Paint Formulation Science

Contents

- What is paint
- Why we use Paint
- Paint Component Materials
- Mixture Theory
- Formulation Relationships
- Formulation Science
- Formulating Strategy
- Experimental Design for Formulation

Some Paint Definitions

- Paint - a pigmented coating material, in liquid paste or powder form, which when applied to a substrate, forms an opaque film having protective, decorative or specific technical properties.
- Distinct from a transparent varnish, clear-coat or semi-transparent stain.

Formal definitions are sometimes used for specifications

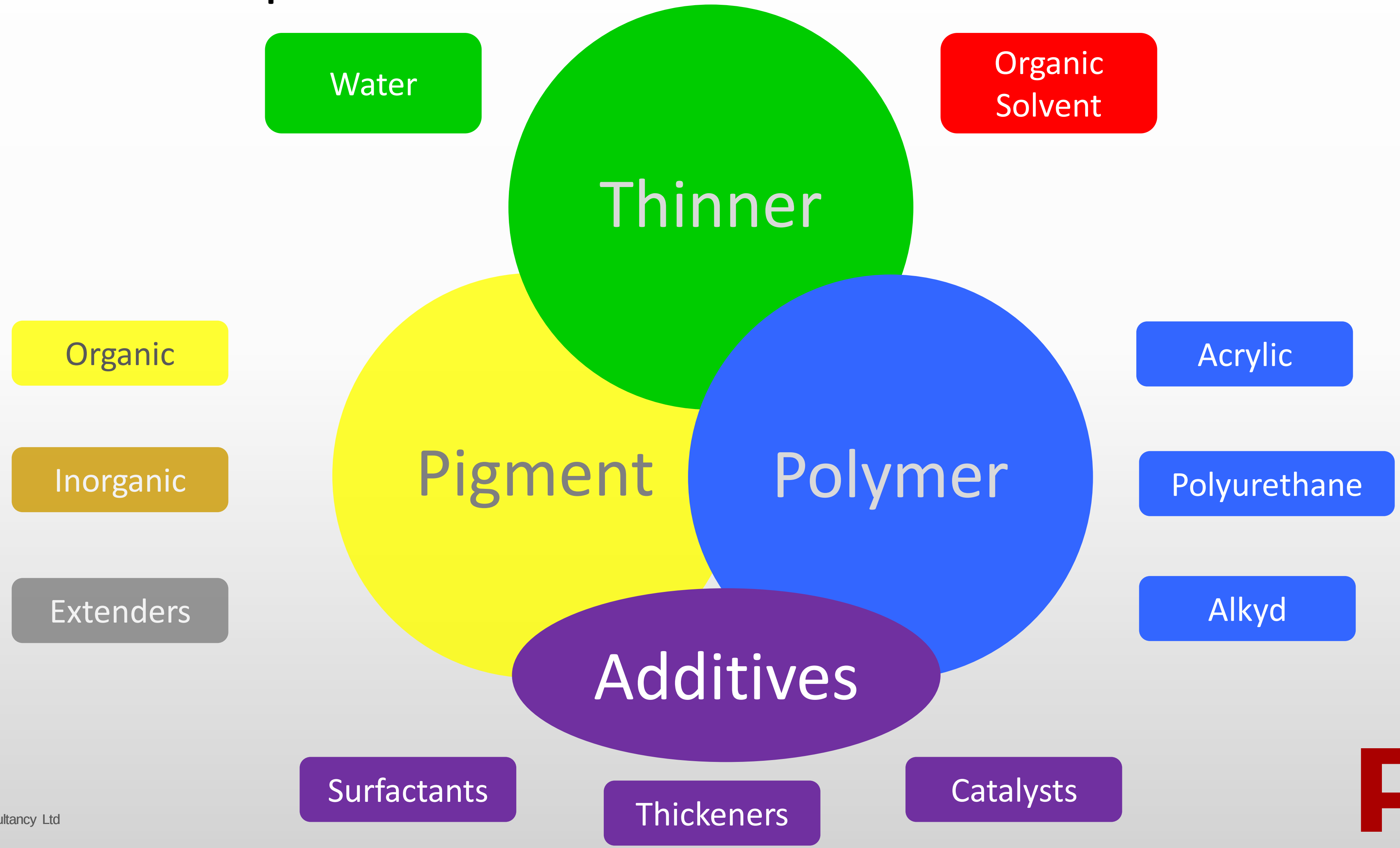
- BS EN ISO 4618:201 Paints and varnishes –Terms and definitions[1]
  Provides a useful glossary of paint related terms.
- ASTM D16-19 Standard Terminology for Paint, Related Coatings, Materials, and Applications[2]

Why do we use paint?

Mostly to decorate & protect surfaces of structures & items

- Decoration
  - Colour
  - Sheen
- Protection
  - Moisture
  - Sunlight
  - Microbial colonisation
  - Oxidation / Corrosion
  - Wear
  - Dirt
- Other functions
  - Anti-icing
  - Smart coatings

