Cracking in coatings from colloidal dispersions
An industrial perspective

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Overview

- Acknowledgements
- Introduction to “mud-cracking”
- Why is AkzoNobel concerned with cracking?
- Cracking development during drying
- Theoretical considerations of cracking
- Drying stress
- Influence of drying rate
- Influence of specific surface area
- Particle blends
- Conclusions
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Gerrards Cross village pond circa 1960

Gerrards Cross village pond
Summer 2006
Sahara desert – photo taken during 2007 Marathon De Sables
Why is AkzoNobel concerned with cracking?
Why is AkzoNobel concerned with cracking?

- Significant proportion of AN’s business is within the coatings sector
- Cracking restricts the available formulation space

- Cracking specifically becomes an issue as we;
  - Drive cost reduction whilst maintaining performance
  - Reformulate to meet legislative drive for VOC reduction
  - Reduce binder levels to increase “sustainability”

- Cracking impacts upon product performance;
  - Aesthetic appearance of decorative paints
  - Mechanical properties and integrity
  - Transport/barrier properties in general
Why is AkzoNobel concerned with cracking?

When it all goes wrong...........
Why is AkzoNobel concerned with cracking?

More typical examples of the problems caused by cracking:

- Cracking of conductive tracks produced by printing dispersions of silver nano-particles.
- Curling of a flexible substrate induced by drying stress.
- Cracking in decorative paints.
Restriction of the available formulation space

Consider the role of VOC’s in waterborne paints

Latex film formation process

- Good film properties depend upon latex coalescence
- Latex coalescence depends upon polymer $T_g < T_{amb}$

Polymer latex dispersion

Drying and ordering

$T_{amb} < T_g$
No film formation

$T_{amb} > T_g$
Film formation
Restriction of the available formulation space

Polymer $T_g$ is reduced by added VOC’s (volatile plasticisers)
Loss of VOC’s post film formation to regain $T_g$

“Soft” polymer phase helps to control the drying stresses
Why is AkzoNobel concerned with cracking?

- Removing VOC’s from w/b paints introduces several challenges
- Not least of which is controlling the cracking
- Using a softer polymer is not an option in most applications
  - Introduces blocking/dirt pick up issues
- Legislative pressure to reduce solvents within paints (2007/2010)
- Routes to low and zero solvent containing paints have to maintain the property balance whilst addressing the cracking
Why is AkzoNobel concerned with cracking?

• Sustainability has become a key driver in many business sectors

• Decorative paints is no exception

• Removal of solvents is just one aspect of this driver

• Sustainability forces one to consider the whole supply chain
Why is AkzoNobel concerned with cracking?

Relative contribution to the carbon footprint of the components in a typical matt paint

- The latex forms a significant part of the embodied carbon in a can of paint.
- It also consumes “non-renewable” petrochemicals feedstock.
- Reducing latex levels in paints makes a positive contribution to “sustainability.”
- However, it will also compromise the ability of the paint to resist cracking.
Our approach

Which means…

• We are on a journey and we are serious about it
• Open and honest approach
• With Integrity
Summary

• Cracking imposes restrictions on our formulation space
• It limits our ability to formulate solvent-free, more sustainable and cheaper products

• Developing a comprehensive understanding of the factors that control and govern cracking is important for the realisation of next generation products
• A critical step in this journey is to understand how the individual components contribute to crack behaviour
Cracking development during drying
Cracking development during drying

Drying and cracking of an aqueous pyrogenic silica dispersion
How cracking develops

MMA/EHA latex: $T_g = 45 \, ^\circ\text{C}$ with a wet film thickness of 400µm

j. After 66min
Drying forms a random close packed dispersion of particles. Capillary pressure compresses the particle network causing densification.

Drying forms a flocculated network of particles. Particle network strength is greater than the compressive stress induced by capillary pressure and a porous coating results.
Typically observe 3 “discreet” regions during drying

A critical observation is that the cracks run into the “wet” region.
In some systems a trace of particles is left at the initial cracking point. This allows an estimate of the volume shrinkage after cracking. In stable systems this typically equates to around 20-30vol%.
Cracking development during drying

Drying and cracking of an aqueous latex dispersion (T_g ~30°C)
These images provide insight into how cracks first develop:

Cracks open up from the top of the coating to the bottom.

