ROWAN TECHNOLOGY GROUP
Linking Global Technologies with Markets

Structural Materials and Coatings

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Rowan Technology Group

Nanotechnology Business Roadmap for Industry
Chicago, October 2002

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Summary

- **Structural materials**
- **Coatings**
- **What types of products and markets will make use of nanomaterials?**
  - **Where are they used now?**
  - **Where are they likely to be used?**
- **What are the drivers and barriers?**
- **How can we make money at it?**

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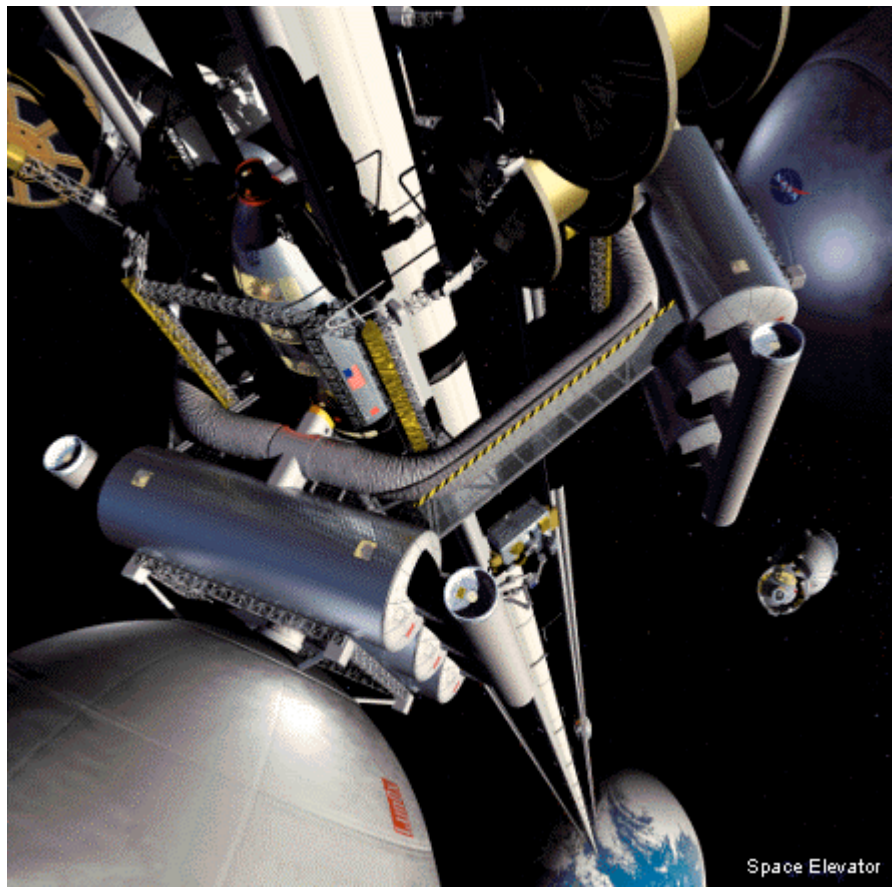
Structural materials



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What are structural materials?

They are the materials that actually make up engineering structures

Can be as big as a bridge…

…or as small as a pin

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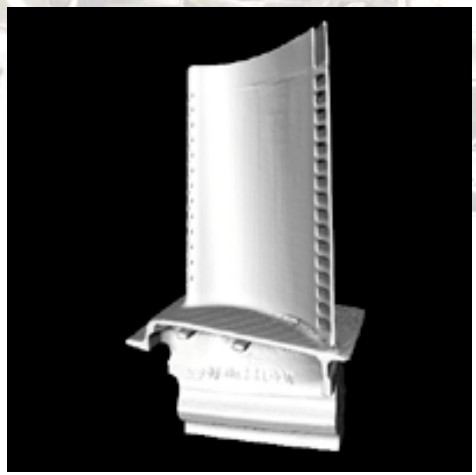
Where are advanced structural materials used?



