Paint: Interesting Facts

A jumbo jet needs 2 tons of paint.

The world's shipping fleet would produce an extra 70 million tons of greenhouse gasses and nearly 6 million tons of acid-rain-producing sulfur dioxide if ships were not treated with anti-fouling paints.
Coatings Market

- 50+ billion USD worldwide, divided into 3 main segments
  - **Architectural**: Paints, varnishes, and lacquers for direct application to interior or exterior surfaces of buildings
    - ~50% of total market, but lowest profit margin
    - Generally air-dried
    - Sherwin-Williams, Benjamin Moore, ICI Paints
  - **OEM/Product**: Applied to equipment in a manufacture process
    - Appliances, cars, industrial machinery, furniture, ...
    - ~35% of total market, higher profits
    - Baked, radiation-cured, electrostatic-spray
    - Automotive: PPG, DuPont, BASF
  - **Specialty Market**: Everything else
    - Auto refinish, traffic marking, ...
    - ~15%, usually high-value
    - Air or force dried
    - PPG, DuPont, Akzo Nobel, ...

OEM = original equipment manufacturer
Thermosetting Binders: Combination

- Copolymerization of an acid-functionalized acrylic resin and an epoxy resin yields a cross linked, block copolymer coating.

\[
2 \left( \text{CH}_2\text{CH}_2 \right)_n + \text{CH}_2\text{CH}_n \text{ResinCHCH}_2\text{O} + \text{CH}_2\text{CH}_n \text{ResinCHCH}_2\text{O} \\
\overset{\text{Acid functionalized acrylic resin}}{\text{COOH}} + \overset{\text{Epoxy resin}}{\text{C}=\text{O}}
\]
While alkyds can be classified as polyesters, the term is reserved for oil-based finishes.

Oils are first transformed into monoglycerides:

\[ \text{Oil} + 2 \text{Glycerol} \rightarrow \text{α Monoglyceride} + \text{β Monoglyceride} \]

Film formation results from condensation polymerization with diacid as well as oxidative cure.
Pigments are selected on the basis of:

<table>
<thead>
<tr>
<th>Particle size</th>
<th>Particle shape</th>
<th>Refractive Index</th>
<th>Tinting strength</th>
<th>Lightfastness</th>
<th>Hiding Power</th>
<th>Thermal Stability</th>
<th>Chemical Reactivity</th>
<th>Density (cost)</th>
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- **Property**          | **Preference** | **Reasons**
- **(1) Brilliance and Organic**
  - clarity of hue | Organic | The most attractive, cleanest colours are obtained with organic pigments.
- **(2) White and Inorganic**
  - black paints | Inorganic | The purest white pigment is TiO₂ and the most jet black, carbon.
- **(3) Non-bleeding Inorganic**
  - | Inorganic | Inorganic compounds have negligible solubilities in organic solvents. Some organics are very insoluble.
- **(4) Light fastness Inorganic**
  - | Inorganic | Inorganic compounds are generally more stable to UV than organics.
- **(5) Heat stability Inorganic**
  - | Inorganic | Very few organic compounds are stable above 300°C.
Aesthetic Properties of Dried Film Coatings

- **Opacity**
  - Extent of substrate coverage, as determined by pigments, extenders and other occlusions in the film.
  - Dependent on refractive index of fillers relative to the polymeric binder.

- **Surface Finish**
  - Gloss is a function of surface irregularity, as determined by the film formation process and dispersion of pigments/fillers.

- **Color**
  - Inorganic and organic colourants that are soluble or dispersed in the film (may or may not provide opacity).
Spraying (charged particles)

Curing (Infrared oven)
Complex Inorganic Colour Pigments

This term usually refers to metal oxide pigments that are derived from spinel \( \text{MgAl}_2\text{O}_4 \), rutile \( \text{TiO}_2 \), hematite \( \alpha\text{-Fe}_2\text{O}_3 \), or bixbyite \( \alpha\text{-Mn}_2\text{O}_3 \) structures. Substitution of metal ions in the host lattice by other chromophoric metal ions opens up a broad color spectrum.

The complex inorganic pigments generally exhibit outstanding lightfastness and resistance to weathering, heat, and chemicals.

Heavy-metal ions can only exert their toxic effects in dissolved form. Since these pigments are sparingly soluble, they may be classified as toxicologically innocuous. Around 25% of the world production of ca. 25 000 t in 1995 was processed into coating materials.

Commercial products include Heucodur (Dr. H. Heubach), Irgacolor (Ciba-Geigy), Kerafast (Blythe Colours), lightfast pigments (Bayer), and Sicopal. Sicotan (BASF), other producers are Cerdec, Ferro Corp., Shephard Chem. Corp. and Ishihama SK.
Bismuth Pigments

The development of pigments based on bismuth orthovanadate [14059-33-71, BiVO₄] is relatively recent. Bismuth pigments are also produced as the two-phase system BiV₀ₓ, Bi,MoO₃, to improve their colorfastness.

The colors of this group of pigments are similar to these of cadmium yellow. Worldwide production in 1995 is estimated at 500 t.