It is necessary for a network to exist for crack propagation.
Critical cracking thickness (CCT)

For any given formulation that is prone to cracking there will be a coat thickness below which no cracking is observed.

Microscope images of dried films of a high $T_g$ latex

Below critical coat thickness

Above critical coat thickness

Much of our work has concentrated on understanding on how to maximise the CCT.
Critical cracking thickness – Syloid silica
Summary

• Both inorganic and “hard” organic particulate dispersions are prone to cracking

• Crack propagation appears to follow the drying fronts within a coating

• Cracks run from the dry region into the saturated, networked region of the coating

• For any given colloidal dispersion there is a breakpoint with increasing coating thickness from crack free to cracked – the so called critical cracking thickness
Theoretical considerations of cracking
The capillary pressure puts the particle network into compression and therefore the liquid into tension – it is this that causes the coating to crack.

The capillary pressure arises due to dewetting of the particles by the liquid – this generates a negative pressure in the fluid.

For soft particles, e.g. low $T_g$ polymer latices, it is the capillary pressure that causes particle deformation and closure of voids within the coating.

\[ P_{cap} = \frac{\Sigma \gamma \cos \theta \phi}{(1 - \phi)} \]

$\Sigma$ = surface area/unit volume of solid
$\gamma$ = surface tension
$\theta$ = contact angle
$\phi$ = particle volume fraction

Influence of particle size on $P_{cap}$

<table>
<thead>
<tr>
<th>Particle radius</th>
<th>$P_{cap}$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 µm</td>
<td>1</td>
</tr>
<tr>
<td>100 nm</td>
<td>10</td>
</tr>
<tr>
<td>10 nm</td>
<td>100</td>
</tr>
</tbody>
</table>

approx. maximum capillary pressure at $\phi = 0.64$ for monodisperse spheres in water
Cracking style and critical cracking thickness

The balance of capillary pressure, particle network strength and substrate affinity determine the cracking style and critical cracking thickness.

The above considerations determine when and how the solid phase “sets up” and begins to support stress elastically, especially in a flocculated system.

How does a system resist the imposed shrinkage strain due to drying?
Griffiths fracture criterion

- From the available data (see later);

\[ CCT \propto P_{\text{cap}}^{-1.8} \propto \Sigma^{-1.8} \]

- If we were dealing with a linear, elastic solid film then the usual way of explaining this relationship would be to balance the elastic energy release rate with the rate of increase in surface energy.

- Doing so gives an exponent of -2.

- We, however, are dealing with a wet film comprising particles.

- The case of a porous film comprising deformable particles has been considered by Russel & Tirumkudulu who find an exponent of -1.5.
Theoretical considerations of cracking

- Tirumkudulu et al. have gone on to derive a relationship to describe the CCT
- For hard particles this critical thickness is dependent upon;
  - the shear modulus of the particles (G)
  - the maximum capillary pressure (-P_{max})
  - the solvent-air interfacial tension
  - the co-ordination number (M)
  - the particle volume fraction (\(\Phi_{rcp}\)) and particle size (R)

\[
CCT = 0.64 \left[ \frac{GM\Phi_{rcp}R^3}{2\gamma} \right]^{1/2} \left[ \frac{2\gamma}{(-P_{max})R} \right]^{3/2}
\]

Critical Cracking Thickness regimes

\[ h = h_{rcp} \phi_{rcp} \]

\[ \frac{28}{3} \frac{(-P_{sv})}{M G \phi_{rcp}} > 1 - \phi_{rcp} \]

\[ \frac{28}{3} \frac{(-P_{sv})}{M G \phi_{rcp}} < 1 - \phi_{rcp} \]

Shear Modulus, \( G \)


