DOUBLE BOND CHEMICAL

UV Products
Introduction
一、UV Curing System
二、UV Monomers
三、UV Oligomers
四、UV Photoinitiators
五、UV Applications
一、UV Curing system
The Future Trend of Coating Development

- Low VOC (Volatile organic compound)
- Energy-Reduced
- High Production Efficiency
  - High-Solid
  - Water-Based
  - Powder Coating
  - Radiation Curable
Commercial Application Areas Using Radiation Curable Materials

- Coatings
- Printing Inks
- Adhesives
- Electronics and Communications Materials
- Plastics and Rubber Materials
The Main Components of UV Curable Coating

- Oligomers or Prepolymers
- Monomers or Reactive Diluents
- Photoinitiators (or Photosensitizers)
- Additives (or Waxes)
- Optional
  - Pigments (Dye)
  - Fillers - such as talc, etc.
  - Matting Agents (silica), etc.
The Main Components of UV Curable Coating

- **Photo-initiator**
  - Absorb actinic radiation & break form the primary reactive species, usually free radicals
  - Consumed in the reaction

- **Photo-sensitizer**
  - Absorb, then transfer energy to another molecule that forms a primary reactive species
  - Not consumed or structurally altered
  - May be regarded as a photo-catalyst
Comparison with Thermal Curing System

**UV Radiation Curing**
- Oligomers
- Monomers
- Additives
- Photoinitiators
- Fillers
- Etc.

**Thermal Curing**
- Resins (Polymers)
- Solvents or water
- Additives
- Curing Agents (Hardeners)
- Fillers
- Etc.
A Generalized Un-Pigmented Acrylate Based Formulation

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Parts by Weight, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligomers</td>
<td>30-50</td>
</tr>
<tr>
<td>Multi-functional monomers</td>
<td>10-30</td>
</tr>
<tr>
<td>Mono- or Di- functional monomers</td>
<td>10-40</td>
</tr>
<tr>
<td>Photoinitiators</td>
<td>0.5-20</td>
</tr>
<tr>
<td>Non-reactive specialty additives</td>
<td>1-20</td>
</tr>
<tr>
<td>Total</td>
<td>100 Base</td>
</tr>
</tbody>
</table>
There are four Curing Mechanisms of UV Coating Commercially Nowadays

- **Free Radical**
  - Unsaturated Polyester/Styrene
  - Thiol-polyene
  - Acrylate

- **Cationic**
  - Epoxy/Vinyl ether

The acrylate-based is the most successful and popular in the market place
The Photo-Reactivity of a General Unsaturated Function

- **Acrylate** > **Methacrylate** > **Vinyl** > **Allyl** > **Internal**

Acrylate

\[
\text{O} \quad \bigg| \\
\text{R-O-C-CH=CH}_2
\]

Methacrylate

\[
\text{O} \quad \text{CH}_3 \\
\text{R-O-C-C=CH}_2
\]

Allyl

\[
\text{R-CH}_2\text{-CH=CH}_2
\]

Vinyl

\[
\text{R-CH=CH}_2
\]

Internal

\[
\text{R-CH=CH-R’}
\]
The Chemical Structure of a General Acrylate-Based Oligomer

\[
\text{CH}_2=\text{CH-}\text{C-O} \quad \text{R}^* \quad \text{O-C-CH}=\text{CH}_2
\]

Where \( R^* \) represents:
- Urethane
- Epoxy
- Polyester
- Polyether
- Acrylic
- Etc.

The properties of coating film are mainly supplied by oligomers!!
二、UV Monomers
UV Monomers

The function of monomers in UV curing

- To dilute oligomers and to reduce viscosity for operation
- To take part in cross-linking reaction and to improve curing more completely
- To improve the properties of coating film
Classified from Functionality of UV Monomers

- **Mono-functional**
  - 2-Ethyl hexyl acrylate (2-EHA), Isobornyl acrylate (IBOA), Benzyl acrylate (BZA), etc.

- **Di-functional**
  - TPGDA, HDDA, etc.