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Primary structural materials markets

- **Aerospace**
  - **push the envelope, but conservative**
- **Automotive**
  - **highly cost driven**
- **Biomedical**
  - **conservative, limited materials knowledge base**
- **Optical and electronic**
  - **innovative, short product cycles**
- **Sports equipment**
  - **innovative, willing to take risks, very short product cycles**

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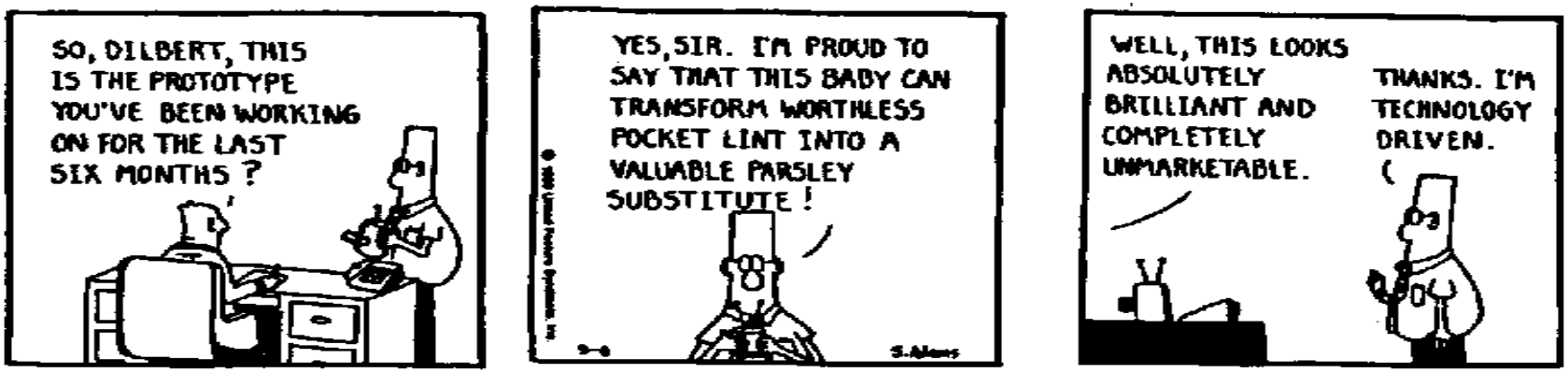
What do people look for in structural materials?

- **Better performance**
  - **harder**
  - **stronger**
  - **tougher**
  - **stiffer or more elastic**
  - **more corrosion-resistant**
  - **sometimes a unique combination of properties**
    - **hard and tough, strong and light, tough and transparent**
- **Lower cost**
  - **you use a lot of it, so it must be cheap**

Who cares?



- Materials engineers are technology-driven
- Mechanical engineers are performance- and cost-driven
  - To get structural materials to market they must offer a real performance advantage that people are willing to *pay for*
  - Nanomaterials can *improve* properties
    - Incremental, not revolutionary - sometimes a little is worth a lot
    - Is there anything you cannot do another way?

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Drivers and barriers

Drivers

- Extreme properties
  - hardness, corrosion
- Unique combinations of properties
  - hardness + toughness
- Unique processing capabilities
  - accurate near-net fabrication
- Incremental improvements that get you past a barrier
  - 100°C increase in turbine blade alloy temperature

Barriers

- Time to market for new materials historically 20 yrs
- Cost sensitive
  - strong barrier, even in aerospace/military
- Structural markets conservative
  - long product cycles, high risks
  - look for incremental improvements
  - many ways to skin the cat

