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WETTING OF BINARY POWDER MIXTURES

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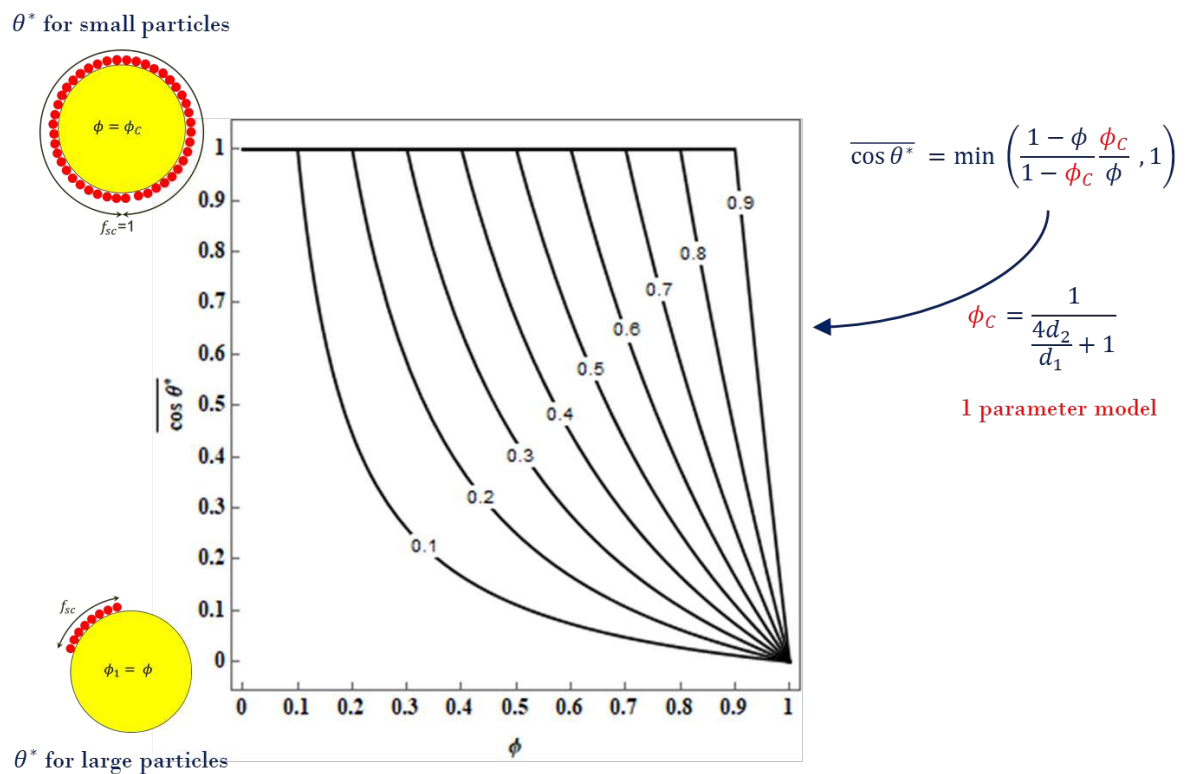
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Abstract

The wetting process involved when a liquid droplet comes into contact with a mixture of particles is a complex phenomenon which is often understood by reference to Cassie-Baxter theory. However, various authors have applied the Cassie-Baxter theory for the prediction of contact angles on two-component mixtures without success. We hypothesise that the main difficulty in applying the Cassie-Baxter theory to mixtures is that if the particles differ in size, it is possible for the small particles to coat the large particles, so reducing the available surface area of the large particles. This leads to the view that bulk volume fractions are not good estimates of surface fractions of the components within the mixture. We argue that the Cassie-Baxter theory over represents the influence of large particles and that below a certain critical volume fraction they exert no influence. We present a simple geometrical model that relates the critical surface coverage volume fraction to the Sauter mean particle size of the binary mixture components. As a consequence, the wetting behaviour can be determined from the bulk volume fractions and the calculated critical surface coverage volume fraction, by means of a simple geometric model. We show that the simple model describes the five two-

23 components systems reported here and a further four systems reported in the literature,
 24 irrespective of whether the larger or small particles are hydrophobic/hydrophilic. With this
 25 model, it is possible to predict the wetting behaviour of mixtures of particles that coat each
 26 other using very simple characterisation methods, so reducing the development time in the
 27 creation of formulations in the pharmaceutical industry.

28 **Graphical Abstract: Surface coverage wetting model**



29

30 **Keywords**

31 Contact angle, Wetting, Surface coverage

32 **1. Introduction**

33 We review the applicability of the Cassie-Baxter theory [1,2] of the prediction of liquid
 34 contact angles on surfaces made from two-component mixtures consisting of
 35 hydrophilic/hydrophobic particles [3,4]. Cassie-Baxter theory was derived on the basis that