- **Tri-functional**
  - TMPTA, Glyceryl propoxyl triacrylate (G(PO)nTA), etc.

- **Multi-functional**
  - Pentaerythritol tetra-acrylate (PET4A), etc.
The Second Generation Monomers

- Modified the first generation monomers with Ethylene oxide (EO) or Propylene oxide (PO)

- The main improvements
  - Skin irritation (toxicity)
  - Volume shrinkage
  - Other
    - Cure speed, Diluent efficiency, More flexible, Low odor, etc.
Mono-Functional Monomers

- **PHEA**

- **EOEOEA**

- **IBOA**

- **LA**

- **B-CEA**

- **CTFA**
Di-Functional Monomers

HDDA

BPA(EO)m+nDA

NPGm+n(PO)DA

PEG(XXX)DA

DPGDA
Tri-Functional Monomers

THEICTA

PET3A

TMPTA
Multi-Functional Monomers

PET4A

DiTMPTA

DPHA
High RI monomers-BPEA

DM® BPEA is a specially-designed aromatic acrylate monomer with low odor, low volatility and high refractive index properties that could be used in uv-curing of optical film applications.

- **Appearance @ 25°C**: clear pale yellow liquid
- **Viscosity (mPa.s/25°C)**: 100-200
- **Inhibitor (MEHQ ppm)**: 500
- **Refractive Index**: nD(20)=1.5720-1.5750
- **Color (APHA)**: 100 max.
- **Acid value, mg KOH/g**: 0.5 max.
三、UV Oligomers
(1) Epoxy Acrylate Oligomers
(2) Urethane Acrylate Oligomers
(3) PE Acrylate Oligomers
(4) Full acrylate Oligomers
(1) Epoxy Acrylate Oligomers

Advantage:
- Cheap
- Fast curing speed
- High gloss
- High hardness
- Good chemical resistance

Disadvantage:
- Yellowing
- High viscosity
- Easy crack
- Bad flexibility
Epoxy Acrylate Oligomers

introduction

1. DM 127
2. DM 129
3. DM 176
4. DM 188
5. DM 186
6. DM 1701
7. DM 1703
8. DM 1636
9. DM 1283C
10. DM 156
DM 156

DM 156 is epoxy diacrylate oligomer. This resin is characterized by high refractive index performance, fast cure, light color, chemical and heat resistance with high gloss and hardness. It belongs to the most common typical UV oligomer used in various UV/EB applications such as inks, coatings and overprinting varnishes.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Clear liquid</td>
</tr>
<tr>
<td>Viscosity at 25°C, cps</td>
<td>---</td>
</tr>
<tr>
<td>Color, Gardner</td>
<td>2 max.</td>
</tr>
<tr>
<td>Acid value, mg KOH/g</td>
<td>1 max.</td>
</tr>
<tr>
<td>Refractive Index, 25°C</td>
<td>1.5560-1.5620</td>
</tr>
</tbody>
</table>
DM 188

- DM 188 is a high functional aromatic Epoxy acrylate oligomer which provides very fast cure response.
- Cured films of DM 188 exhibit excellent hardness (>9H) and solvent resistance.
- It can use in inks and primer of Vacuum metalization.

Properties:
- Viscosity @ 25°C, cps approx. 130,000
- Acid value, mg KOH/g approx. 3
DM188 for Vacuum Metalization

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
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<tbody>
<tr>
<td>DM-188</td>
<td>30 ~ 45 P</td>
</tr>
<tr>
<td>HDDA</td>
<td>10 ~ 15 P</td>
</tr>
<tr>
<td>TMPTA</td>
<td>7 ~ 10 P</td>
</tr>
<tr>
<td>GPTA</td>
<td>5 ~ 10 P</td>
</tr>
<tr>
<td>9166</td>
<td>1 ~ 3 P</td>
</tr>
<tr>
<td>Solvent</td>
<td>20 ~ 30 P</td>
</tr>
</tbody>
</table>
(2) Urethane Acrylate Oligomers

