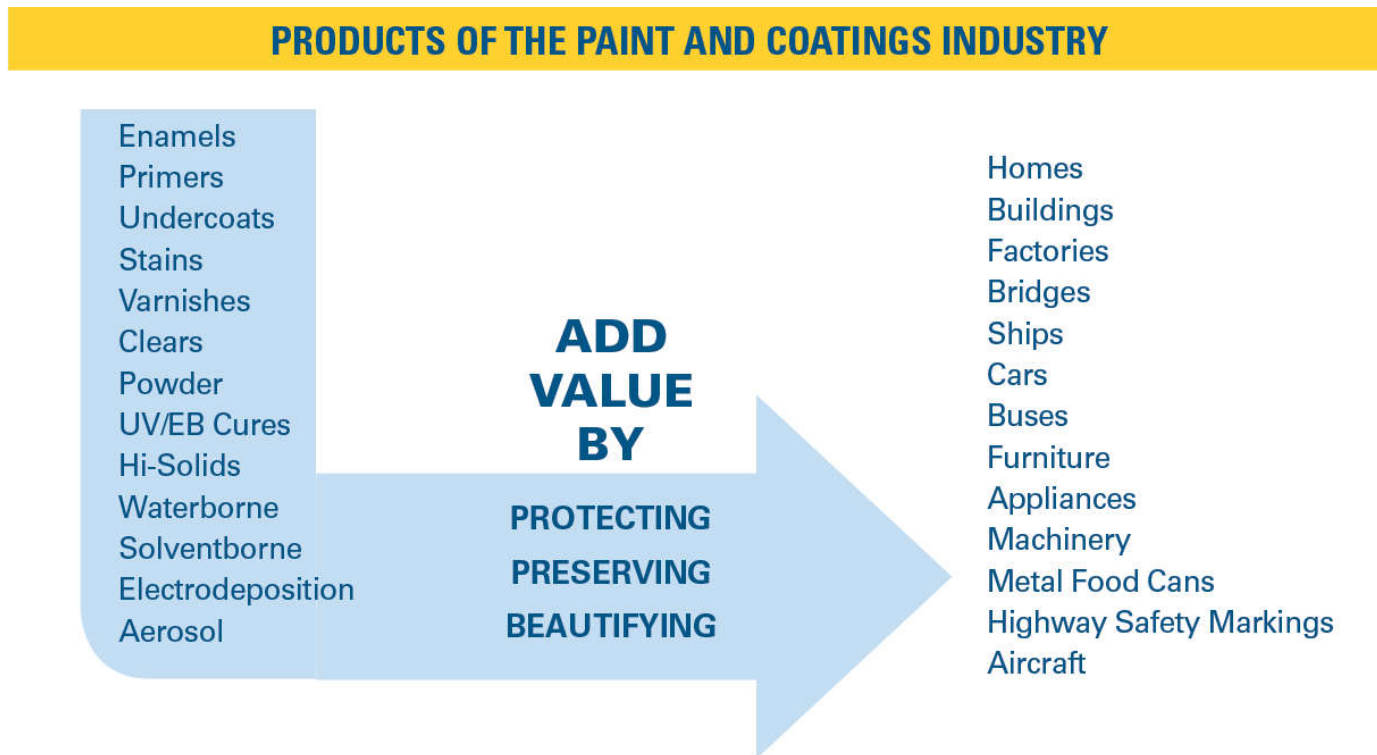


Consumer Coatings in the Home: Fact and Fiction

Dr. Michael J. Michalczyk
Chelate Consulting, LLC
April 13, 2016

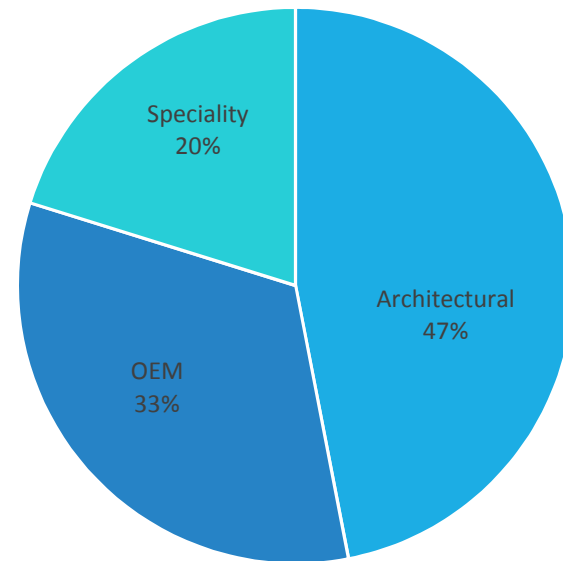
Why do we need Paints and Coatings?