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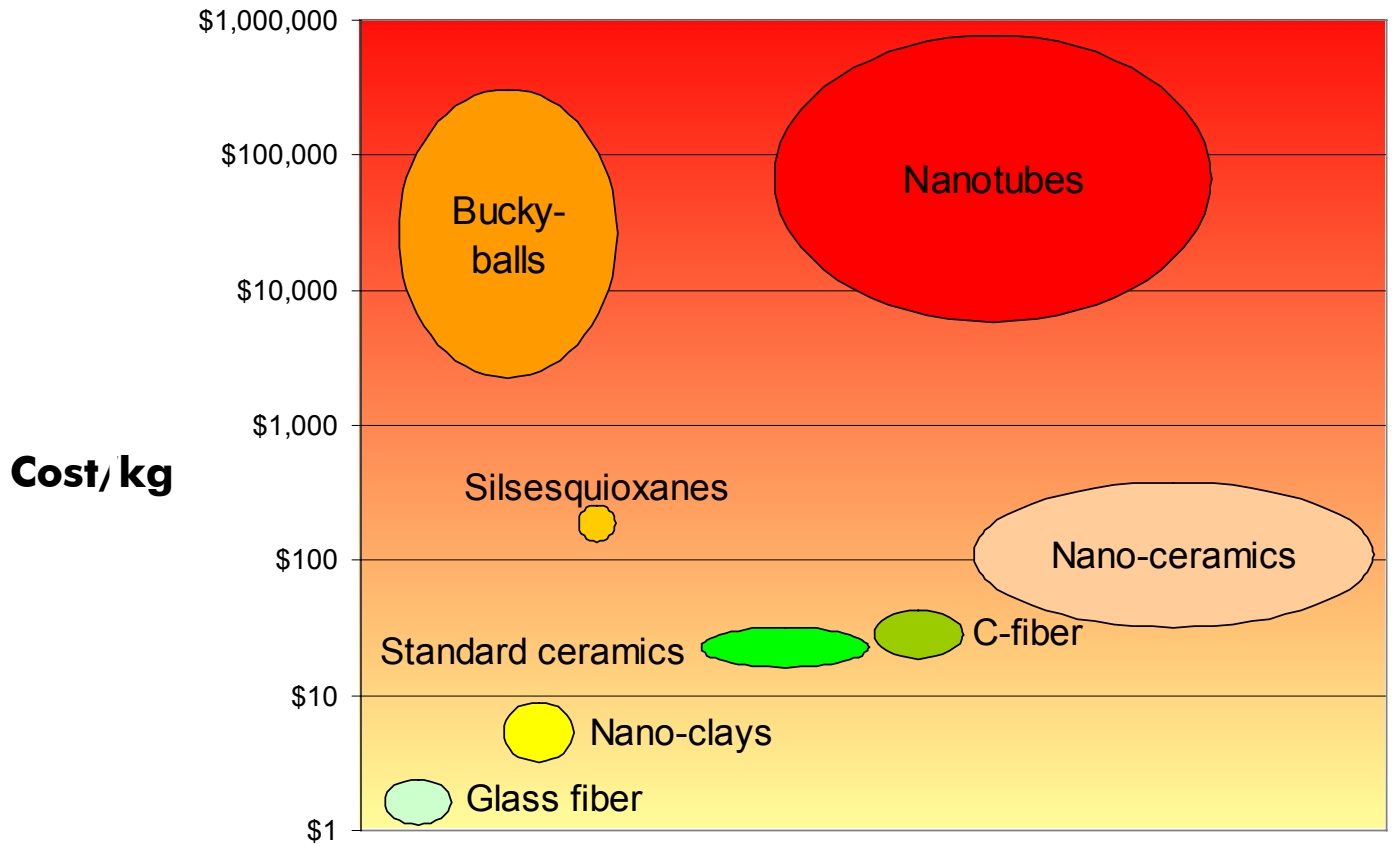
Cost of nanomaterials



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Where are structural nanomaterials used today?

- **Nanograin ceramics**
  - **sintered nanoparticles**
  - **improved ductility, especially at high temperature**
  - **near-net forming**
  - **superplastic forming**
- **Very little commercial usage**
  - **Good application potential, but cost vs performance issue**

***Note*: Because finely powdered metals can be explosively reactive, most nanopowders are oxides and other ceramics. Qinetiq Nanomaterials, UK, making Al, W, Ce, Ni, Cu Technanogy (CA) nano-Al for propellants and munitions.**

