

3M Advanced Materials Division

Dirt Pick Up and Stain Resistance Evaluations of 3M™ Fluorochemical Additives for Architectural/Decorative Paints





Outline

- Dirt pick up and stain resistant background
- 3M™ Fluorochemical surfactants and additives
- Dirt pick up resistance evaluation in paint formulations
- Stain resistance improvement of commercial paints with 3M surfactant and additives
- Conclusion





Dirt Pick up and Stain Resistant Performance Factors

Environmental:

- Pollution / airborne dust
- Humidity / rain
- Weather
- Temperature
- Algae growth
- Finger print / oily stains
- Graffiti

Coating Formulation

- Resin Type and Tg (stickiness)
 - Pigment Volume Concentration (PVC) ratio (surface porosity)
 - VOC (solvent) level (cured film)
 - Static Dissipation (dirt particle attraction)
 - Surface smoothness
 - Surface Energy
 - Hydrophobicity
 - Oleophobicity
- } FC additives can help





Hydrophilic vs. Hydrophobic Surface

■ Hydrophilic Surface

- Lower water contact angle
- Water will evenly wet the surface and wash away the dirt
- Rain can do the cleaning

- May be good for exterior paint self-cleaning

■ Hydrophobic Surface

- Higher water contact angle, water drop beads up
- Liquid does not wet surface
- Water may lead to streak marks
- Rain can not wet the surface and can not wash away the dirt

- May be good for interior paint for easy cleaning

While Hydrophobic / Hydrophilic characteristics are important, Oil repellency is necessary to reduce dirt pick up and remove dust

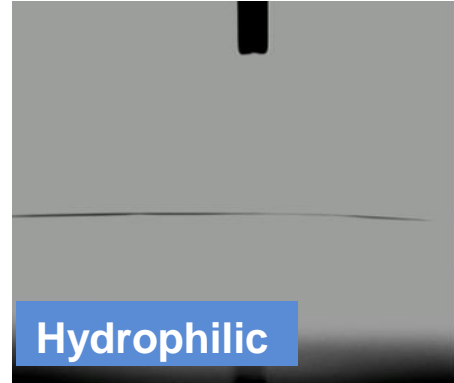




Contact Angle – Hydrophobic vs. Hydrophilic Surface



Water beads up



Water wets out



Oil beads up
(oleophobic)

Oil wets out

3M™ Fluorochemical surfactants FC-4430, FC-4432 and FC-4434 are oleophobic (higher oil contact angles)

3M™ Fluorochemical surfactants FC-4430, FC-4432 and FC-4434 are hydrophilic (lower water contact angles)

Hydrophilicity helps surfaces be self-cleaning with water

Oleophobicity aids in preventing build up of oily contamination that attracts dirt





3M™ Fluorochemical Surfactants and Additives

- FC-4430/FC-4432/FC-4434 Surfactants provide
 - A hydrophilic and oleophobic surface (dried paints)
 - Hydrophilic characteristic generally provides easy clean surface
 - Durable repellency to oil stains and soils
 - Good wetting and leveling
 - Supplied as a polymeric nonionic surfactants (soluble/dispersible in water-based paints)
 - Very low use level (typically 0.05-0.2%)
- SRC-220 Additive provides
 - A coating with both hydrophobic and oleophobic characteristics
 - Low surface energy surface when dried
 - Supplied as a fluorinated polyurethane dispersion (soluble/dispersible in water-based paints)
 - Low use level (typically 0.2-1.0%)





3M™ Fluorochemical Surfactants Profile

	FC-4430	FC-4432	FC-4434	FC-5120
Physical Properties				
Surfactant Types	Non-ionic	Non-ionic	Non-ionic	Anionic
Solid %	98	95	25	25
Solvent	DPM	DPM	DPM	Water/IPA
Viscosity cp (25°C)	1,000 - 10,000	1000 - 10,000	< 20	< 10
Flash point (°C)	82	82	78	25
Solvent based systems	Yes	Yes	Yes	No
Polar solvent	Yes	Yes	Yes	Varies*
Non Polar solvent	Varies*	Varies*	Varies*	No
Water based systems	Yes	Yes	Yes	Yes

3M™ surfactants can be used in polar solvent and water borne coatings, high solid coatings (epoxy, PU and acrylic) UV and EB cured coatings, adhesives and solder flux.

* Varies on the solubility, FC-4430/FC-4432 are soluble in aromatic solvents, but not in hydrocarbons.





Multiple Performance Attributes for Paint and Coating Formulations

- Wetting Agent
- Leveling Agent
- Low Foaming
- Stain Removal
- Dirt Pick up Resistance
- Open Time Improvement

These are characteristics of dried paints and are addressed in this presentation





Paints and Coatings Definitions

- Stain Removal
- Dirt Pick up Resistance
- Open Time Improvement
- VAE formulations
- Acrylic formulations
- Easy Clean
- Reflectance Recovery
- Delta E (DE) is a measure of the color difference between the original sample and the sample after performing the dry dirt test





Test Methods

- **Dirt Pick-up Resistance (DPUR): Exterior Paints & Coatings**
 - Exterior weathering tests (Florida/Arizona)
 - Dry dirt tests
 - Washability
- **Washability & Cleanability (Stain removal): Interior Paints & Coatings**
 - ASTM D-3450 modified
 - carbon black oil stain and sponge method- used 10% Dawn soap & 50 cycles
- **Open-Time: Exterior & Interior Paints & Coatings**
 - ASTM D-7488
 - Rated visibility of “X”





3M Lab Evaluation: Paint Formulations and Testing

■ Paint Formulations

- Varying Pigment Volume Concentration (PVC) levels (from 45% - 60%)
- FC-4432 or FC-4434 added in the letdown stage (from 0% to 0.5% active)
- 3M™ Ceramic Microspheres W-410 evaluated in combination with FC surfactants
- SRC-220 evaluated in combination with FC-4432

■ Testing

- Washability and dirt pick up resistance evaluated based on the test methods described in the previous slide
- Weatherability has yet to be completed (in-process, results expected Q2, 2014)





Vinyl Acetate Ethylene (VAE) Formulations Evaluated:

MATERIAL	Amount(lbs) Formulation A	Amount(lbs) Formulation B	Amount(lbs) Formulation C	Amount(lbs) Formulation D
Natrosol [®] 250 MHR	3.39	3.39	2.75	3.39
Water	343.60	343.90	279.40	343.35
Popylene Glycol	9.16	9.15	7.45	9.16
AMP-95 [®]	2.57	2.56	2.08	2.56
Skane [™] M-8	3.05	3.05	2.48	3.05
Rhodoline [®] 643	1.51	1.51	1.23	1.51
TAMOL [®] 851	2.75	2.41	2.23	2.75
Triton [™] CF-10	2.29	2.29	1.86	2.29
Ti-Pure [®] R-706	79.38	79.37	74.46	109.87
Iceberg [®] calcined particle	167.93	114.47	136.51	53.40
Duramite [®]	193.88	140.42	157.61	65.60
3M [™] W-410 Ceramic Microspheres	0.00	96.16	0*	199.90
Ucar [™] polyphobe TR-116	3.74	3.73	3.04	3.74
EcovVAE [®] 401 Resin	152.66	152.60	289.15	152.60
Water	152.66	152.60	124.10	152.60
Rhodoline [®] 643	1.14	1.14	0.93	1.14
Eastman Texanol [™] ester alcohol/Butyl Carbitol [™] solvent (70/30)	4.58	4.58	3.72	4.58
UCAR [™] Polyphobe [™] TR-116	8.78	8.78	7.13	8.78
3M [™] FC-4434* add here*	0.2% equates to 9 lbs	0.2% equates to 9 lbs	0.2% equates to 9 lbs	0.2% equates to 9 lbs
TOTALS(LBS)	1133.06	1122.11	1096.13	1116.88
TOTALS (Gallons)	100	100	100	100.00