Source: American Coatings Association (www.paint.org)

Global Coatings Market

- Global market was \$128 billion in 2014
 - US market was \$24 billion
- Product Segments
 - Architectural/Decorative coatings
 - Industrial/OEM Coatings
 - Special Purpose Coatings
 - Auto Refinish
 - Industrial Maintenance
 - Marine
 - Traffic marking paint
- Trends – low VOC, higher quality



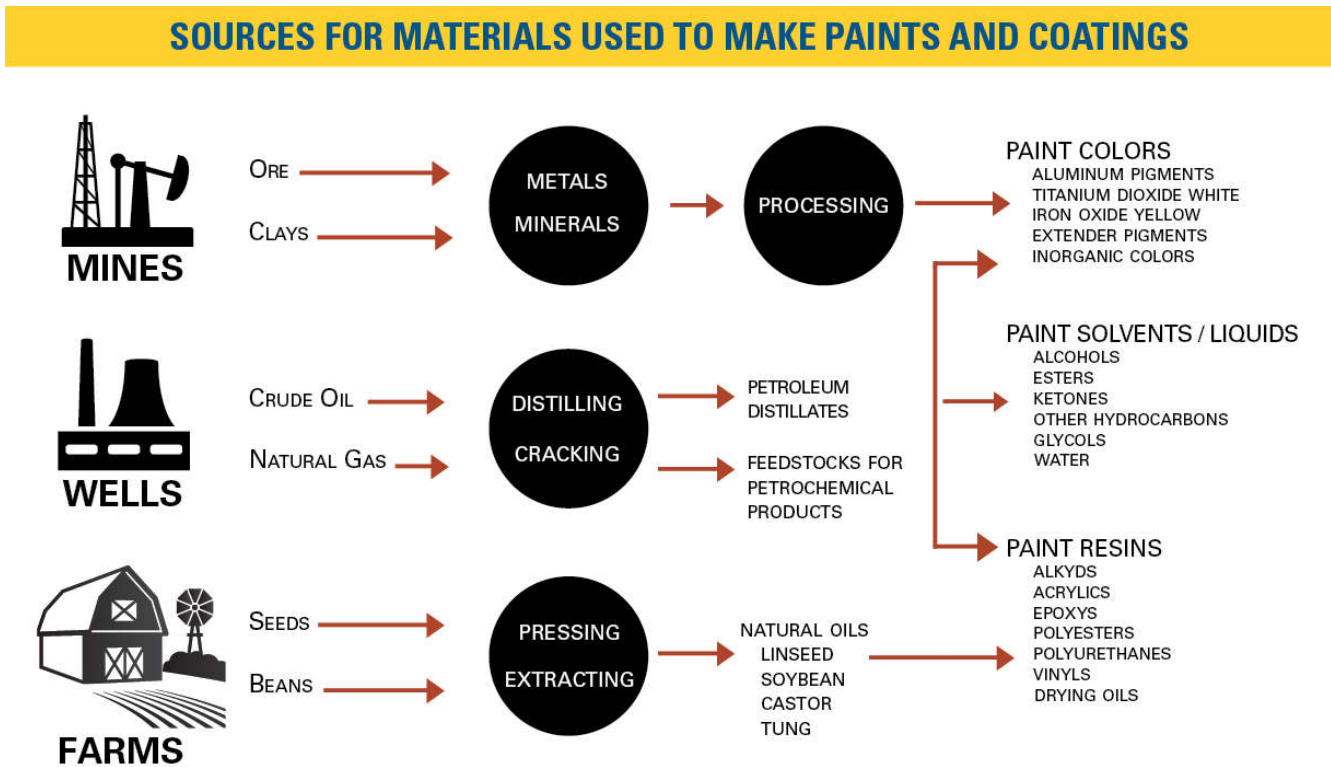
US Market 2014

Source: P&S Market Research; American Coatings Association

Global Coatings Industry

- Major players:
 - PPG Industries
 - Sherwin-Williams Company
 - Valspar Corporation
 - Akzo Nobel
 - Axalta Coating Systems
 - Kansai Paint Co.
 - Henkel AG & Co.
 - Asian Paints Limited
 - RPM International

