Radiation Curable Additives
Enabling Excellent Paint Surfaces

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When and why do we need additives?

- Introduction
- Leveling and Flow
- Foam
- Rheology
When and why do we need additives?

- **Introduction**
- Leveling and Flow
- Foam
- Rheology
When and why do we need additives?

- Defects in the paint film are deviations in evenness and uniform smoothness of the paint surface and are judged to be an indication of an imperfect coating process.

- Most defects are related to surface tension phenomena, which arise in a liquid because the forces in the air/liquid interface differ from those inside the liquid phase. To prevent or reduce such defects, flow and leveling additives are used.

- Examples of defects: orange peel, brush marks, peaks, craters, fish eyes, and pinholes.

MODAFLOW®, CYCAT®, ADDITOL®
Surface tension effects drive two different mechanisms of flow:

1. To minimize the surface area of a liquid;
2. To minimize the surface tension differential (or surface tension gradient) to cover areas/liquids of high surface tension with lower ones.

Observation:
Besides Surface Tension Differential, flow and leveling are influenced also by the following factors:

- Surface Roughness of the Substrate
- Wet Film Thickness
- Rheological Behavior after Application
- Drying Time/Flash Off Time and Speed of Solvent Evaporation
Surface Tension - Concept

The concept of the surface energy can be more easily understood when looking to a liquid as an example. Atoms and molecules of the liquid may freely move in order to reach positions with lower potential energy (thermodynamics law). In other words, a “place” where the forces (attractive and repulsive) acting in all directions are in equilibrium. On the other hand the particles in the surface of the material experience only forces directed to the center of the liquid.

Due to this, the surfaces are always high energy regions. And precisely this difference between the energies on the surface and on the interior is called SURFACE TENSION.
When and why do we need additives?

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- **Leveling and Flow**
- Foam
- Rheology
Surface Tension - Substrate Wetting

Ideal - Substrate wetting: Substrate Surface Tension > Coating Surface Tension

Surface Tension in Radiation Curing

A challenge in radiation curing formulations when dealing with SURFACE TENSION comes from a often polar profile of the regularly used components, which leads to higher liquid surface tensions (or energies), impacting the leveling and mainly adhesion on some substrates.

This polarity is essentially determined by the type and number of functional groups. Polar groups, such as hydroxyl or carboxyl groups, increase the surface tension, while nonpolar groups, such as long alkyl chains, siloxanes, or (fluoro)alkyl groups, reduce it.

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbr.</th>
<th>F</th>
<th>Surface tension/mN/m (25 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>isobornyl acrylate</td>
<td>IBOA</td>
<td>1</td>
<td>32</td>
</tr>
<tr>
<td>isodecyl acrylate</td>
<td>IDA</td>
<td>1</td>
<td>29</td>
</tr>
<tr>
<td>octyl/decyl acrylate</td>
<td>ODA</td>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>hexanediol diacrylate</td>
<td>HDDA</td>
<td>2</td>
<td>36</td>
</tr>
<tr>
<td>dipropylene glycol diacrylate</td>
<td>DPGDA</td>
<td>2</td>
<td>35</td>
</tr>
<tr>
<td>tripropylene glycol diacrylate</td>
<td>TPGDA</td>
<td>2</td>
<td>34</td>
</tr>
<tr>
<td>trimethylolpropane triacrylate</td>
<td>TMPTA</td>
<td>3</td>
<td>38</td>
</tr>
</tbody>
</table>

[Table of Surface Energies of Untreated Polymers]

MODAFLOW®, CYCAT®, ADDITOL®
Defects

What happens in a non-ideal situation?
Defects

What happens in a non-ideal situation?

Example: Cratering

Low surface tension

High surface tension

Spraymist contamination

MODAFLOW®, CYCAT®, ADDITOL®
Fixing the Defects - Chemistries

- (Meth-) Acrylic copolymers
- Silicones
- Fluoro surfactants
(Meth-) Acrylic Copolymers

No surface tension reduction

\[
\begin{align*}
R^1 & = H \quad (\text{Acrylate}) \\
& \quad \text{CH}_3 \quad (\text{Methacrylate}) \\
R^2 & = \text{Alkyl} \\
& \quad \text{Polyester/Polyether} \\
& \quad \text{Salt} \\
& \quad \text{HO-functional} \\
& \quad \text{COOH-functional}
\end{align*}
\]
Silicones

Modes of action depends on

- Silicone backbone
- Modification
- Reactive / non reactive
- Dosage

MODAFLOW®, CYCAT®, ADDITOL®
Silicones

Polydimethylsiloxanes

\[ X = \begin{array}{cccc}
2 - 27 & 45 - 230 & 380 - 1500 & 1800 - 2900 \\
\text{Levelling} & \text{Slip} & \text{Defoaming} & \text{Special Effects}
\end{array} \]

\[ \begin{array}{c}
(\text{CH}_3)_3\text{Si} - \text{O} \\
\text{Si} - \text{O} \\
\text{CH}_3 \\
\end{array} \]

X

MODAFLOW®, CYCAT®, ADDITOL®
Silicones

Modifications

Reduction of surface tension and/or slip improvement

- Polyester
- Polyether
- Alkyl
- Reactive:
  - Acryl
  - COOH
  - OH

organic Modif.