Rideal – Cracking 20th April 2009
Summary

- The theory of cracking during drying of particulate dispersions has made great strides over the past decade or so.
- Ultimately it is the capillary pressure generated during the drying that is responsible for cracking.
- How the capillary pressure is balanced against the particle network strength and the affinity of the coating for the substrate will determine if and how the coating will crack.
- The problem can be addressed by Griffiths fracture criterion which suggests a correlation between the capillary pressure and the coating thickness at which cracking is observed.
- Recent theory developments suggest approaches that might be taken to reduce or eliminate cracking in coatings.
Drying stress
Drying stress

- Stress is caused by **dimensional changes** occurring within the coating as it is **losing volume** and becoming **anchored to the substrate**
- Measuring the **instantaneous drying stress** within a coating has been tackled by cantilever beam methods
- Due to inhomogeneous drying, driven by edge drying, what is measured is an averaged drying stress
- Coupled with gravimetric data such measurements can provide insight into **stress growth** and **relaxation** processes and the factors that influence them
Drying stress

Drying stress

Drying

Film/network strength

Drying stress
Drying stress

Crossover
⇒ CRACKING

Film/network strength
Drying stress
Measuring the drying stress
Measuring the drying stress
Measuring the drying stress

For many commercial materials the starting solids is such that stress begins to accumulate as soon as drying begins. From theory, we can now consider strategies to influence different parts of the drying stress profile.
Managing the drying stress

Magnitude of the stress

Impact of formulation components

- Larger particle size/lower SSA
- Thin coatings
- Low surface tension
- Gel the continuous phase
- Soft particles (low Tg)
- Volatile plasticisers
Managing the drying stress

Timing of the stress development

Impact of “open time”

1. Slow drying
   a) Humectants
   b) Cosolvents
2. Improve mobility vs. solids
   a) Particle packing
Managing the drying stress

Retained stress

Drying stress

Drying time

Stress relaxation
- Coating modulus
- Film formation
- Cracking
Managing the drying stress

Many paints possess a high level of “retained” stress after drying. However, it is possible to manage this stress to improve service life.
Summary

• Drying stress generated by the capillary pressure during drying can be measured by cantilever bending tests.

• These measurements, whilst not absolute, do provide insight into the dynamics of drying and stress rise.

• Most, if not all, industrial/commercial materials are “high solids” materials and as such typically begin to develop drying stress immediately upon application.

• Compressional rheology measurements can also provide insights into network consolidation and strength under drying/dewatering.
Taking stock.....

- Particulate networks are put under compression during drying by capillary forces.
- The capillary forces are balanced against the yield stress of the concentrating particle network.
- Consolidation during drying strengthens the particle network.
- If the yield stress of the network is greater than the maximum capillary pressure then liquid recedes into packed particle network.
- Alternatively the coating cracks under the transverse stresses caused by shrinkage strain imposed by the pinning of the coating to the substrate.
Taking stock…..

- Theory suggests coating cracking should depend on;
  - Capillary pressure
    - Specific surface area, surface tension, volume fraction and contact angle
  - Coating thickness
  - Wetting of the substrate
  - Evaporation rate
  - Particle deformability ($T_g$) & shear modulus
- How well do these guidelines predict the behaviour of industrial systems?
Influence of drying rate
Influence of drying rate

Latex with following properties

- Particle size: 200nm
- Polymer T<sub>g</sub>: 17°C
- MFFT: 15°C
- CCT*: 10µm

150µm coating – after 50mins drying time
Time for complete drying – 70mins

*20°C/50% RH
Influence of drying rate

Despite a CCT of only 10µm, it is possible to produce thick, crack free coatings – if you are willing to wait long enough.

Faster drying results in increased propensities to cracking.
Slower drying influences network strength development during consolidation.
e.g. Timeframe for visco-elastic response of latex particles.
Influence of drying rate

As latex particle size is reduced there is a greater influence of drying rate. SEM images reveal greater porosity in fast dried coatings.
Influence of drying rate

Particle packing is highly ordered – unusual triangular symmetry
HCP interrupted with regions of random packing
Triangular patterns are due to highly ordered packing.