Sources of Materials used in the Coatings Market



Source: American Coatings Association (www.paint.org)

Consumer Coatings in the Home

Type of Coating	Benefit
<ul style="list-style-type: none">• Architectural – exterior, interior paints• Furniture – wood, metal finishes• Automotive – paint, corrosion• Packaging – can interiors, labels, printed packages• Electronics – wire coatings• Appliance• Glass - eyewear	<ul style="list-style-type: none">• Beauty• Protection• Increased value• Insulation• Anti-stain/non-stick• Easy clean• Thermal Stable• Anti-reflective

Appliance Coatings

- Appliance coating market
 - Refrigeration
 - Cooking appliance (stoves, cookware, bakeware, rice cookers, grills)
 - Laundry (washer/dryers)
 - Miscellaneous kitchen appliances (dishwasher, microwave, and others)
- Coatings mainly epoxy-based exterior coatings to protect metal and provide color
- Interior coatings provide metal protection and easy clean benefits

Cookware and Bakeware Coatings

- Main benefit is non-stick surface which provides easy clean up
- Best coatings are oleophobic and acid-resistant
- Sold as branded coatings (i.e. Teflon[®] Platinum) or unbranded
- Ingredients used in cookware/bakeware coatings have to be compliant with FDA regulations (21 CFR 175.300)
- Many choices for the consumer depending on how they cook

Bakeware

- Made of carbon steel, aluminum, glass or silicone elastomer
- Consumer bakeware coated with non-stick silicone
- Industrial bakeware coated with non-stick fluoropolymer
- Glass bakeware is usually uncoated



Top of Range (TOR) Cookware

- Made of aluminum, hard-anodized aluminum, stainless steel or clad (Al core/SS cladding)
- Stainless steel and clad tends to be uncoated
- Aluminum is always coated with a non-stick interior coating
- Hard-anodized can be uncoated or coated
- Exterior can have an optional coating for scratch-resistance or color



Types of Cookware coatings

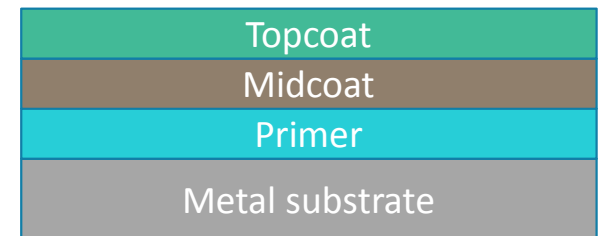
- Seasoned metal
 - Cast iron skillets, carbon steel woks
- Porcelain
 - Old ceramic coatings, TOR exteriors, broilers and grills
- Silicone
 - Most consumer bakeware, some TOR cookware, rice cookers
- Fluoropolymer
 - TOR cookware, industrial bakeware and high-end rice cookers
- Ceramic/Sol-gel
 - TOR cookware marketed as “green” alternative to PTFE-based coatings

Materials Used in Cookware/Bakeware Coatings

- Materials used in coatings must have high use temperatures
 - Silicone, fluoropolymer, polyimide, ceramic, pigments
- Maximum oven temperature 500°F (250°C)
- Maximum stove top temperatures
 - Gas: 428°F (220°C)
 - Induction: 666°F (352°C)
 - Electric: 742°F (394°C)
- Food/water in the pan reduces temperature of cookware and the cookware coating

Cookware and Bakeware Coating Systems

- Formulated as solvent or water-based paint
- Usually 2-coat or 3-coat systems
- Primers typically are silicone or polyamide imides
- Topcoats are typically fluoropolymer and silicone
- Pigments and fillers added to primers and midcoats for scratch and abrasion resistance
- Applied between 1-1.5 mil (25-38 μm) and baked at high temperatures
 - 500-550°F for silicone coatings
 - 800°F for PTFE/fluoropolymer coatings