Grind

Let down



General Formulation Properties:

Formulation	60 degree gloss	85 degree gloss	Opacity	PVC
Formula A	2.3	1.9	96-97	65
Formula B	2.1	1.6	94-95	65
Formula C	2.4	1.7	90-91	45
Formula D	2.1	1.2	91-91.5	65

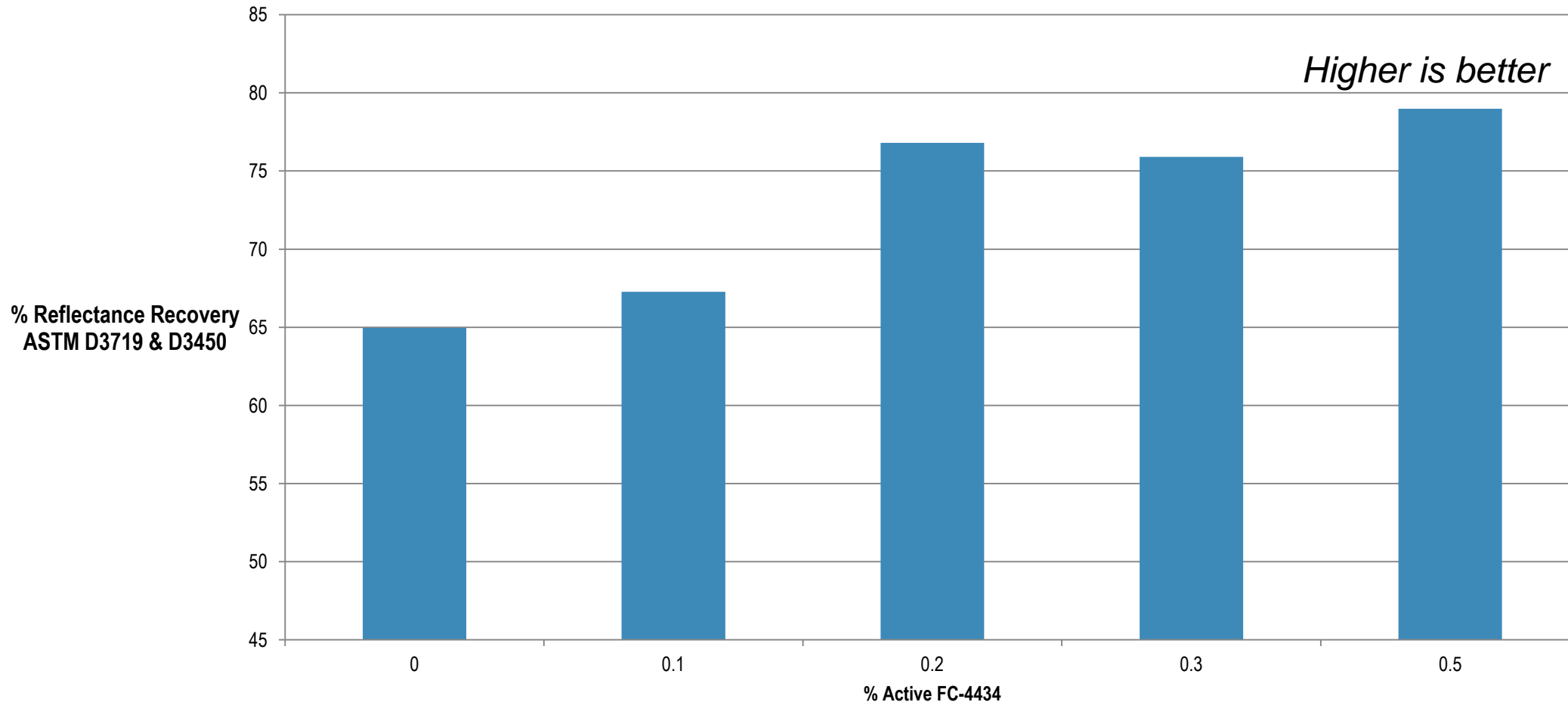
Viscosity: 90-100 ku's





FC-4434 Ladder Study in Formulation A (VAE flat, PVC = 65%)

Leneta Black Stain test- 50 cycles with (10% Dawn® Soap)

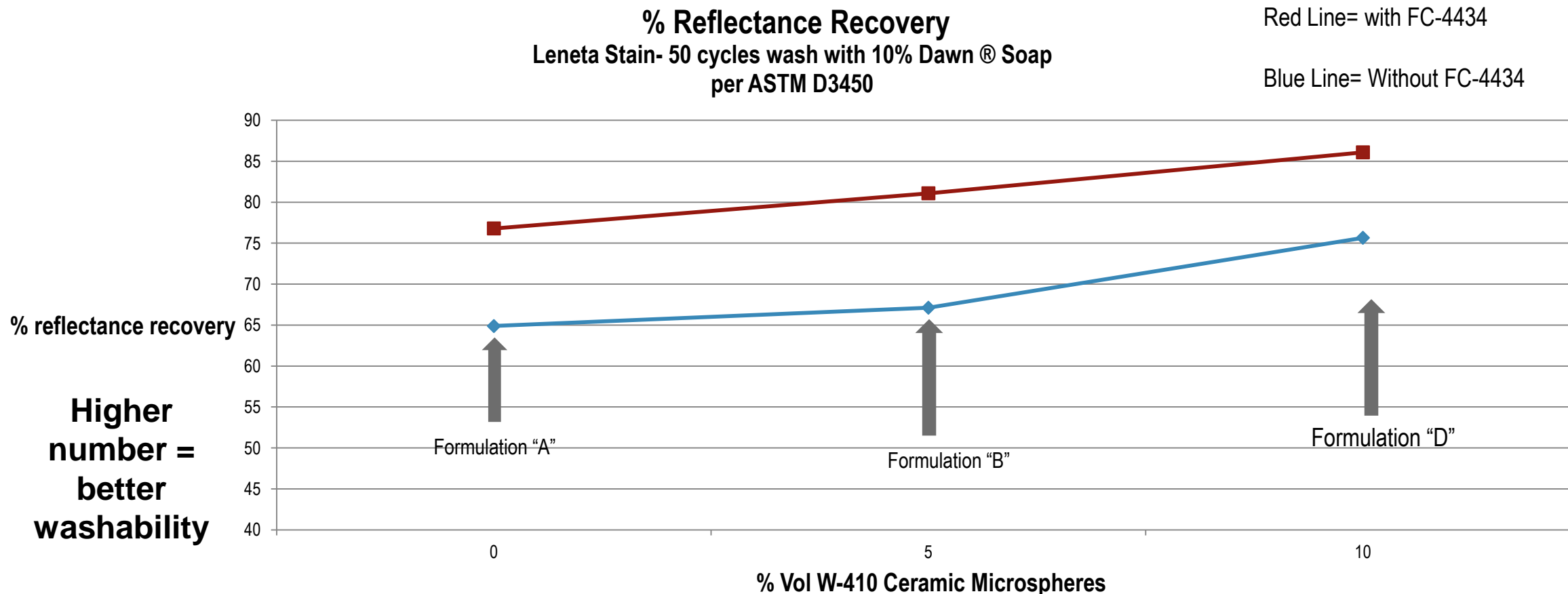


Addition of FC-4434 additive can improve stain resistance of this formula.
0.2% addition of FC-4434 in this formulation offers optimum cost performance benefit.