Paint Component Materials



Binder - Thinner Relationships

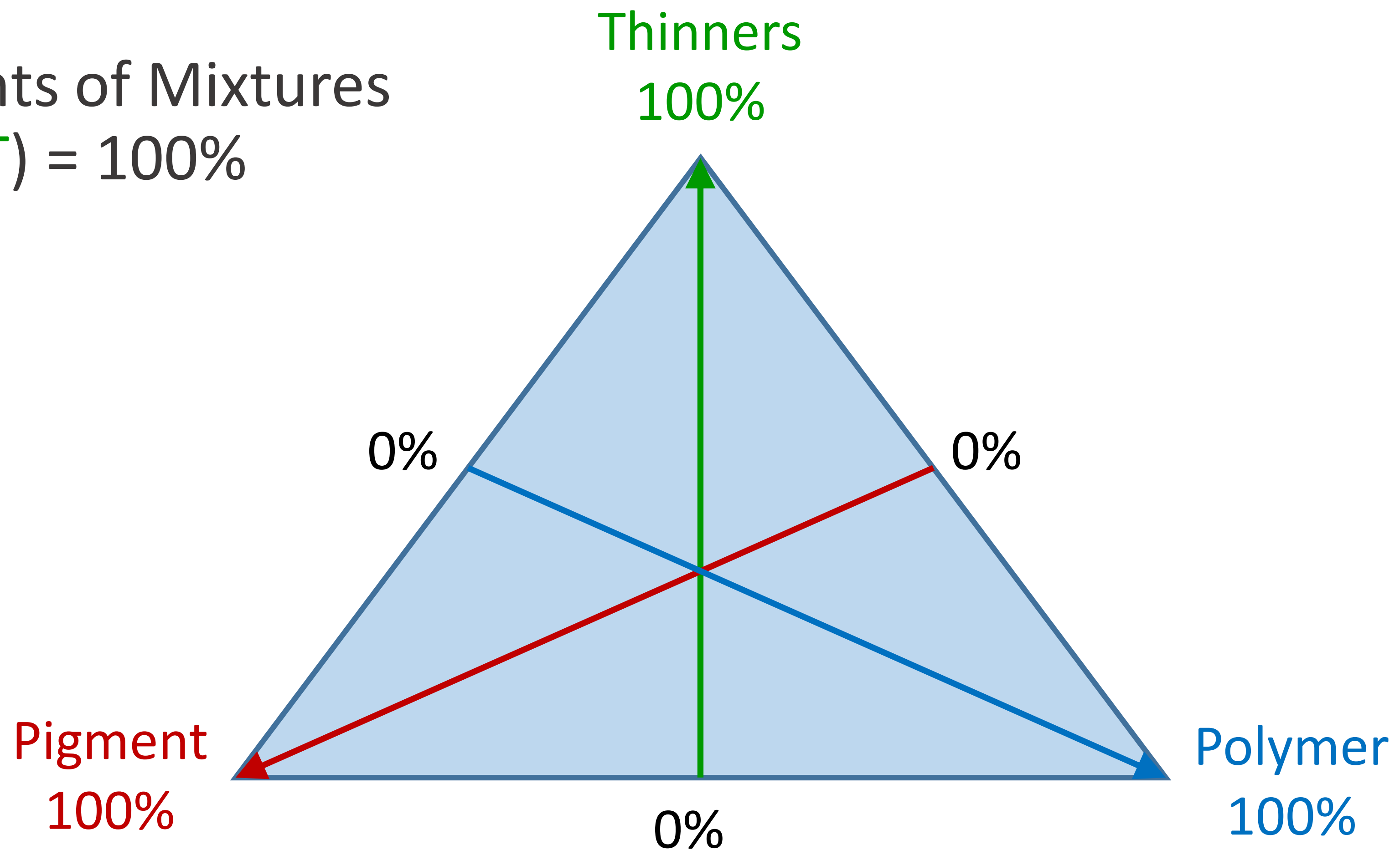
	Organic solvent 'Solventborne'	Aqueous 'Waterborne'
Solution Polymer	Alkyd resins Acrylic resins Polyurethane resins* Epoxy resins*	
Dispersion Polymer		Acrylic Latex Alkyd Emulsion Alkyd/Acrylic Hybrids