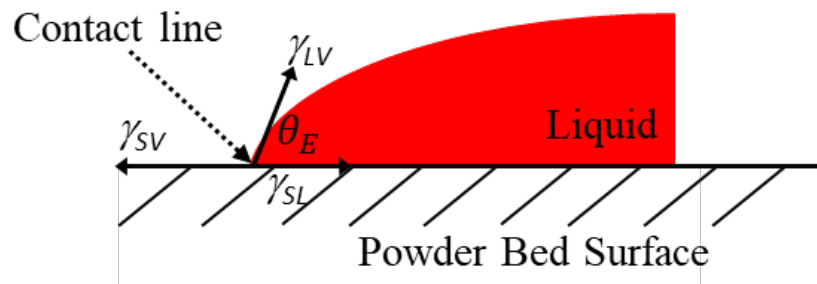
36 contact angles are determined by the interactions within the interfacial contact area of the liquid
37 and solid surface [1,2]. To validate their theory, Cassie-Baxter studied systems in which the
38 components were not free to rearrange and so the surface fraction of each component was fixed
39 and simple to determine. However, several authors have questioned the validity of the Cassie-
40 Baxter theory and suggested that the three-phase contact line alone and not the interfacial
41 contact area is important in determining the contact angle behavior [5–10]. This result was
42 attributed to the difference in behavior of solid and liquid molecules. At the three-phase contact
43 line, solid molecules are not mobile and cannot contact to obey area minimization when a liquid
44 droplet is placed on them. Put simply, the laws of liquids cannot be directly applied to solids.
45 The aim of our paper is to highlight the misconceptions and restrictions of Cassie-Baxter theory
46 in predicting contact angles on surfaces made from two-component particulate mixtures.
47 Consequentially, we put forward a new theory which is supported by detailed experimental
48 investigations that allows the prediction of contact angles on two-component particulate
49 mixtures.

50 **2. Background**

51 When a liquid droplet comes into contact with a solid surface, the liquid droplet wets the
52 constituent particles. This wetting phenomenon is determined by the interactions between the
53 molecules of the two phases coming into contact, forming a three-phase contact line, where the
54 liquid, powder bed surface and vapour co-exist. The three-phase contact line will continue to
55 advance to an equilibrium contact angle (θ_E) in which the liquid droplet takes the shape that
56 minimizes the total free energy of the system, (see Figure 1).

57 A well-known relation for θ_E was developed by Young (1805) assuming an idealized
58 smooth and homogeneous solid surface and that the liquid droplet does not spread further after
59 reaching its equilibrium contact line radius [11]. A liquid is said to wet a surface if $\gamma_{SV} - \gamma_{SL} \geq$

60 γ_{LV} ($\cos \theta \leq 1$) and be non-wetting if $\gamma_{SV} < \gamma_{SL}$ ($\cos \theta$ is negative). However, in reality solid
61 surfaces are not ideal, particularly pharmaceutical powders where there are several factors that
62 affect the measured apparent contact angle (θ^*) such as contact line surface heterogeneities,
63 chemical composition of the liquid and solid surface [1,2,12,13].



64

65 **Figure 1. Cross sectional contact angle profile of a liquid droplet on a solid surface at a three phase**
66 **contact line**

67 Wenzel (1936) first related the θ^* to solid surface heterogeneities (roughness) assuming that
68 the liquid droplet fills the grooves of a rough solid surface completely [12]. Wenzel's theory
69 suggests that for $\theta^* > 90^\circ$, surface roughness enhances its wetting behaviour since there is a
70 greater net energy decrease to induce spreading. However for $\theta^* < 90^\circ$, the non-wetting
71 behaviour of a solid surface is exaggerated with surface roughness. However, Wenzel's theory
72 was conceived for homogeneous, one-component solid systems.

73 In the pharmaceutical industry, solid systems are however frequently mixtures [4,14–16,
74 21]. For two-component mixtures of fibres in a cloth, Cassie-Baxter related the θ^* with the
75 wetted fraction of surface area of a solid based on the assumption that the cloth surface is
76 smooth and consists of a grid of cylinders, using the following expression [1]:

77
$$\cos \theta^* = f_1 \cos \theta_1^* + f_2 \cos \theta_2^*$$

78
$$f_1 + f_2 = 1$$

79 **Equation 1**

80 where θ^* is the apparent equilibrium contact angle, f_1 and f_2 are the area fractions of fibres
81 1 and 2 with apparent contact angles of θ_1^* and θ_2^* respectively.

82 There are a number of limitations in seeking to applying Cassie-Baxter to powders: a) in
83 practise real solid surfaces do not consist of cylindrical particles and have complex pore
84 structures in which the liquid droplet ‘may’ spread on the solid surface and fill the pores in any
85 direction depending on the contact angle formed [17,18] and b) Cassie-Baxter studied systems
86 in which the components were not free to rearrange and so the surface fraction of each
87 component was fixed and simple to determine. In seeking to apply their result to mixtures of
88 particles it has to be assumed that the surface fraction of each component is equal to the known
89 volume fraction; a situation that arises naturally if particles can rearrange in the surface of the
90 mixture i.e. in 2D, but not vertically i.e. in 3D. Then Equation 1 is rewritten as:

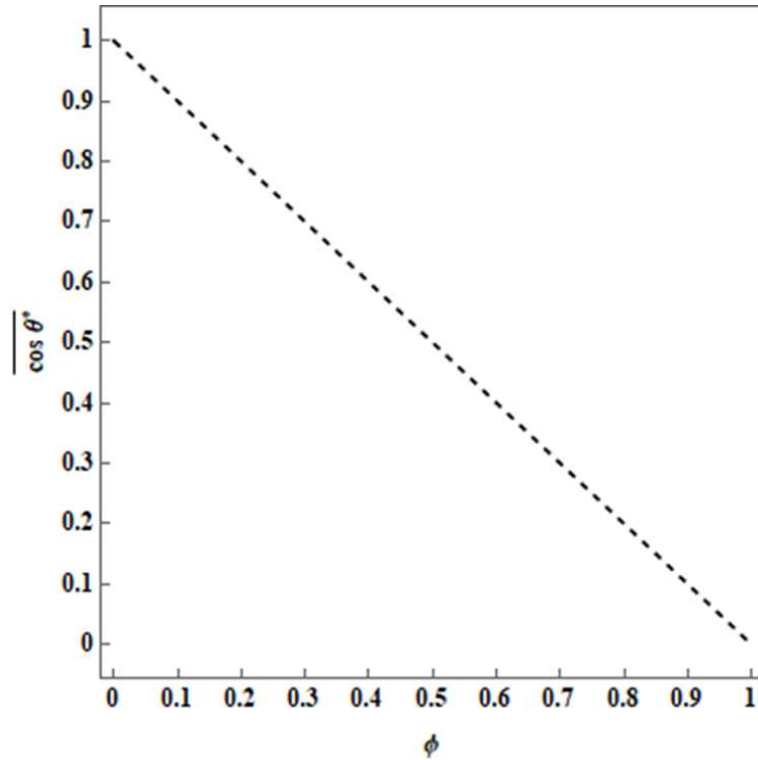
91
$$\cos \theta^* = (\phi) \cos \theta_1^* + (1 - \phi) \cos \theta_2^*$$