Effect of FC-4434 & W-410 ceramic microspheres in 65% PVC-VAE Paints -Washability/Stain Removal Test



The addition of FC-4434 and W-410 ceramic microspheres improves washability.





100% Acrylic Flat Paint- Formulation “E”

Material	Amount(lbs)	WPG	Amount (GAL)
Natrosol [®] 250 MHR	2.60	11.50	0.23
water	244.90	8.34	29.36
TAMOL [®] 851	10.37	9.90	1.05
Potassium tripolyphosphate	1.55	21.15	0.07
TRITON [™] CF-10	2.27	8.97	0.25
Rhodamine [®] 643	1.03	7.09	0.15
Ti-Pure [®] R-706	181.00	33.40	5.42
Zinc Oxide	25.86	46.70	0.55
Minex [®] 4	54.90	21.70	2.53
Iceberg [®] calcined particle	36.69	21.93	1.67
Duramite [®]	54.93	22.70	2.42
3M[™] Ceramic Microspheres W410	100.20	20.00	5.01
Attagel [®] 50	5.17	19.70	0.26
Skane [™] M-8	2.22	8.60	0.26
Rhoplex [™] VSR-50	406.32	8.80	46.17
Rhodoline [®] 643	3.67	7.09	0.52
Eastman Texanol [™] ester alcohol/Butyl Carbitol [™] solvent (70/30)	9.74	7.92	1.23
Propylene glycol	6.71	8.63	0.78
Acrysol [™] RM-2020 NPR	18.00	8.67	2.08
3M[™] FC-4434* add here*	0.2% equates to 9.3 lbs		
TOTALS	1168.12		100.01



General Formulation Properties:

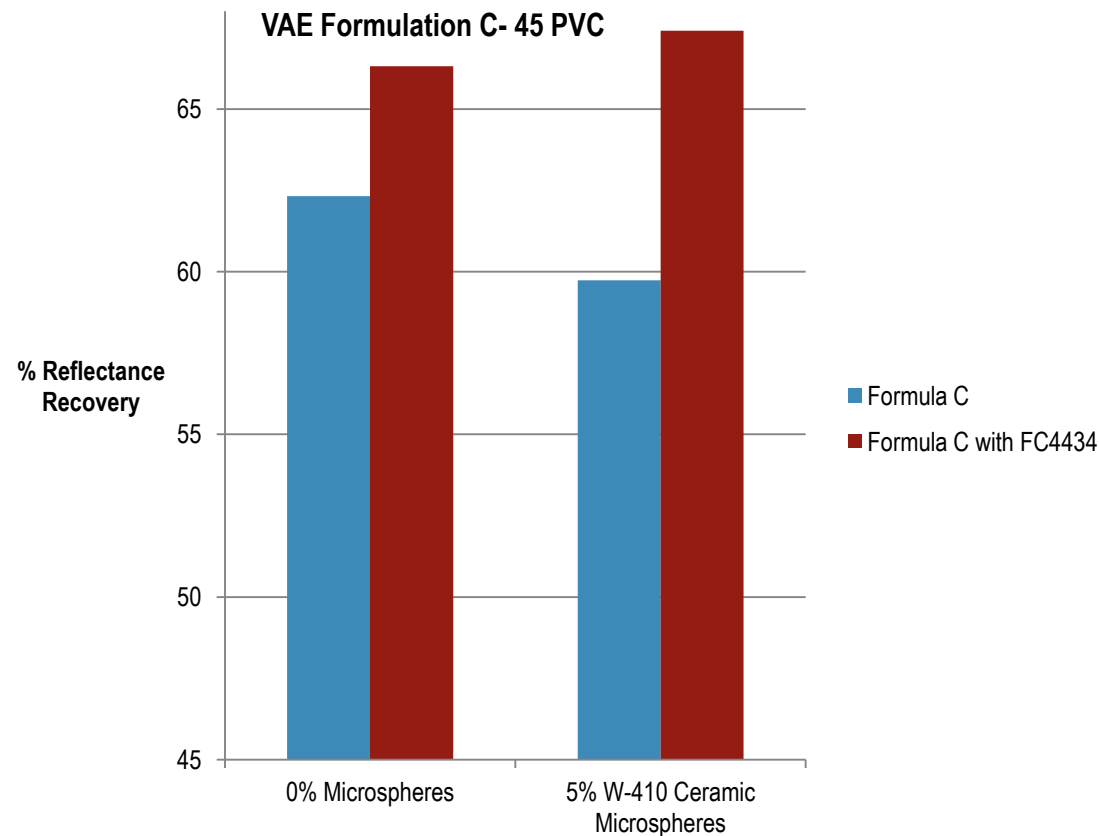
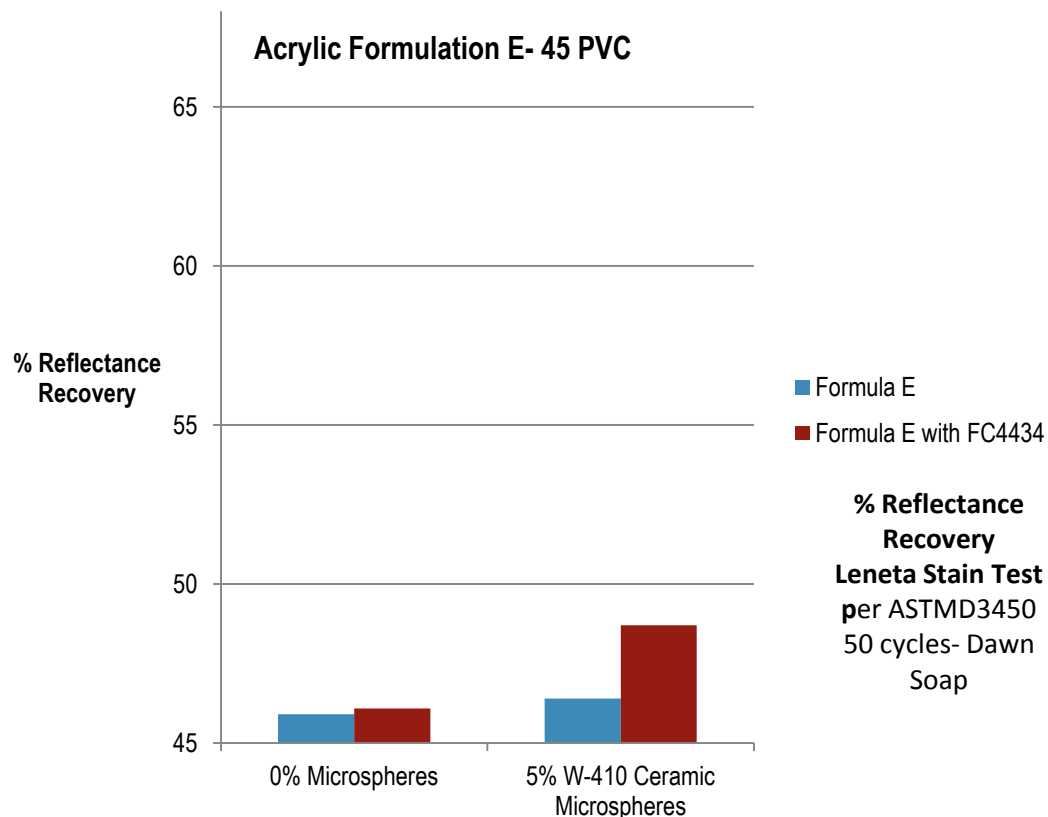
Formulation	60 degree gloss	85 degree gloss	Opacity	PVC
Formula E	3.3	2.6	96-97	45