**Advantage:**
- Good flexibility
- High gloss
- High hardness
- Wide application
- Non-Yellowing

**Disadvantage:**
- Expensive
- High viscosity
Urethane Acrylate Oligomers

Introduction

1. DM 566
2. DM 583
3. DM 584
4. DM 585
5. DM 586
6. DM 5812
7. DM 571
8. DM 87A
9. DM 566
10. DM 564
11. DM 850
<table>
<thead>
<tr>
<th>Function</th>
<th>DM 583</th>
<th>DM 584</th>
<th>DM 585</th>
<th>DM 586</th>
<th>DM 571</th>
<th>DM 87A</th>
<th>DM 588</th>
<th>DM 5812</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Flexibility</td>
<td>ok</td>
<td>Excellent</td>
<td>Excellent</td>
<td>good</td>
<td>OK</td>
<td>Bad</td>
<td>Bad</td>
<td>OK</td>
</tr>
<tr>
<td>Hardness</td>
<td>2H</td>
<td>2H</td>
<td>3~4H</td>
<td>4~5H</td>
<td>6~7H</td>
<td>6~7H</td>
<td>&gt;9H</td>
<td>&gt;9H</td>
</tr>
<tr>
<td>Flow</td>
<td>OK</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>OK</td>
<td>Bad</td>
<td>Bad</td>
<td>Good</td>
</tr>
<tr>
<td>MW</td>
<td>1200</td>
<td>1500</td>
<td>2500</td>
<td>2500</td>
<td>900</td>
<td>900</td>
<td>1500</td>
<td>3500</td>
</tr>
</tbody>
</table>

Flow: Flow,

2010/3/16
DM 584

- DM 584 is an 2-f aliphatic urethane acrylate oligomer diluted with 12% HDDA.
- Films of DM 584 impart excellent exterior durability, flexibility, toughness and the non-yellowing properties.
- DM 584 also has good adhesion for ABS、PC、PET.
- It also can be used in coating of carbon fiber and plastic.

Properties :
Viscosity @ 23°C, cps approx. 100,000
Hardness (pencil) : 1~2H
DM 585

- DM 585 is an 4-f aliphatic urethane acrylate oligomer diluted with 12% HDDA.
- Films of DM 585 impart excellent exterior durability, flexibility, toughness, hardness and the non-yellowing properties.
- DM 585 has good adhesion for ABS、PC、PET.

Properties:
Viscosity @ 25°C, cps approx. 130,000
Gardner Color Value approx. 2
Form supplied ca 88% in HDDA
Hardness (pencil) : 3~4H
DM 588

- DM 588 is a 10-functional aliphatic urethane acrylate oligomer. Generally, it is used in combination with 3% Chivacure 173 to reach an >9H hardness.
- It can be applied in clear hard coatings or scratch resistant coatings on plastic, wood coating and fillers, improving cured speed and gloss

Properties:
- Viscosity @ 25°C, cps approx. 200,000
- Gardner Color Value approx. 2
- Hardness (pencil) : >9H
Process of Mold-Printing
Keypad product
Plastic Special Surface Deal
DM 850

- DM 850 is designed for plastic spray coating which provides **excellent leveling**, significantly reduces surface defeat caused by frame effect.
- It also offers very good adhesion, **good hardness** and high toughness with ABS/PC.

**Properties:**
- Appearance white muddy, viscous liquid
- Viscosity at 25°C, cps 6000±500
- Functionality, theoretical 5-8
DM 850

Physical Properties

- Hardness 2 – 3 H/1kg at 20 – 30um
- Gloss 60°>80 at 20 – 30um
- Suitable Substrates ABS, PC, ABS/PC
DM 850 used in Keyboard
DM 850 used on PC/ABS
DM 566

DM 566 is an aliphatic urethane diacrylate resin, characterized by its light color and low viscosity. Films of DM 566 cured are very soft and has excellent flexibility. It can be used as an additive to improve the flexibility of finished formulations.

