of the speckle image created by scattered light by the particles in the coatings. Micro dynamics are large at the beginning of film formation due to fast movement of particles in the liquid coating sample and small at the end due to slow motion of particles in the coatings film. This scan provides information on various stages of film formation,[6,7] such as water evaporation-concentration, particle packing, particle deformation, and particle coalescence-interdiffusion in water-based paints[8,9]. The end of concentration, particle packing, and particle deformation stages are denoted by tc 1, tc 2, tc 3, respectively, as shown in **Figure 4**.

The paints were drawn down using a 120µm gap drawdown bar on Leneta Form P121-10N black scrub test panel for testing the paint drying process. The tests were carried out at 75 °F and 50% relative humidity.

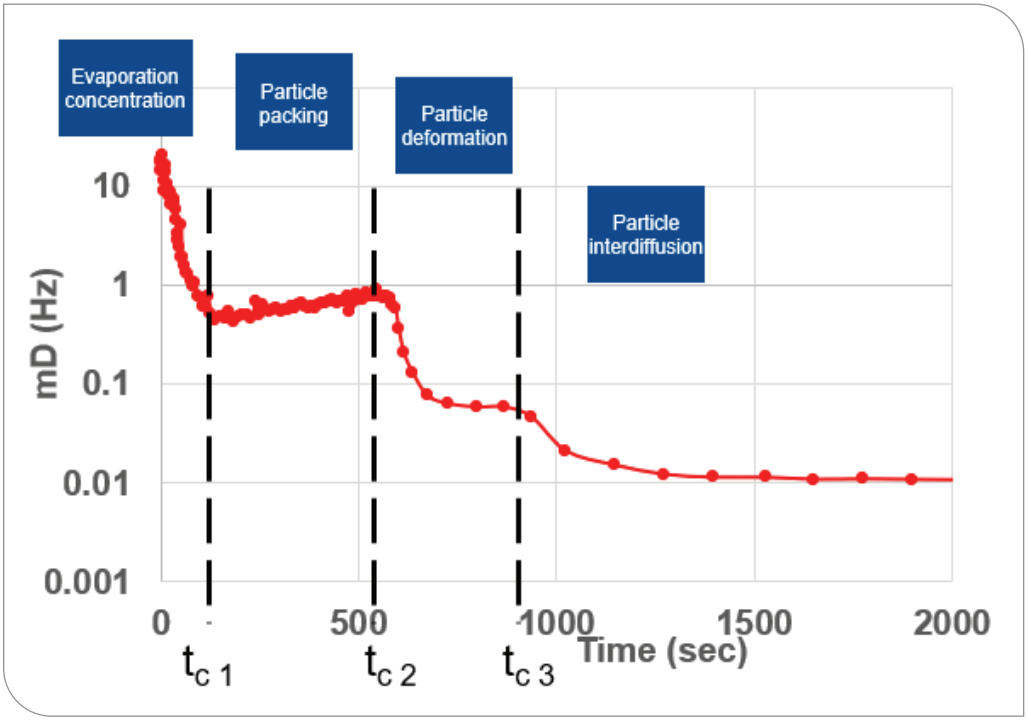


FIGURE 4 CurinScan™ showing change in micro dynamics mD (Hz) of particles in a drying paint.

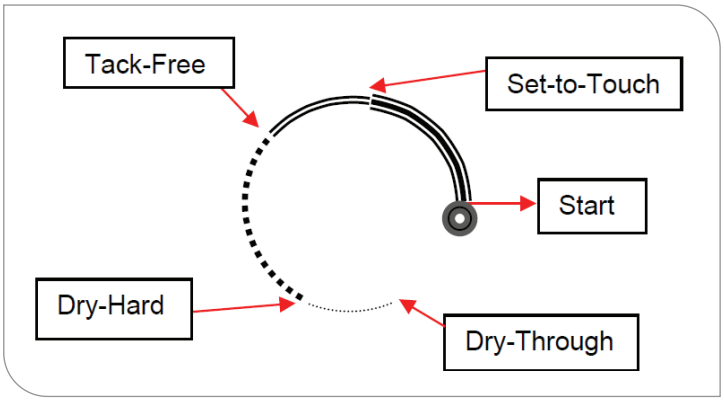


FIGURE 5 Various stages in the paint drying process.