Viscosity: 90-100 ku's





Effect of FC-4434 & W-410 ceramic microspheres in 45% PVC Paints Washability/Stain Removal



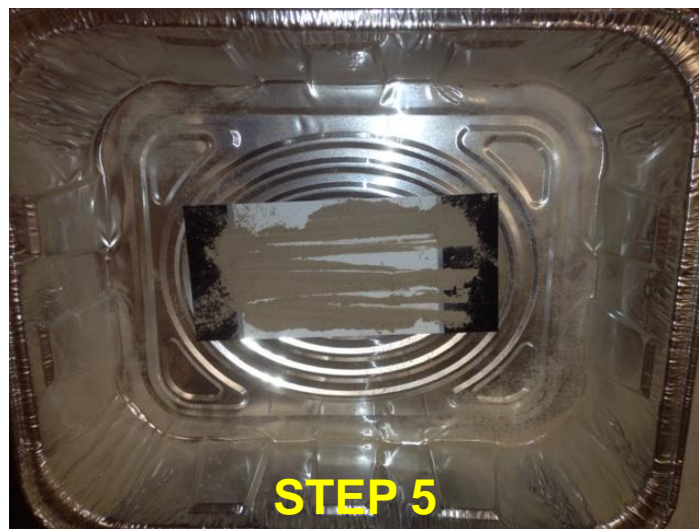
Higher Number = Better Washability



FC-4434 has more pronounced effect in VAE Paint at 45 PVC level



"Preliminary" Dry Dirt Test



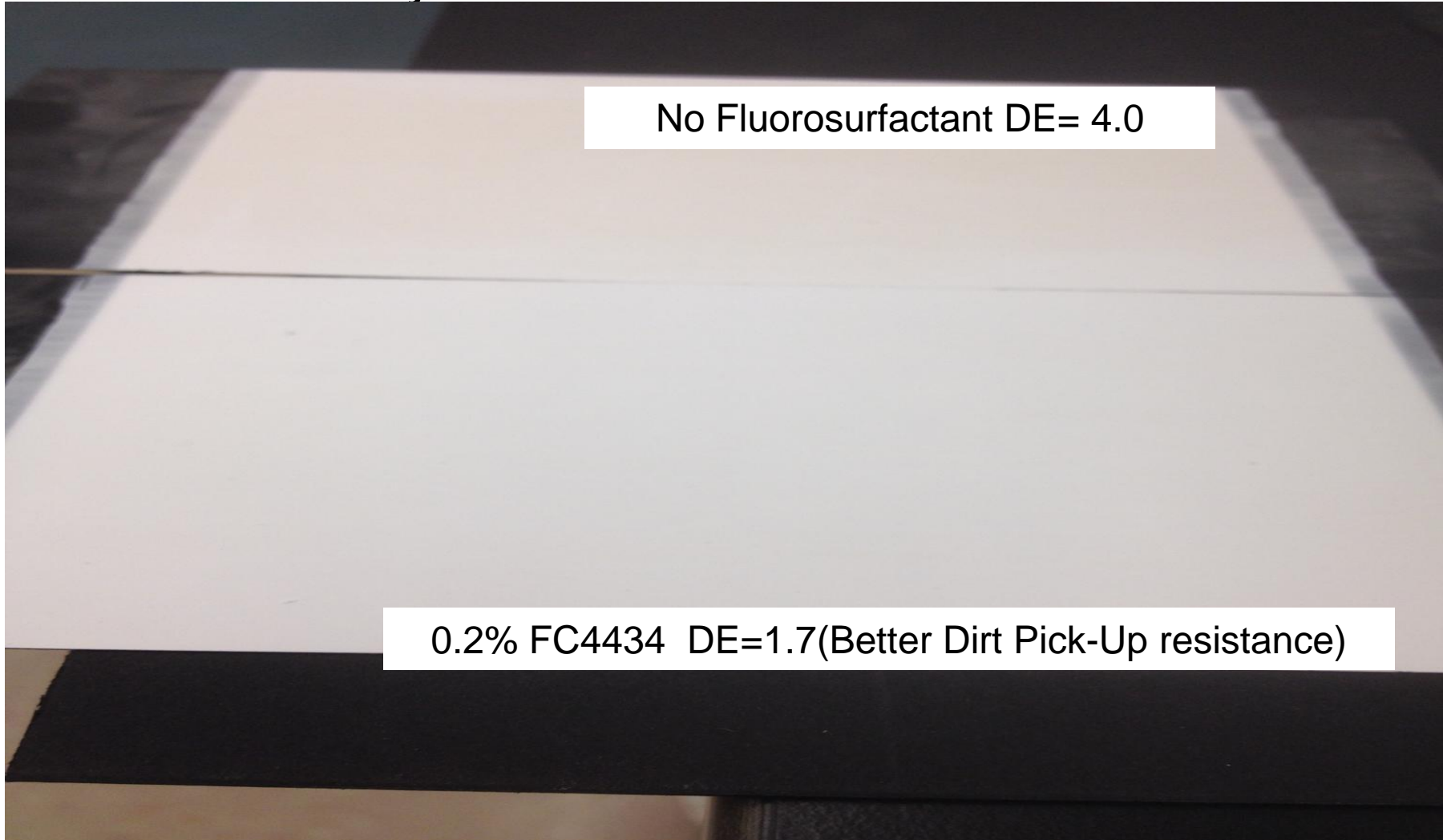
Materials: Commercial Dry Dirt (Arizona 0-70 micron brown dirt(60722K) from PTI or equivalent), Gloss meter, spectrophotometer, balance, stopwatch, temp/humidity gauge, spatula.