Properties:
- Viscosity @ 25°C, cps approx. 15000
- Gardner Color Value approx. 1
(3) PE Acrylate Oligomers

Advantage:
- General flexibility
- General hardness
- Good pigments wetting
- Low viscosity
- Non yellowing (Aliphatic)

Disadvantage:
- Dark color
- Low curing speed
PE Acrylate Oligomers

Introduction

1. DM 236
2. DM 245
3. DM 257
4. DM 287
5. DM 281
6. DM 284
7. DM 272
8. DM 276
9. DM 278
10. DM 279
11. DM 2015
12. DM 2019
DM 2015

- DM 2015 is a 19-f polyester acrylate oligomer.
- It has high M.W(3000) and very low viscosity (800cps@25C).
- Cured films of DM 2015 also exhibit excellent adhesion and lower shrinkage (10~15%) compared to DPHA.

Appearance: Light yellowish liquid
Viscosity: 600 - 800 mPa.s @ 25°C
Molecular weight: 3000
Acid value: <1 mg KOH/g
DM 2019

- DM 2015 is a 19-f polyester metha-acrylate oligomer.
- It has high M.W(3000) and very low viscosity (1000cps@25C).
- Cured films of DM 2015 also exhibit excellent adhesion and lower shrinkage (10~15%) compared to DPHA.

Appearance: Light yellowish liquid
Viscosity: App.1000 mPa.s @ 25°C
Molecular weight: 3000
Acid value: <1 mg KOH/g
(4) Full acrylate Oligomers

Introduction

1. DM 321H
2. DM 321HC
3. DM 321HS
4. DM 345
5. DM 353
6. DM 3710
7. DM 347-1
8. DM 350A
DM 321HC

DOUBLEMER 321HC is an acrylic oligomer for applications required high gloss, high flexibility and improved adhesion to difficult substrates after UV curing. It provides excellent adhesion on metal and plastic.

- Appearance: Slightly muddy white liquid
- Viscosity at 25°C, cps: >20000
- Color, Gardner: 1 max.
- Acid value, mg KOH/g: 5 max
- Pencil Hardness: >H
DM 321HS

- DM 321HS has good compatibility with ink, especially suitable for metal ink.
- DM 321HS can also improve the adhesion for PP and PE.
- DM 321HS is suggested to be used in UV curing system, and thermal curing system in order to increase the toughness.
- DM 321HS can also be applied in pigmented ink.

Appearance : Slightly muddy, high viscous liquid
Viscosity@25°C : 9200±500cps
Solid content : 60%
Solvent : MEK
DM 347-1

- DOUBLEMER 347-1 is an acrylic oligomer diluted with 50% Butyl Acetate (BAC).
- This resin is designed as an additive to provide flexibility and improved adhesion to inorganic substrates.

Properties:
- Viscosity @ 25°C, cps : approx. 500~2500
- Gardner Color Value : approx. 2
- Form supplied ca 50% in BAc
- Hardness (pencil) : 3H
四、Photoinitiators
Introduction
**Photoinitiators**

- **Photo-reaction Process**
  - Absorb radiation: \( \text{PI} \xrightarrow{h \nu} \text{PI}^* \) (excited state)
  - Energy transfer: \( \text{PI}^* \xrightarrow{} \text{I} \cdot \) (Free radical)
  - Polymerization: \( \text{I} \cdot + \text{M} \rightarrow \text{Polymers (network)} \)

Note: PI and M stand for photoinitiators and monomers / oligomers, respectively.
Two Mechanisms from Photochemistry

Homolytic cleavage

\[ \text{R-C-R'} \xrightarrow{\text{O}} \text{R-C} \cdot + \text{R'} \cdot \]

Norrish I reaction

Hydrogen abstraction

\[ \text{Ph-C-Ph} \xrightarrow{h \nu} (\text{Ph-C-Ph})^* \xrightarrow{\text{O}} (\text{Ph-C-Ph})^* \xrightarrow{\text{O}} \text{Ph-C-Ph} \cdot + \text{RH} \]