CH₃
Si
O

CH₃
Si
O

CH₃
Si
O

Si(CH₃)₃

mN/m

CH₃  21
CH₂CH₃  26
(CH₂)₉CH₃  32

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Silicones and Interlayer Adhesion

Influence on interlayer adhesion

- Non thermostable Silicones
- Reactive Silicones
- Overdose

To ensure no influence on interlayer adhesion

- Low molecular weight silicones
- Modification (compatibility)
- Right dosage

Dosage

- 0.01%
- 0.1%
- 0.2%

Cure Temperature

- 130°C/27°F
- 150°C/30°F
- 170°C/34°F
Fluoro Surfactants

Nonionic / Ionic

Strong reduction of surface tension

Silicone vs. Fluoro Surfactants

PF — (EO)ₙ

- Decreased Foam Stabilisation
- Comparable Influence On Surface Tension

MODAFLOW®, CYCAT®, ADDITOL®
- Mobile polymer design for optimal dynamic surface tension reduction. Surface tension (< 22 mN/m)

- Comparable efficiency with Fluoro modified polymers.

- Low foam stabilization
- Strong anti-crater efficiency
- No influence on interlayer adhesion
When and why do we need additives?

- Introduction
- Leveling and Flow
- Foam
- Rheology
Incorporation of Air and Foam Generation

- Production
- Pumping and filtration
- Manipulation
- Application
- During lacquer manufacturing
- Application (airless/airmix)
- Chemical reaction (e.g. NCO/H₂O)
- Porous substrates

!! Stabilised by the use of surface active substances - Surfactants !!

In some radiation curing formulations, foam can be a critical factor. The viscosity and rheological patterns, as well as the application conditions including the cure speed, can result in a more stabilized foam in the paint. Conventional actions such as viscosity lowering, addition of co-solvents, and decreasing line speed, do not effectively collapse the foam. In this case, the use of additives are a very important part of the formulation.

MODAFLOW®, CYCAT®, ADDITOL®
Foam Generation - Stabilizing effects

- Gibbs elasticity
- Marangoni effect
- Electrostatic effects
- High surface viscosity

Air

Lamella

Air/Gas

Liquid

Hydrophobic

Hydrophilic

MODAFLOW®, CYCAT®, ADDITOL®
Foam Generation - Negative Impacts

- Blisters
- Pinholes
- Macro Foam

MODAFLOW®, CYCAT®, ADDITOL®
Foam Generation

Negative impacts

- Poor pigment grinding
- Increase of volume
- Blisters
- Pin holes
- Poor gloss

Reduction in film quality

Foam prevention or destruction by using Defoamer and Air-release Agents

MODAFLOW®, CYCAT®, ADDITOL®
**Defoamer**
- Org. modified silicones
- Silicone oils
- Aliph. / arom. Mineral oils
- Special polymers
- Fatty acid derivatives
- Silica
- Waxes

**Deaerator**
- Org. modified silicones
- Silicone oils
- Aliph. / arom. Mineral oils
- Special polymers
- Fatty acid derivatives

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**ADDITOL® VXL 4951N**
“Best in class” for Leveling/Defoaming on UV/EB formulations

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**MODAFLOW®, CYCAT®, ADDITOL®**
Defoaming and Air Release agents

Macrofoam

Interface

DEFOAMER

AIR-RELEASE AGENTS

Microfoam
Defoaming mechanism

Air

DEFOAMER

Lamella
Deaerating mechanism

Destabilising effect

Apolaric substance

MODAFLOW®, CYCAT®, ADDITOL®
Deaerating mechanism

Coalescence

Apolaric substance

\[ V \sim \frac{r^2}{\eta} \]
When and why do we need additives?

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Rheology is the study of the flow, or movement, of a substance in liquid form or solid under conditions where it exists a flow profile in stationary conditions under shear forces (e.g. agitation, roll application, spray gun pressure). The Rheological profile of a fluid impacts directly on its applicability, drying, leveling, gloss and substrate wetting.

* OBS.: Radiation curing formulations are 100% solids fluids with a flow profile.
Thickeners

Inorganic
- Montmorillonite
- Hectocrite
- Silica

Organic
- Water-Phase
  - Cellulose derivates
  - Starch derivates
  - Acrylic derivates

Associative Thickeners
- PUR - Thickener
- Associative acrylic thickeners
- Associative cellulose ethers

MODAFLOW®, CYCAT®, ADDITOL®
Associative Thickeners - Mechanism

ADDITOL® VXW 6360 / ADDITOL® VXW 6388
Conclusions

Additives play an important role on:

• Adjusting rheological profiles, leveling & flow parameters and breaking down the stabilized foam. Important characteristics in radiation curing coatings;

• Fixing defects and resolving deviations from the evenness and uniform smoothness of the paint surface, improving the final performance of the coating and optimizing the quality of the film leading to excellent finishes.
In early April 2013, Cytec Coating Resins became an Advent International portfolio company. Please visit us at www.mycoatingresins.com.