Procedure:

1. Measure Initial Gloss and Color(not shown)
2. Record Room Temp and %RH- control humidity or run controls with each study.
3. Weigh out 5 grams dirt in metal spatula
4. Transfer to sample(3x6")
5. Spread evenly on surface and wait 30 min
6. Tap off dirt and measure gloss & color and compare with initial readings.(not shown)



Formulation A – Dry Dirt Test



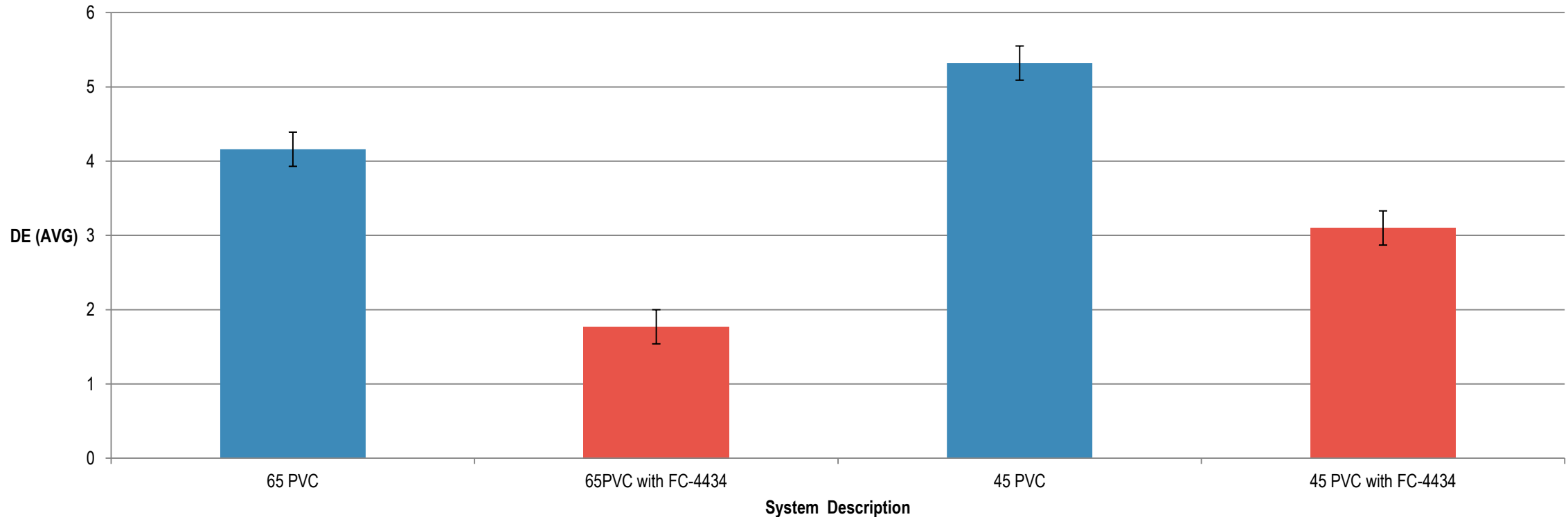
A difference of 1.0 Delta E is significant



"VAE" Paint- Dry Dirt Test

Delta E , DE, is a measure of the color difference between the original sample and the sample after performing the dry dirt test

DE Arizona (0-70 micron) Dry Dirt Test VAE Flat Paints



65PVC= Formulation A
45 PVC= Formulation C

The addition of FC-4434 improves dry dirt pick-up





Additional Formulation Study with FC-4432 as Additive

- FC-4432 (without any solvent) was used in a commercial interior paint
- Formulation Dependent, Two paint formulations studied and commercialized
 - Acrylic resin
 - Styrene/Acrylic resin
- Washability Improvement
 - 45 down to 4 – 15 strokes for FS141 grease
- Delta E Improvement
 - The Delta E is a measure of the color difference between the original sample and the same sample after performing the greasy test and clean. After cleaning, the treated paint should come back to within 2 Delta E of the original Color
 - 8 – 10 vs. 0.2 – 0.5 Delta E





Testing Method and Screen (DOE) for Performance

- Used black carbon grease washability testing (ASTM D-3450)
- FC-4432 FC polymer (100% active) was used for evaluation
- Various PVC level (pigment volume concentration)
- FC concentration vs. washability performance
- Also the impact on other paint characteristics (no negative impact)





Example of Evaluated Acrylic Paint Formulation with FC-4432

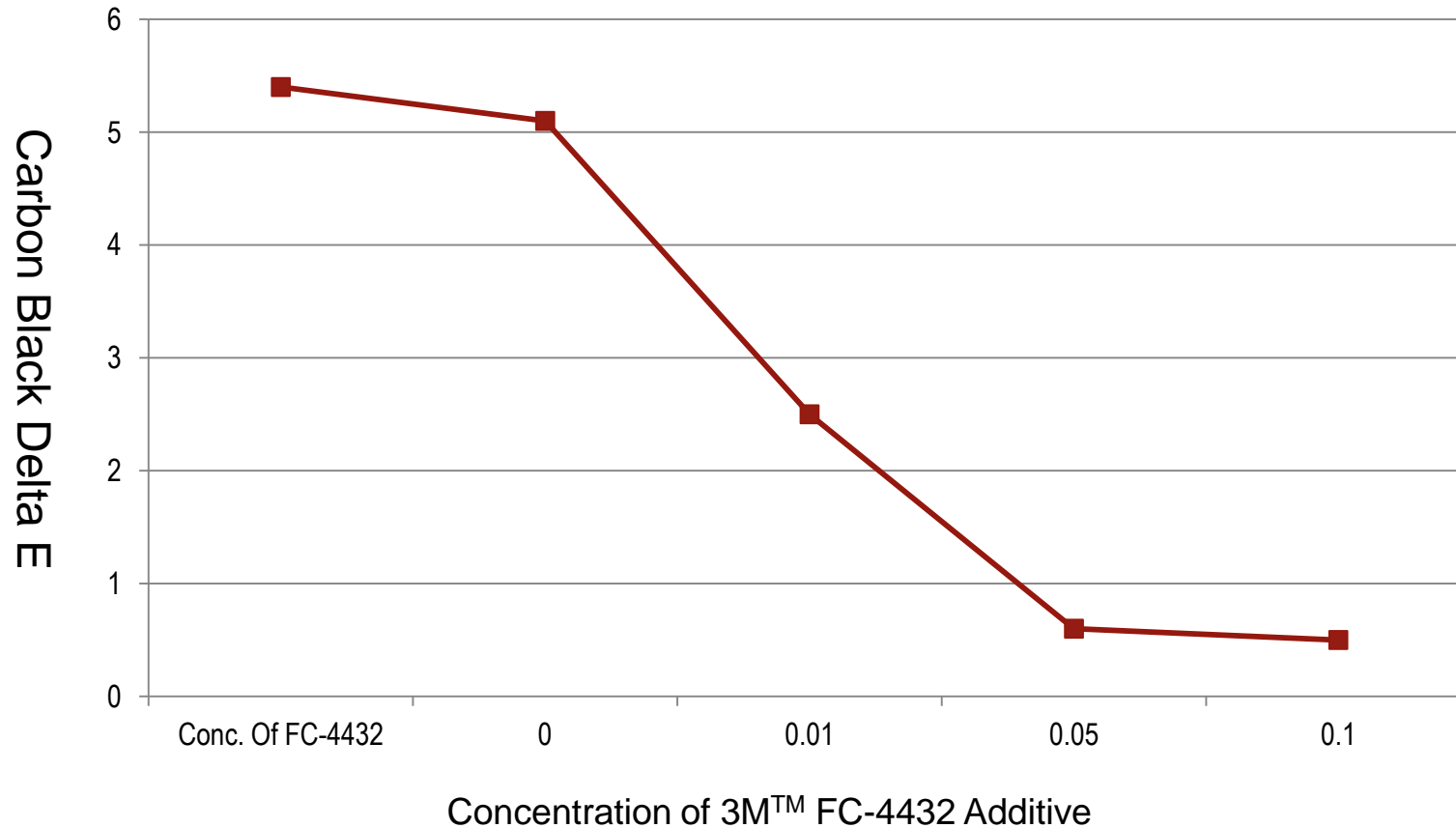
	Material	Pounds	Volume
Grind	Joncryl ® 537 Latex	240	27.39
	Propylene glycol	15	1.61
	Drewplus ™ L475	2	0.27
	Ti-Pure ® R-900	200	5.93
	OPACIMITE ® calcium carbonate	33.2	1.47
	Novacite ® silica	210	9.50
	Attagel ® 40	10	0.51
Letdown	Joncryl ®537 Latex	135.85	15.50
	Water	264	31.63
	Ammonia	1.5	0.18
	Drewplus ™ L475	1	0.13
	Acrysol ® QR-708	15	1.67
	Eastman Texanol ™ ester alcohol/Butyl Carbitol ™ solvent (70/30)	38.04	4.13
	3M ™ FC-4432	1.2	0.15
	Tinting color 1:10	5.36	0.64
	Biocide	2.5	0.30
	Total	1174.65	101.01





