



Carbon Blacks in Coatings: Overview and case studies

Dr Richard Abbott



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Overview



- Fundamental Properties of Carbon Black and Test Methods
- Applications Performance
 - High Color – effect of dispersion
 - Tint study
 - Drop in tint replacement



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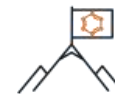
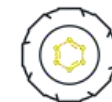




Fundamental Properties



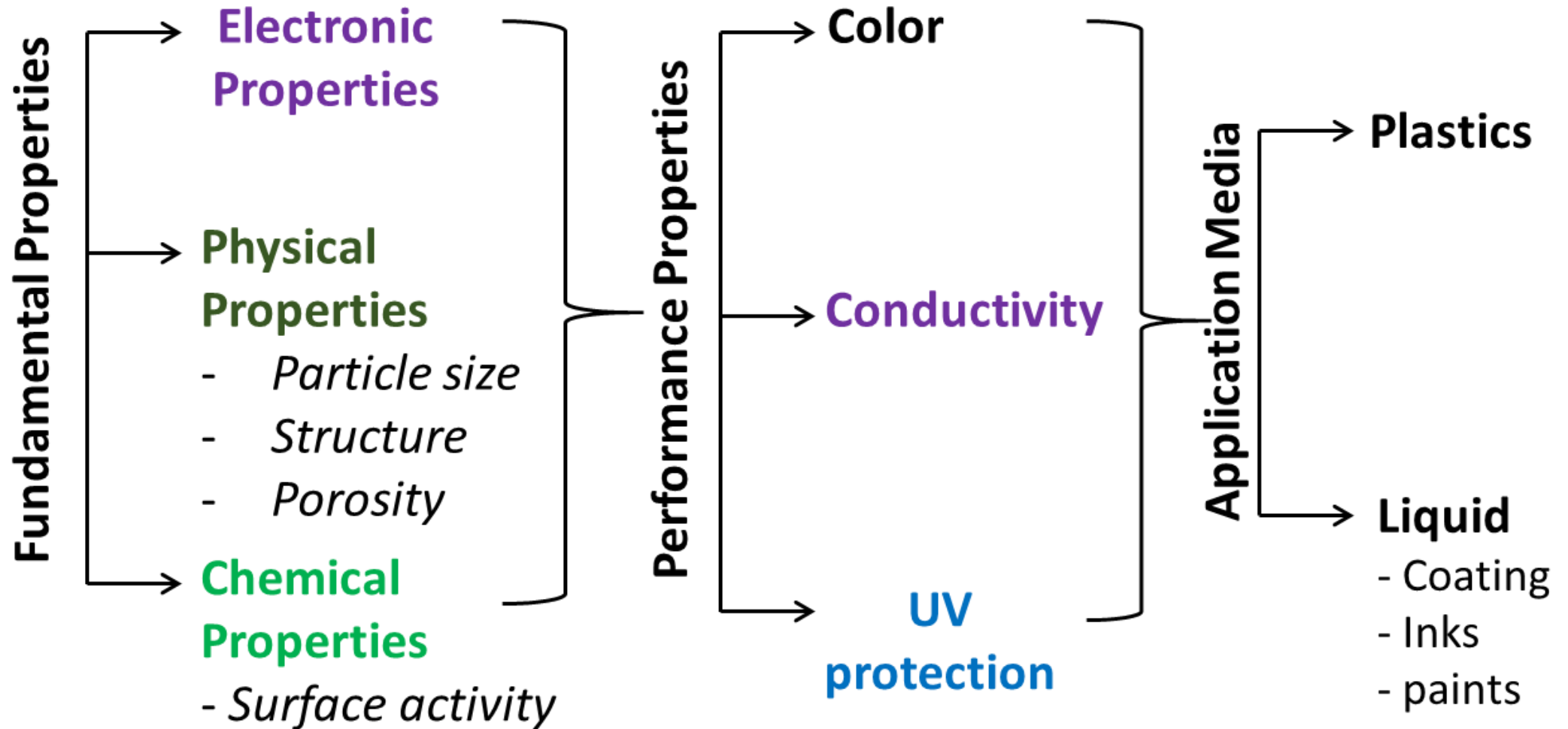
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Carbon Black and Specialty Applications

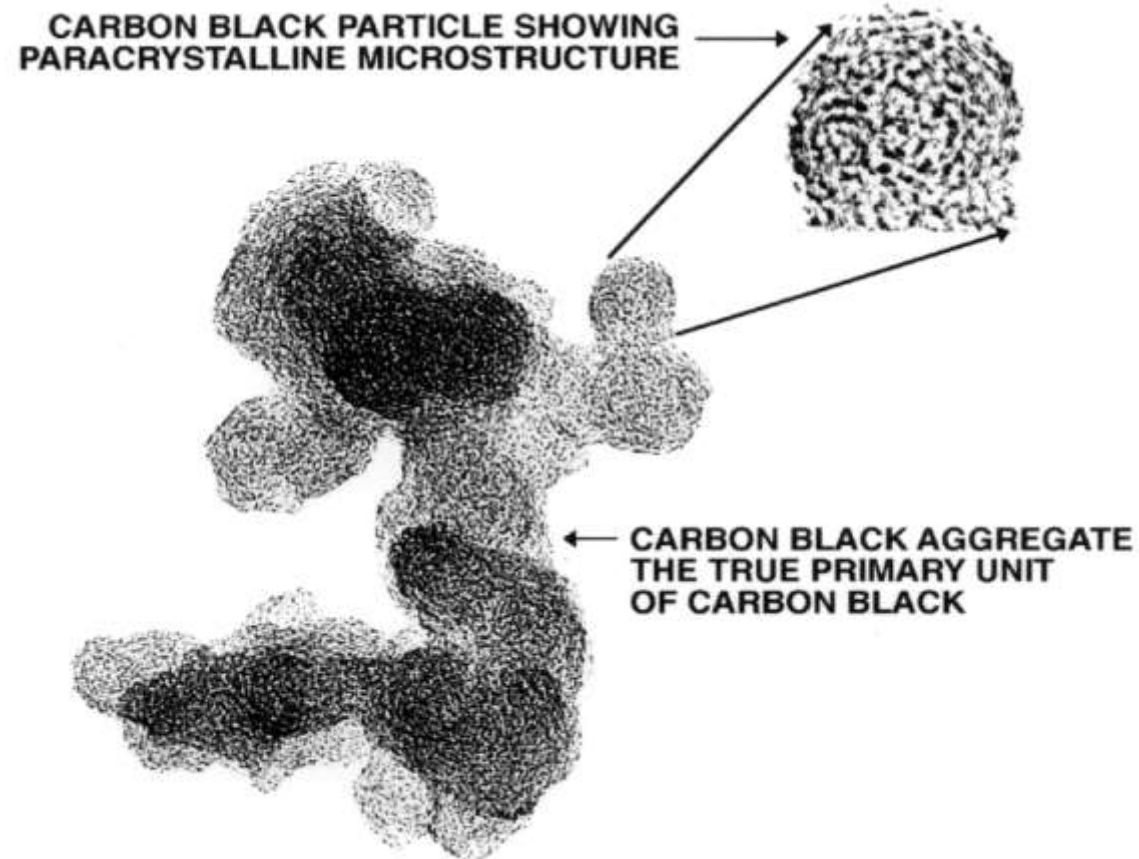


Carbon Black



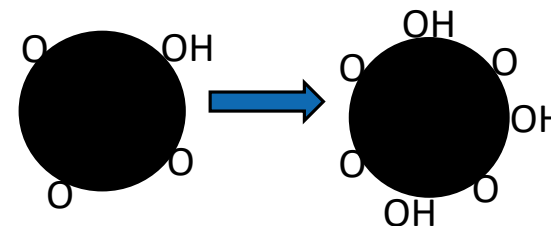
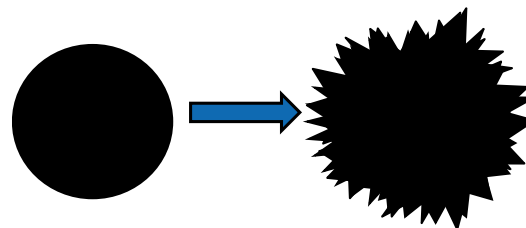
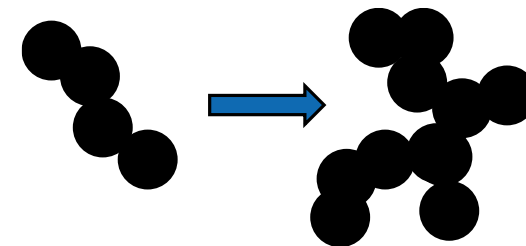
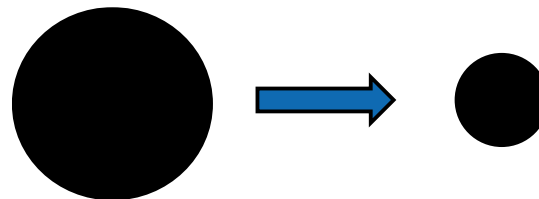
Introduction to Carbon Black

- Carbon Black is a pure form of amorphous carbon produced by a thermal decomposition of hydrocarbons under very limited air supply
- Carbon black is composed of multiple near spherical primary particles fused into aggregates



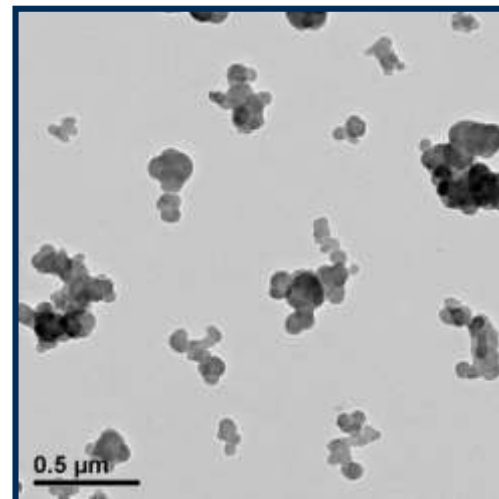
Fundamental Properties of Carbon Black

- Fineness
 - Particle Size Distribution
 - NSA/STSA, EMSA, & ISA
- Structure
 - Aggregate Size/Shape Distribution
 - OAN
- Porosity
 - Pore Size Distribution
 - NSA-STSA
- Surface Activity
 - Surface Functionality Distribution
 - Volatile Content

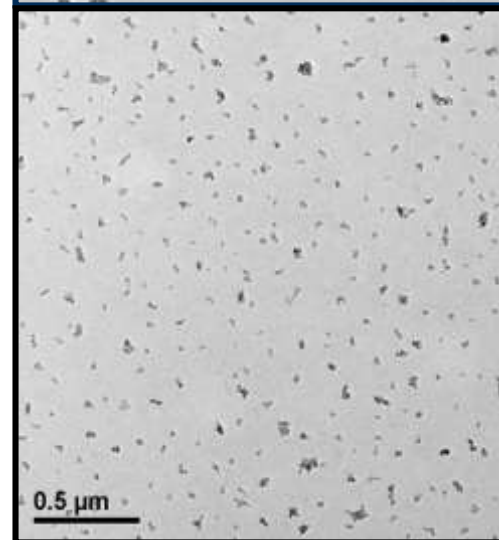


Properties of Carbon Black - Primary Particle Size

- Most significant property in determining performance
- Measured via
 - Electron Microscopy
 - Particle Size Distribution
 - Aggregate Size Distribution
 - EMSA
 - Surface Area
 - NSA and STSA
 - Iodine Number
 - Tinting Strength



Raven 410
100 nm



Raven 5000 Ultra II
8 nm

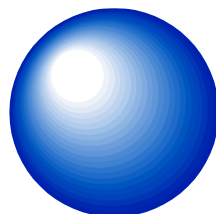


Particle Size and Surface Area

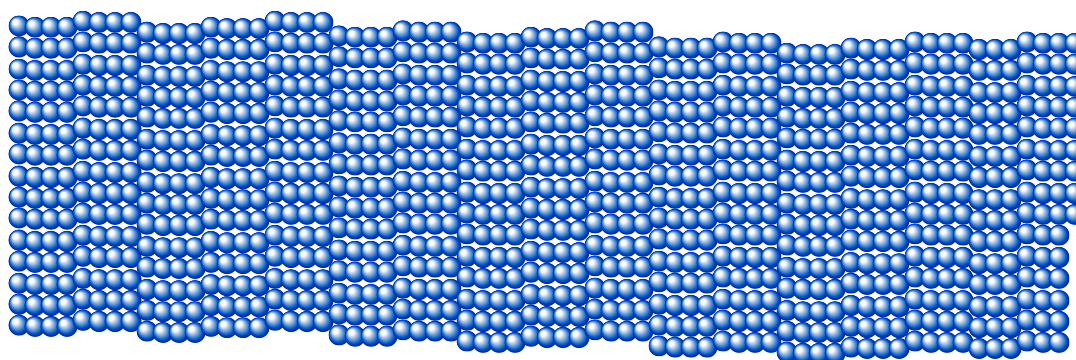
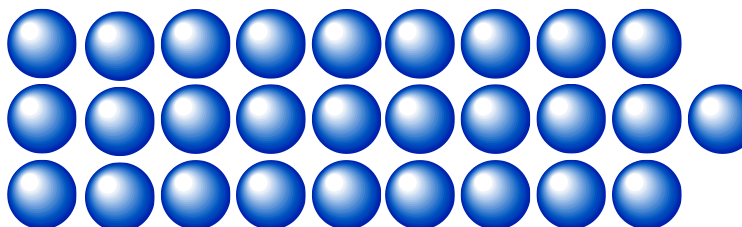
- **Surface Area**

- At equal mass, reducing the particle size increases the available surface area.