Influence of drying rate

Courtesy of Mervyn Shannon Intertek MSG
Influence of drying rate

AFM images of the surface of fast dried coatings

Particle packing is still ordered – but less so than in the slow dry case.
Grain boundaries/possible Bernard cell structure visible
Such small differences in the network order influence the CCT
Influence of specific surface area (SSA)
Influence of specific surface area

- The SSA influences the maximum attainable capillary pressure
- Particle size itself shows a poor correlation with the CCT
- Surface roughness/internal porosity contribute to the capillary pressure

- We have measured the CCT for a wide range of inorganic and organic particles
Styles of cracking for various inorganics

Colloid silica

Titanium dioxide

Calcined kaolin

Rideal – Cracking 20th April 2009
Styles of cracking for various inorganics

- Indium tin oxide
- Mica
- Yellow oxide
Styles of cracking for various inorganics

Kaolin
Influence of specific surface area

All of this data is based upon stable dispersions without added binder.
Crack-free binderless coatings are possible – of limited use.
Influence of specific surface area

The SSA is the dominant factor – particle shape is a secondary influence.
Many pigments have CCT’s below the typical thickness of decorative paints. Necessitates formulation with lower SSA extenders and film forming latices.
The role of SSA still holds true for latices. However, we have a narrower experimental range available to us. Polymeric particles are more prone to cracking than the inorganic materials. This is due to the lower inherent modulus of the (non-film forming) polymeric materials.
Summary

• Out of all the factors we have studied by far the greatest to influence cracking behaviour is the particle SSA.
• For hard particles it has an over-riding effect on the CCT.
• The CCT shows a remarkable correlation with SSA over a wide experimental space.
• Other factors such as drying mechanism and particle shape are secondary.
• This makes the SSA a valuable tool for formulators in industry.
• Directs the choice of particle to maximise the CCT.
• Useful if particle function isn’t related to SSA.
Particle blends
Particle blends

- What we have reviewed so far only covers model systems comprised of single particle types
- Obviously for industry this is far removed from reality
- Do the same formulating rules and guidelines apply when we start to blend particles?
- Does the capillary pressure generated by the smaller particles dominate the cracking behaviour?

- We have considered inorganic/inorganic particle blends and then hard/soft polymer latex blends
Particle blends

Generally blends of inorganic particles results in intermediate behaviour. The CCT can be predicted by averaging the SSA of individual particles. However in some cases particle segregation can cause one SSA to dominate.
• Blends of greatly different particle sizes can lead to greater packing efficiencies

• E.g. the well known “Farris effect” can be used to reduce the viscosity of formulations at equivalent volume fraction

• The theory relies upon blending large/small with size ratios of >6:1 and in volume ratios of ~70:30

- 2nd, 3rd generational packing
- Increasing number of particle-particle contacts
- Increasing network “strength”
- Increased resistance to cracking
Excess of small particles leads to lower than expected CCT. However, there is a “sweet spot” with higher than expected CCT. This comes from efficient packing of the small/large particles.
For latices the polymer $T_g$ has an over-riding influence on crack behaviour.

As the coating temperature approaches the polymer $T_g$ the CCT tends to infinity.

Below the $T_g$, the SSA of the latex dominates the CCT.

What happens if we blend soft latex with hard latex?
- Mimic of filler inclusion in film forming latex.

How is the CCT affected?
- Latices with $T_g$’s of 15°C and 60°C (same particle size of 128nm) blended in various ratios & CCT measured at 25°C.
### Hard/soft latex blends

<table>
<thead>
<tr>
<th>Blend (soft:hard)</th>
<th>CCT (µm)</th>
<th>$T_g$ (°C measured/Fox)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>None</td>
<td>15</td>
</tr>
<tr>
<td>75:25</td>
<td>None</td>
<td>25</td>
</tr>
<tr>
<td>50:50</td>
<td>6</td>
<td>35</td>
</tr>
<tr>
<td>25:75</td>
<td>6</td>
<td>45</td>
</tr>
<tr>
<td>0:100</td>
<td>6</td>
<td>60</td>
</tr>
</tbody>
</table>

When coated at 25°C the soft latex doesn’t exhibit any cracking.