Formulation Performance – Delta E (Acrylic formulation)

(The Delta E is a measure of the color difference between the original sample and the same sample after performing the greasy test and clean)



Lower Delta E means better washability

3M™ FC-4432 improved the performance even at low level





General Performance Trend with FC-4432 (Concentration and PVC Formulation dependent, you need to do the testing on your formulation

- For the acrylic and acrylic/styrene tested in the lab:
 - The higher the FC-4432 concentration, the better the performance (black carbon grease washability testing, with PVC at 50%), some formulation may need more FC-4432 than others
 - As PVC increases, the washability deteriorates (at 0.2% FC-4432)
- Very formulation dependent (resins, PVC, solvent etc), customers would need to run their own evaluation





Stain Resistant Additives for Paints – Performance Evaluation with the Combination of FC-4432 and SRC-220 on the Commercially Available Paints from the DIY Market

- **Question:** Can a poor quality paint be turned into a good quality paint by adding 3M Fluorochemical surfactants and additives?
- **Study:** Conduct a series of experiments looking into the “design space” of FC-4432, FC-4434 and SRC-220 in various commercially available paints purchased locally from Menards, Home Depot and Lowe’s.
- **Testing:** Test panels were prepared for 3 levels of additive for each additive, for each paint and a control. Then performed 4 separate test methods (listed below) on each panel to gather data about the effect of the additives.
 - Contact Angles
 - Visual Stain Beadability
 - Visual Beadability
 - Recoatability





Additives, Concentration, Procedure and Test Paint Coupons

- FC-4432 and FC-4434: 0.05, 0.1 and 0.3% active level (total wet weight%)
- SRC-220 0.2 and 0.6% level (same wet weight%)
- Competitive FC surfactant 0.05, 0.1 and 0.3% active level
- Procedure:
 - Post adding to the commercial paints (mixer)
 - Mix using an air motor / paint mixer
- Test Paint Coupons as shown (painted on dry wall)





Paints Tested in this Study (from local DIY stores)

Letter	Paint	Price
A	Interior Flat	12.99
B	Interior Flat Latex Waterbase Wall Paint	6.97
E	Flat Ultra White Latex Wall Paint	16.88
F	Interior Flat	19.89
G	Matte finish Wall Paint Interior 100% acrylic	23.98
J	Matte Flat Enamel with Scotchgard(TM) Protector	31.99
K	Matte Finish	30.99
L	Interior Flat Wall Paint Acrylic Latex	26.49
M	Interior Matte Finish	37.99
N	Wall Latex Flat	18.97
O	Interior Wall Paint	23.98
P	Interior Flat Enamel	20.98
Q	Interior Flat	16.98