Diameter = 100
Surface Area = 31,416



Diameter = 33
Total Surface Area = 95,200



Diameter = 10
Total Surface Area = 314,159



Tinting Strength (ASTM D3265)

- Tint

- Primarily a function of particle size, it is additionally influenced by dispersibility or structure
- The reflectance of a paste of carbon black and zinc oxide relative to an industry standard carbon black (%ITRB)



Effect of on Surface Area Performance

Higher surface area leads to

- Greater jetness and tint strength
- Lower dispersibility
- Higher vehicle demand and viscosity
- Higher electrical and thermal conductivity
- Higher UV Absorption



Four Fundamental Properties-Structure

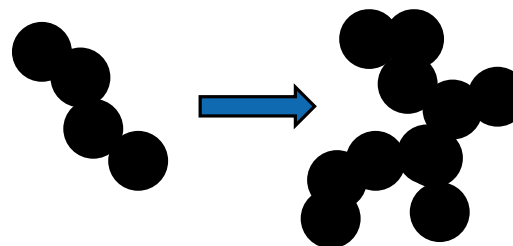
- Fineness

- Particle Size Distribution



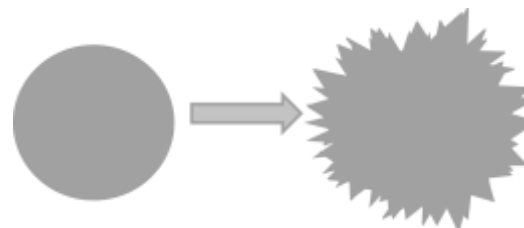
- Structure

- Aggregate Size/Shape Distribution



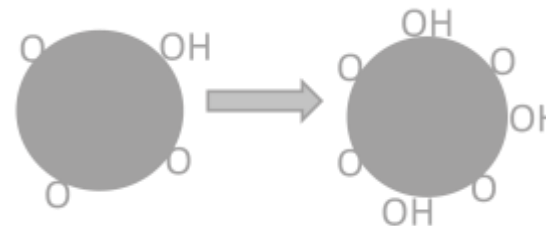
- Porosity

- Pore Size Distribution



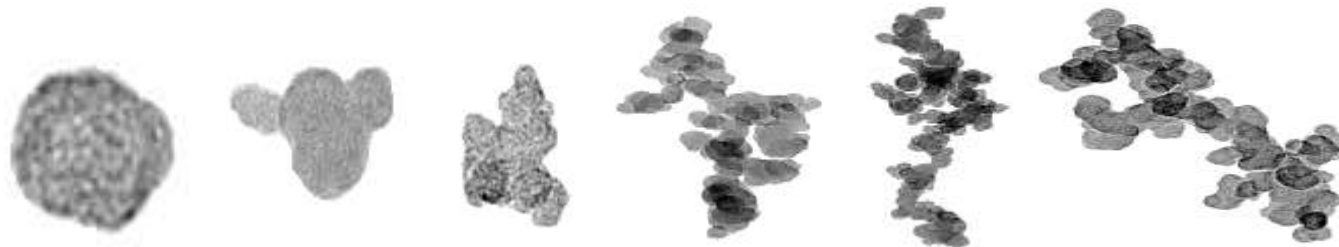
- Surface Activity

- Surface Functionality Distribution



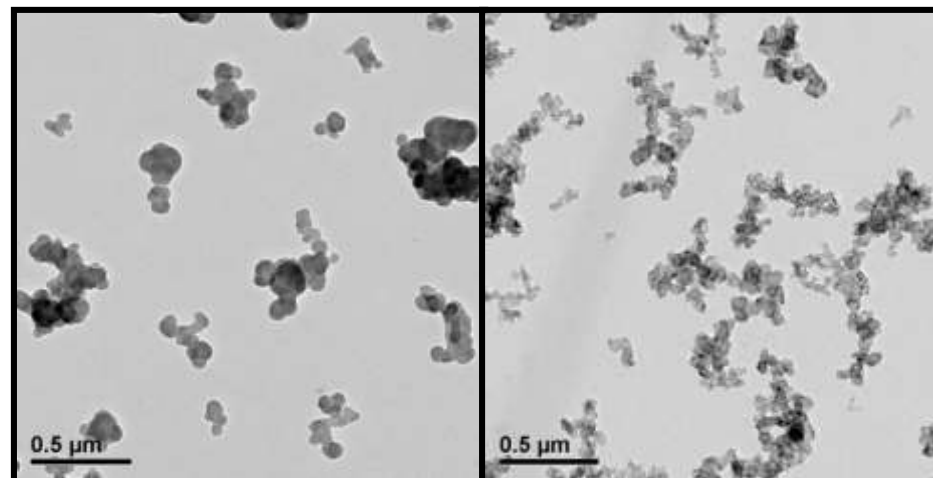
Structure & Aggregate Shape Classification

- Structure is a term used to describe the relative complexity and shape of aggregates
- Simple VS Complex/Highly Branched



- Measured via Oil Absorption Number (OAN) and TEM

Raven 410
65 cm³/100g



Conductex 7055 Ultra
170 cm³/100g



Structure – Oil Absorption Number (ASTM D2414)

- Oil Absorption Number, primarily influenced by aggregate size/shape, may be influenced by porosity
- The amount of oil to reach a peak torque, results given as cubic centimetres of oil per 100 g carbon black



Effect of Structure on Performance



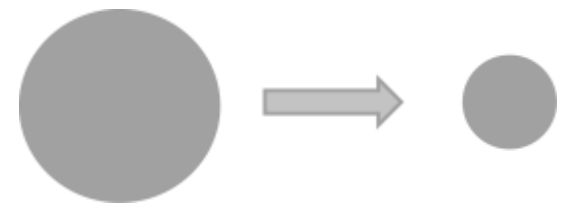
Higher structure (OAN) leads to

- Slightly lower blackness and tint strength
- Better dispersibility
- Higher viscosity and vehicle demand
- Higher electrical and thermal conductivity

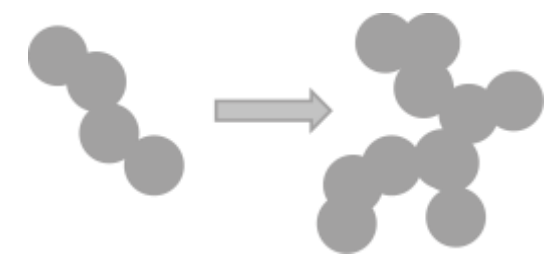


Fundamental Properties-Porosity

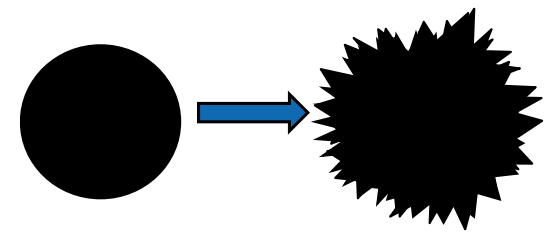
- Fineness
 - Particle Size Distribution



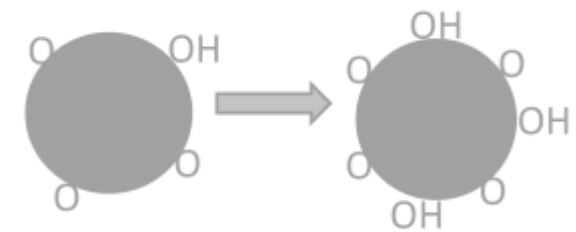
- Structure
 - Aggregate Size/Shape Distribution



- Porosity
 - Pore Size Distribution

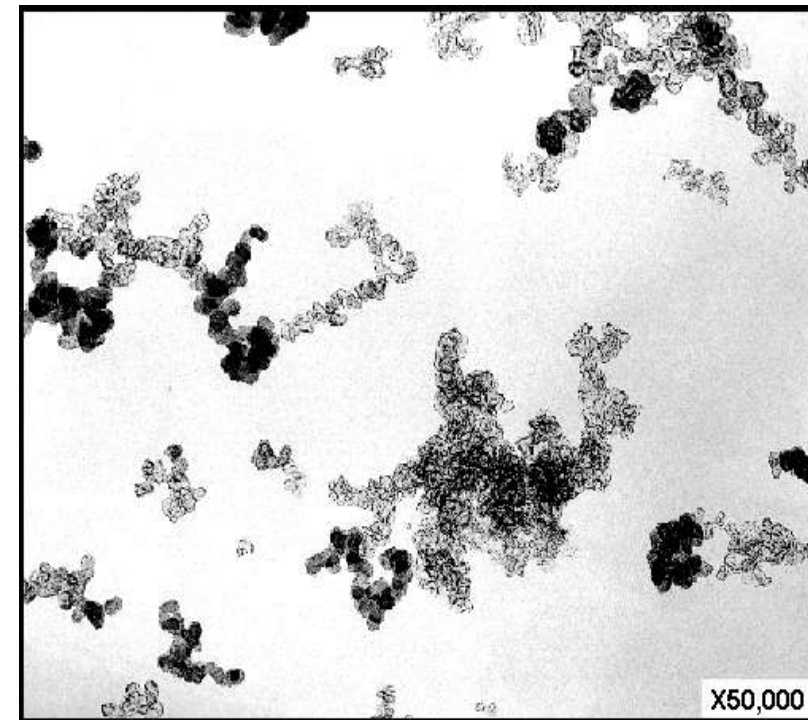


- Surface Activity
 - Surface Functionality Distribution



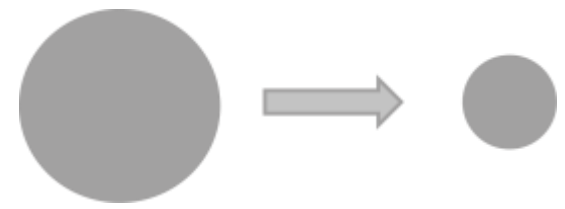
Porosity and its Influence

- Porosity is caused by oxidation in the reactor and is controlled by residence time
 - The freshly formed carbon black gets oxidized by carbon dioxide and water present in the reactor off-gas
 - Earlier the freshly formed carbon black is quenched, the lower its porosity
- Indicated by a difference between Nitrogen Surface Area & Statistical Thickness Surface Area
- Increasing porosity yields
 - Improved Conductivity
 - More Binder Demand
 - Higher Viscosity
 - Greater Moisture Pickup
 - Reduction in Gloss