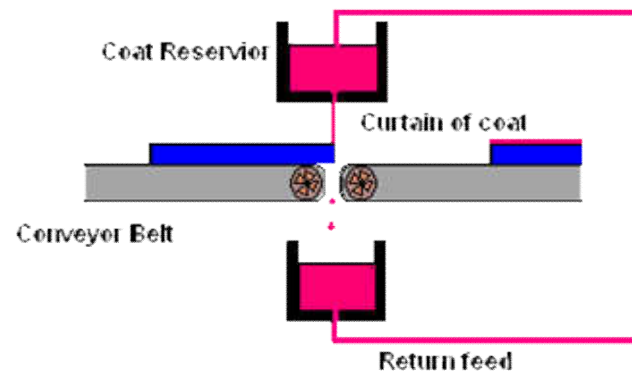


Application of Coatings

- Non-stick coatings are applied using printing and spray processes
- Coil coating process is mainly used for bakeware



Roller coat



Curtain coat



Spray coat

Ref: GMM Coatings, www.kerone.com, chuangzhitz.en.alibaba.com

Types of Testing Used in Cookware Coatings

- Adhesion
- Durability
 - Abrasion and scratch resistance
 - Dishwasher cycles
- Real time cooking and baking
 - Egg release
 - Cake/cookie release
- Accelerated failure testing



Seasoned Metal

- Probably discovered 2000 years ago with cast iron use in China
- Used now in cast iron skillets and carbon steel woks
- Provides a great easy clean, non-stick coating
- Non-stick surface is thought to be formed by oxidation and degradation of cooking oil and fats
- Seasoning must be reapplied to keep surface non-stick
 - Little consensus on best oil and temperatures for seasoning
- High acidic foods and the dishwasher can strip the seasoning



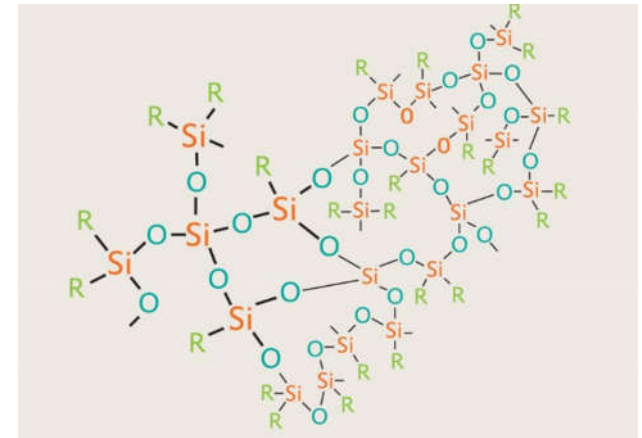
Porcelain

- True ceramic coating
- Used on aluminum and steel
- Very high temperature resistance
 - Ceramic is fired at 1200 – 1400 °C
- Benefit – high temperature resistance
- Has poor non-stick properties
- Color palette limited to high temperature pigments
- Mainly used in frying pan exteriors and on grill grates



Silicone Coatings

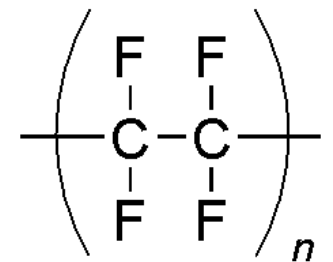
- First use was as baking mats in France in the 1980's by Silpat
- Used mainly on bakeware due to high temperature resistance of silicone 675°F (360°C)
- Coatings use methyl phenyl siloxane
- Silicone rubber used in flexible bakeware
- Benefit – good non-stick for baking goods but will lose non-stick over time
 - Silicones are hydrophobic but not oleophobic
- Clear, colorless coatings allow wide array of colors



Structure of a silicone resin (Tego)

Fluoropolymer Coatings

- Developed by DuPont in 1951 for industrial bakeware
- Tefal developed use on TOR cookware in 1954
- Coatings use PTFE (polytetrafluoroethylene) dispersion
 - PFOA (C8) was a surfactant/soap used in the manufacture of PTFE
- Benefit – coating is oleophobic, hydrophobic and chemically inert
- Excellent non-stick and easy-clean properties
- Limited colors due to primer and bake temperature