*1 pack & 2 pack

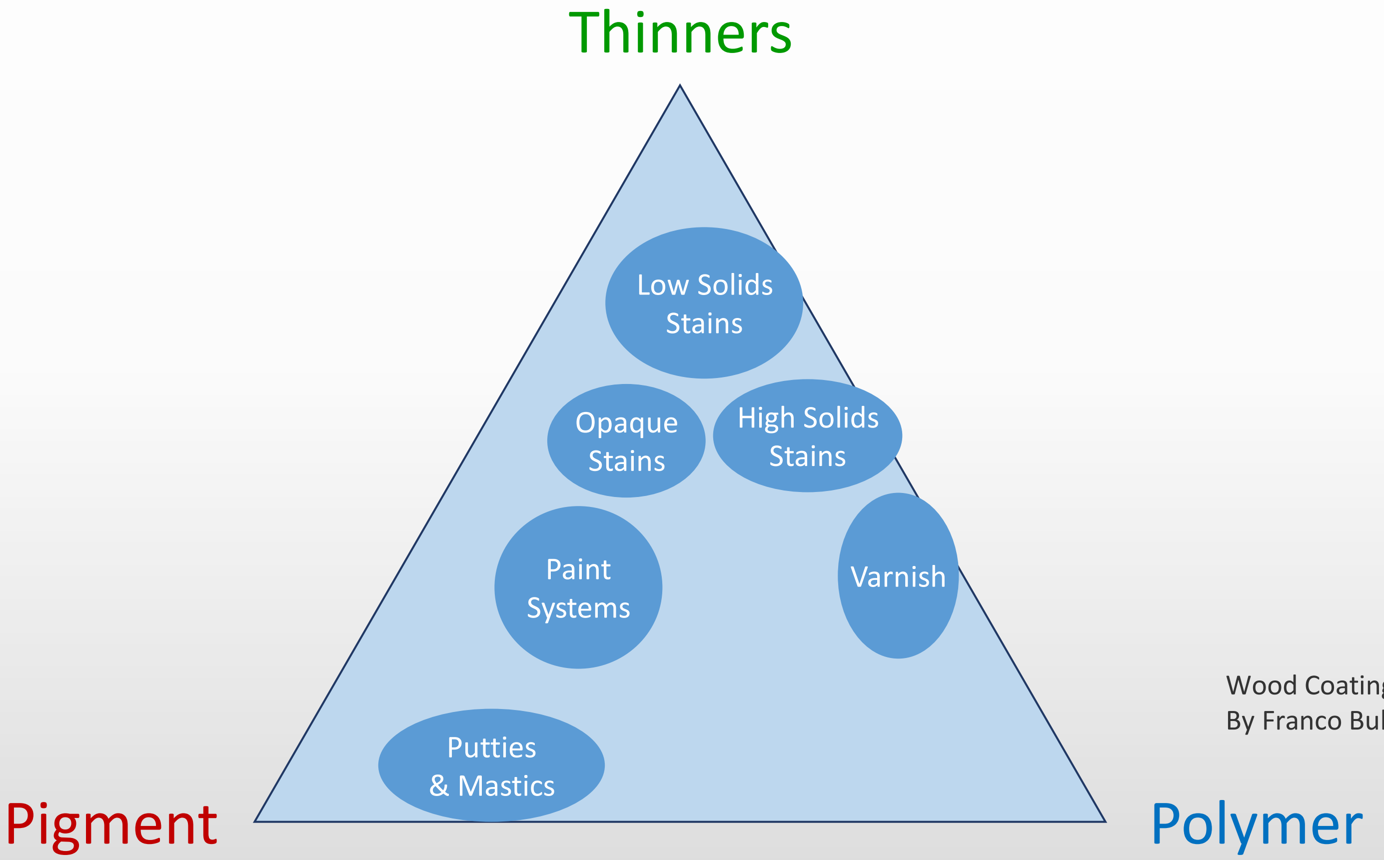
Mixture Theory

Components of Mixtures

$\Sigma (P + B + T) = 100\%$



Formulating Relationships

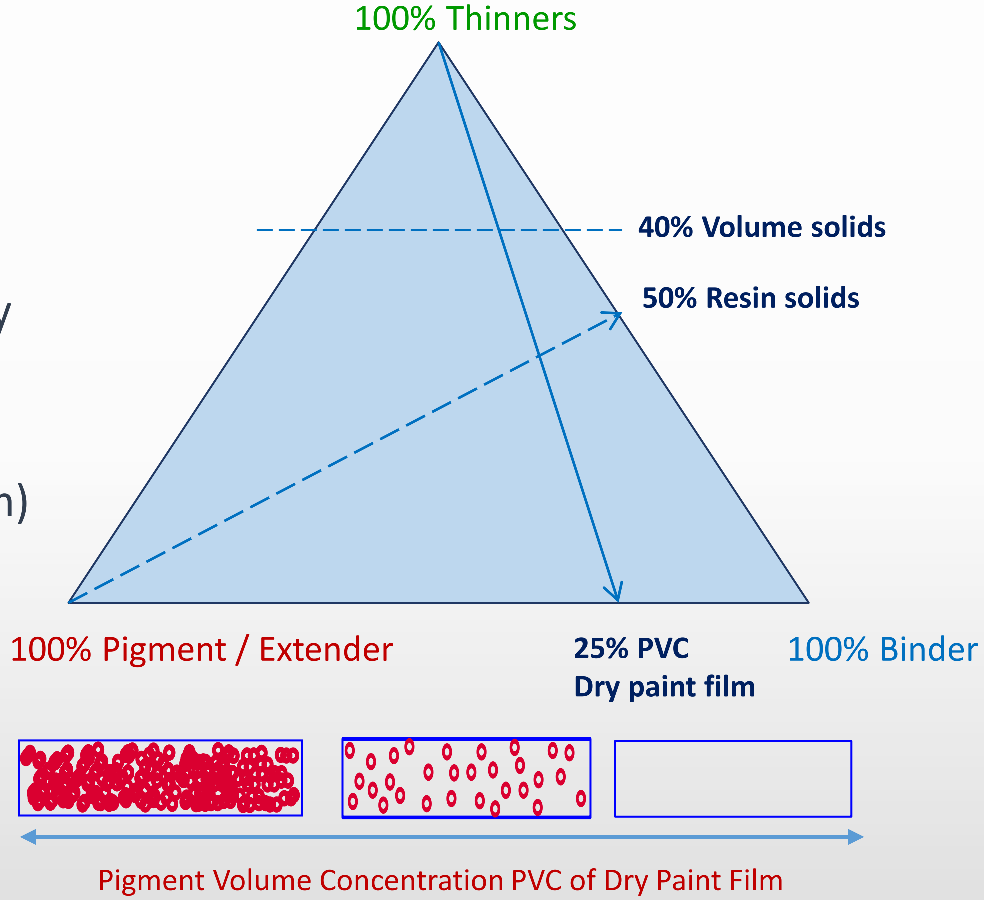


Wood Coatings: Theory and Practice
By Franco Bulian, Jon Graystone[3]

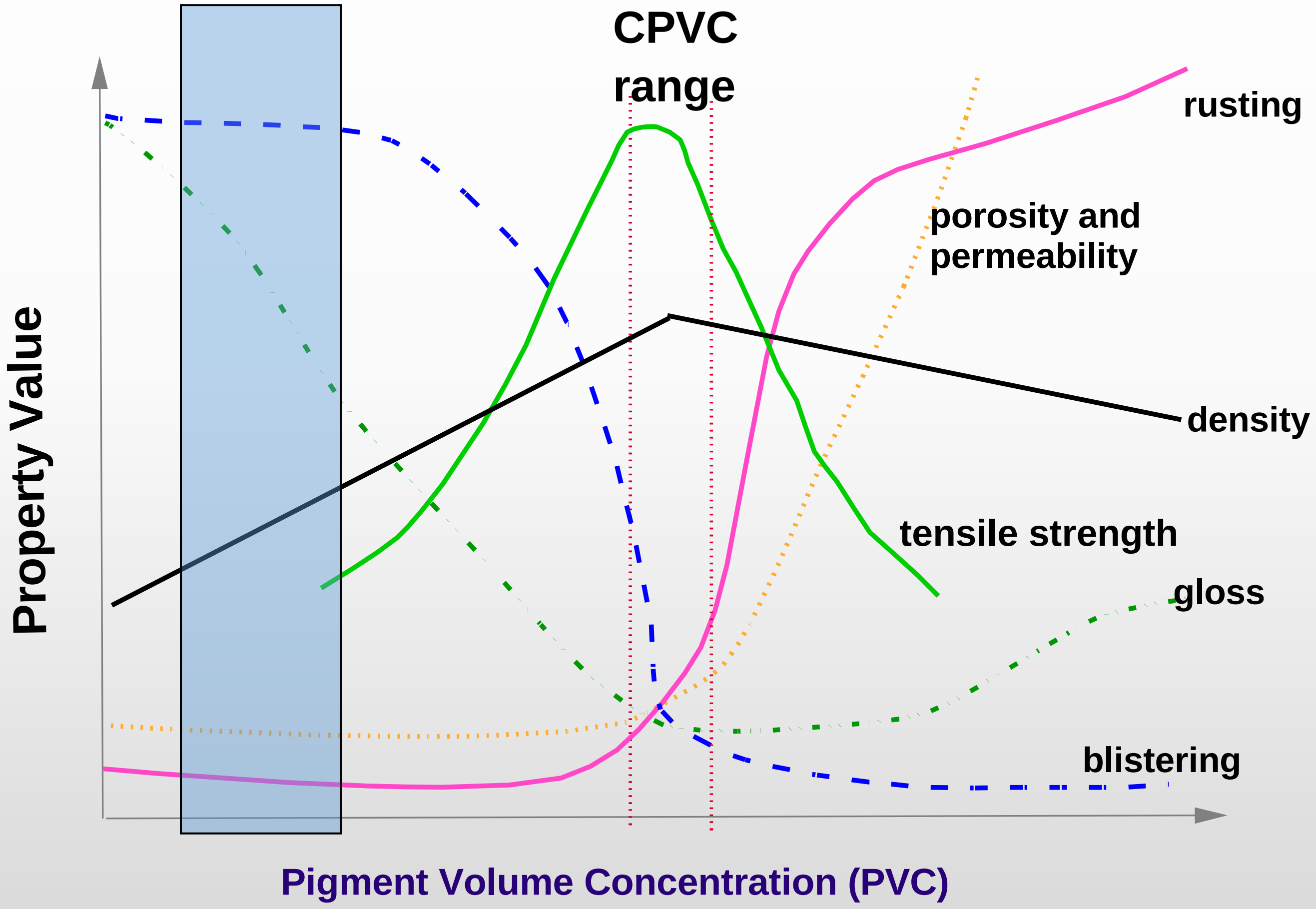
Formulating Relationships

	Volume %
Thinner	60
Binder	30
Pigment	10

- Solids content is the total amount of non-volatile material – dry film, expressed by volume or weight % e.g. 40% volume solids
- Spreading rate (m^2/litre) determines the wet film thickness (µm) and volume solids determines the dry film thickness (µm)
- Pigment : Binder ratio impacts dry film properties sometimes expressed as P:B (w/w) ratio
  or more often
  Pigment Volume Concentration PVC (v/v%) e.g. 25%