Testing paint dry time using circular dry time recorder

The Gardco Quadracycle dry time recorder was used to record the paint drying process. This recording device enables the identification of different stages of paint drying such as set-to-touch, tack-free, dry-hard, and dry-through stages as shown in **Figure 5**.

The set-to-touch time (Q-STT) corresponds to the point in time where the paint's ability to backflow and fill the track created by the moving ball no longer exists. This point marks the end of the open time of the paint.

The testing was conducted following the ASTM D 5895-03 test method in a controlled environment with a constant temperature and relative humidity of 75°F and 50%. The paints were applied using a 7 mil Dow drawdown bar onto Leneta Form WB plain white sealed charts for the study.

Results and Discussion

The flat paints formulated with design of experiment polymers were tested for early rain resistance and open time and the data is given in **Table 4**. The results demonstrate that the open time can be significantly altered by adjusting the composition of the polymer dispersions. The range of ASTM open time observed varied from 2 to 10 minutes as shown in **Table 4**.

The results demonstrate that the open time can be significantly altered by adjusting the composition of the polymer dispersions.

TABLE 4
ASTM Open Time, Quadracycle Dry Time, CurinScan™ DWS Time and Early Rain Resistance Data

Polymer	ASTM open time (min)	Q-STT[1] (min)	tc 1[2] (min)	tc 2[3] (min)	(tc 2 - tc 1)[4] (min)	ERR[5] (min)
2	2	1.7	2.4	14.4	12	60
3	2	3	3.4	16.3	12.9	65
4	2	2.7	2.5	15.5	13	60
5	5	4.5	4.3	14	9.7	65
6	4	4.3	3.9	19.6	15.7	65
7	2	2.7	3.1	19.1	16	65
8	2	2.8	3.1	17.1	14	65
9	8	6.5	5.9	15.6	9.7	65
10	6	4.2	4.4	15.2	10.8	70
11	4	5.5	3.6	14.4	10.8	65
12	3	3	3	11.9	8.9	75
13	5	5.3	3.8	15.3	11.5	75
15	10	9.2	5.7	20.3	14.6	65
16	5	5.2	4.8	13.7	8.9	65
Control Paint[6]	7	7.6	3.5	15	11.5	65

*Polymer descriptions in Table 2
1: Q-STT = Quadracycle set-to-touch time
2: tc 1 = Diffusing wave spectroscopy end of concentration time
3: tc 2 = Diffusing wave spectroscopy end of particle packing time
4: (tc 2 – tc 1) = particle packing time
5: ERR = Paint dry time @ 45 °F and 75% RH to pass the ERR shower test
6: Paint formulated using the control polymer. The design of experiment is centered around this polymer.

The ASTM open time data was analyzed using the JMP® statistical software. The analysis revealed that two structure factors, namely the polymer particle stabilizer and the T_g (glass transition temperature) of the polymer, have a significant influence on the open time, as shown in **Figure 6**.

A very similar conclusion was obtained (**Figure 7**) from the analysis of Q-STT.

The open time, measured according to ASTM D 7488-11, was compared with the Quadracycle set-to-touch (Q-STT) time. The comparison revealed a strong correlation between the two methods, as depicted in **Figure 8**. The linear fit analysis yielded an R^2 value of 0.87, indicating a good relationship between the open time and the Q-STT time.

FIGURE 6
JMP® analysis of ASTM open time data.