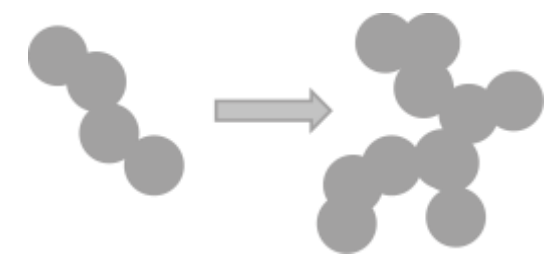


Fundamental Properties-Porosity

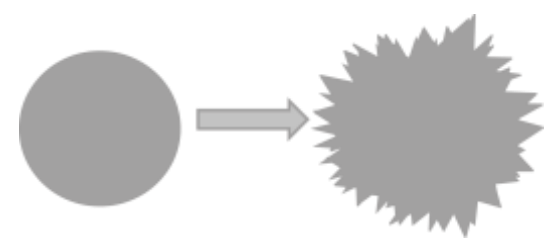
- Fineness
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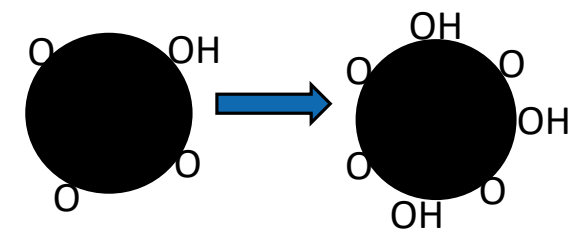
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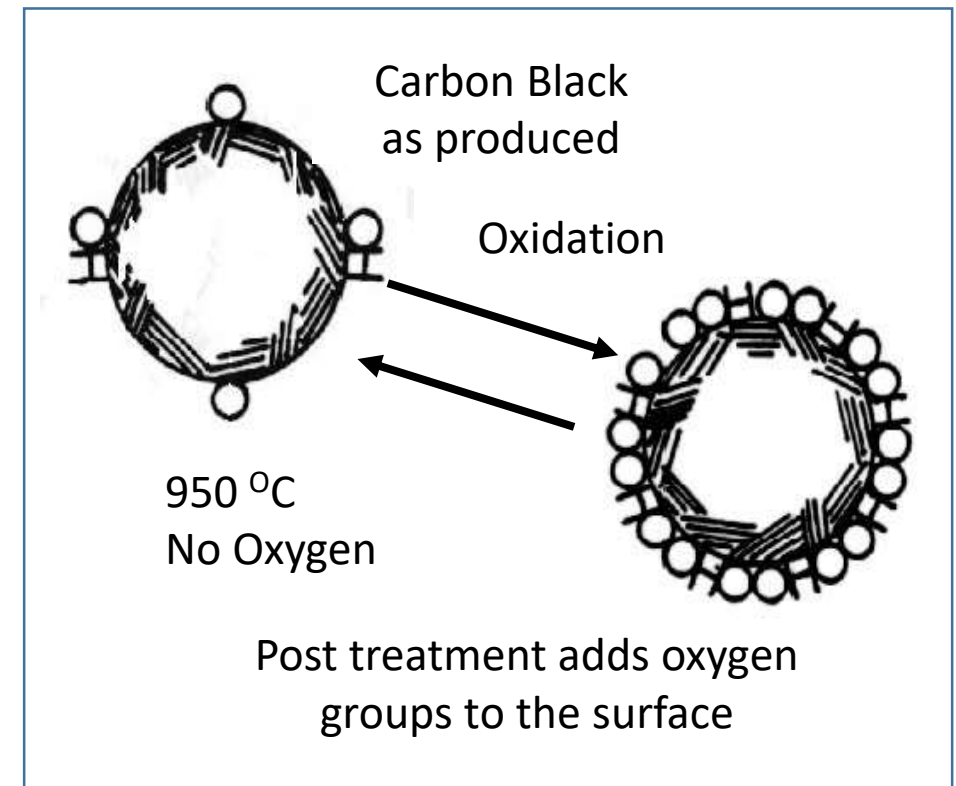


- Surface Activity
 - Surface Functionality Distribution



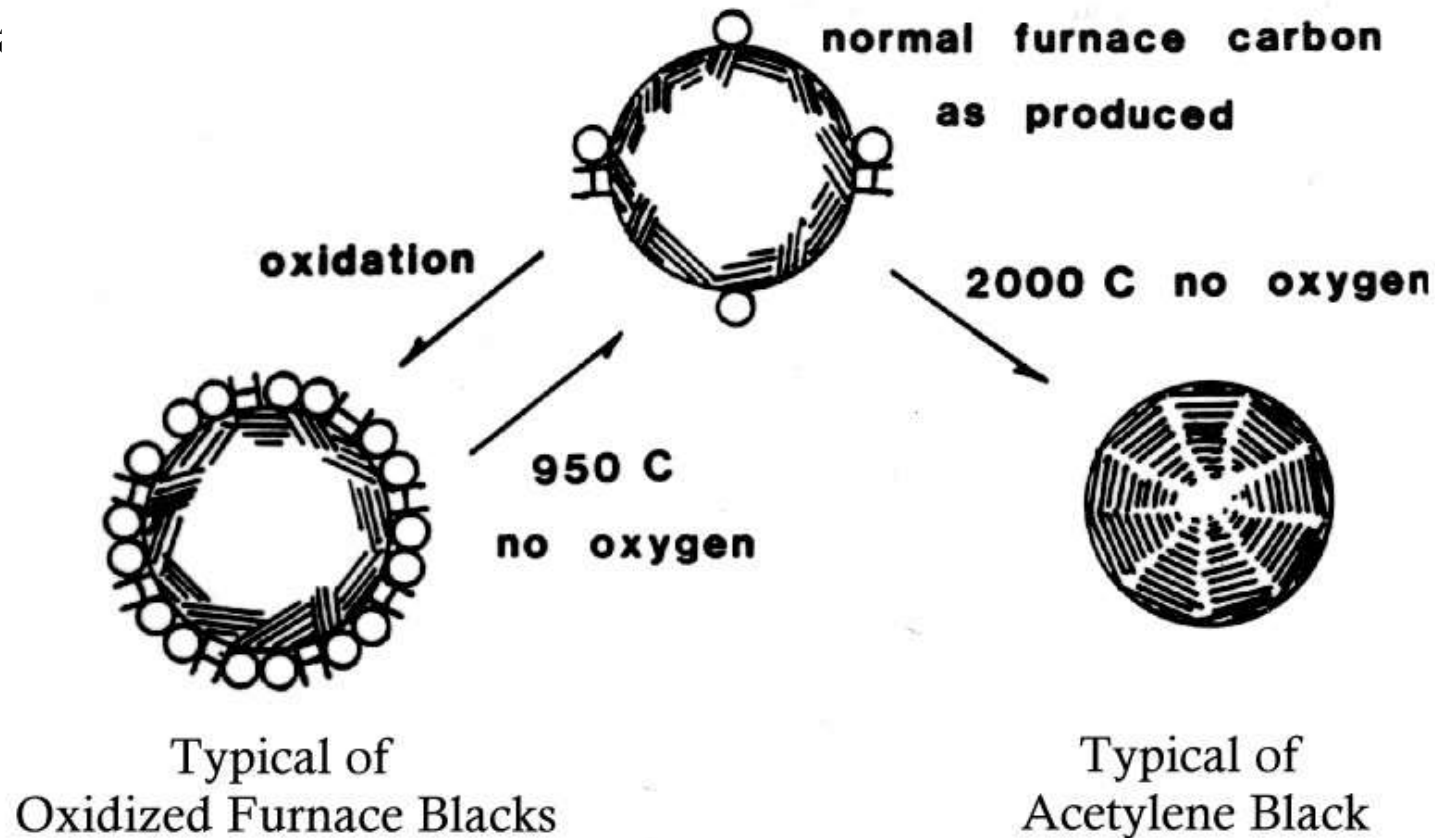
Surface Activity and its Influence

- Property describing the interaction of a carbon black surface with its surroundings
- Furnace Carbon Blacks
 - Post-oxidative treatment that increases the polarity/surface activity
 - Mimics Channel Black Performance
- Surface Treatment can
 - Improve Dispersion
 - Improved Wetting
 - Improved Color
 - Reduce viscosity
 - Liquid systems
 - Reduce conductivity

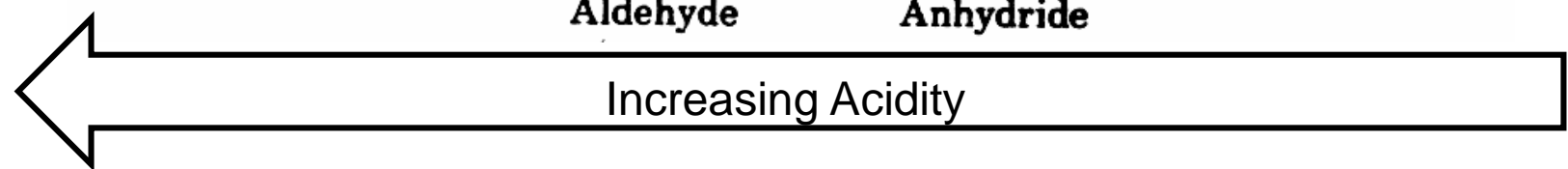
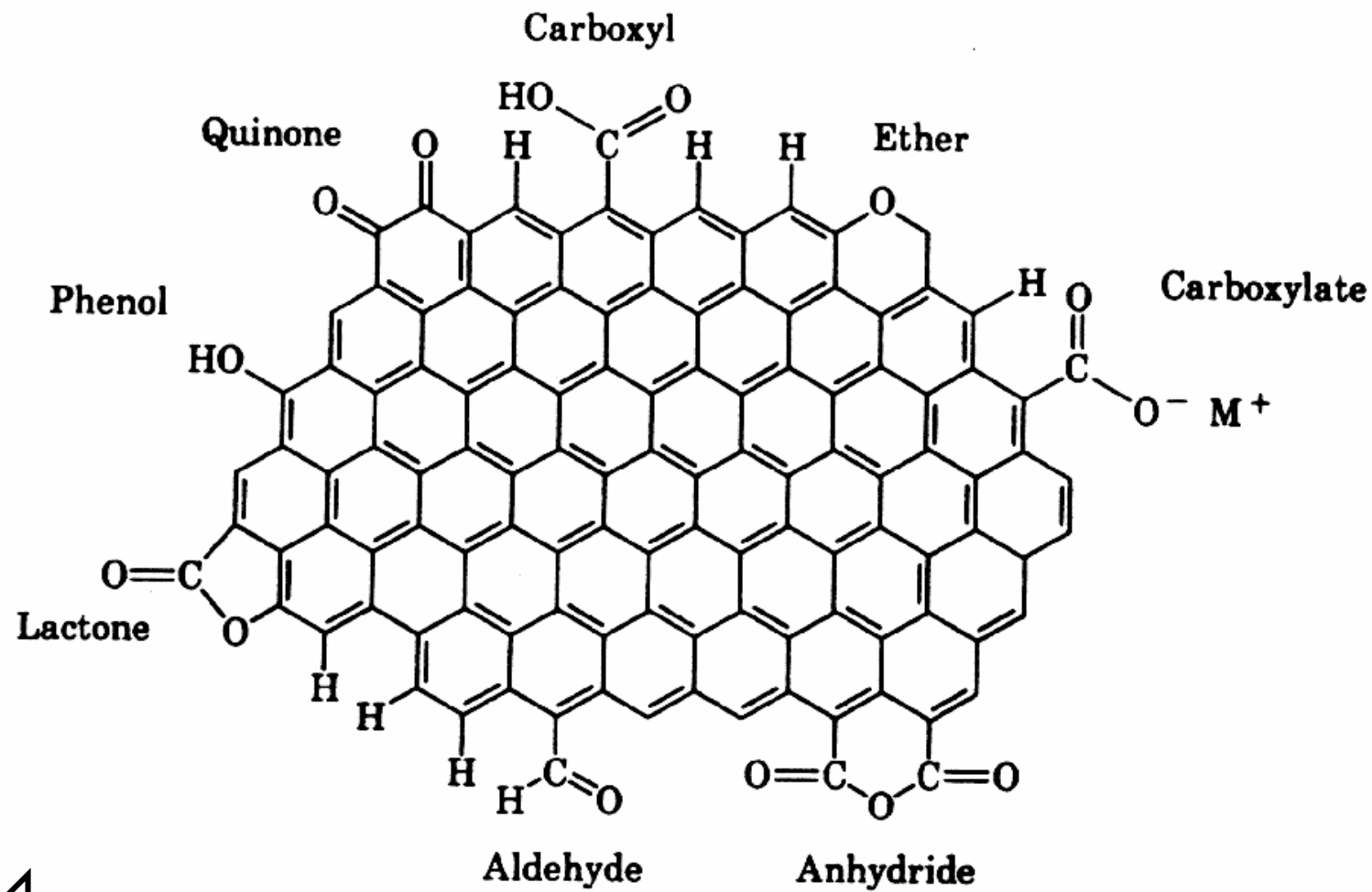