92 **Equation 2**

93
$$1 - \phi = \frac{\cos \theta^* - \cos \theta_1^*}{\cos \theta_2^* - \cos \theta_1^*} = \overline{\cos \theta^*}$$

94 **Equation 3**

95 where ϕ is the volume fraction of particles of type 1 and $\overline{\cos \theta^*}$ is the normalized wetting
96 parameter.



97

98

99

Figure 2. Relationship between the normalized contact angle and the volume fraction of particles of type 1 according to Cassie-Baxter, from Equation 3.

100

101

102

103

104

Figure 2 shows how the normalized wetting parameter ($\overline{\cos \theta^*}$) depends on the volume fraction of particles of type 1. The implication of Equation 3 is that a plot of $\overline{\cos \theta^*}$ versus the volume fraction (ϕ) of the particles in the powder mixture, gives a linear relationship (see Figure 2). This shows that as ϕ increases there is a corresponding reduction in the value of $\overline{\cos \theta^*}$.

105

106

107

However, in this paper we will hypothesise that there is a non-linear relationship between $\overline{\cos \theta^*}$ versus ϕ if the particles differ in size, as it is possible for the small particles to coat the large particles thus changing the apparent contact angle.

108

3. Revised Theory

109

110

We propose a model that considers a two-component powder system consisting of particles of differing chemical composition, using the following assumptions to complete the derivation:

- 111 1. Particles are treated as spheres.
112 2. The presence of air is neglected.
113 3. The solid surface is smooth.

114 We consider a unit volume of a mixture in which the volume fraction of large particles is ϕ .

115 Volume fraction of large particles

116
$$v_1 = \phi_1 = \phi$$

117 **Equation 4**

118 Volume fraction of small particles

119
$$v_2 = \phi_2 = 1 - \phi$$

120 **Equation 5**

121 From this, the surface area per unit volume, s_1 of the large particles is:

122
$$s_1 = \frac{6\phi}{d_1}$$

123 **Equation 6**

124 The projected area of small particles, p_2 is given by:

125
$$p_2 = \frac{3(1 - \phi)}{2d_2}$$

126 **Equation 7**

127 If small particles cover the large ones, surface coverage of larger particles by small particles
128 is related to s_1 and p_2 by:

129
$$f_{sc} = \frac{\text{projected area}}{\text{surface area}}$$

130 **Equation 8**

131 where f_{sc} is fractional surface coverage of larger particles by the small

132 Substituting Equation 6 and 7 into 8 gives:

133
$$f_{sc} = \frac{1(1-\phi)d_1}{4\phi d_2}$$

134 **Equation 9**

135 If we equate Equation 9 to $f_{sc} = 1$ and denote the volume fraction of larger particles at
136 which this occurs as the critical surface coverage, ϕ_c substituting $\phi = \phi_c$ then solving for ϕ_c ,
137 yields the critical value fraction at which larger particles are completely covered by the small
138 particles, rearrangement gives:

139
$$\phi_c = \frac{1}{\frac{4d_2}{d_1} + 1}$$

140 **Equation 10**

141 The value of d_1 and d_2 can be easily determined allowing ϕ_c to be predicted without
142 conducting extensive analysis.

143 Equation 9 and 10 are solved to give the proposed surface coverage, f_{sc} as:

144
$$f_{sc} = \frac{1 - \phi}{1 - \phi_c} \frac{\phi_c}{\phi} \quad \text{if } \phi \geq \phi_c$$