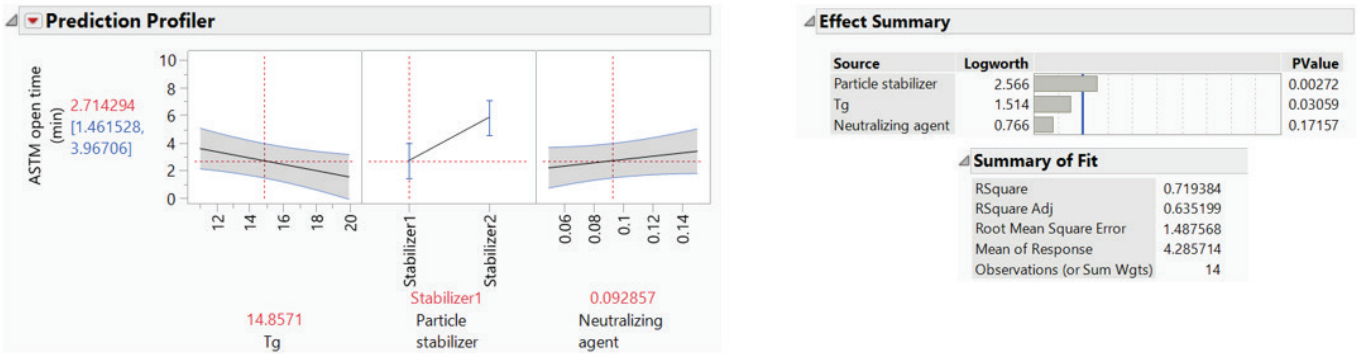


FIGURE 7
Analysis of Quadracycle set-to-touch time (Q-STT) Data by JMP.®

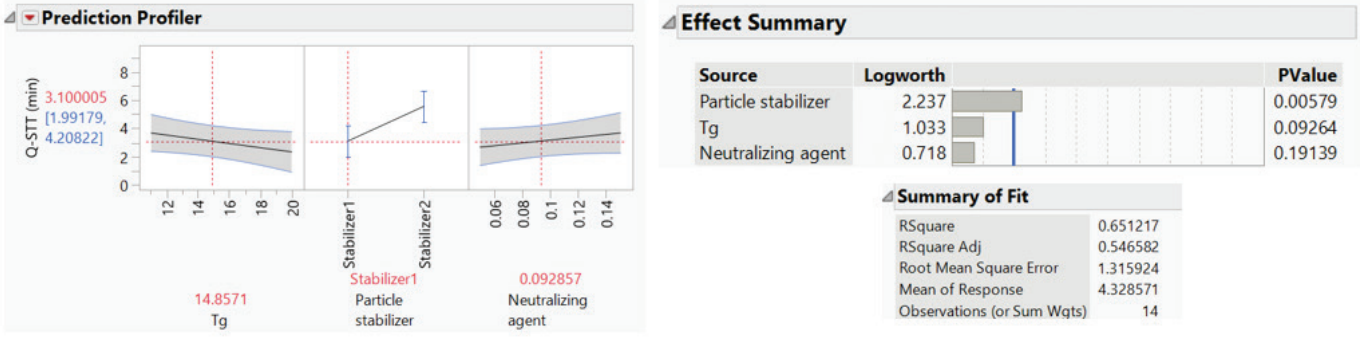
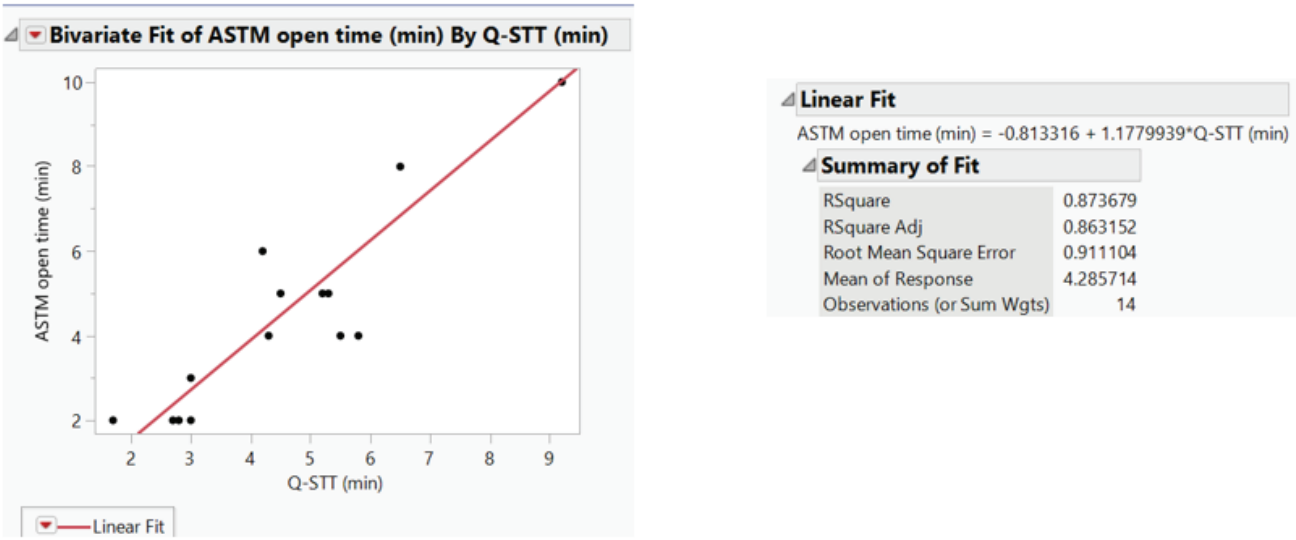


FIGURE 8
ASTM open time vs. Quadracycle set-to-touch (Q-STT) time.