Surface Activity and its Influence

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Oxygen Functionality



Carboxyl Phenol Aldehyde Lactone Quinone Anhydride Ether



Measurement of Surface Activity

- Volatile (Mass loss at 950 °C)
 - Usually indicative of oxygen function groups, sometimes influenced by moisture, sulfur and toluene extract
- pH (ASTM D1512)
 - Generally assumed to indicate surface acidity by oxygen functional groups, often strongly influenced by sulfur levels
 - Non-treated products (7-10 pH)
 - Post-Treated and Channel/Gas products (≤ 5 pH)
- Oxygen Content
 - Direct measure of bulk oxygen
- XPS Analysis (Outside Test)
 - Measure of surface composition by atomic type, and some qualitative information on oxygen functionalities



Elemental Composition and Impurities

- Sulfur (ASTM D1619)
 - Component of feedstock that is found in carbon black in two forms
 - Free Sulfur: Reactive - generally nil or in trace (ppm) amounts.
 - Bound Sulfur: Very stable - does not affect plastic performance directly
- Ash (ASTM D1506)
 - Non-combustible content
 - Salts, Metallurgy, and Inorganic Particulates
 - Process water, Feedstock Oil, Manufacturing Equipment, and Refractory
- Water Wash Residue (ASTM D1514)
 - Inorganic Particulates, Hard Carbonaceous Material, and Compacted Carbon Black
 - Manufacturing Equipment and Refractory

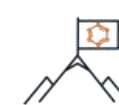




Dispersion



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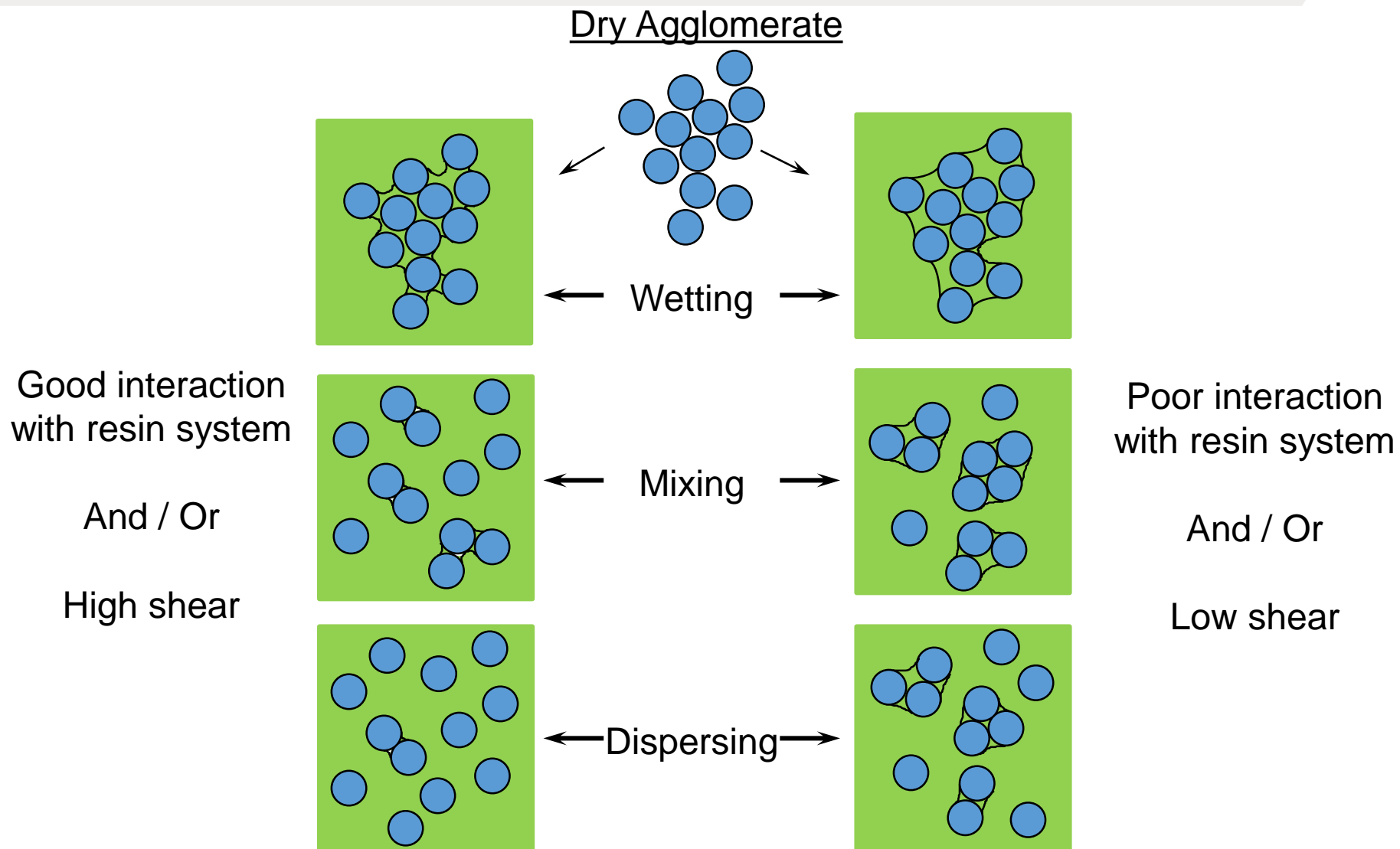
Carbon Black and Liquid Dispersion



- Correct selection of carbon black plus dispersion equipment/process + binder/additive + optimal ratio of ingredients leads to the perfect dispersion
- A new carbon black product in to an existing formulation is “never a one to one” replacement. There will always be a need to fine tuning of formulation / process to optimise the performance
- Dispersion is a uniform distribution of suspended pigment particles in liquid
- Air voids are replaced with liquid binder, large agglomerates are broken to smaller agglomerates and further to the level of aggregates.
- In most of the liquid dispersions, suspended particles keep moving under Brownian motion, increasing possibility of agglomeration.
- For a pigment, the optimum performance is:
 - Good color
 - Good stability
 - Good Image
 - Good dispersion
 - UV Protection (Optional)



Good Dispersion is Critical for Functionality



Why Carbon Black is Difficult to Disperse?

- Very fine “particles” (avg. aggregate size ~50 - 300 nm) with high surface area
- Aggregates are bounded with force of attraction due to van der Waals forces (plus possibly dipolar interactions)
- Poor stability / re-agglomeration due to high force of attraction
- High shear force required to break the agglomerates
- Equipment wear due to abrasive nature
- In some cases, high oil absorption, meaning the presence of hard to remove air in fine voids
- Higher viscosity of dispersion

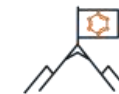
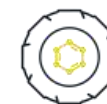




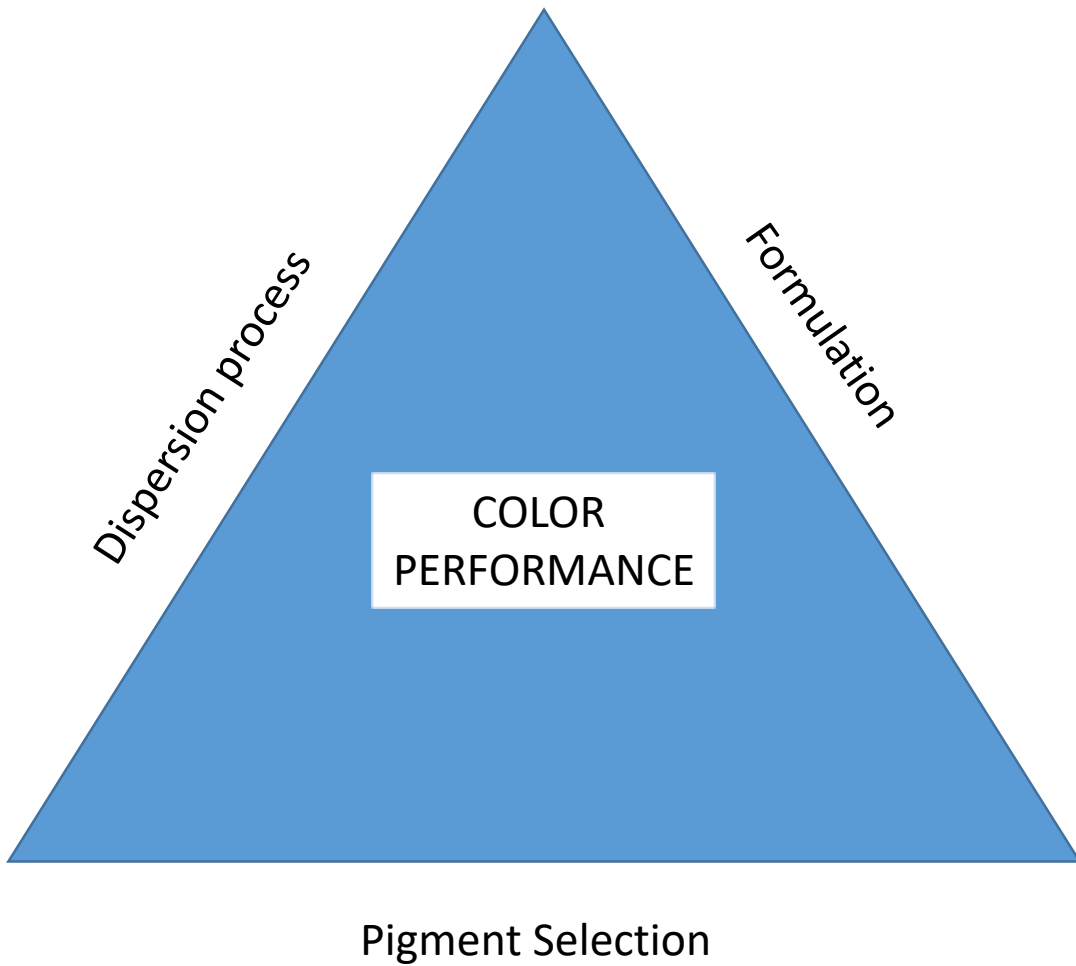
Color Performance



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Where Does Color Performance Come From ?