Cracking only occurs when the level of hard latex reaches 50wt%.

There is no correlation of CCT with predicted $T_g$ for the blends.
Despite no change in CCT the crack spacing changes
Hard/soft latex blends

Once the hard phase percolates a CCT is observed
Summary

• Systems consisting of more than one particle can exhibit a range of cracking behaviours

• In the simplest case the CCT can be predicted by the averaged SSA of the individual components

• However it is often the case that particle segregation, stratification and percolation thresholds influence the cracking behaviour making it more difficult to predict

• Prediction in such systems relies on an understanding of the final film morphology and any heterogeneities
Conclusions
Where have we got to?

- Current trends in legislation and private & public sentiment are driving formulators down paths that lead to cracking.
- Industry has to address these needs without compromising other coating properties and profitability.

Dulux

30% Lower Carbon Footprint*

*As compared to Dulux Matt 2008 formulation, to find out how we have calculated the reductions, visit www.dulux.co.uk/environment.
Where have we got to?

• Significant advances have been made in the last decade regarding the factors that control and influence the cracking upon drying of colloidal dispersions

• It is the capillary pressure generated during the drying of particulate dispersions that is responsible for the stresses that cause cracking

• The over-riding contribution to the capillary pressure is the specific surface area of the particles

• The simplest handle a formulator has control over when facing a mud-cracking problem is the SSA of the component particles
Where have we got to?

- A critical coating thickness exists for colloidal coatings – this represents a transition point between crack-free and cracked coatings.
- The CCT correlates with the SSA over a wide experimental space, particularly for inorganic particles.
- The mechanism of drying and cracking does not seem to influence this correlation.
- A robust predictive model exists to describe the CCT of both inorganic and polymeric hard particles.
Where have we got to?

- Polymer latex particles only exhibit cracking during drying if the polymer $T_g$ is higher than the coating temperature.
- Film forming latices do not crack – the drying stress is relaxed by the deformation of the polymer particles.
- The shear modulus of the particles influences the CCT, such that polymer particles are more sensitive to cracking than hard inorganic particles.
- The drying rate does have a role to play in defining the cracking behaviour, particularly for polymer latices, however commercial exploitation of this effect is limited.
Where have we got to?

- Blending of particles introduces further complexities.
- For many hard particle mixtures the CCT can be predicted from the average SSA of the particle mix.
- For hard/soft particle mixtures, it is the percolating phase that defines the CCT behaviour, although the crack spacing may change irrespective of the CCT.
- However in both cases segregation of the particles, or structuring of the particles can have either a positive or negative effect on the CCT.
- Controlling the film morphology to control the cracking behaviour is an area that offers potential.
What remains to be done?

• Our understanding of blends and mixtures is beginning to grow but there is a lot of ground to cover

• In particular we currently have a limited understanding of the critical factors when hard particles are blended with a binder

• The binder introduces a number of other variables;
  • E.g. Overall modulus of the coating, drying kinetics
  • Viscosity vs. solids profile, coating morphology
  • Mechanism of drying stress relaxation

• The interplay of these factors means that the role of the binder is not simple but also means that there are several handles we can turn
What remains to be done?

- Most - but not all - of the work in this field has been concerned with stable dispersions
- Flocculation changes the co-ordination number, final volume fraction and network strength
- Thus we would expect flocculation to have a significant influence on the cracking behaviour
- Tirumkudulu et al. have shown that the CCT of flocculated systems can be predicted using the current models
- This learning needs to be assimilated by industry
Finally…how do you avoid cracking?

• Soft particles - low $T_g$ polymers, volatile plasticisers
• Dry slowly – low boiling co-solvents, humectants
• Larger particle size/lower SSA
• Low surface tension
• Thin coatings

• Strengthen the particle network
• Controlled particle blending

Alternatively we need to educate our customers to appreciate the beauty of cracking