Diffusing wave spectroscopy

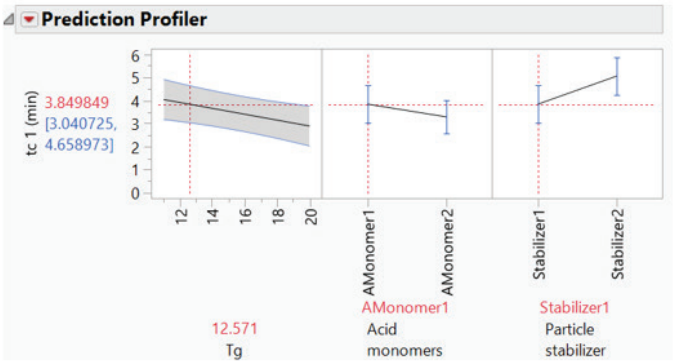
Diffusing wave spectroscopy[8] provides insight into various stages of film formation, including water evaporation-concentration, particle packing, particle deformation, and particle coalescence-interdiffusion. The evaporation-concentration time (tc 1) was analyzed by JMP®. The results, as shown in **Figure 9**, indicate that the tc 1 time is strongly influenced by polymer structure factors, namely particle stabilizer and T_g (glass transition temperature). This observation aligns with the ASTM open time (**Figure 6**) and Q-STT (**Figure 7**) measurements.

The data obtained from ASTM D 7488-11 was compared with the diffusing wave spectroscopy data tc 1 time. The comparison revealed a good correlation between the two methods as illustrated in **Figure 10**. The linear fit analysis showed an R^2 value of 0.86, indicating a good relationship between the open time measured by ASTM D 7488-11 and the tc 1 time measured by diffusing wave spectroscopy.

The open time measured by ASTM D 7488-11 is higher compared to tc 1, especially for paints with a higher ASTM open time. This discrepancy may be attributed to the differences in the two test methods, specifically the differences in the film thickness.

The time difference between the end of particle packing stage and the end of evaporation-concentration stage gives the time taken for the particle packing called particle packing time. The analysis of the particle packing time (tc 2 – tc 1) data showed

FIGURE 9
Analysis of DWS tc 1 Data by JMP®.



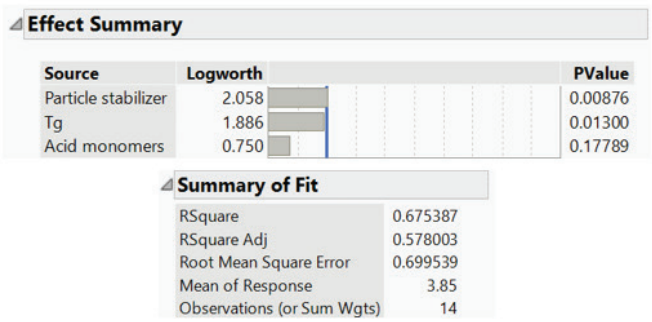
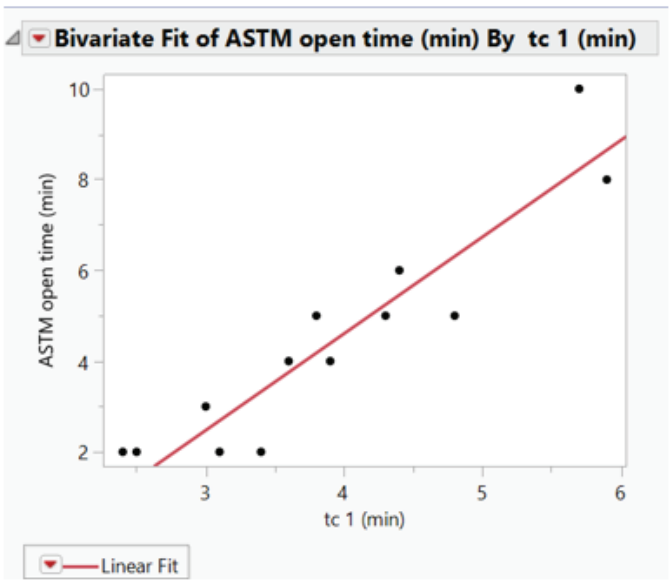


FIGURE 10
Correlation of ASTM open time and DWS tc 1 time.