High Color Carbon Black Portfolio



- Automotive
 - Raven 5000 Ultra II
 - Raven 5100 Ultra
- Other
 - Raven 3500
 - Raven 3000 Ultra
 - Raven 2900 Ultra
 - Raven 2800 Ultra
 - Raven 2500 Ultra



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Color Development over Time



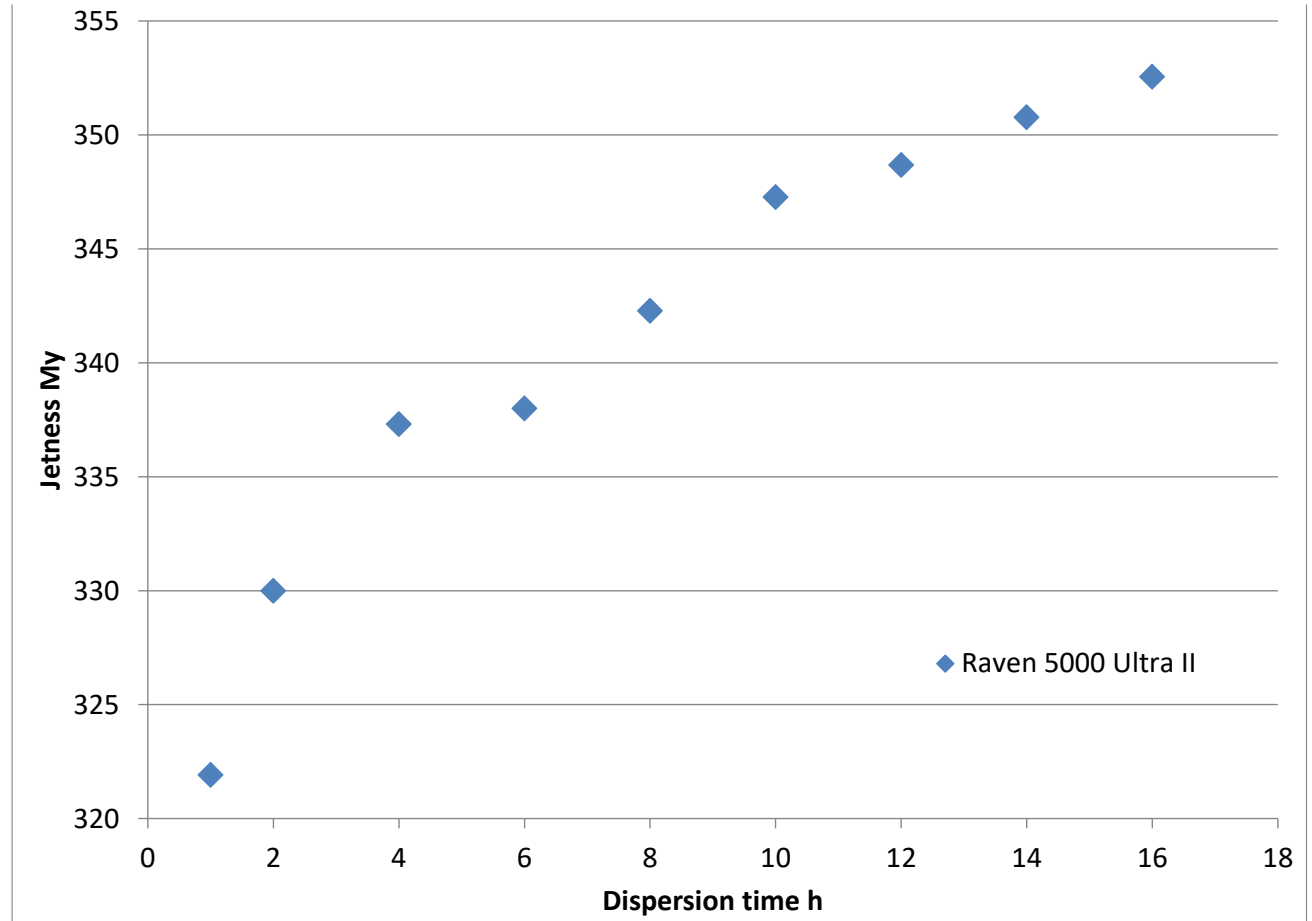
Lau Shaker

0.6 – 0.8 mm Zirconia beads

Color X-Rite CI7800

With a well matched dispersant even 16 hours of Lau shaker hasn't yet reached the ultimate level of performance

Obviously for production efficiency there will be an optimum energy/time and performance balance, that will be determined by the particulars of any given location



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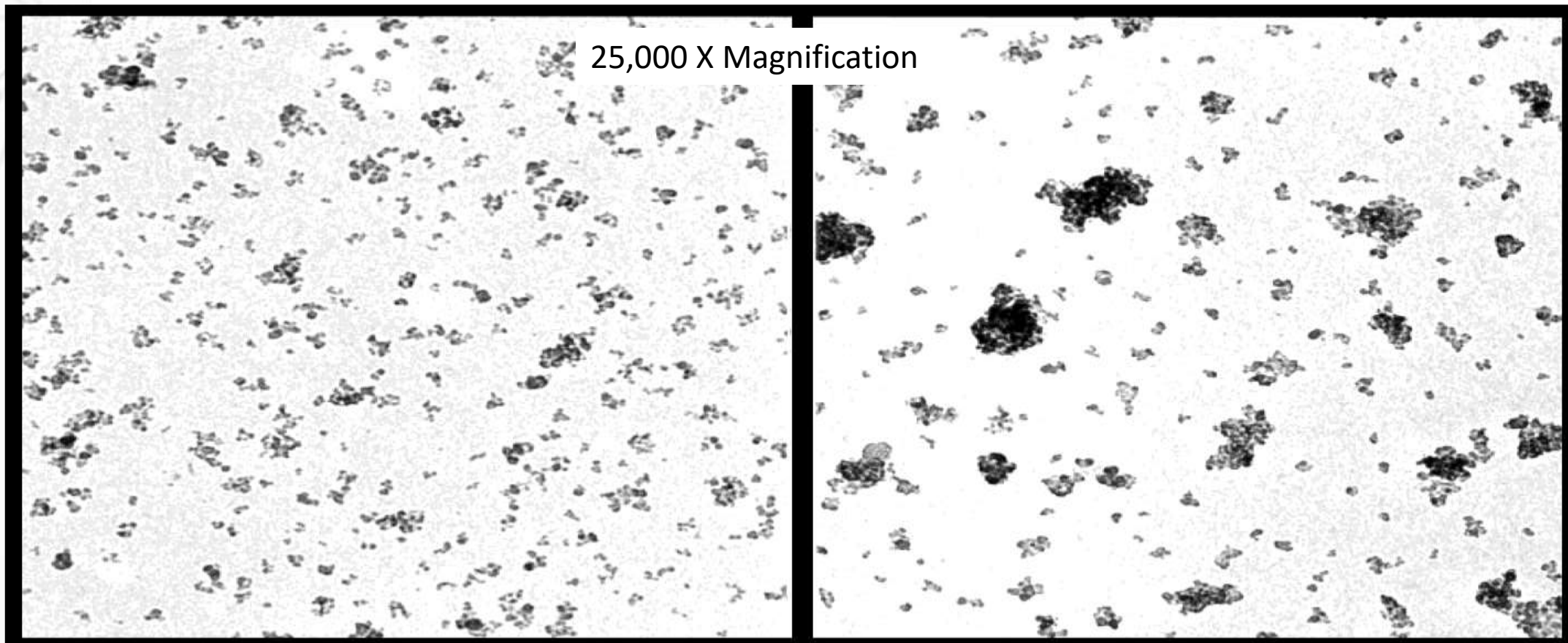


Influence of Dispersion On Color and Undertone

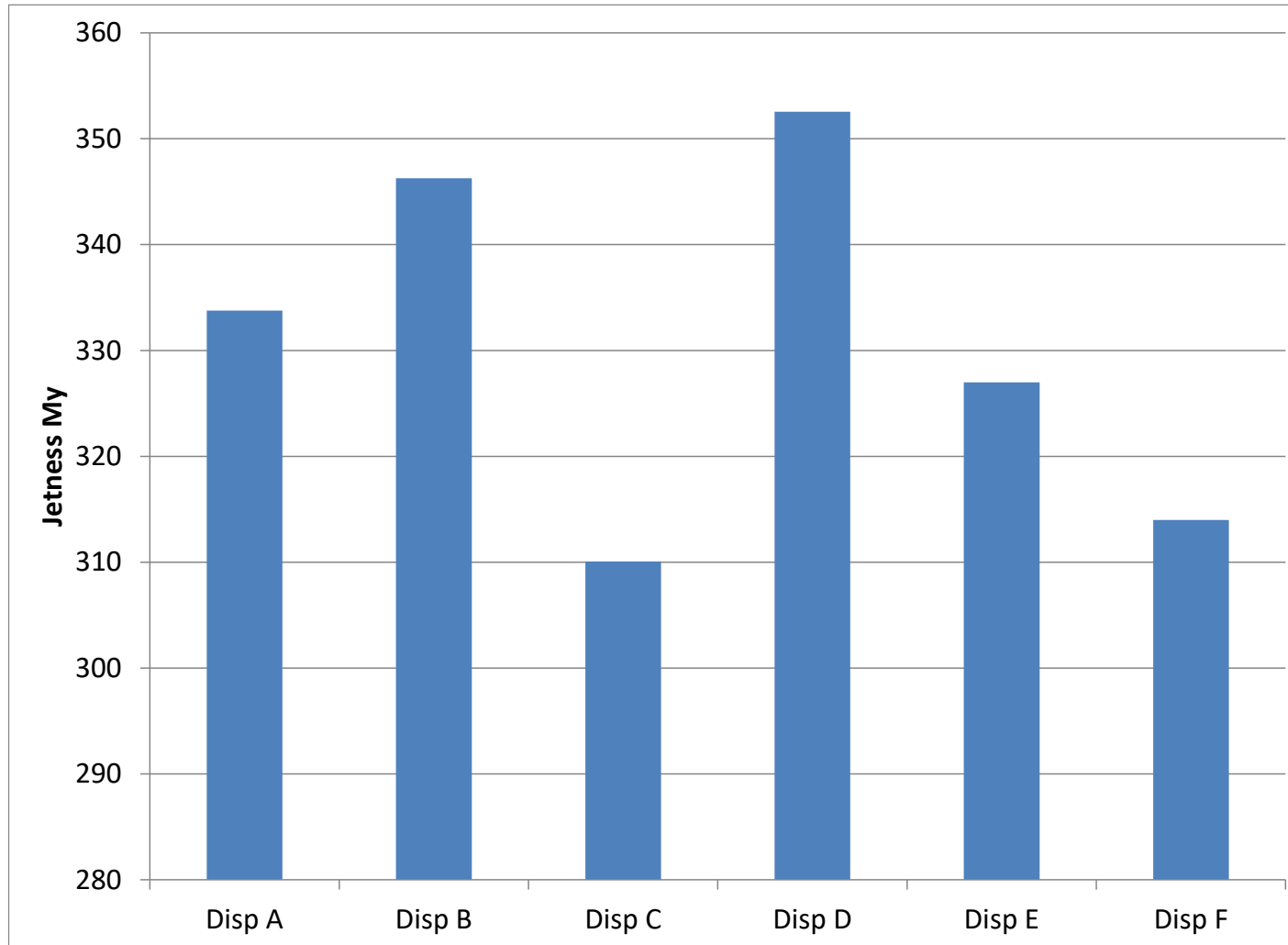
Fully Dispersed
Very Jet & Blue

Raven 5000 Ultra II

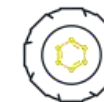
Micro Flocculated
Poor Jetness & Brown



Well Dispersed Raven 5000 Ultra II



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Synergist : Effect is minimal compared to dispersion time/energy