145 **Equation 11**

146 In the style of Cassie-Baxter we expect:

147
$$\overline{\cos \theta^*} = (1 - f) \cos \theta_1^* + f \cos \theta_2^*$$

148 **Equation 12**

149
$$\overline{\cos \theta^*} = f = \min (f_{sc}, 1)$$

150 If $\phi > \phi_c$ then $f_2 = f_{sc}, f_1 = 1 - f_{sc}$

151 If $\phi \leq \phi_c$ then $f_2 = 1, f_1 = 0$

152 **Equation 13**

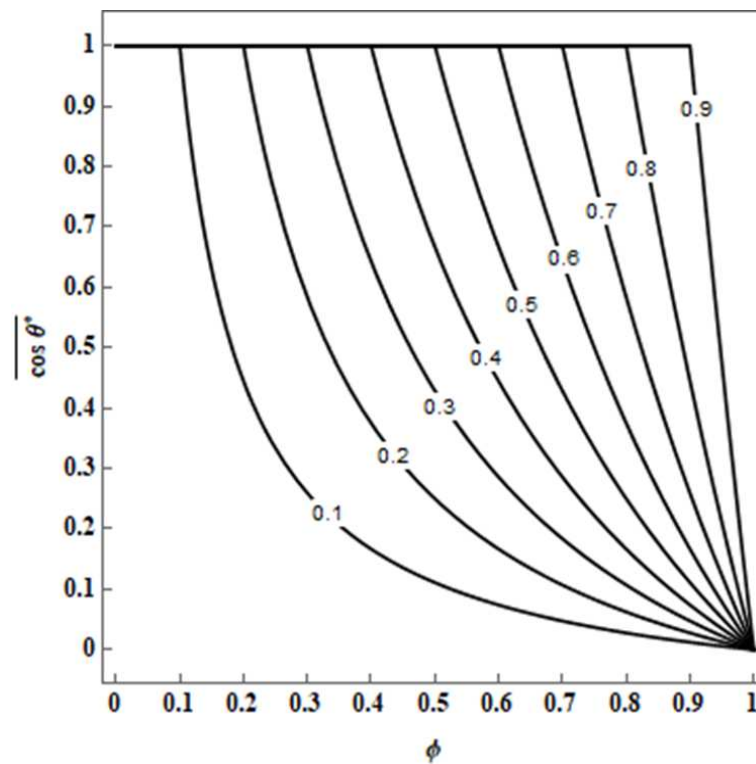
153
$$\overline{\cos \theta^*} = f = \min \left(\frac{1 - \phi}{1 - \phi_c} \frac{\phi_c}{\phi}, 1 \right)$$

154 **Equation 14**

155 Figure 3 shows the behaviour of $\overline{\cos \theta^*}$ from mixtures which is predicted using Equation
 156 14. We see from Figure 3 that Equation 14 predicts a non-linear relationship between the $\overline{\cos \theta^*}$
 157 and ϕ . We have shown that non-linear relationship of $\overline{\cos \theta^*}$ behavior on ϕ arises because
 158 small particles coat the large particles.

159 For a given mixture, if ϕ of large particles is greater than ϕ_c , the contact angle behavior
 160 changes considerably as there is partial surface coverage of larger particles by the small (see
 161 Figure 3). However, if ϕ of large particles is less than or equal to ϕ_c then complete ‘full’

162 surface coverage of the larger particles by the small is achieved, so the mixture behaves entirely
163 as though it had the properties of small particles.



164
165 **Figure 3. The normalized wetting parameter profiles of mixtures with volume fraction of large**
166 **particles, ϕ , predicted from Equation 14 with the critical surface coverage volume fraction of large**
167 **particles, ϕ_c , in the range of 0.1 - 0.9, in increments of 0.1.**

168 Conceptually, Equation 14 is a simple geometrical model that relates the available surface
169 fraction to the underlying bulk volume fractions of the components. This geometrical model
170 depends only on the ratio of particle sizes, which in turn can be described by a ϕ_c at which
171 complete surface coverage of the larger particles by the small is achieved. This approach allows
172 that particles rearrange in 3D (prior, in this case, to being formed into a smooth solid surface),
173 because upon mixing small particles coat larger particles which is in contrast to Cassie-Baxter
174 theory that assumes that the “particles” (actually fibres) lie on the surface. We describe here a
175 series of experiments to test the existing Cassie-Baxter theory and the proposed surface
176 coverage theory described above (for predicting contact angle behaviour of surfaces formed

177 from particulate mixtures). These experiments are intended to introduce a new contention,
 178 relating surface coverage to wetting behaviour.

179 **4. Experiments**

180 Single liquid droplet experiments were conducted to measure the θ^* on the solid surface.
 181 The solid surface was comprised of a wide range of hydrophilic and hydrophobic particles
 182 given in Table 1.

183 **Table 1: Properties of hydrophilic and hydrophobic particles**

Primary Particles	Supplier(s)	True Density¹ (kg/m³)	Sauter mean diameter, d_{3,2} (µm)	Measured θ^{*2} (°)
Micronized Lactose	DFE Pharma	1530	1.2	45
Lactose 100M	DFE Pharma	1150	4.5	20
Lactose 200M	DFE Pharma	1540	22	22
Lactose 350M	DFE Pharma	1390	6.0	35
Calcium Carbonate	Bernegger GmbH	2700-2900	6.5	98
Ethyl cellulose (sieved)	Dow chemical company	1130	6.2	90
Magnesium Stearate	Ligamed	1140	2.5	120
Stearic Acid (sieved)	Merck	0.2980	2.7	105

184 To prepare the solid surface, the two-component hydrophilic and hydrophobic mixtures
 185 given in Table 2 were pre-mixed in a Roto Junior mixer (Zanchetta). For all two-component
 186 mixtures, the different particle densities of the primary powders were accounted for so as to
 187 maintain the same overall volume of the solid in the batch. Powder compacts were then
 188 prepared using a 3300 single column universal system (Instron) at the rate of 1 mm/s until a
 189 cut off load of 450 N (0.64 MPa) is achieved. In this manner powder compacts of diameter 30

¹ True density values were obtained from the suppliers

² Contact angle values measures using liquid binder 1.0 wt.%

190 mm were produced. The porosity was reported to be approximately ~35-40 % for each compact
 191 formed under these conditions [3]. Analysis was carried out using powder compacts in order
 192 to produce powder beds of more ‘regular’ structure to allow a comparative study and ultimately
 193 make sure that results observed can be attributed to wetting effects as opposed to these effects
 194 acting in combination with internal macrovoids [17].