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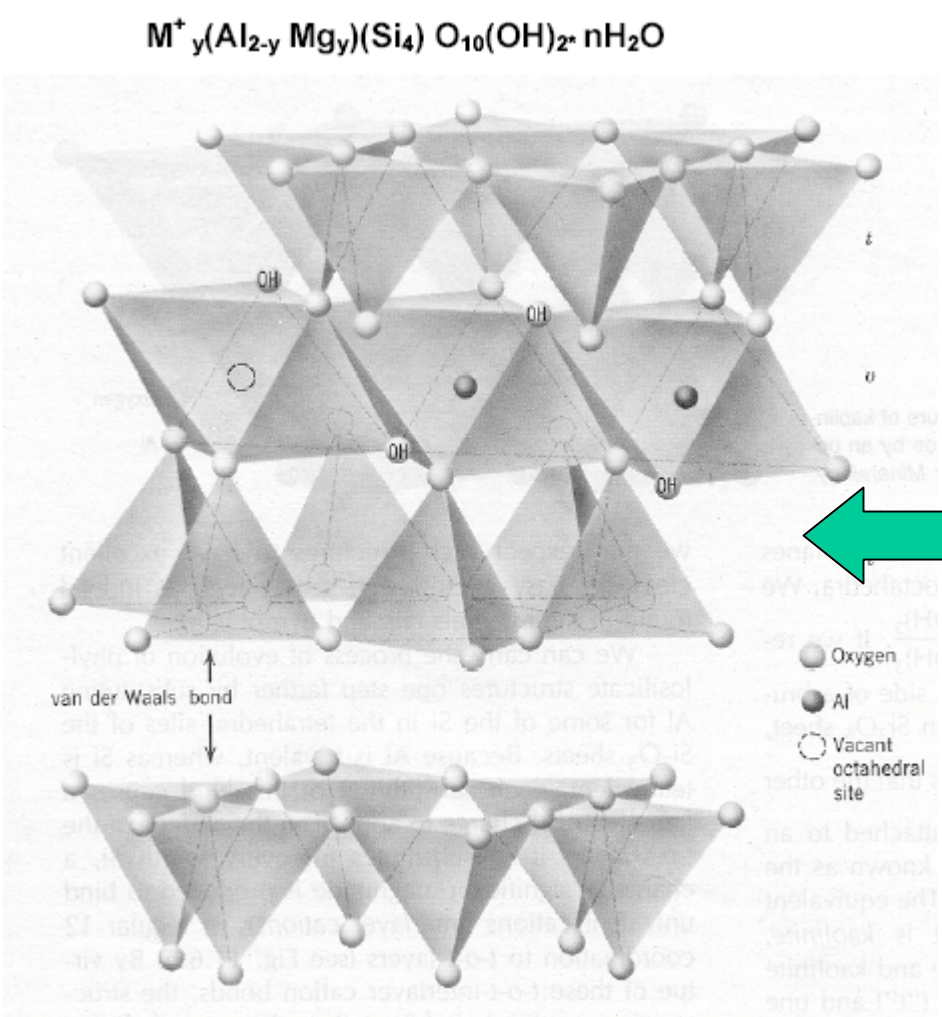
Composites - Filled polymers



- **Composite fillers (for polymers, metals, etc.)**
  - **Carbon black used for years in tires, etc.**
  - **1% Al_2O_3 filled gelatin scratch-resistant film (Kodak)**
  - **Montmorillonite clay (Nanocor, Southern Clay Products)**
    - **particle thickness comparable to polymer molecule sizes**
    - **clean and treat to functionalize**
    - **large surface areas, low loading, less cost**
    - **clear - less light scattering**

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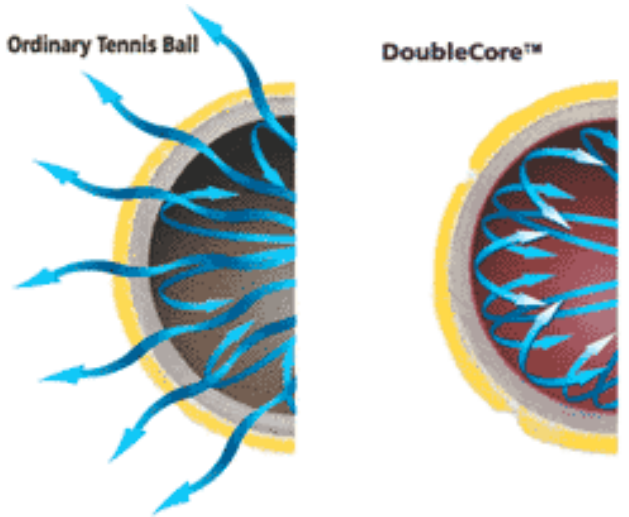
Polymer nanocomposites (smectite clays)