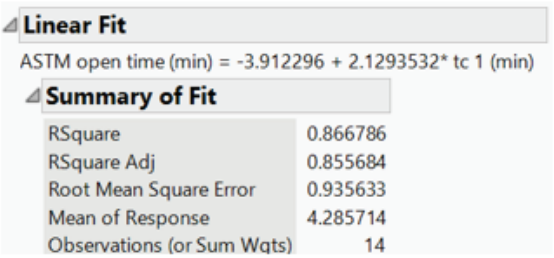
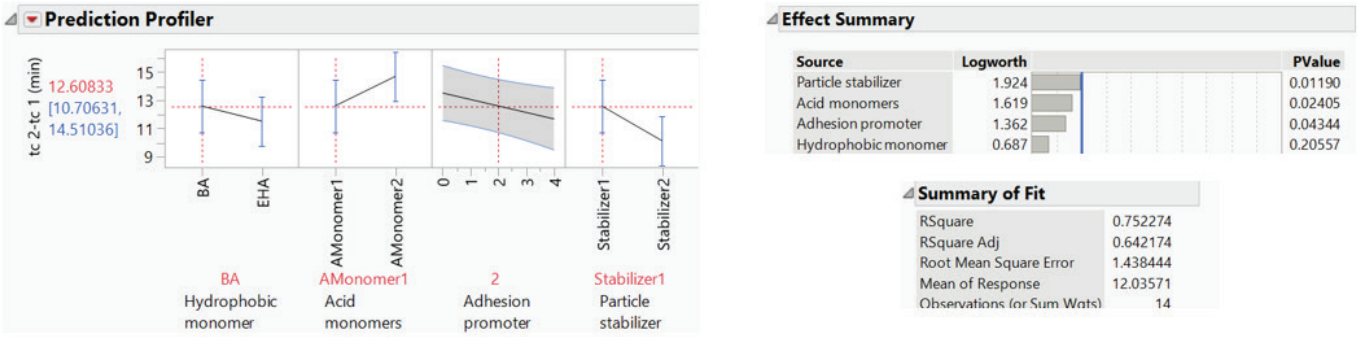


FIGURE 11
Analysis of DWS (tc 2 – tc 1) data by JMP®.



(**Figure 11**) that the particle packing stage is significantly influenced by several polymer structure factors namely particle stabilizer, acid monomers, and adhesion-promoter. Particle stabilizer1 and acid monomer2 were found to increase the particle packing time, while the adhesion promoter reduced it as shown in **Figure 11**.

Thus, diffusing wave spectroscopy provides valuable insights into how the polymer structure influences the water evaporation and particle packing during the drying of the paint.

The polymer dispersion No.15 in **Table 4** offers the best early rain resistance and ASTM open time among the polymer dispersions in the design of experiment. The Quadracycle set-to-touch time (Q-STT) and Diffusing wave spectroscopy (tc 1) data also support this conclusion. This particular polymer dispersion provides rain resistance that is comparable to the control polymer, while also displaying a 40% improvement in open time. Furthermore, this polymer dispersion provides good tint strength, adhesion to various substrates, tannin blocking, surfactant leaching, and accelerated dirt pick-up resistance.

Summary

- The design of the experiment reveals that polymer structure factors significantly influence paint open time.
- Paint open time was improved by 40% by changing the composition of the polymer dispersion without reducing the early rain resistance.
- Diffusing wave spectroscopy provides insights into polymer structure factors that have an influence on water evaporation and particle packing during the film formation.
- Data from ASTM D 7488-11 open time measurement, Quadracycle dry time measurement, and diffusing wave spectroscopy show good alignment and provide valuable insights into the polymer structure factors that influence paint open time. ⁂

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