Perfluorooctate (PFOA)

- 2000: 3M announced removal of PFOS (perfluorosulfonate) products and phased out PFOA production
 - PFOS found to have adverse effects in animal studies and elevated levels in worker's blood (C&EN May 29, 2000)
- 2006: PFOA Stewardship Program formed at request of EPA to provide baseline tox testing and eliminate use by 2015
- Human health effects from PFOA (from EPA 2014 draft report)
 - Positive association in high exposure populations with testicular, kidney, ovarian and prostate cancer and non-Hodgkin's lymphoma
 - Neutral or negative association for other exposure categories

References: EPA and American Cancer Society

Fluoropolymer Cookware Concerns

- Teflon is toxic
 - PTFE coating is inert but can decompose at high temperatures
 - Some deterioration above 500°F (260°C)
 - Significant decomposition above 660°F (349°C)
 - Typical cooking temperatures are less due to oil, water and food in pan

Oil	Smoke Point
EV Olive Oil and Butter	320°F
Canola Oil	400°F
Peanut Oil	450°F

- PTFE cookware should not be overheated

Fluoropolymer Cookware Concerns

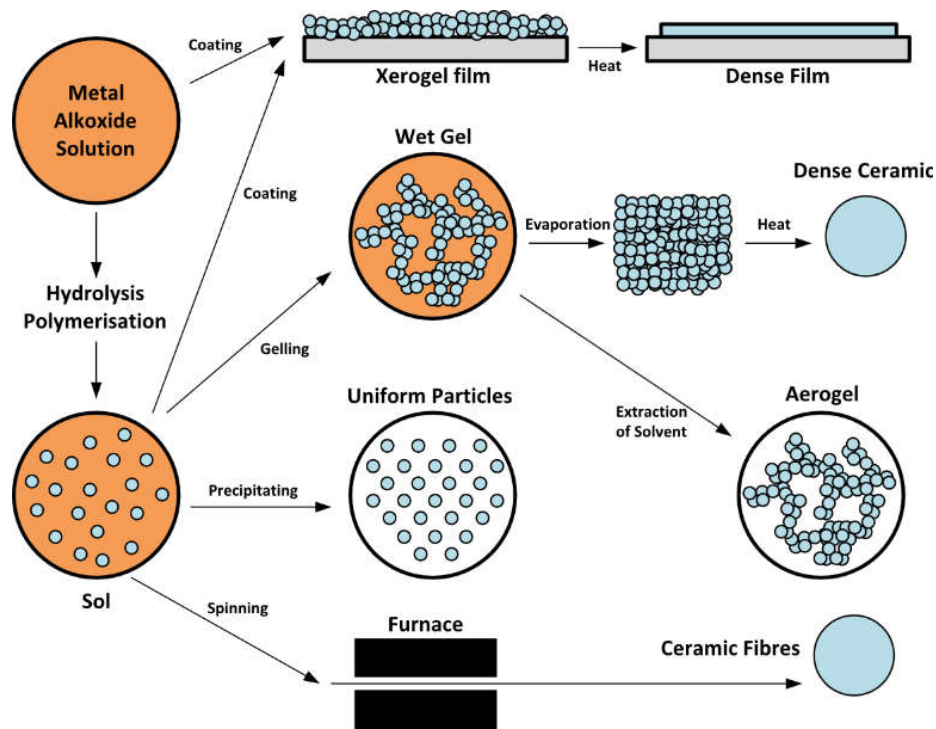
- Coating has come off of my cookware, should I throw it away?
 - PTFE is chemically inert. Primers, pigments and filler are FDA compliant
 - Replace cookware when non-stick benefit is lost
- The non-stick pans may expose my family to PFOA
 - Ammonium PFOA sublimes at 266°F (130°C)
 - PTFE cookware is typically baked at 800°F (427°C)
 - DuPont tested commercial Teflon-branded cookware
 - No PFOA observed at detection limits of 0.1 ppb
 - 2014 EPA Progress Report shows most PTFE manufacturers have reduced or eliminated use of PFOA