195 **Table 2: Two-component mixtures used**

Primary Particles	Particle Description	Mixture	Reference
Lactose 200M Magnesium Stearate	Large Hydrophilic/ Small Hydrophobic	M-1	[3]
Lactose 200M Stearic Acid	Large Hydrophilic/ Small Hydrophobic	M-2	Present work
Micronized Lactose Ethyl Cellulose	Small Hydrophilic/ Large Hydrophobic	M-3	Present work
Lactose 350M Calcium Carbonate	Small Hydrophilic/ Large Hydrophobic	M-4	Present work
Lactose 100M Ethyl cellulose	Small Hydrophilic/ Large Hydrophobic	M-5	Present work
Microcrystalline Cellulose Phenacetin	Large Hydrophilic/ Small Hydrophobic	M-6	[22]
Limestone Tea	Small Hydrophilic/ Large Hydrophobic	M-7	[19]
Di-calcium phosphate dihydrate	Similar size Hydrophilic/ Hydrophobic	M-8	[21]
Jet milled Aspirin Glass Beads	Similar size Hydrophilic/Hydrophobic	M-9	[23]

196 Particle size analysis was carried out before and after compaction of the primary powders
 197 using laser diffraction (Malvern Mastersizer 2000). Similar results were obtained for the
 198 particle size before and after compaction (original particles recovered) as the powders were
 199 compressed under slight compression, producing weak powder compacts, thus suggesting that
 200 there was minimal deformation in the points of contact between the particles, however if
 201 deformation did exist, it is very minimal that the shape of the particles was only slightly
 202 affected.

203 The liquid binder was comprised of Hypromellose (Pharmacoat) (Shin-Etsu) as three
 204 solutions: 1.0 wt.%, 2.5 wt.%, 5 wt.% prepared by dissolving the solid binder in water at 25 °C
 205 under constant agitation. To these solutions the soluble component, (10 g/100 ml) was added
 206 to make saturated solution in order minimise dissolution during experiments. The liquid binder
 207 viscosity and interfacial tension were measured using a rotational rheometer (Malvern) and
 208 Wilhelmy plate tensiometer (Kilbron) respectively. A summary of the liquid binder properties
 209 is given in Table 3. The effect of the concentration of the liquid binder is investigated on the
 210 contact angle behavior as in the pharmaceutical industry viscosity is a critical parameter as it
 211 determines the strength of the liquid bridge between the particles which affects the resultant
 212 granule and final tablet properties.

213

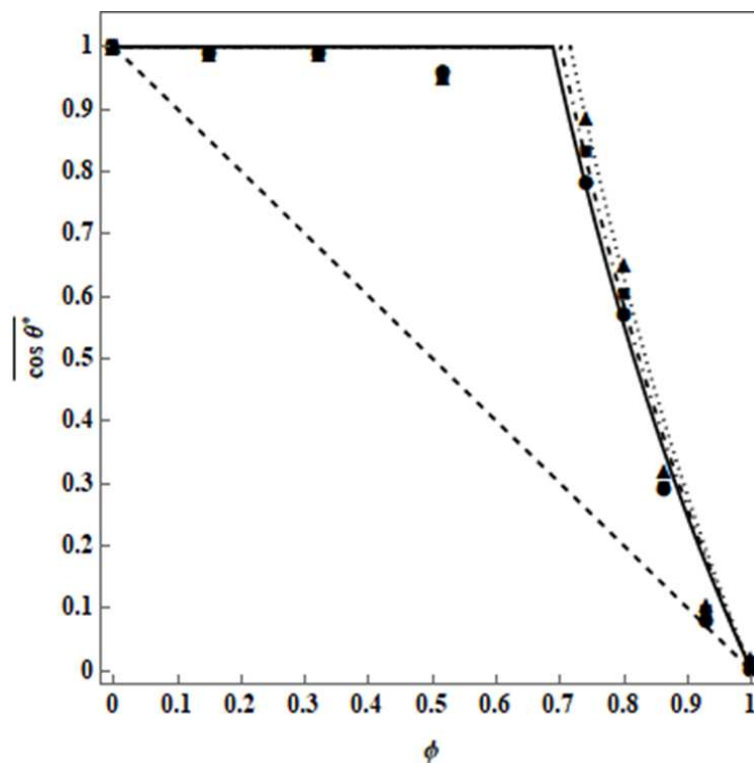
Table 3: Properties of the liquid droplets

Binder	Concentration (wt.%)	Viscosity (mPa · s)	Surface Tension (mN/m)	Droplet volume (µl)
Hypromellose	1.0	3.67±0.08	44±1.40	15
	2.5	6.10±0.12	46±0.70	
	5.0	13.17±0.15	44±0.67	

214 The contact angle measurements of the binary mixtures were then measured by a sessile
 215 drop method First Ten Angstroms FTA 125 goniometer [19]. The sessile drop method was
 216 used to measure the contact angle by using a video camera positioned from the side, adjusting
 217 the lighting to obtain good contrast between the droplet and the background [20]. The liquid
 218 binder droplets of 15 µl were slowly deposited from an electronic pipette onto the solid surface
 219 at 25 °C and the maximum θ^* formed between the liquid droplet and the solid surface was
 220 captured using a camera (Photron) and determined directly using image analysis. The
 221 maximum θ^* is the “advancing” contact angle. The contact angle values reported here are
 222 average of 10 measurements which were taken from different areas of the solid surface.
 223 Analysis is further extended to experimental data reported in the literature which focuses on
 224 two-component particulate mixtures.

225 **5. Results and Discussion**

226 Initial experiments were conducted to assess the dependence of contact angle on binder
 227 concentration. Figure 4 shows the effect of binder concentration on the $\overline{\cos \theta^*}$ vs ϕ profiles for
 228 the particulate mixture M1. Here, Cassie-Baxter Equation 3 and surface coverage wetting
 229 model Equation 14 are fitted to the $\overline{\cos \theta^*}$ vs ϕ profiles and the fitted parameters are given in
 230 Table 4. The surface coverage model provides for an abrupt transition in $\overline{\cos \theta^*}$.