- **Gas barrier films**
  - **Butyl rubber composite in Wilson DoubleCore tennis balls**
    - **gas barrier inhibits gas loss, increases playing time**
- **Being tested in thermoplastic olefin for aftermarket step-assist in GM Safari**
- **Nanocomposite nylons**
  - **more rigid tubing for catheters, etc (Foster)**



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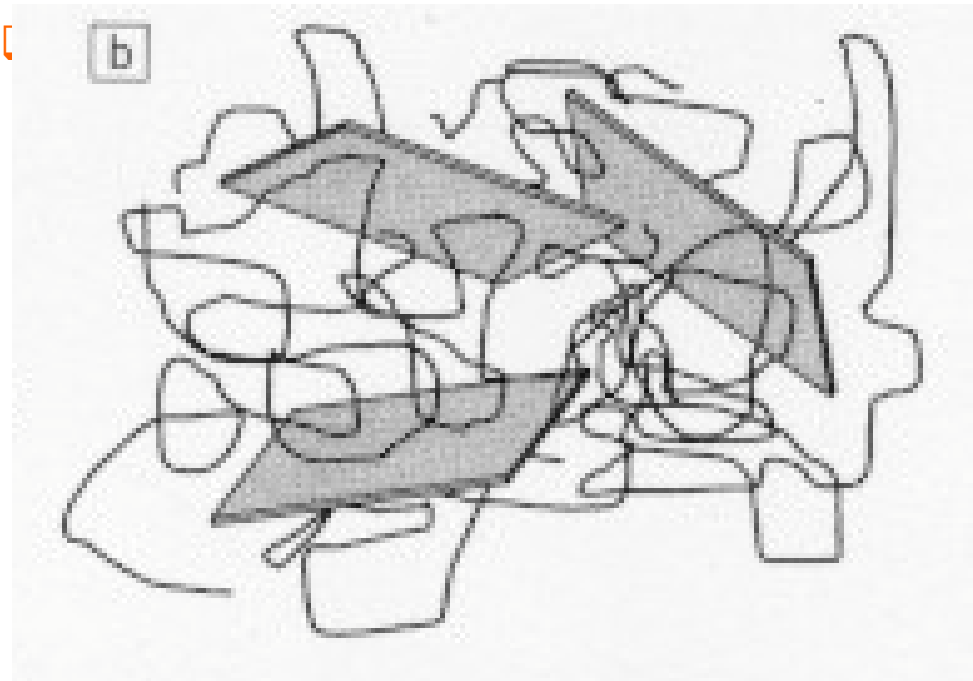
Smectite clays in polymer gas barriers



marketed by

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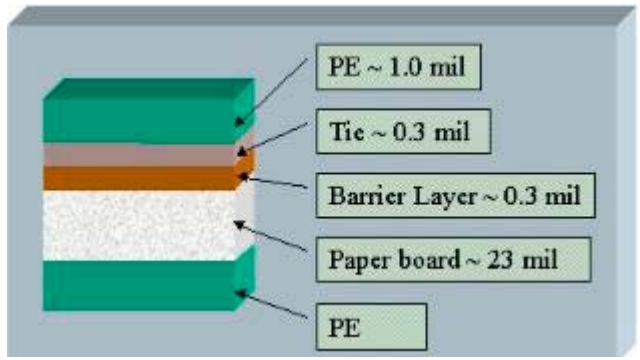