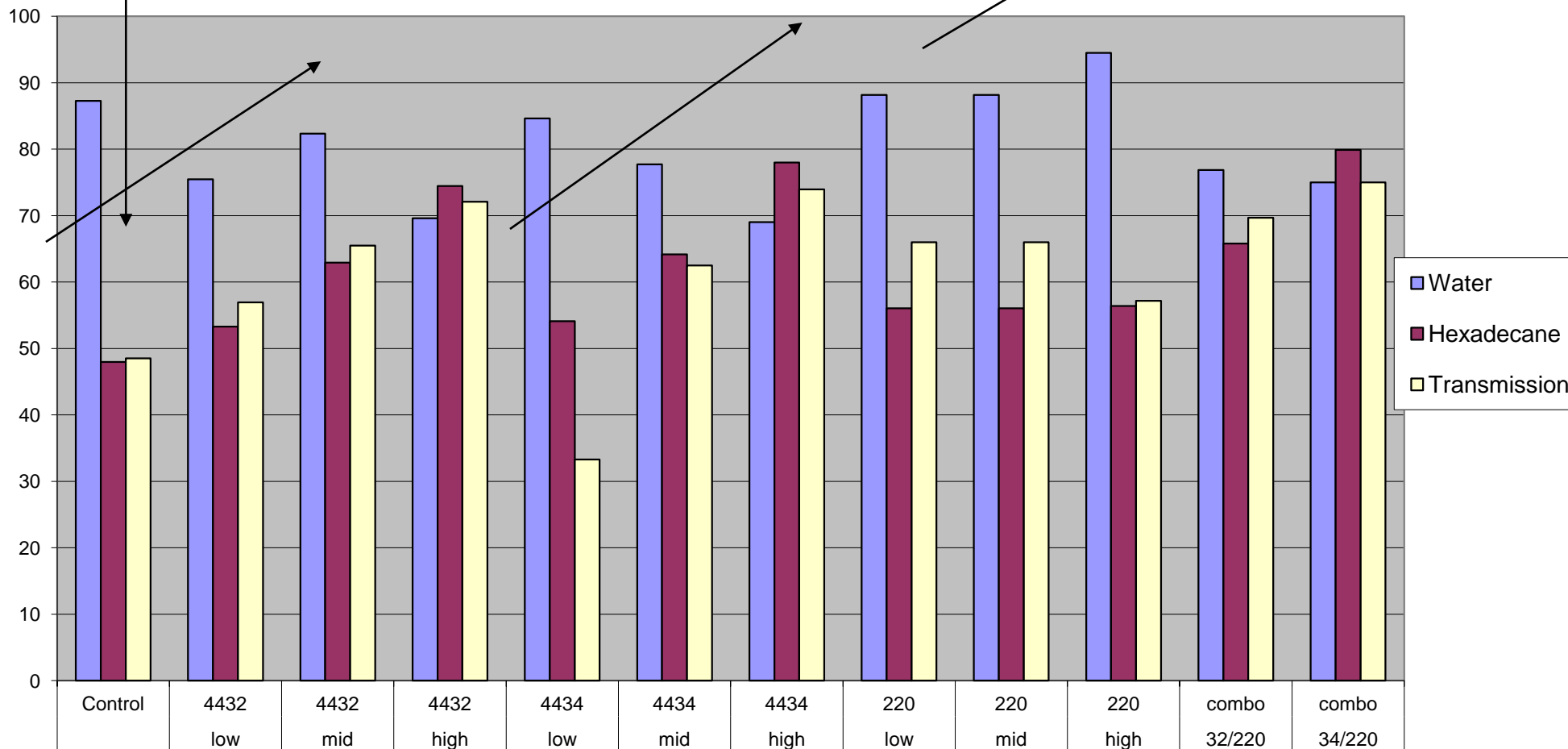




No additives

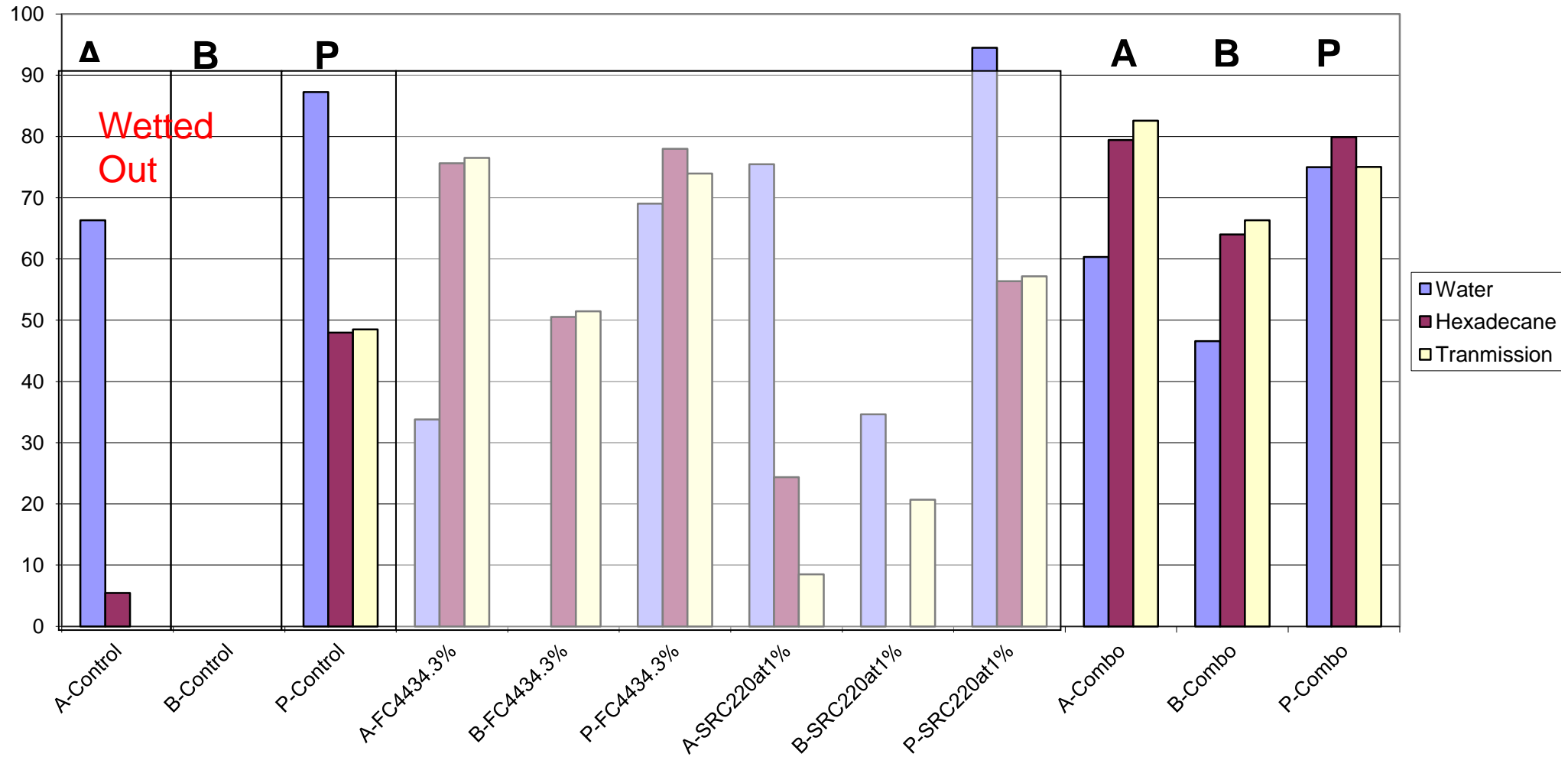
Additives

Contact Angle Data for Paint P Interior Enamel





Contact Angle Results for Paint A, B and P





Contact Angle Conclusion

- FC-4432/FC-4434 increased the oil contact angles (oleophobic)
- FC-4432/FC-4434 have minimum impact to water contact angle, if not lower (hydrophilic)
- SRC-220 increased both water and oil contact angle (hydrophobic and oleophobic)

- **The FC-4432/FC-4434 are similar to FC phosphate based surfactants (hydrophilic and oleophobic)**





Visual Beadability and Stain Resistant Test Method

- **Beadability:** For each stain, the relative “beadability” of the stain was rated 1 – 10 as follows
 - 1 = Flat, stain wets out completely onto coated surface.
 - 5 = Medium, stain wets onto coated surface but stays relatively “contained” .;
 - 10 = Stain stays on surface of coating, beads like water on wax.

- **Stain resistant test:** 24 Hours after staining, test panels will be cleaned using Scotchbrite™ sponge that has been moistened Dawn® dish in water.
 - 1 = Test panel shows high levels of staining.
 - 5 = Test panel shows slight level of staining.
 - 10 = Test panel shows little to no level of staining.