The Formulating Window



Formulation Science

Formulation Problem

To produce a physical mixture of two or more ingredients to develop a final product with two or more, usually conflicting, measure of product quality.[4]

The Range of Formulation

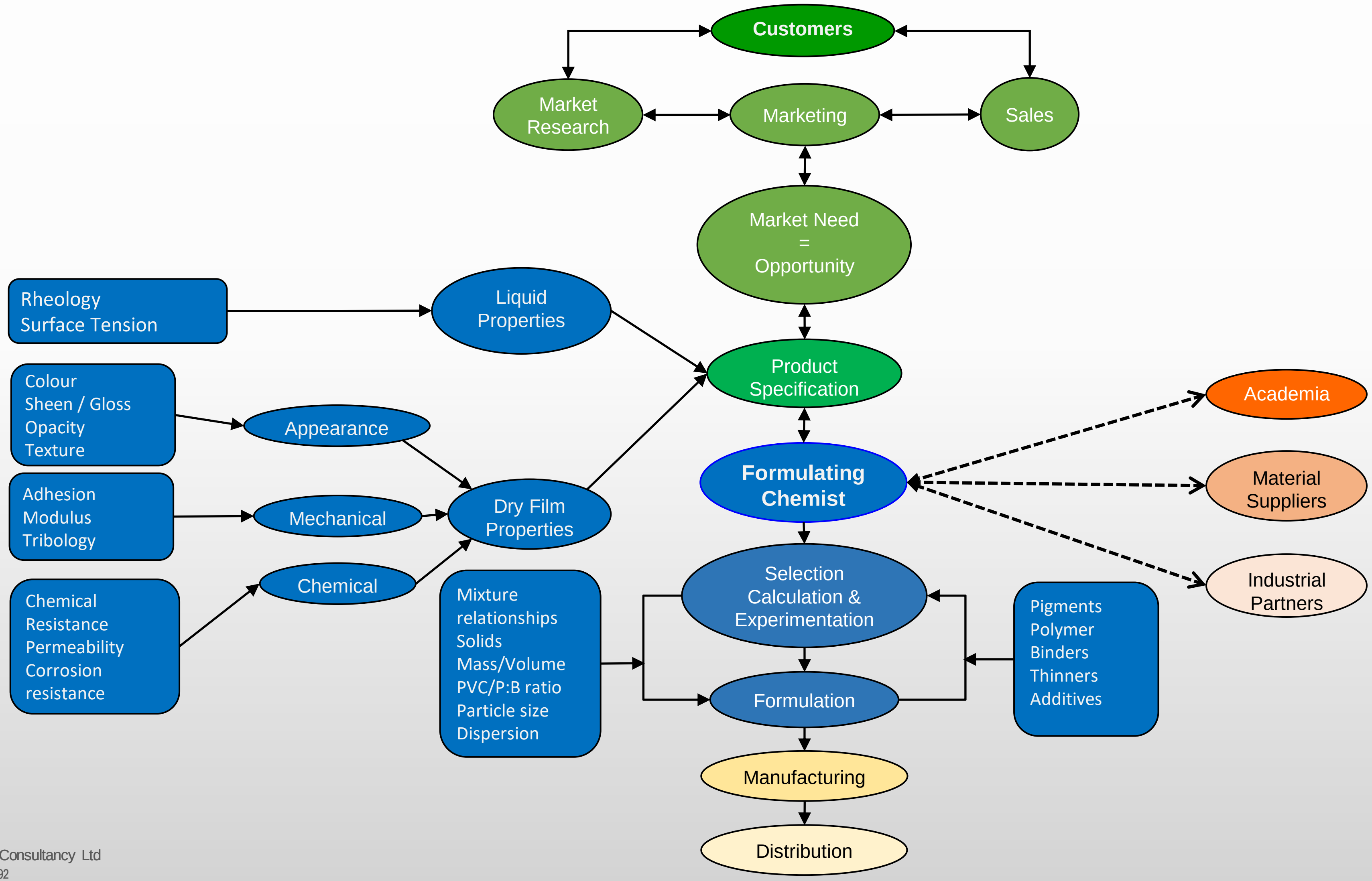
- pharmaceuticals
- cosmetics
- detergents
- bread & cakes
- agrochemicals
- paints
- adhesives
- lubricants
- alloys
- tyres
- formulated process chemicals

What do these categories have in common?

They are all MIXTURES

Interactions are physical rather than chemical

The Role of the Formulating Chemist



Paint Formulation – Art or Science ?

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Formulating Strategy

1. Develop and agree a specification, with property weightings
2. Choose technology type: waterborne, solventborne, powder
3. Choose polymer binder type: acrylic, polyurethane, alkyd
4. Choose pigment and extender types
5. Determine ratios and levels of major components: pigment, binder, thinner
6. Determine necessary additives and levels
7. Prepare small scale samples
8. Test product fully and check storage stability
9. Customer evaluation
10. Scale-up for manufacture

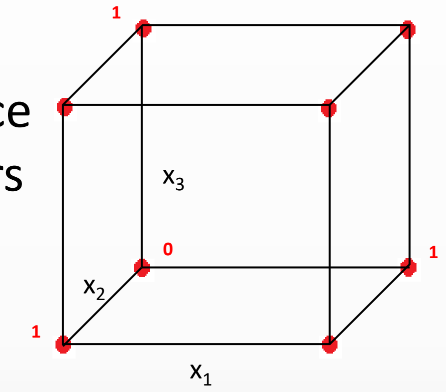
Experimental Designs for Formulation

Factorial Designs[5]

Experimental design space e.g. 3 independent factors

x_1, x_2, x_3

ranging from Low to High often shown as -1, +1 or just - , +



Many more factors are possible but difficult to visualise.

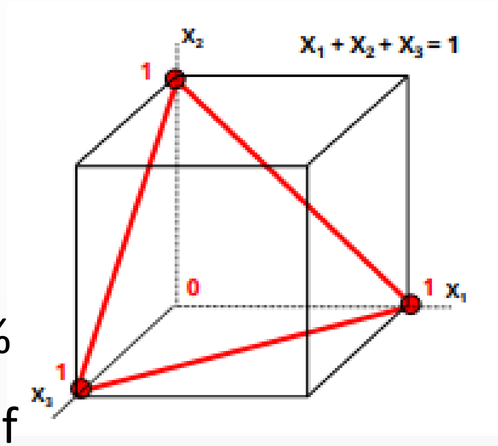
Useful for minor components in a formulation or for process variables.

Mixture Designs[6]

Experimental design space for 3 mixture factors

$x_1 + x_2 + x_3 = 1$

Components always total up to 100%



The formulation always rescales itself in this way.

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Useful for major components in a formulation.