Long paths inhibit gas flow

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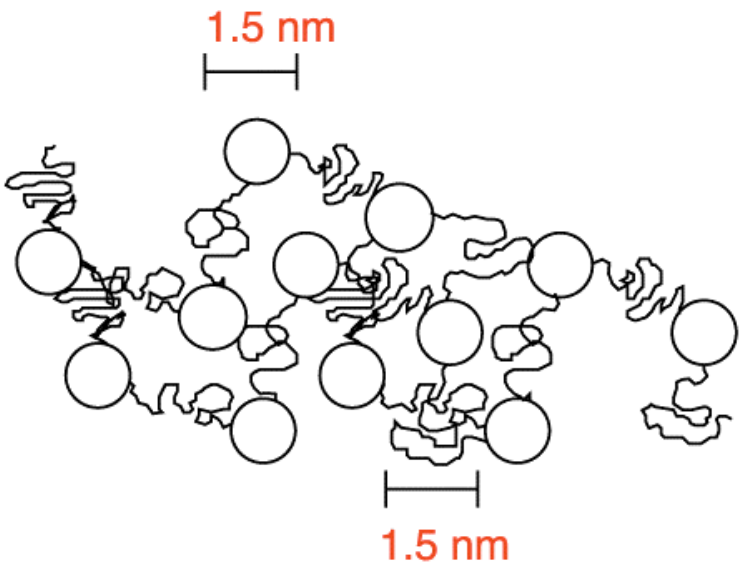
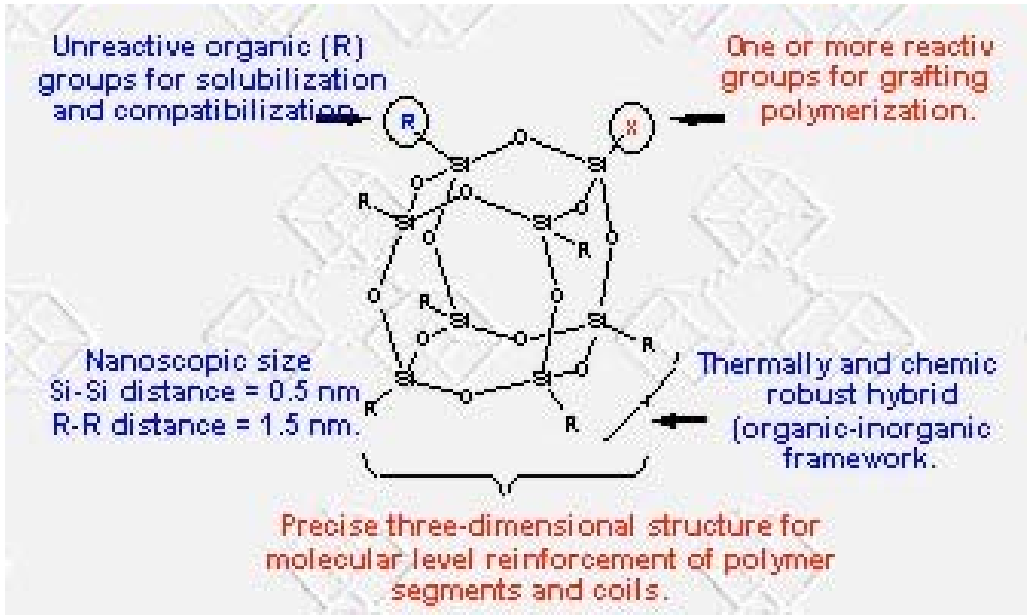
Market potential

- **Market predictions (Packaging Strategies)**
  - **3 million lbs nanocomposites by 2006 - for beer!**
    - **Smectite clay polyamide gas barriers**
  - **100 million lbs by 2011**
    - **50% for carbonated soft drinks**
    - **Beer**
    - **Meats, foods, condiments**

Polyhedral Oligomeric Silsesquioxanes (POSS)

- **Hybrid Plastics, Inc.**
  - **Nanosized compounding material rather than filler**





- **New on market - few production uses**
  - **Dental bonding system**
  - **Fire retardance**