Commercial products include Sicopal Yellow (BASF Lacke und Farben), and Irgacolor (Ciba-Geigy).
Varnish

- **Varnish** is a transparent, hard, protective finish or film primarily used in wood finishing but also for other materials.
- **Varnish** is traditionally a combination of a drying oil, a resin, and a thinner or solvent.
- **Varnish** finishes are usually glossy but may be designed to produce satin or semi-gloss sheens by the addition of "flatting" agents.
- Varnish has little or no color, is transparent, and has no added pigment, as opposed to paints or wood stains, which contain pigment and generally range from opaque to translucent.
- **Varnishes** are also applied over wood stains as a final step to achieve a film for gloss and protection. Some products are marketed as a combined stain and varnish.
Lacquer

- The word *lacquer* refers to quick-drying, solvent-based varnishes or paints. Although their names may be similarly derived, lacquer is not the same as *shellac* and is not dissolved in alcohol. Lacquer is dissolved in lacquer thinner, which is a highly flammable solvent typically containing butyl acetate and xylene or toluene. Lacquer is typically sprayed on, within a spray booth that evacuates overspray and minimizes the risk of combustion.

- Outside America, the rule of thumb is that a clear wood finish formulated to be sprayed is a lacquer, but if it is formulated to be brushed on then it is a varnish. Thus, by far most pieces of wooden furniture are lacquered.

- Lacquer may be considered different from varnish because it can be re-dissolved later by a solvent (such as the one it was dissolved in when it was applied) and does not chemically change to a solid like other varnishes.
Powder Coatings:

History, Types, and Applications
Lacquers

Lack of durability
High maintenance
High VOC content

Fast Drying
Deep shine

-Lack of durability
High maintenance
High VOC content
Acrylics

+ Excellent color, gloss, weather ability
+ Excellent thin film appearance
- Fair flexibility and corrosion resistance

Poly(methyl methacrylate)
The crosslinking during the cure

tri-glycidyl-iso-cyanurate powder

Polyester milled into powder
Disadvantages

- Material must be able to withstand curing temperatures, >260°F (~125°C)
- Forming films thinner than 1.5mil is difficult
- Electrostatic spraying may only be used for electrically conductive materials
- Powder is highly flammable
- Conversion from conventional to powder coating line requires large capital investment
Other Common Applications

- Metal Objects
  - Appliances
  - Highway signs
  - Tools
  - Lawn and garden equipment
  - Office furniture
  - A/V furniture and equipment
  - Sports equipment

- Non-metal Objects
  - Home-office furniture
  - Kitchen cabinets
  - Sinks/shower stalls
  - Ceramics
<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>APPROXIMATE VISCOSITY (in centipoise)</th>
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<tbody>
<tr>
<td>Water @ 70 F</td>
<td>1 to 5</td>
</tr>
<tr>
<td>Blood or Kerosene</td>
<td>10</td>
</tr>
<tr>
<td>Anti-Freeze or Ethylene Glycol</td>
<td>15</td>
</tr>
<tr>
<td>Motor Oil SAE10 or Mazola Corn Oil</td>
<td>50 to 100</td>
</tr>
<tr>
<td>Motor Oil SAE30 or Maple Syrup</td>
<td>150 to 200</td>
</tr>
<tr>
<td>Karo Corn Syrup or Honey</td>
<td>2,000 to 3,000</td>
</tr>
<tr>
<td>Blackstrap Molasses</td>
<td>5,000 to 10,000</td>
</tr>
<tr>
<td>Hershey Chocolate Syrup</td>
<td>10,000 to 25,000</td>
</tr>
<tr>
<td>Heinz Ketchup or French's Mustard</td>
<td>50,000 to 70,000</td>
</tr>
<tr>
<td>Tomato Paste or Peanut Butter</td>
<td>150,000 to 250,000</td>
</tr>
<tr>
<td>Crisco Shortening or Lard</td>
<td>1,000,000 to 2,000,000</td>
</tr>
</tbody>
</table>
1 ENVIRONMENT
The environment required for this test is 25 ±2°C temperature according to standard ASTM D1210-96.

2. TEST REQUIREMENT
The specimen of the materials to be tested shall be visibly homogeneous and free of any foreign materials or air bubbles.

3. EQUIPMENT AND REFERENCE MATERIAL
1 Scraper: Double edged hardened steel, Stainless steel blade.
2 Tapered Gage: hardened stainless steel block.

4- PRECAUTIONS
1 Clean the gage immediately after each use by using a solvent and soft cloth.
2 Do not allow any hard materials to come in contact with the gage surface.
3 Avoid tapping or scratching with others metal.
4 The tested specimen must be free from any bubble
Analysis of Paint

Colour layer analysis
- Requires cross section of paint chip
- Cannot be done on paint smears
- Same number and order of layers
- Relative thickness must be same
- Is a class test (but see case at end of lecture)

Solubility
- Use solvents such as acetone, dichloromethane, pyridine.
  - Acrylic lacquers are soluble in acetone

Pyrolysis GC
- Analysis of film formers
- Bulk technique, all layers analysed together
• One-way systems: Already in use
  - Corrosion sensing
  - Conductive coatings
  - Anti-inflammatory coatings

• Two-way systems: More challenging
  - Shape-memory materials
  - Hydrophobic/hydrophilic switching
  - Thermochromic pigmented coatings
Examples of Smart Coatings

- Antimicrobial and Hygienic
- Antifouling
- Bio-catalytic
- Color shifting
- Conductive
- Corrosion sensing
- Detect degradation sensing
- Light sensing
- Molecular electronics
- Nanotechnology-based
- Optically active

- Photo-catalytic
- Pressure sensing
- Shape-memory polymers
- Self-lubricating
- Self-repair and healing
- Super hydrophobic
- Thermally triggered
Scratch Resistant Self-healing Coating

New scratches

One week later

TOKYO (Dec. 2, 2005)-- Nissan Motor Co., Ltd
Smart Coatings

Self-repair Coatings

Ilhan A. Aksay, Peng Jiang, Dudley A. Saville, Princeton University, Princeton, USA.