231

232 **Figure 4. Effect of liquid binder concentration on the relationship between $\overline{\cos \theta^*}$ and ϕ for mixture**
 233 **M-1. The symbols correspond to the measured $\overline{\cos \theta^*}$ for \bullet 1.0 wt.%, \blacksquare 2.0 wt.% and \blacktriangle 5.0 wt.%**
 234 **binder. The solid, dot-dashed and dashed (tiny) line correspond to the fitted data of Equation 14. The**
 235 **dashed line corresponds to the expected Cassie-Baxter relationship Equation 3.**

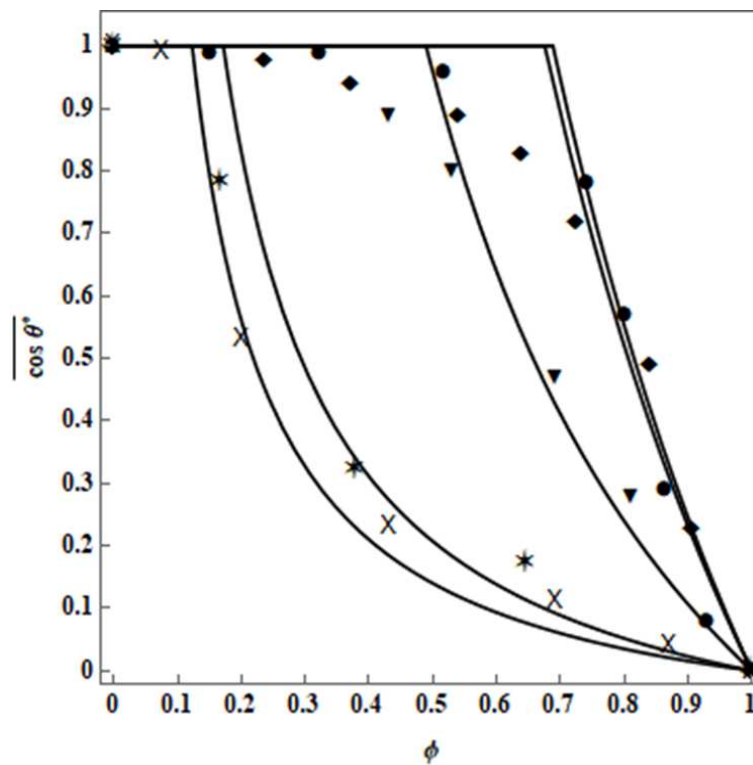
236 We see from Figure 4 that as ϕ decreases, there is a corresponding increase in the values of
 237 $\overline{\cos \theta^*}$ as small particles coat the large particles until ϕ_c is reached and the large particles are
 238 fully coated and the contact angle is constant at the value of the small particles. We observe
 239 essentially identical characteristics in $\overline{\cos \theta^*}$ behaviour when the liquid binder concentration is

240 changed, see Figure 4 and Table 4. That is, changing the liquid binder concentration has little
 241 effect on the $\overline{\cos \theta^*}$ profile, despite substantial changes in viscosity because the surface tensions
 242 associated with the liquid change little, see Table 3.

243 **Table 4: The fitted parameters for two-component mixture M-1.**

Liquid binder concentration (wt.%)	1.0	2.5	5.0	Global Fitting
Φ_c	0.688	0.699	0.715	0.702
Standard Error	0.0082	0.0085	0.0077	0.005
t-statistic	83.44	82.92	93.22	140
P-value	4.75×10^{-13}	4.99×10^{-13}	1.96×10^{-13}	5.72×10^{-39}

244



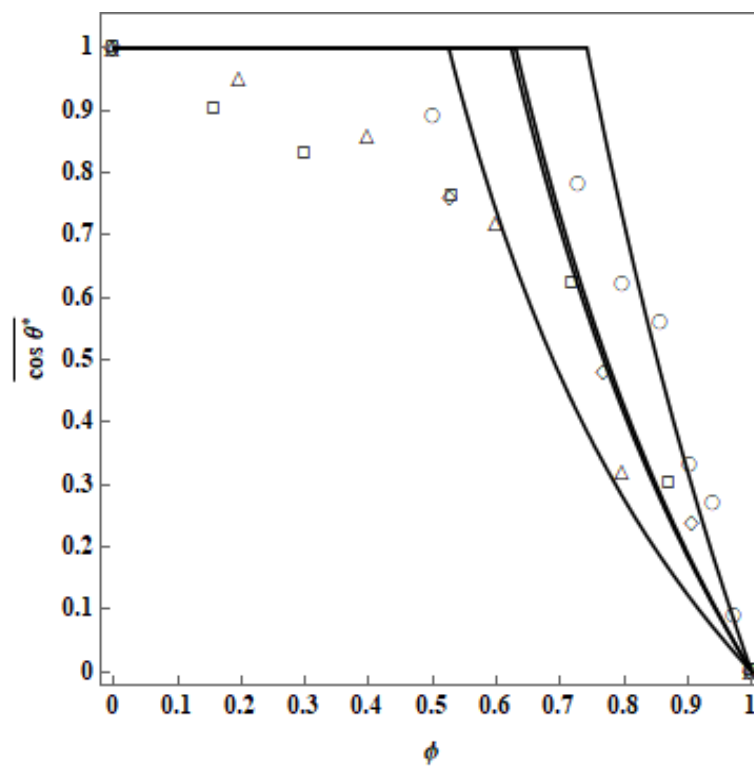
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246 **Figure 5. Effect of particle size on the relationship between $\overline{\cos \theta^*}$ and ϕ for mixture M-1 (●), M-2**
 247 **(▴), M-3 (◻) M-4 (○), and M-5 (×) . The solid lines correspond to the fitted data of Equation 14.**

248 The $\overline{\cos \theta^*}$ behaviour observed is in agreement with the implications from the surface
 249 coverage wetting model Equation 14, where $\overline{\cos \theta^*}$ behaviour is expected to increase non-
 250 linearly as ϕ decreases, as small particles coat the large particles (see Table 6). The non-linear
 251 relationship observed between $\overline{\cos \theta^*}$ versus ϕ does not follow the trend expected from the

252 Cassie-Baxter Equation 3. In each case, Equation 14 gives an excellent prediction of $\overline{\cos \theta^*}$
253 behaviour.