H donor (i.e. 3° amine)

\[ \text{Ph-C-Ph} \cdot + \text{R} \cdot \]
Photoinitiators

Doublecure TPO

Doublecure 107

Doublecure 173

Doublecure 184

Doublecure 200

Doublecure BDK
Photosensitizers

- Doublecure BMS
- Doublecure EMK
- Doublecure BP
- Doublecure OMB
- Doublecure LBP
- Doublecure ITX

2010/3/16
Aminesynergist

\[ \text{Doublecure EPD} \]

\[ \text{Doublecure OPD} \]
Special photoinitiators

- High molecule weight
  Ex: PolyQ102 (MW>900)

- With Acrylate functionality
  Ex: PolyQ101 (1 Functionality)

Properties: Non-Migration, Low odor
DC 184L

1. Liquid type photoinitiator
2. Have good surface curing speed.
3. Non-yellowing
4. Have better deep-curing effect compared to DC 184.
DC 184L
Surface Curing Speed Test

<table>
<thead>
<tr>
<th>%</th>
<th>PI</th>
<th>DC 184</th>
<th>DC 184L</th>
<th>DC 173</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%</td>
<td>×</td>
<td>×</td>
<td>○</td>
<td></td>
</tr>
<tr>
<td>4%</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
</tr>
<tr>
<td>6%</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
</tr>
</tbody>
</table>

- DM 127TP20
- Coating thickness : 30 μm
- Curing Speed : 30 m/min
# DC 184L

Surface Curing Speed Test

<table>
<thead>
<tr>
<th>PI</th>
<th>DC 184</th>
<th>DC 184L</th>
<th>DC173</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface curing</td>
<td>○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>Deep curing</td>
<td>×</td>
<td>○</td>
<td>×</td>
</tr>
</tbody>
</table>

- DM 127TP20+4% PI
- Coating thickness : 1.5 mm
- Curing Speed : 10 m/min
五、UV Applications
How to design an UV. Curable formulation?

Properties demanded by customers
(What substrate? Coating method? Film properties?)

↓

Oligomers, Monomers & photoinitiators

↓

Formulation ← Pigments and Fillers

Additives

↓

End use ← UV. Oven / EB Accelerators

Application Machines

(Trial & Errors)
Factors Affecting Cure Rate

<table>
<thead>
<tr>
<th>Lamp System</th>
<th>Chemical System</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV. Dose</td>
<td>Reactivity</td>
</tr>
<tr>
<td>Intensity</td>
<td>Absorption</td>
</tr>
<tr>
<td>Wavelength</td>
<td>Coating Weight</td>
</tr>
<tr>
<td>IR Content</td>
<td>Pigmentation</td>
</tr>
</tbody>
</table>

Temperature
Oxygen Inhibition
Coating/Substrate Interaction
UV Coating Methods

- 噴塗 (Spray)
- 滾筒塗佈 (Roller Coating)
- 淋幕塗佈 (Curtain Coating)
- 旋轉塗佈 (Spin Coating)
- 浸塗 (Dipping Coating)
- 其他 (Draw-down Bars, Slot Die, etc.)
UV Inks coating methods

- 凸版印刷 (Relief printing)
- 平版印刷/膠版印刷 (Offset Lithography)
- 凹版印刷 (Gravure)
- 孔版印刷 (Screen inks)
- 柔版印刷 (Flexo inks)
- 其他特種印刷 (轉印, printing, etc.)
Application

(1) ABS plastic
    Ex: Motorbike case, mobile phone

(2) ABS/PC plastic
    Ex: cosmetic box, mobile phone, safe hat

(3) PS plastic
    Ex: toy
Application

(4) PVC film
   Ex: Furniture

(5) PET、PC film
   Ex: Protect film、手機面板(IML)、

(6) PC、PMMA
   Ex: Eyeglass、car lampshade
Application

(7) BMC、Nelon
   Ex: car lampshade

(8) Wood coating

(9) Others: metals、glass
   Ex: touch panel、phone panel、computer case
Thank you !!!