“Determination of Perfluorooctanoic Acid (PFOA) Extractable from the Surface of Commercial Cookware Under Simulated Cooking Conditions By LS/MS/MS.” C. R. Powley, M. J. Michalczyk, M. A. Kaiser, L. W. Buxton, *The Analyst*, 130, 1299 (2005)

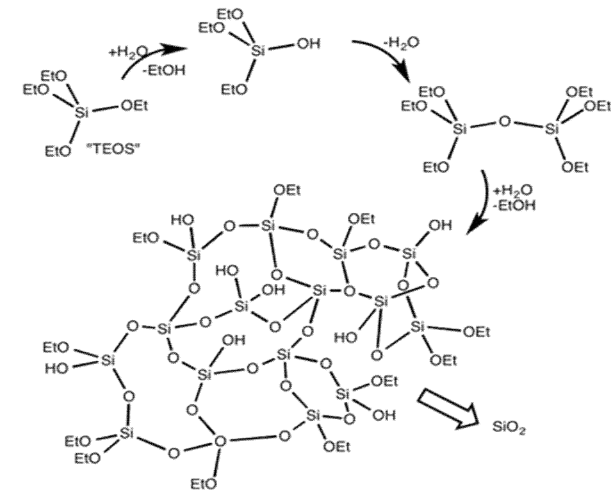
Ceramic/Sol-Gel Coatings

- Developed due to consumer concerns of PFOA and PTFE
- Coating is mainly organosilica/silicone formed using sol-gel
- Silicone oil is added to surface to provide non-stick feel
- Benefit - coating is very scratch-resistant
- Non-stick surface similar to silicone bakeware
- Does not provide long-term easy-clean, non-stick properties
- Same color palette as in silicone bakeware