254 Figure 5 shows the effect of primary particle size on the $\overline{\cos \theta^*}$ vs ϕ profiles for the different
255 mixtures. The effect of primary particle size on the $\overline{\cos \theta^*}$ vs ϕ profiles was also investigated
256 on a further four particulate mixture systems reported in literature, (see Figure 6). Here, Cassie-
257 Baxter Equation 3 and surface coverage wetting model Equation 14 are fitted to the $\overline{\cos \theta^*}$ vs
258 ϕ profiles and the fitted parameters are given in Table 5.



259


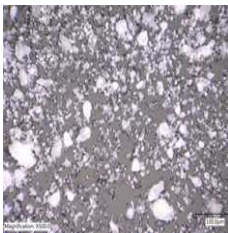

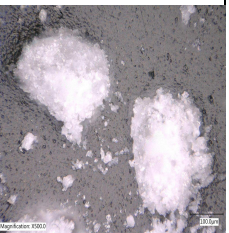
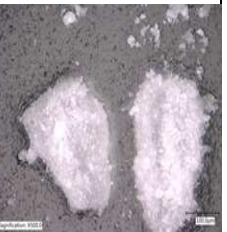
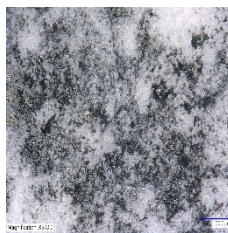
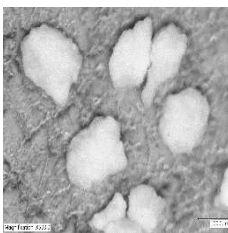
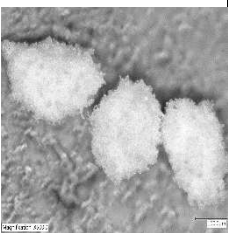
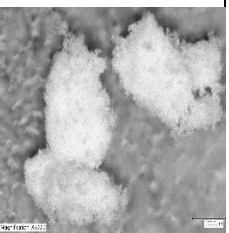
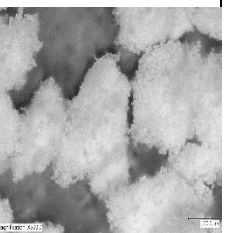

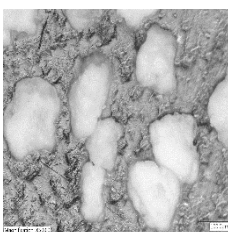

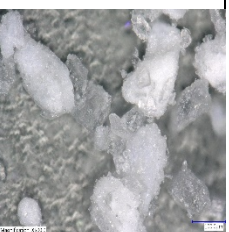

260 **Figure 6. Analysis of experimental data reported in literature for mixtures M-6 (\circ), M-7 (\square), M-8 (Δ),**
261 **M-9 (\square with dot). The solid lines correspond to the fitted data of Equation 14 and the dashed line correspond to**
262 **the expected Cassie-Baxter relationship.**

263 It is evident that changing the primary particle size, particularly the ratio of the particle size
264 of the two components, has a marked effect on $\overline{\cos \theta^*}$ behavior since it is this ratio that
265 determines the extent to which surface coverage of large particles by small particles is possible,
266 (see Figures 5-6 and Table 6).

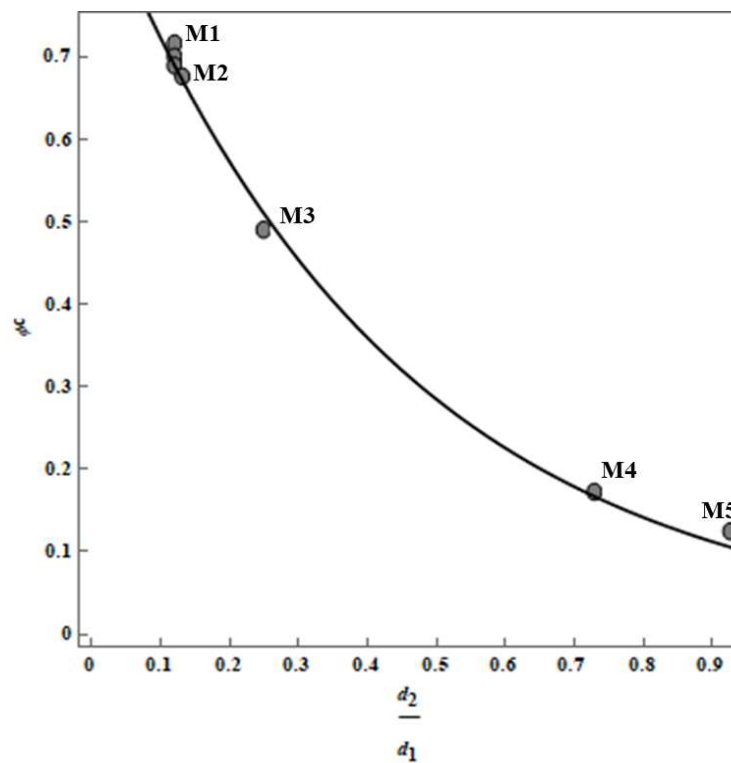
Table 5: The fitted parameters for various two-component mixtures.