Overall Test Data

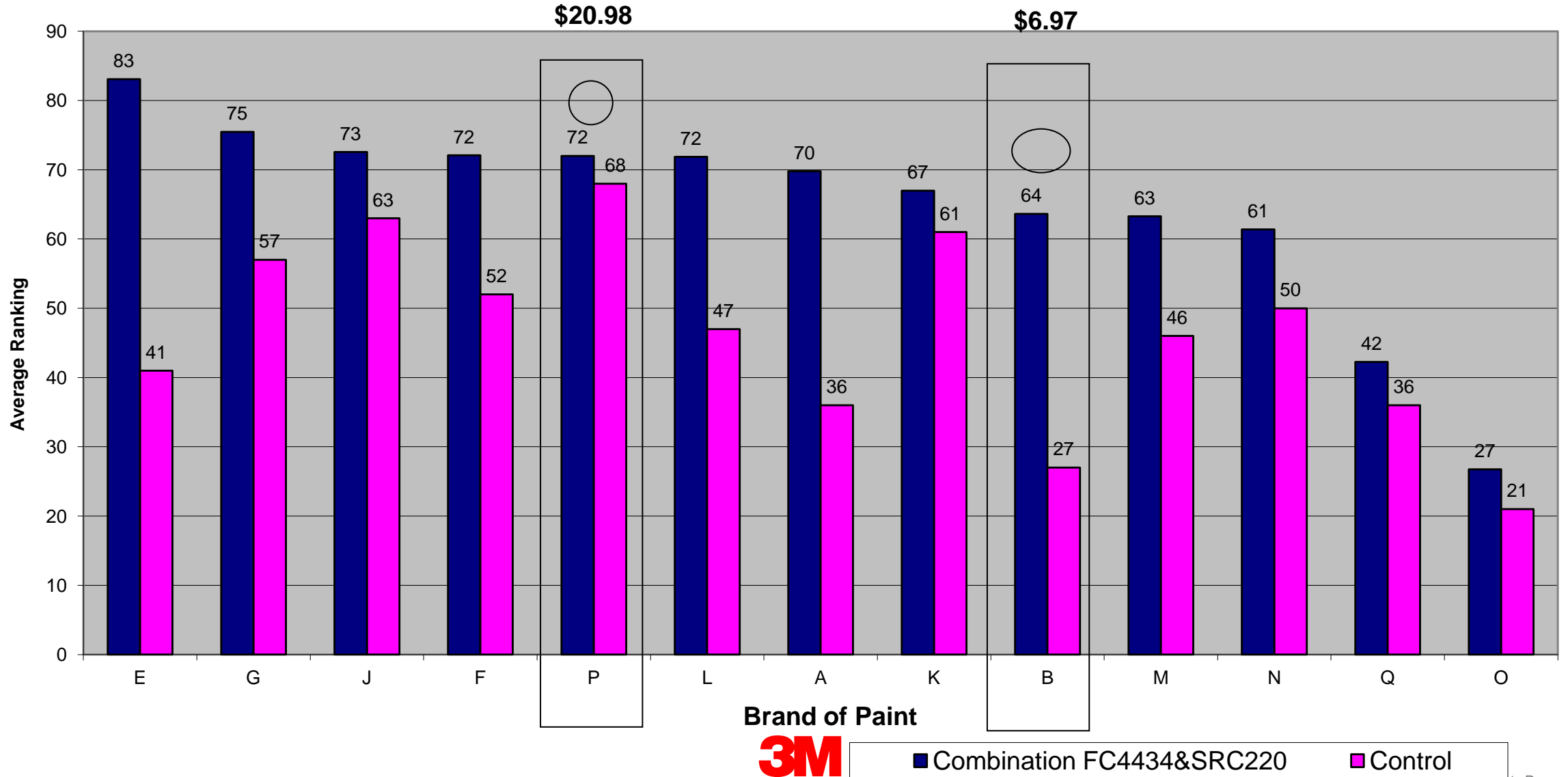
- Visual Test A – Beadability (50 μ L)
- Visual Test B – Stain resistant (easy to clean)
- Goniometer – Contact angles (3 substances) (5 μ L)
- Recoating – Dry/Stain Coverage

Since each of these readings and averages were then rated on a 100 point scale, the collection of data provides an overall ranking for each brand of paint used.





Overall Test Results and Ranking of Paints

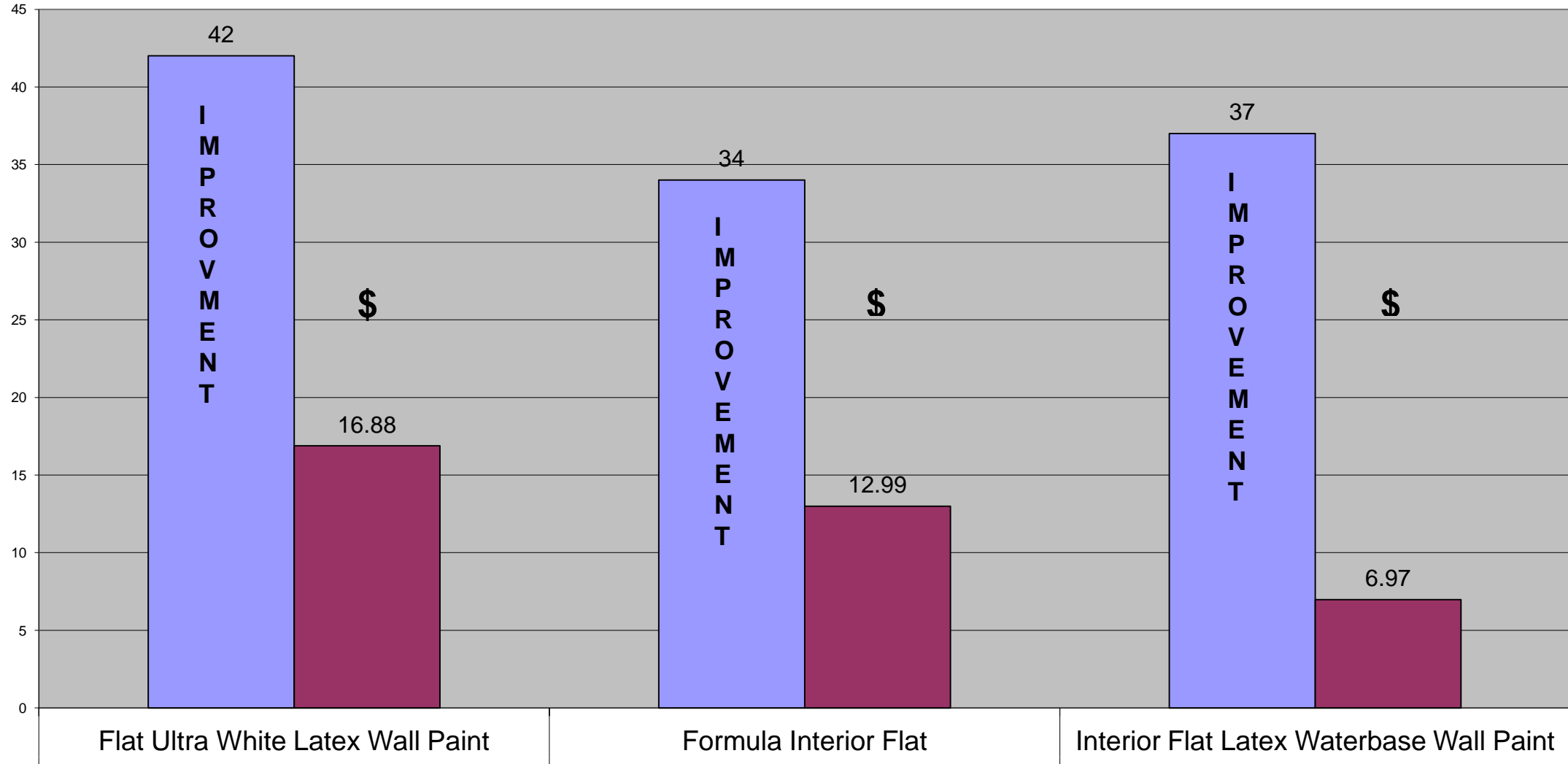


■ Combination FC4434&SRC220

■ Control



Low Cost Paints – Vast Improvement with 3M™ Additives (FC-4432 & SRC-220)





Open Time Testing on VAE Paint

System	Open Time(min)
	<i>ASTM D7488</i>
Formulation "A"	7
Formulation "A" with 0.2% FC4434	12

For open time, higher number means the paint remained open longer for workability.





Conclusions:

- 3M™ Fluorosurfactants can improve washability, stain resistance and dirt pick up especially in high PVC VAE binder paints.
- 3M™ Fluorosurfactants can also improve washability & stain resistance in other binder systems such as exterior acrylic(s) depending on formulation parameters.
- 3M™ Fluorosurfactants combined with 3M ceramic microspheres can significantly improve the washability & stain and dirt resistance of various paints.
- 3M™ Fluorosurfactants combined with SRC-220 can improve the stain resistance of commercially available paints
- 3M™ Fluorosurfactants can improve the open time of the paint formulations





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