Sol-Gel Process and Chemistry

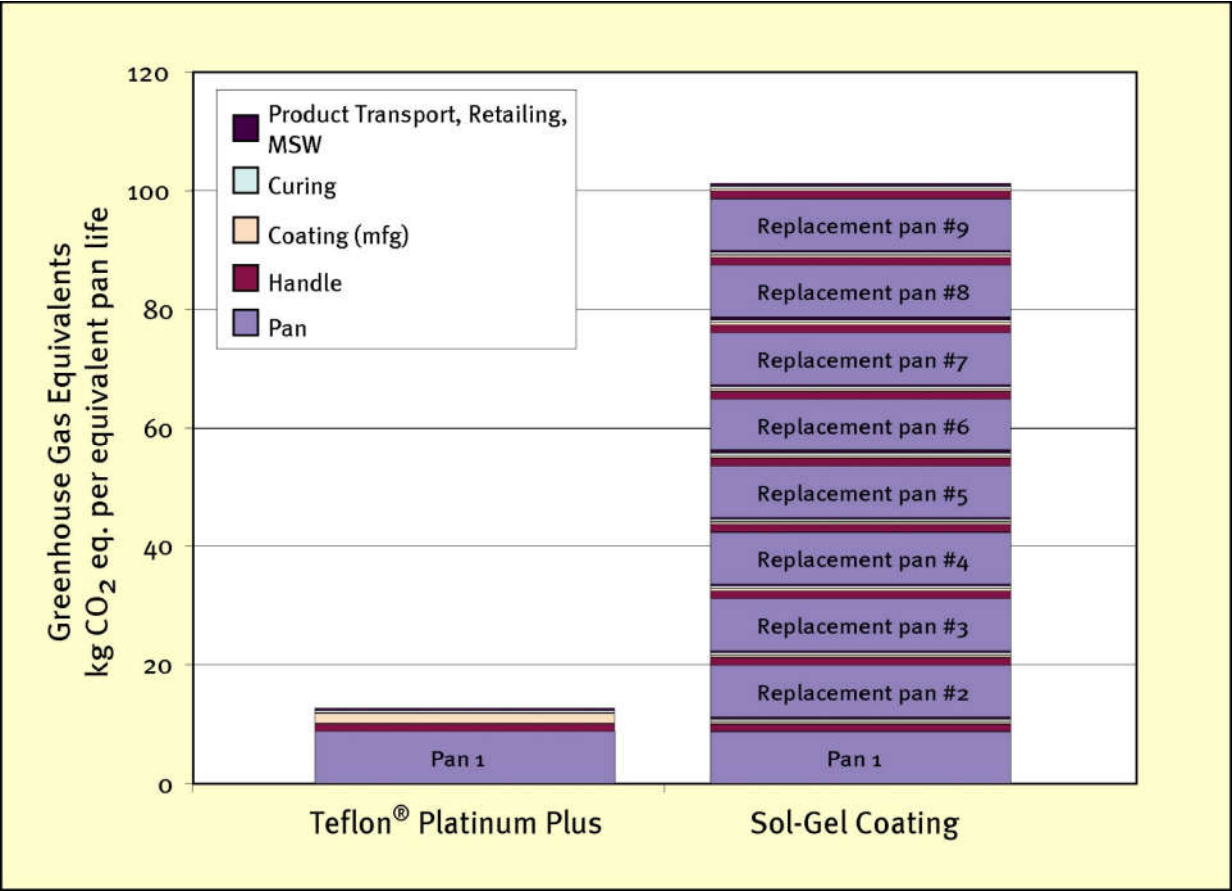


- Developed as a process to make metal oxides at low temperatures
- In cookware coatings, blends of $\text{Si}(\text{OEt})_4$ and $\text{MeSi}(\text{OMe})_3$ are used to increase durability and provide non-stick



References Wikipedia: Sol-gel, By Claudionico - Own work, inspired in Brinker and Scherer book ("Sol-gel Science: The Physics and Chemistry of Sol-gel Processing"), Sol-gel, by Smokefoot - Own work, CC BY-SA 3.0

Performance of Ceramic Coatings vs. Teflon[®]



- Results of a 2008 DuPont study on simulated equivalent nonstick cooking life
- One pan made with Teflon[®] nonstick lasts longer than 9 pans coated with sol-gel ceramic or silicone

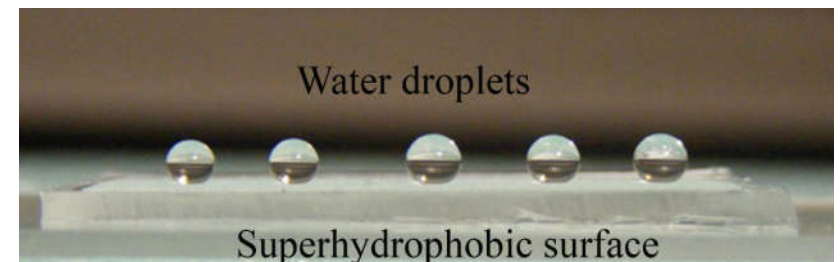
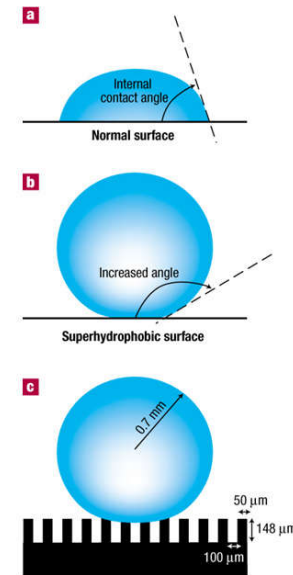
Ref: DuPont Media Center

New Coatings Innovations

- Superhydrophobic coatings
- Smart Materials
- Green solvents
- Optical coatings

Superhydrophobic Surfaces

- Rough surface causes water to bead – “Lotus effect”
- Benefit is never wet and self cleaning
- Ongoing research on superoleophobic surfaces to repel oil
- Durability is critical issue for commercial applications
- Self cleaning challenge is to repel environmental grime



Ref: D. Quere, Nature Materials, 1 (2002) pg 14; MTFI Research. U. Texas

How to Purchase Quality Cookware

- Decide on your use and what benefit is important
 - *Non-stick coating or non-coated metal*
- Stick with a reputable cookware and coating brand
- Heavy is better than light
 - *Thicker metal is better (~ 1/8" or 10 gauge)*
 - *"A proper sauté pan should cause serious head injury if brought down hard against someone's skull" Anthony Bourdain*
- Riveted handles with silicone grip



“A nonstick sauté pan is a thing of beauty”
Anthony Bourdain