Mixture	ϕ_c	Standard Error	t-statistic	P-value
M-2	0.675	0.02	31.98	9.95×10^{-10}
M-3	0.489	0.02	30.24	7.42×10^{-7}
M-4	0.171	0.05	3.81	1.89×10^{-2}
M-5	0.123	0.006	22.11	5.59×10^{-7}
M-6	0.742	0.02	34.77	5.12×10^{-10}
M-7	0.630	0.06	11.40	3.38×10^{-4}
M-8	0.623	0.044	14.05	8.11×10^{-6}
M-9	0.525	0.022	23.749	2.47×10^{-6}

Table 6. Microscopic images of particles

Lactose 200M particles	Magnesium Stearate particles	Binary Mixture (coated particles) [M1]		
				
Micronized Lactose particles	Ethyl Cellulose particles	Binary Mixture (coated particles) [M3]		
				
Lactose 100M particles	Ethyl Cellulose particles	Binary Mixture (coated particles) [M5]		
				

270 According to the surface coverage theory presented earlier, the critical volume fraction, ϕ_c ,
271 should depend only on the ration of the particle sizes in the two-component mixture via
272 Equation 10. In Figure 7 the fitted values of ϕ_c are shown as a function of size ratio, as in
273 Equation 10. It is apparent that the experimental data conform entirely to the theory. This
274 means that $\overline{\cos \theta^*}$ behavior can be predicted from the particle size ratio without conducting
275 extensive and expensive pharmaceutical research and development studies.



276

277 **Figure 7. Effect of particle size ratio of different mixtures on ϕ_c . The line is the result predicted,**
278 **without adjustable parameters, by Equation 10.**

279 In the pharmaceutical industry, mixtures consist of components with different particle sizes,
280 making surface coverage of one constituent over another inevitable, providing substantial
281 motivation for the present work (see Table 6). The authors are aware that small particles usually
282 agglomerate, and that the degree of dry coating of larger particles with smaller particles is
283 process dependent [14,16]. However, quantification of the agglomeration effect and the extent
284 of this influence is not within the scope of this study. In our experiments we have chosen to

285 work on compresses formed from the binary mixtures for reasons of accuracy of measurement,
286 rather than on loose powder beds as might be found at the point of binder addition in a
287 granulation process. Our contention is that the proposed relationship, based on surface
288 coverage of particles, will be useful in describing wetting of powder systems and in
289 understanding the significant deviations from the Cassie-Baxter relationship reported in many
290 publications. For potential future additional benefits, the surface coverage wetting model
291 presented here may be further enhanced by unifying it with the works of Cassie-Baxter as our
292 model required that any sort of particles will coat larger particles to a certain extent, whereas
293 some solids might not interact in this way.

294 **6. Conclusion**

295 This paper considers the dependence of wetting behaviour of surfaces formed from binary
296 mixture of particles having different sizes and wetting behaviours. Cassie and Baxter studied
297 systems in which the components were not free to rearrange and so the surface fraction of each
298 component was fixed and simple to determine. In seeking to apply their result to mixtures of
299 particles it has to be assumed that the surface fraction of each component is equal to the known
300 volume fraction; a situation that arises naturally if particles maintain a random spatial
301 distribution, but not if some process, such as surface coating, yields a non-random spatial
302 distribution.

303 In contrast, we propose that if the particles differ in size, it is possible for the small particles
304 to coat the large particles, so reducing the available surface fraction of the large particles. In
305 this paper we propose a simple geometrical model that relates the available surface fraction to
306 the underlying bulk volume fractions of the components. This geometrical model depends only
307 on the ratio of particle sizes, which in turn can be described by a critical component volume
308 fraction at which full coverage of the larger particles by the small is achieved. We observe that

309 with this correction, we are able to describe the wetting of two-component
 310 hydrophobic/hydrophilic systems using a range of binder solutions. We find that changing the
 311 binder concentration has little effect, despite substantial changes in viscosity.

312 By contrast, changing the size of the solid phase particles, and particularly the ratio of sizes
 313 of the two components, has a marked effect, since it is this ratio that determines the extent to
 314 which surface coverage of large particles by small is possible. Although many models that
 315 predict contact angle behaviour have been presented in literature, to the author's knowledge,
 316 this surface coverage wetting model represents the first quantitative model that predicts wetting
 317 based on surface coverage of one solid by another. The objective in developing this model is
 318 to enable a simple approach to theoretical prediction, which is expected to be of value in
 319 particle wetting applications pertaining to various industries. This is especially so in the
 320 pharmaceutical industry, where wetting knowledge of solid surfaces is important in
 321 formulation development, to enable effective design of product that achieves the desired
 322 properties.

323 **Nomenclature**

324 **Greek**

Symbol	Meaning
d	Sauter mean diameter
f	Area fraction of components
f_{sc}	Fractional surface coverage of large particles by small particle
p_2	Projected area of small particles
s_1	Surface area of larger particles
θ	Liquid-solid contact angle
θ^*	Apparent contact angle
$\overline{\cos \theta^*}$	Normalized wetting parameter
ϕ	Volume fraction of larger particles
ϕ_1, ϕ_2	Volume fraction of particle types 1 and 2
ϕ_c	Critical volume fraction
γ	Surface tension

325

326 **Subscripts**

Symbol	Meaning
1	Of particle type 1, the larger particle
2	Of particle type 2, the smaller particle
<i>E</i>	Equilibrium
<i>S</i>	Solid
<i>L</i>	Liquid
<i>V</i>	Vapour

327

328 7. **Acknowledgement**

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