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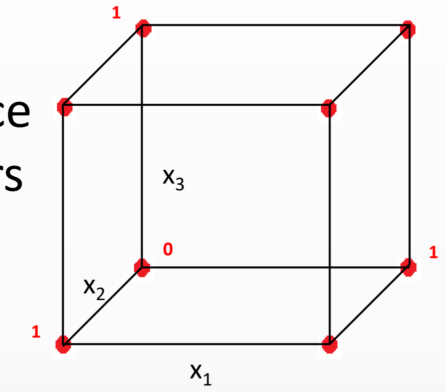

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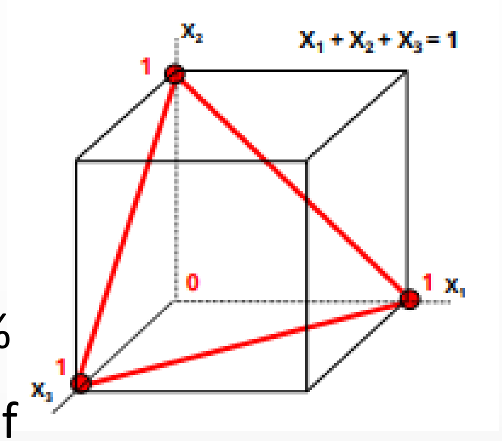
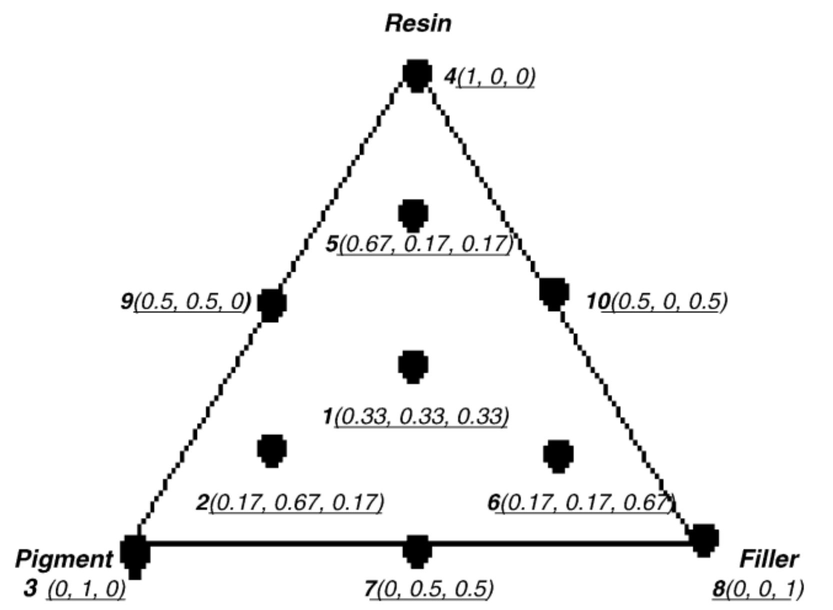


Road-Marking Paint – Mixture Design

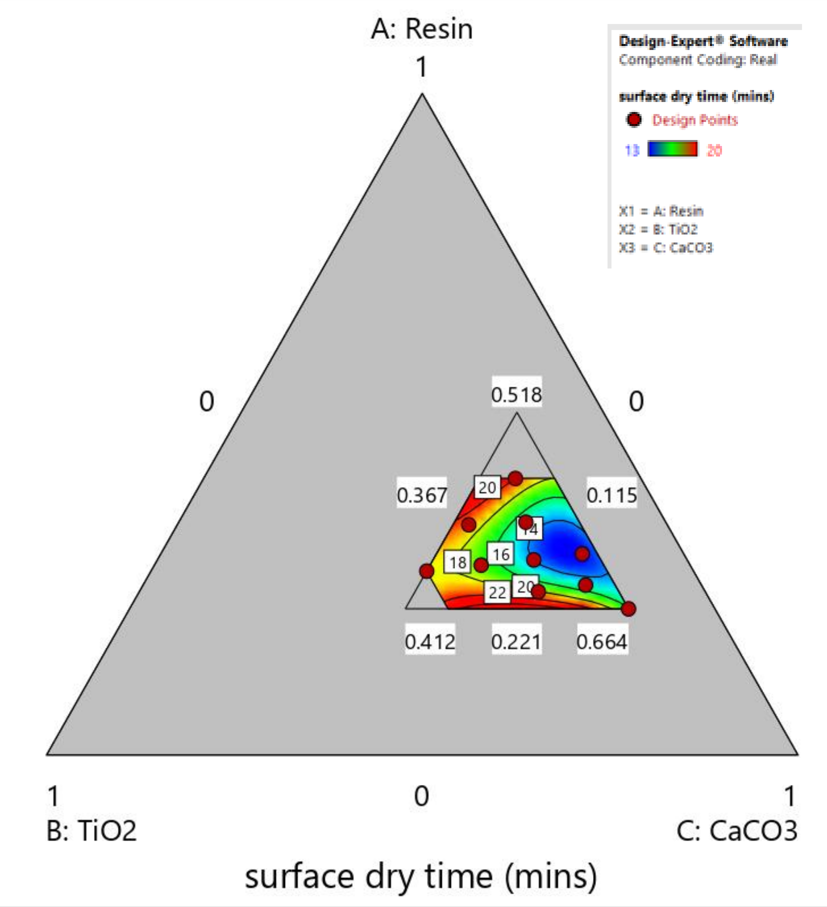
Paint Formulation, Input Variables / Factors (wt%)				
	Resin	TiO2	CaCo3	Totals
1	29.5	20.4	50.1	100
2	28.7	27.8	43.5	100
3	27.8	35.5	36.7	100
4	41.8	16.7	41.5	100
5	35.2	18.6	46.2	100
6	25.7	15.4	58.9	100
7	24.7	22.2	53.1	100
8	22.1	11.5	66.4	100
9	34.8	26.4	38.8	100
10	30.4	13.5	56.1	100