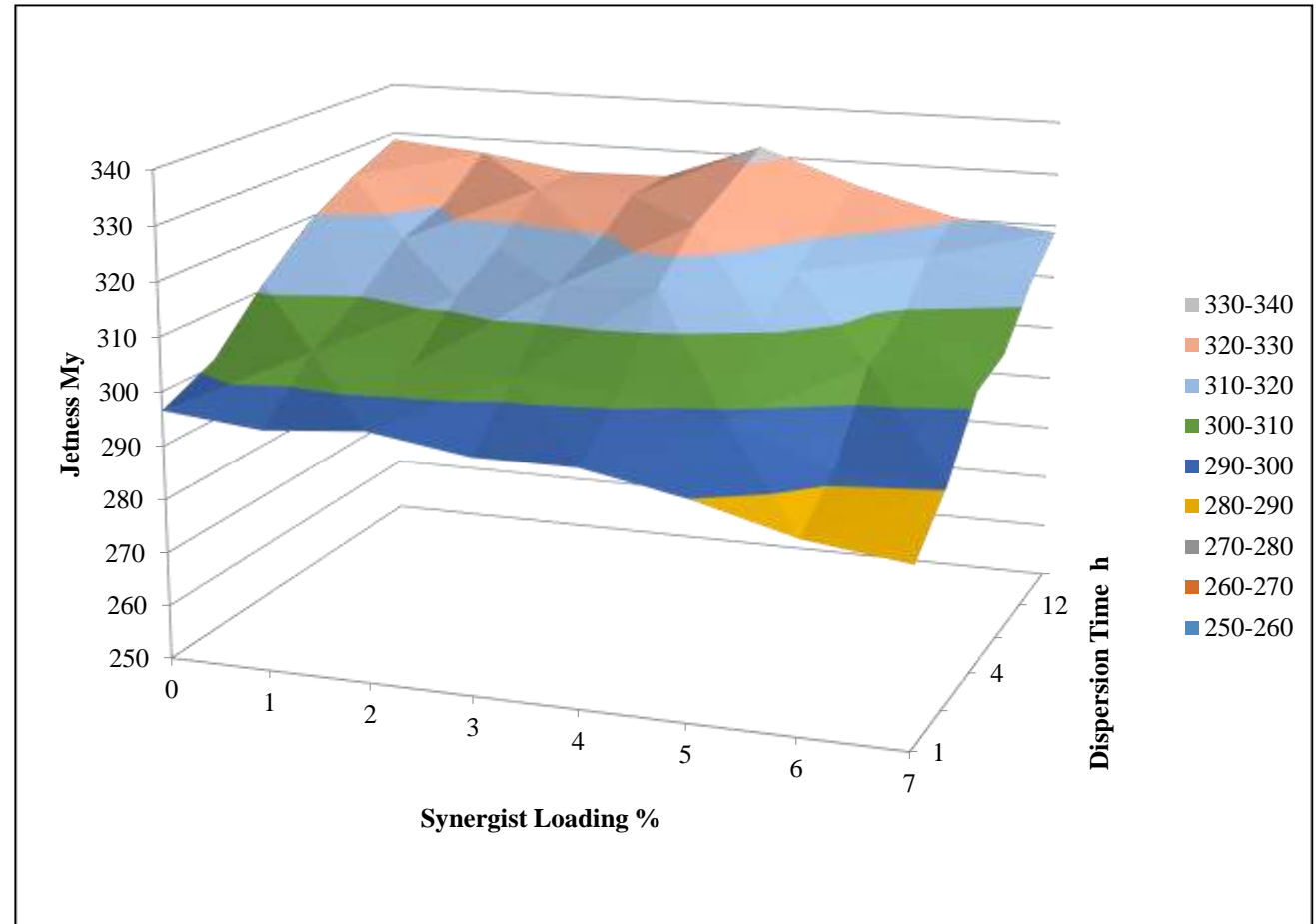


Lau Shaker

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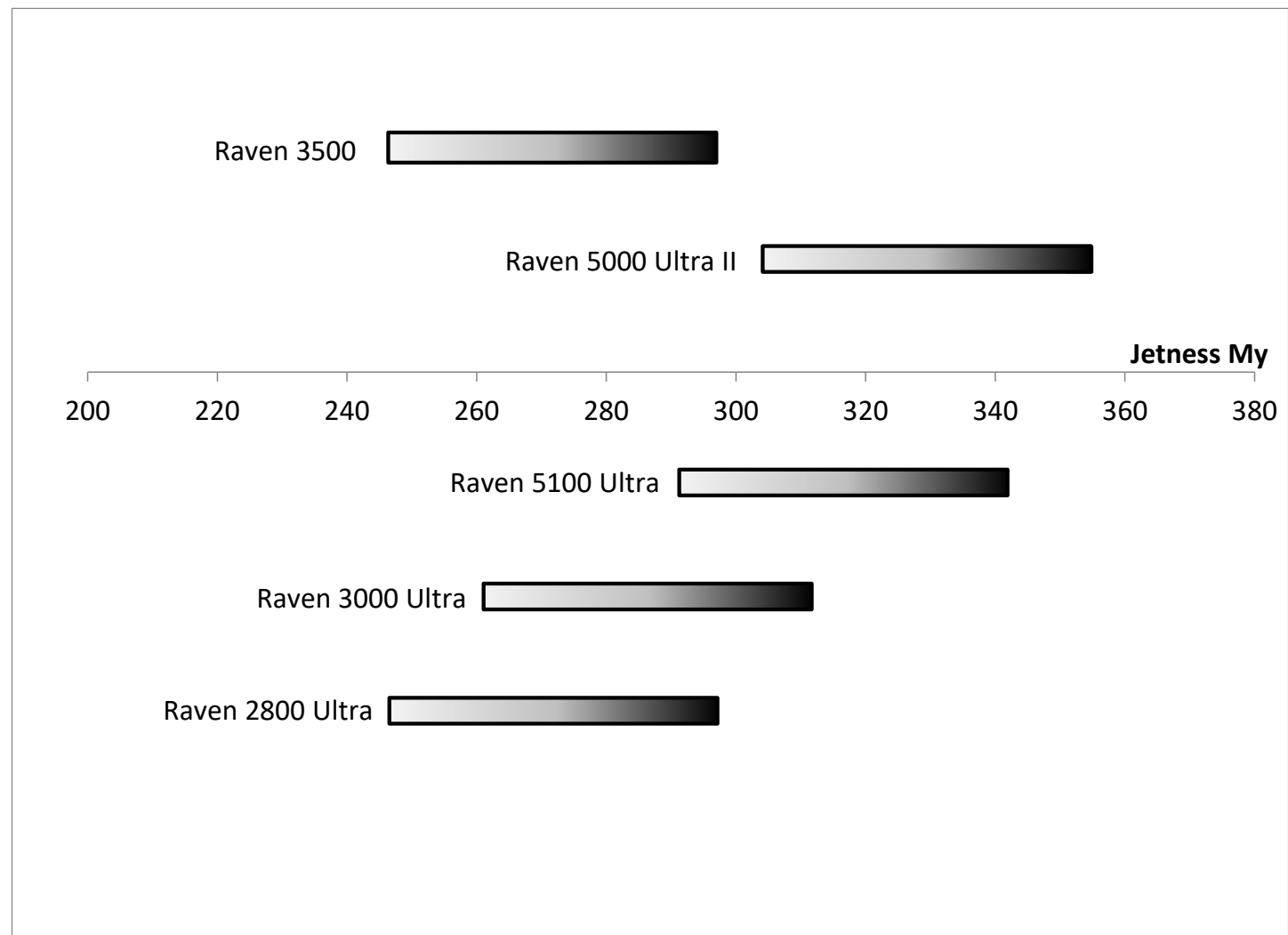
There is a clear ridge of performance improvement at 4% loading for the synergist



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Pigment Color Space isn't a point

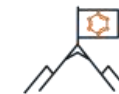
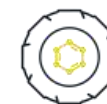




Tint Study



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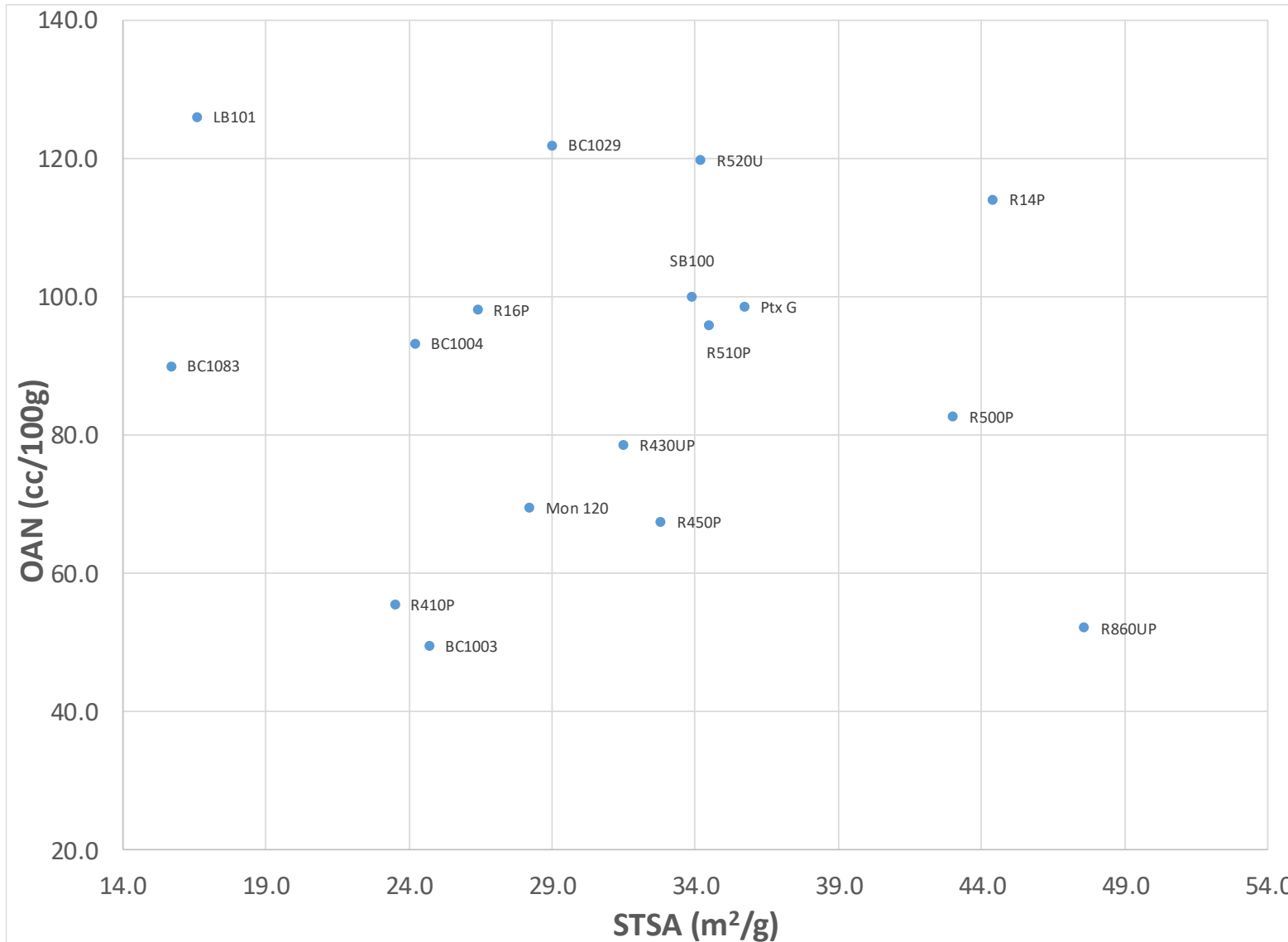
Measured Material Properties

Sample	Product	NSA (m ² /g)	STSA (m ² /g)	OAN (cm ³ /100g)	IAN (mg/g)	pH
A-88036	BC1083	16.5	15.7	90.0	21.5	8.7
A-90579	LB101	26.0	16.6	126.0	40.0	8.0
A-90617	R410P	25.2	23.5	55.5	26.4	9.7
A-87986	BC1004	24.7	24.2	93.3	27.9	8.7
A-89170	BC1003	25.0	24.7	49.6	26.5	9.6
A-71710	R16P	28.8	26.4	98.1	25.8	8.6
A-83721	Mon 120	28.0	28.2	69.5	---	---
A-81414	BC1029	29.3	29.0	121.9	32.6	8.6
A-90618	R430UP	32.4	31.5	78.6	36.4	9.4
A-59409	R450P	34.2	32.8	67.5	31.6	9.3
A-87628	SB100	36.6	33.9	100*	---	3.4
A-87318	R520U	34.1	34.2	119.7	38.7	8.3
A-90317	R510P	34.8	34.5	95.8	41.0	9.4
A-90585	Ptx G	36.4	35.7	98.5	39.3	8.6
A-60567	R500P	43.2	43.0	82.6	48.6	8.1
A-63316	R14P	46.9	44.4	114*	---	3.8
A-75170	R860UP	47.8	47.6	52.1	49.6	10.3

*Value Quoted in Literature



Product Plot with Measured Material Properties



Waterborne Pigment Concentrate



Resinless Pigment Concentrate Formulation

Component	Amount (g)
Water	50.80
Dynol 604	0.20
Borchi Gen 0851 (50 % solids at 20 %SOP)	14.00
Carbon Black	35.00
Total	100.00

Tinting

- Architectural Exterior White Semi-Gloss Acrylic
- Architectural Interior White Semi-Gloss Latex
- Architectural Interior/Exterior Alkyd Urethane Enamel High-Gloss White

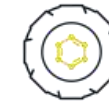
Final Carbon Black Loadings (%)
0.2
0.5
1.0
1.5