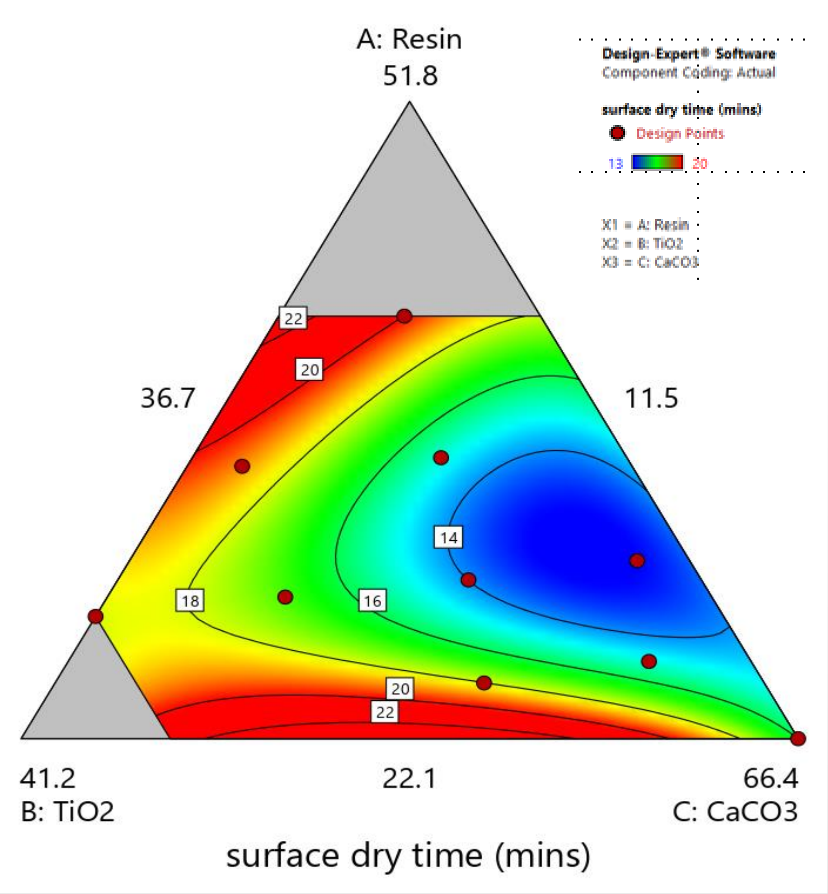
Test Results (Response Variables) Measured / Calculated				
Surface Dry Time / mins	Taber Abrasion / mg	Gloss / %	PVC / %	Cost / $
14	94.0	4	55.44	1.629
17	94.7	4	55.59	1.734
18	90.5	6	54.9	1.954
20	107.2	5	44.65	1.778
15	100.3	5	50.55	1.682
15	82.9	3	60	1.407
18	74.8	4	59.09	1.589
16	63.8	3	63.21	1.251
19	95.0	5	49.59	1.774
13	91.0	4	55.16	1.940



S. Fatemi et al. / Progress in Organic Coatings 55 (2006) 337–344

Road-Marking Paint – Mixture Analysis





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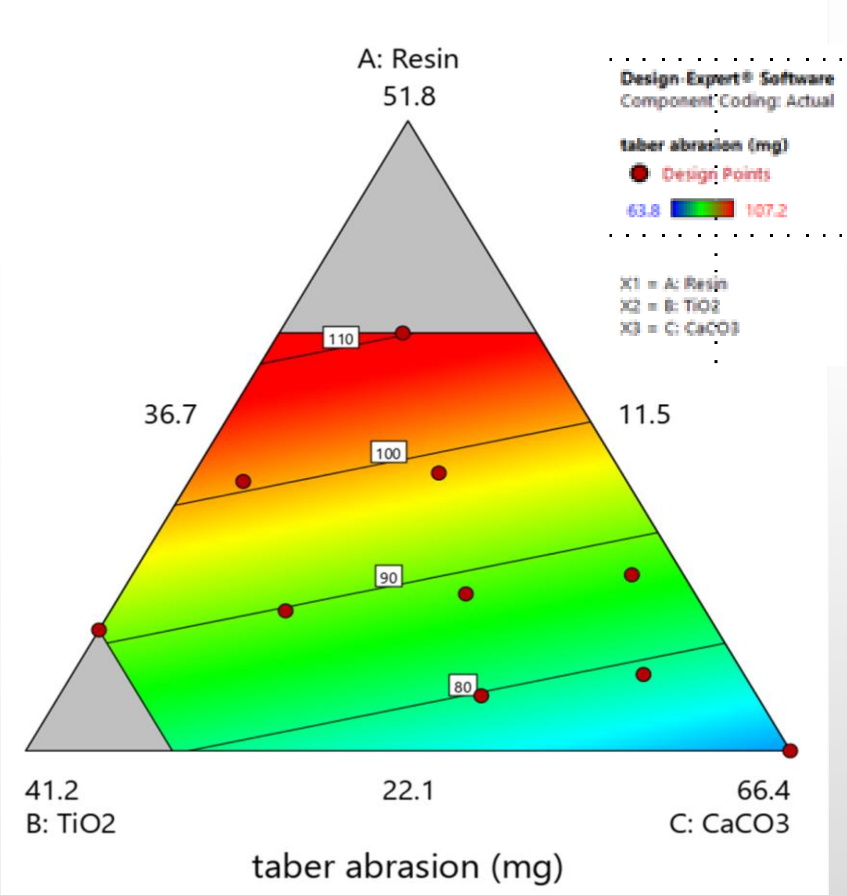
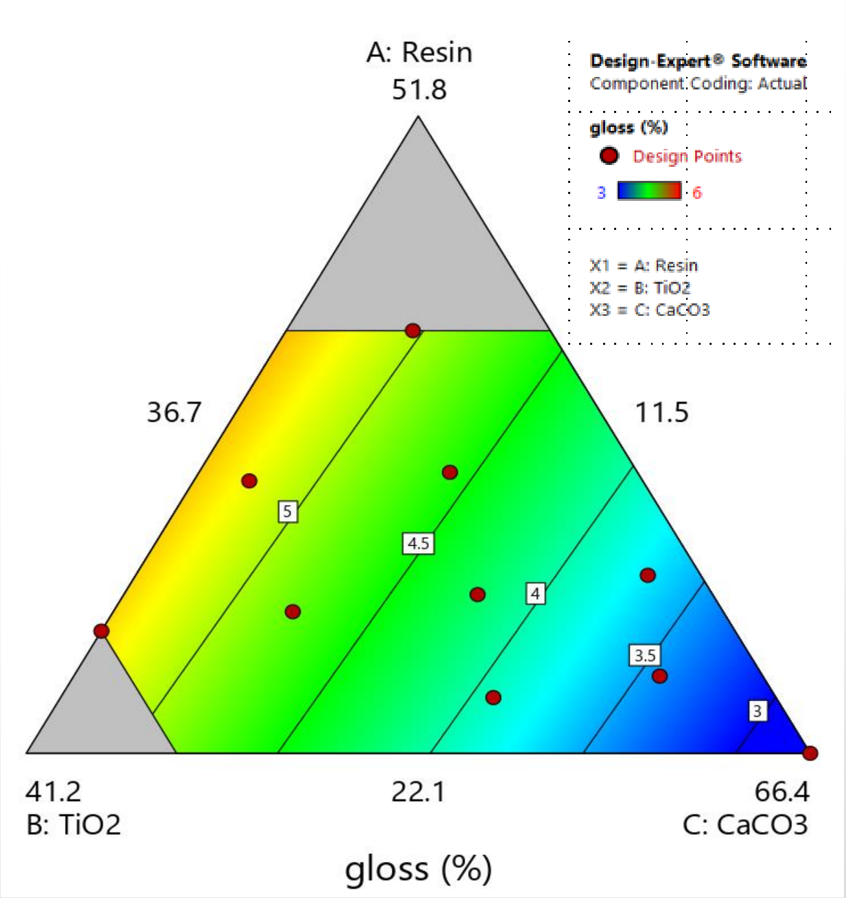
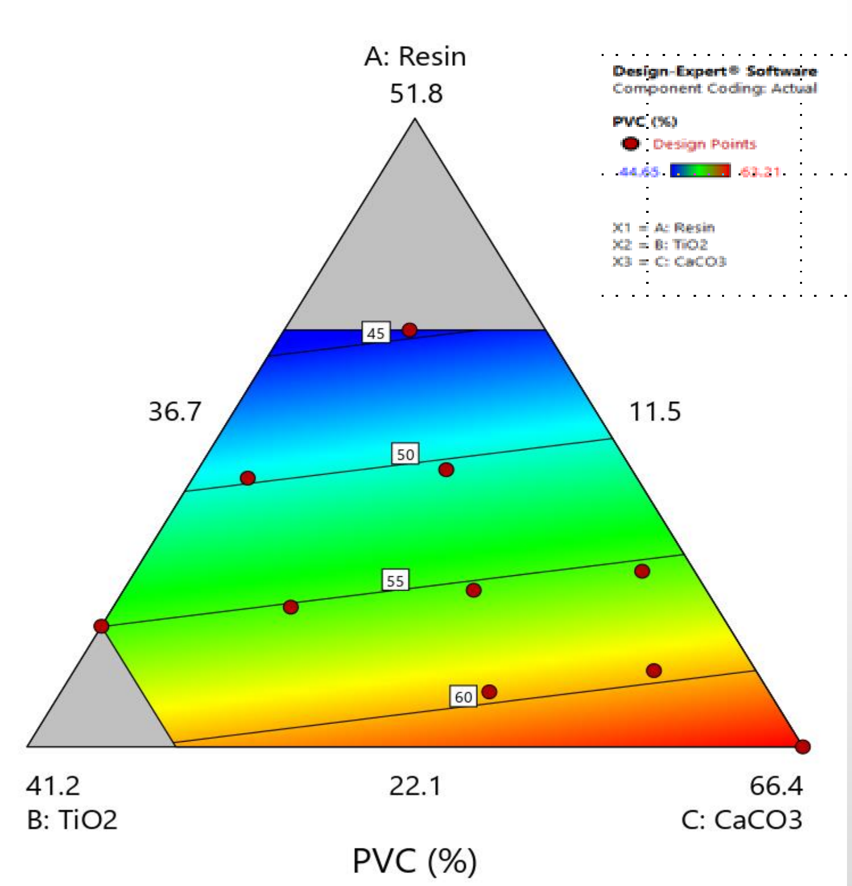
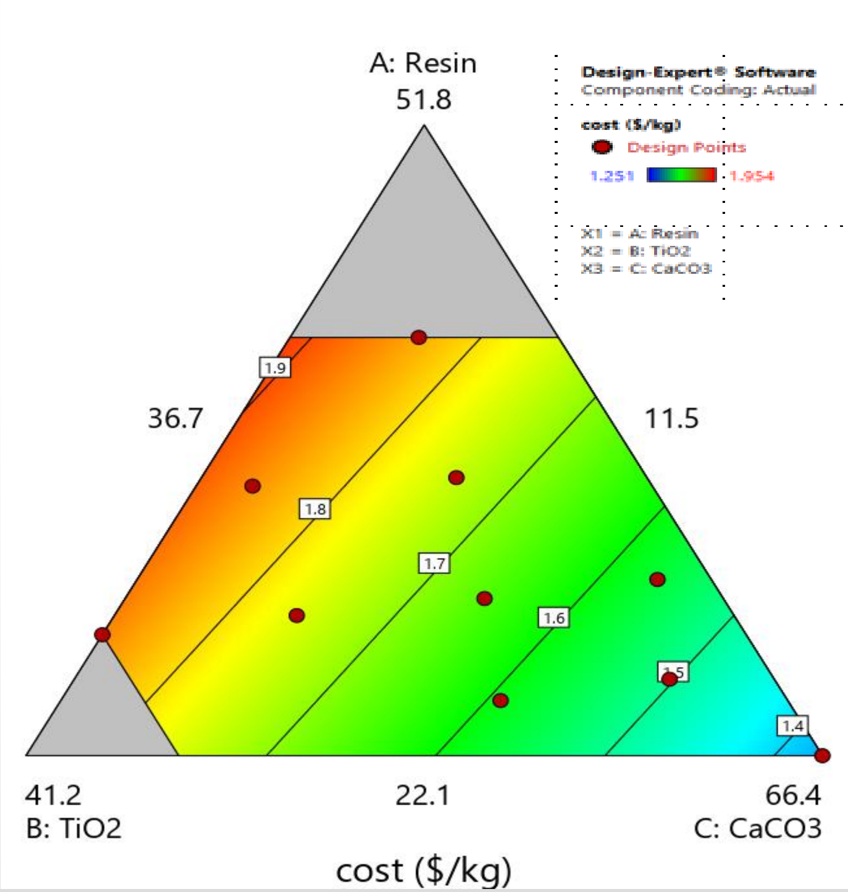




Road-Marking Paint – Mixture Analysis





Road-Marking Paint – Mixture Optimisation

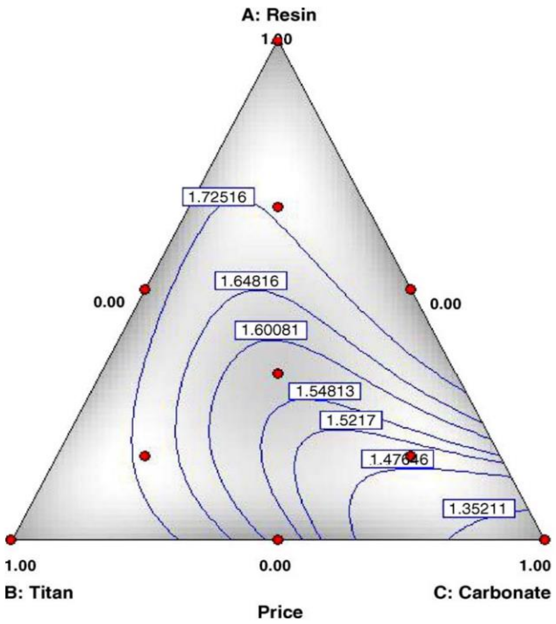


Fig. 11. Price (US$/kg).