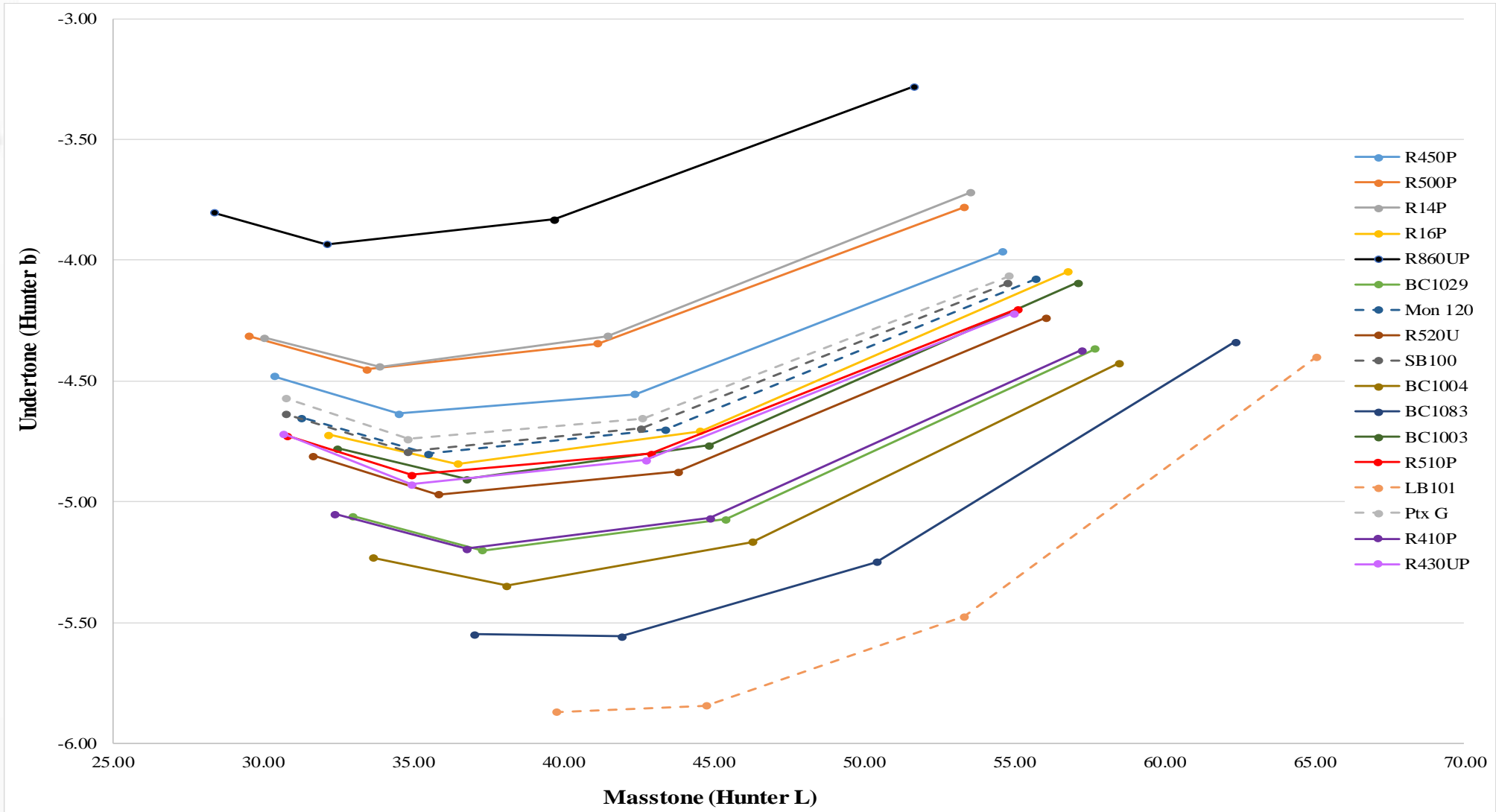
Waterborne Pigment Concentrate Dispersion Process



Step	Description
1	Grind vehicle components mixed in batch form on flacktek speedmixer
2	Weigh 65g of grind into HDPE Bottles (2.25x5.5", ODxh)
3	Add 35g of CB to each bottle
4	Add 400g of Ce-TzP zirconium oxide media (1.7-2.4 mm)
5	Disperse on Lau Disperser DAS 200 for 1 hour
6	Remove sample and filter with 190 um filter into sealable container.

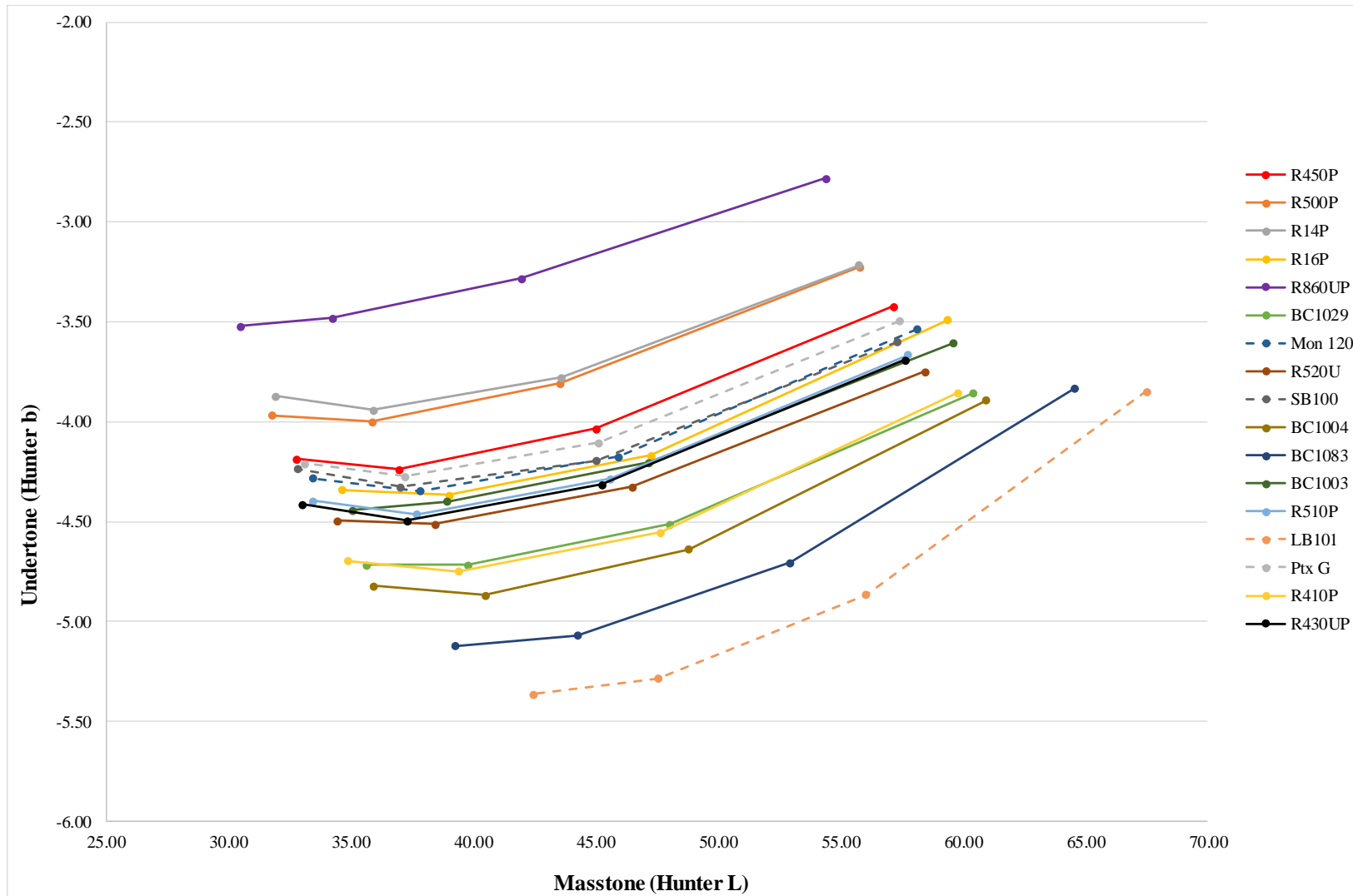


Waterborne Acrylic Performance Overview

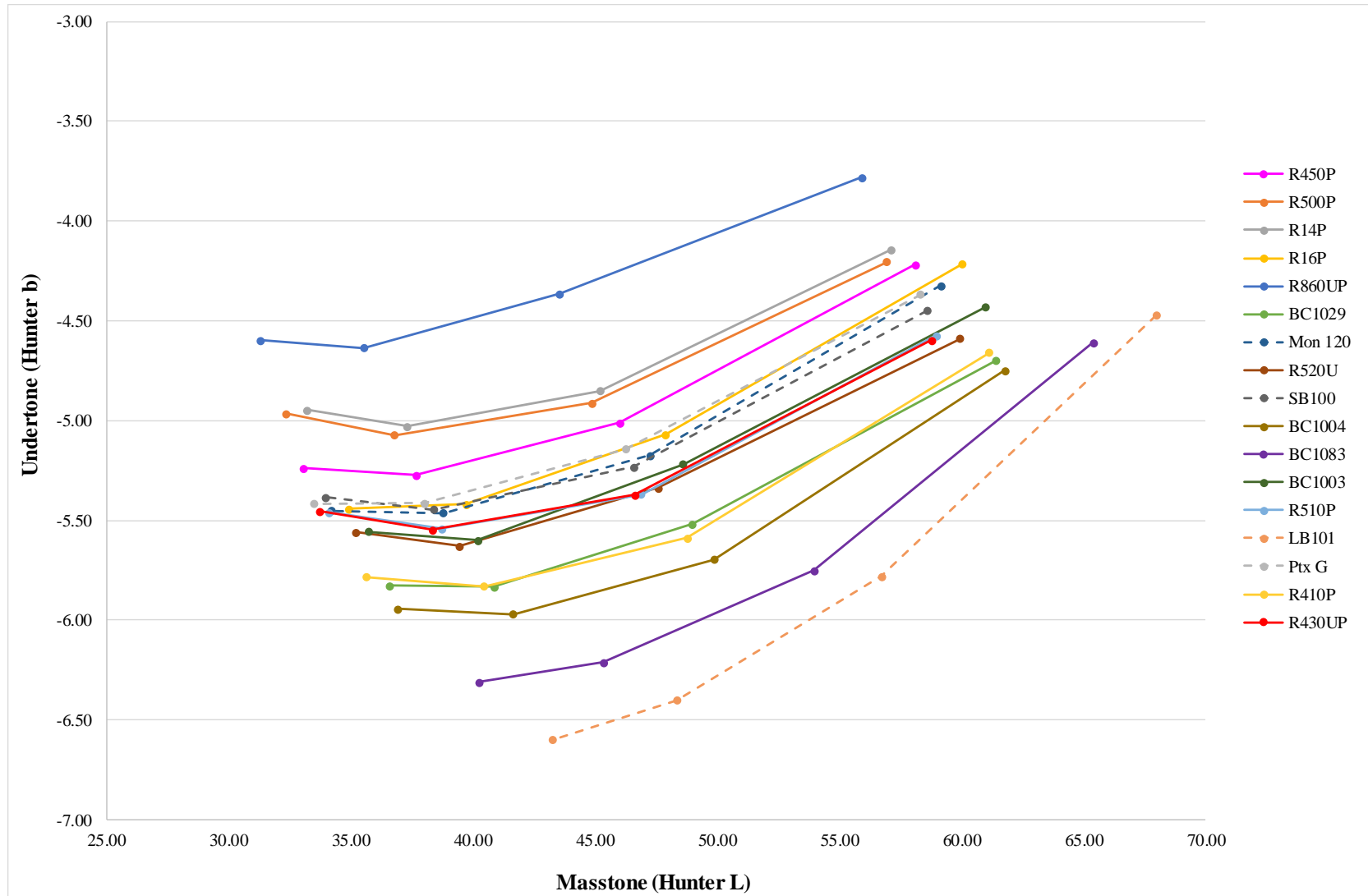


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Waterborne Latex Performance Overview



Waterborne Urethane-Alkyd Performance Overview



Solventborne Pigment Concentrate

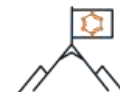
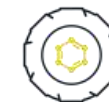
Pigment Concentrate Formulation

Component	Amount (g)
Laropol A81	10
MPA	27
Xylene	27
Tego Disperse 1010 (100% solids @ 20 %SOP)	6
Carbon Black	30
Total	100

Tinting

- Architectural Interior/Exterior White Semi-Gloss Medium Oil Alkyd

Final Carbon Black Loadings (%)
0.2
0.5
1.0
1.5



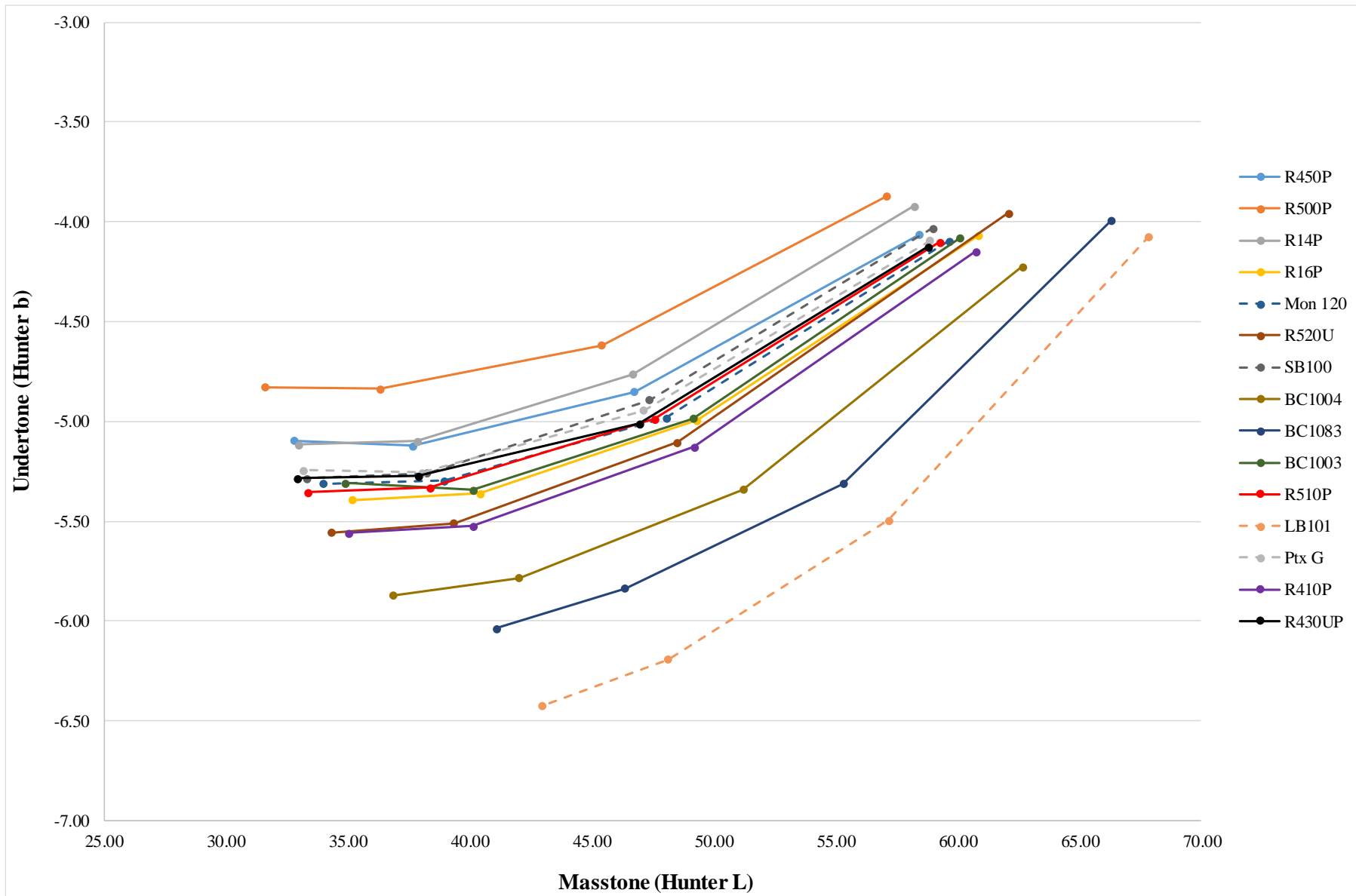
Solventborne Dispersion Process



Step	Description
1	Prepare grind vehicle in batch form on HSD
2	Weigh 70g of grind into a HDPE bottle (1.75"x4.00" ldxh)
3	Add 30g of CB to each bottle
4	Add 400g of Stainless Steel Media (3/32")
5	Disperse on Lau Disperser DAS 200 for 1 hour
6	Remove sample and filter with 190 um filter



Solventborne Alkyd Color Performance Overview



Formulation Results Summary



- Waterborne pigments concentrates
 - exhibited a low viscosity and good flow properties. Based on this, the formulation should be optimized to increase the pigment loading
 - The waterborne pigment concentrates showed good compatibility with all letdown systems, exhibiting little color shifted when subjected to rub-out testing
 - Lamp black 101 was noted to exhibit significant settling after a 1 week storage period at room temperature
 - Other products exhibit no settling over this same time frame.
- Solventborne pigment concentrates
 - exhibited a low viscosity and higher pigment loadings could be possible.
 - Showed incompatibilities with the PU and Acrylic tinting bases which prevented evaluations in these systems
 - Showed evidence of some pigment flooding in the medium oil alkyd tinting base with a reduction in color strength following the rub-out testing.
 - Showed no settling after a week at room temperature
- At the low carbon black loadings (0.2% CB), material properties were less effective in predicting tinting performance and the data tended to be more scattered. This essentially means performance at low carbon black loadings will be harder to match.



Material Property-Performance Relationships Summary



- Increasing the carbon black loading in the final coating was noted in increase color strength and shift the tone in a more blue direction
 - Blue tone increased initially with the carbon black loadings, but was observed to plateau or begin to decrease at the highest carbon black loading of 1.5% CB. This is most likely a result of the carbon black beginning to become a more prominent pigment in the system
- Regression Analysis and Main Effects plots
 - Due to similarity in data trends, analysis was only carried out on the Waterborne Latex and Solventborne alkyd systems
 - Masstone and Blue tone were observed to show a strong correlation with increases in color strength resulting in lower blue tone performance
 - STSA was identified as the main factor in influencing performance
 - OAN appeared to have little to no effect on color performance
 - Further studies on aggregate size-performance relationship should be performed as OAN can effect this property, but shifts in aggregate size due to OAN changes could be masked by particle size changes

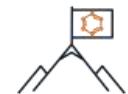
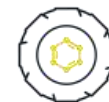




“Drop in Replacement” for a Tint Base



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Problem Summary



- The Customer approached Birla carbon with the following problem:
- They used a large amount of one particular Birla product in tint bases, but it was single sourced with no alternatives and their risk management people had flagged this as a business risk to be addressed
- An additional constraint was that any alternative carbon black could not be solely produced at the same location
- They asked if we could offer an alternative, that required no reformulation of other ingredients and offered a close match
- After the initial work, the customer better defined the targets as $\Delta E < 0.2$ in pastel base, and $\Delta E < 0.3$ in full color



Initial Work, promising but not close enough

		Let Down Pastel						
Internal #	Sample	Grind (g)	Base (g)	L	a	b	%STR-WSUM	ΔE
A-73472	R500P	0.47	19.53	53.13	-1.22	-4.39	100	0.0
A-73519	R430UP	0.47	19.53	55.61	-1.24	-4.94	82	2.8
A-73520	R510UP	0.47	19.53	54.17	-1.22	-4.91	91	1.4
A-73520	R510UP 0.16%	0.50	19.50	53.78	-1.31	-4.92	95	0.8
A-73520	R510UP 0.27%	0.52	19.48	53.19	-1.30	-4.92	99	0.5
A-73520	R510UP 0.5%	0.57	19.43	51.97	-1.25	-4.95	107	1.3
A-73520	R510UP 1.0%	0.67	19.33	49.92	-1.26	-5.04	123	3.3
A-73520	R510UP 1.5%	0.77	19.23	48.10	-1.22	-5.05	139	5.1

		Let Down Masstone						
Internal #	Sample	Grind (g)	Base (g)	L	a	b	%STR-WSUM	ΔE
A-73472	R500P	1.55	18.45	24.68	-0.39	-2.80	100	0.0
A-73519	R430UP	1.55	18.45	25.96	-0.49	-3.30	86	1.7
A-73520	R510UP	1.55	18.45	24.94	-0.45	-3.13	95	0.7
A-73520	R510UP 0.5%	1.65	18.35	24.71	-0.44	-3.01	99	0.2
A-73520	R510UP 1.0%	1.75	18.25	24.25	-0.41	-2.95	104	0.5
A-73520	R510UP 1.5%	1.85	18.15	23.81	-0.41	-2.92	108	0.9



2nd round got closer but still not close enough

Pastel Base									
Internal #	Sample	CB %	Grind (g)	Base (g)	L	a	b	%STR-WSUM	ΔE
A-73472	R500P	17.55	0.47	19.53	52.47	-1.10	-4.46	100	0.00
A-73524	R510UP	18.00	0.47	19.53	53.53	-1.15	-4.34	93	1.07
A-73528	R510UP	19.00	0.47	19.53	52.63	-1.14	-4.88	98	0.45
A-73528	R510UP	19.50	0.47	19.53	52.33	-1.15	-4.88	100	0.44

Masstone Letdown									
Internal #	Sample	CB %	Grind (g)	Base (g)	L	a	b	%STR-WSUM	ΔE
A-73472	R500P	17.55	1.55	18.45	24.42	-0.33	-2.80	100	0.00
A-73520	R510UP	18.00	1.55	18.45	24.94	-0.41	-3.05	95	0.58
A-73520	R510UP	19.00	1.55	18.45	24.18	-0.36	-2.99	102	0.31
A-73521	R510UP	19.50	1.55	18.45	23.97	-0.36	-2.99	104	0.49



Problem (Revisted)



- To reach the customer targets of $\Delta E < 0.2$ in pastel base, and $\Delta E < 0.3$ in full color it became clear that a single carbon black could not be used without other major reformulations
- The Raven 510 Ultra Powder was close but was simply too blue
- A blending of carbon blacks approach was adopted.



Carbon Black Blend – Pastel Base



Sample	Description	Carbon Black Loading (g)	L	a	b	%STR-WSUM	ΔE
A-73472	R500P	17.55	52.78	-1.18	-4.37	100.0	0.00
A-74030	80% R510UP/ 20% RLP	16.00	54.17	-1.20	-4.39	87.2	1.39
		16.50	53.78	-1.24	-4.37	89.6	1.00
		17.00	53.49	-1.21	-4.40	91.3	0.71
		17.50	53.03	-1.18	-4.44	94.1	0.26
		18.00	53.00	-1.20	-4.45	98.6	0.23
		18.25	52.70	-1.20	-4.49	100.5	0.15
		A-74031	60% R510UP/ 40% RLP	15.33	53.55	-1.18	-4.00
		15.67	53.26	-1.12	-4.08	93.1	0.56
		16.17	52.68	-1.16	-4.13	96.7	0.26
A-74032	62.5% R510UP/ 37.5% RLP	16.80	52.56	-1.12	-4.17	97.5	0.30
		17.12	52.32	-1.11	-4.19	99.0	0.50
		17.60	51.86	-1.11	-4.22	102.1	0.93
A-74033	66.2% R510UP/ 33.8% RLP	16.61	52.69	-1.17	-4.13	96.7	0.26
		17.06	50.62	-1.13	-4.38	110.7	2.16
		17.52	52.37	-1.16	-4.18	98.7	0.45
		17.97	50.16	-1.18	-4.42	114.2	2.62



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Carbon Black Blend – Masstone Base

Sample	Description	Carbon Black Loading (g)	L	a	b	%STR-WSUM	ΔE
A-73472	R500P	17.55	24.32	-0.39	-2.72	100.0	0.00
A-74030	80% R510UP/ 20% RLP	18.00	24.44	-0.37	-2.80	98.3	0.15
		18.25	24.28	-0.38	-2.78	99.8	0.08



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Solution Attained



- To reach the color performance of the single carbon black a blend of two other carbon blacks was used and met the customers very tight requirements.
- To satisfy the disaster recovery/business risk neither of the carbon blacks proposed was from the same production location as the currently used pigment
- The customer carried out lab tests and confirmed the results carried out in the Birla Lab
- The cost of the tint base made using the alternative was slightly higher than the incumbent.





Thank You



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