Selected range of optimized paint properties

Property	Range
Taber abrasion (mg)	≤85
Hardness (N)	≥8
No pick up time (min)	≤18
Gloss (%)	≥3
|LCPVC – PVC| (%)	<2
PVC (%)	>58

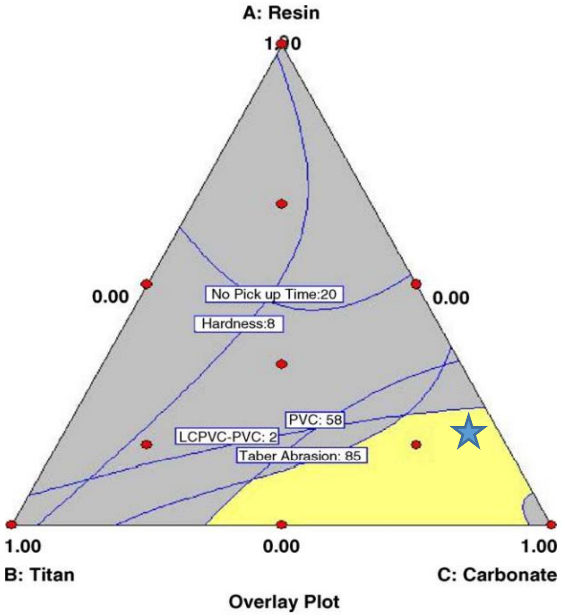


Fig. 12. Results of running optimization program in desired ranges.

CPVC:	61.4641
PVC:	60.14
LCPVC-P:	1.32964
No Pick	15.7503
Surface	13.8901
Gloss:	3.14105
Hardness	8.49913
Price:	1.53673
Taber Ab	78.5816
Density:	1.74267
Gloss aft	2.61476
X1	0.19
X2	0.07
X3	0.74

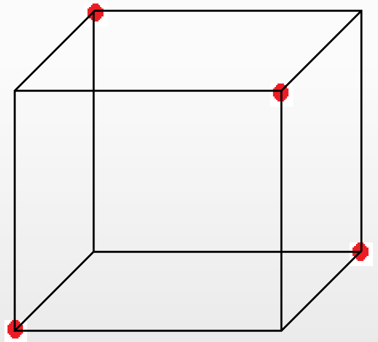
Comparison of the results obtained from experiment and statistical model

Property	LPVC (%) – PVC (%)	Taber (mg)	Gloss (%)	Hardness (N)	No pick up time (min)	Drying time (min)	Price (US$/kg)
Exp.	1.4	77	3	9	15	13	1.5
Model	1.32	78.58	3.14	8.5	15.75	13.89	1.54

Fractional Factorial Screening Designs

- Used to discover which factors are significant
- Does not provide a detailed model
- Minimises the number of runs

Half fraction of
a 3 factor design



- Highly fractionated designs for many factors are possible, e.g. Plackett Burman designs[7]

Millbase Fractional Factorial Design

Using a “Plackett Burman”, fractional factorial design to discover the important factors in a sandmill dispersion

	FACTOR	Low (-)	High (+)
A	disc speed	1500 rpm	4500 rpm
B	vessel size	11.8 cm	16.1 cm
C	disc diameter	4.5 cm	9.0 cm
D	milling time	10 mins	30 mins
E	no of discs	1	2
F	pigment concentration	7.50%	12.50%
G	pigment/binder ratio	1:4	1:2
H	premix time	0.5 hours	6 hours
I	milling media size	Fixed	
J	milling media chargd	16%	24%
K	formulation charge	16%	24%
L	milling temperature	20oC	55oC
M	type of milling media	Glass	Sand
N	thickness of discs	0.5 cm	1.5 cm
O	Order of charging vessel	Fixed	

Trial	FACTOR LEVEL															RESPONSE
No.	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	K/S
1	+	+	+	+	-	+	-	+		-	-	+	-	-		0.593
2	-	+	+	-	-	+	-	-		+	+	+	+	-		0.64
3	+	+	+	-	+	-	+	+		-	+	-	-	-		0.454
4	-	-	+	+	+	+	-	+		+	+	-	-	+		0.93
5	+	+	-	-	-	+	+	+		-	+	-	+	+		0.564
6	-	+	+	+	+	-	+	-	F	+	-	-	+	-	F	0.473
7	+	+	-	-	+	-	-	-	I	+	+	+	-	+	I	0.417
8	-	-	-	-	+	+	+	+	X	+	-	+	+	-	X	0.624
9	+	+	-	+	-	+	+	-	E	+	-	-	-	+	E	0.493
10	-	-	-	-	-	-	-	-	D	-	-	-	-	-	D	0.356
11	+	-	+	+	-	-	+	-		-	+	+	+	+		0.701
12	-	-	-	-	-	-	+	+		+	-	+	-	+		0.487
13	+	-	-	-	+	+	-	-		-	-	-	+	+		0.76
14	-	-	+	+	-	-	-	+		+	+	-	+	-		0.76
15	+	-	+	+	+	+	+	-		-	+	+	-	-		0.435
16	-	+	+	+	+	-	-	+		-	-	+	+	+		0.481

W.Carr & A. Kelly
“Factors which affect the efficiency of sand grinding, J. Oil Col. Chem. Assoc., Vol 62 No. 6, (1979), p 183-198

Millbase Fractional Factorial – Analysis

ANOVA for Reduced Linear model

Response 1: K/S

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.3107	12	0.0259	1.63	0.3797	not significant
A-disc speed	0.0119	1	0.0119	0.7501	0.4501	
B-vessel size	0.0550	1	0.0550	3.47	0.1593	
C-disc diameter	0.0515	1	0.0515	3.25	0.1690	
D-milling time	0.0199	1	0.0199	1.26	0.3442	
E-no of discs	0.0000	1	0.0000	0.0016	0.9708	
F-pigment concentration	0.0518	1	0.0518	3.27	0.1684	
G-pigment/binder ratio	0.0312	1	0.0312	1.97	0.2553	
H-premix time	0.0239	1	0.0239	1.51	0.3071	
J-milling media charge	0.0144	1	0.0144	0.9092	0.4107	
K-formulation charge	0.0251	1	0.0251	1.59	0.2969	
L-milling temperature	0.0106	1	0.0106	0.6698	0.4731	
M-thickness of discs	0.0155	1	0.0155	0.9786	0.3955	
Residual	0.0475	3	0.0158			
Cor Total	0.3582	15				

Factor coding is **Coded**.
Sum of squares is **Type III - Partial**

The **Model F-value** of 1.63 implies the model is not significant relative to the noise. There is a 37.97% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case there are no significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The most important factors were found to be…

B. Vessel size
F. Pigment concentration
C. Disc diameter
G. Pigment/binder ratio

The Way Forward – Lab Automation and AI

Labman[10]

Chemspeed Formax[11]

Acknowledgements

Thanks to the PRA for permission to use a number of the slides shown, taken from their Professional Paint Formulation Course

I would particularly like to thank Laura Pilon of PRA who kindly input most of the data used in these slides into DesignExpert software and analysed the results to provide many of the charts shown to you.

Labman for permission to use images from their website

Chemspeed for permission to use images from their website

Finally I would like to acknowledge my friend and mentor Jon Graystone, who has taught me most of what I know about paint formulation.

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