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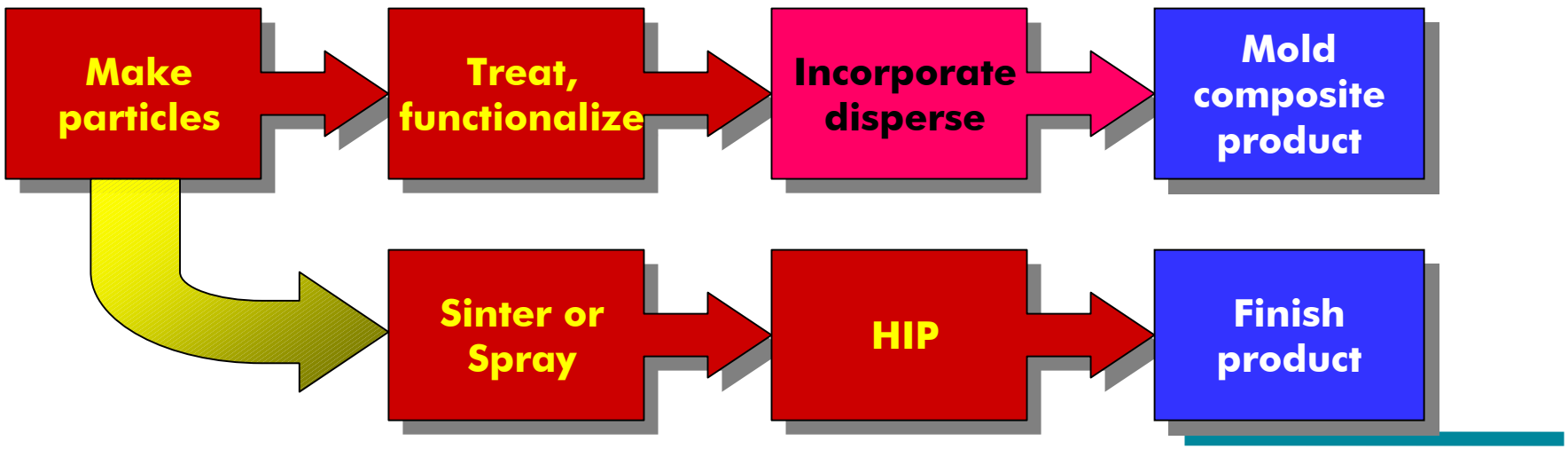
Turning nanomaterials into structures

- Some steps very expensive
  - Particle manufacture usually much more expensive than for standard particles
    - Exception nanoclays
  - Treating, functionalizing to be organophilic, etc is key
- On other hand amount of material needed often much less
  - 5% loading instead of 30%



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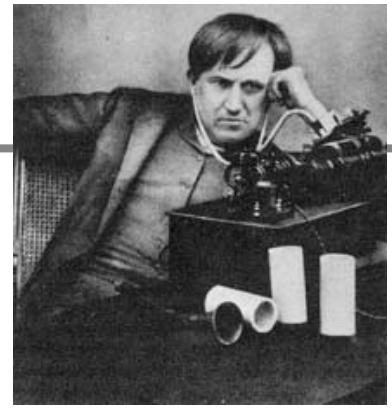
Bringing down the cost

- **Very expensive to manufacture nanomaterial separately from the final material**
  - **Few cost-effective nanomaterials**
    - **Smectite clay, carbon black**
- **A better approach**
  - **Form the nanophase as part of the process of forming the material**
    - **Uses the advantages of nanomaterials without the pain of making them**
    - **Gets around the cost issue - about the same cost as non-nano material**
    - **Nanophase metals made by Severe Plastic Deformation processing have higher strength and ductility**
      - **Aerospace industry now uses Friction Stir Welding to make joints stronger than the original metal**

Computational Design



- **Making the better approach work**
  - **Discard the old Edisonian approach**
    - **Very slow and inefficient**
  - **Design the material**
    - **Uses computational methods to design the material rather than experimental methods to develop it**
      - **Requires sophisticated computer modeling and high level of materials knowledge**
        - **Understand the science and turn it into engineering**
        - **Essential to cost-effective and rapid materials creation**
        - **Replaces years of experiment with weeks or months of calculation**

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Designer materials – e.g. High Strength Stainless Landing Gear Steel

C-17

- **Want a corrosion-resistant landing gear just as strong as a normal high strength steel**
  - **But stainless is inherently weaker**
  - **How to solve?**
    - **Design the chemistry and processing to precipitate nano-carbides during the steelmaking process**
    - **Intrinsic nanocomposite**

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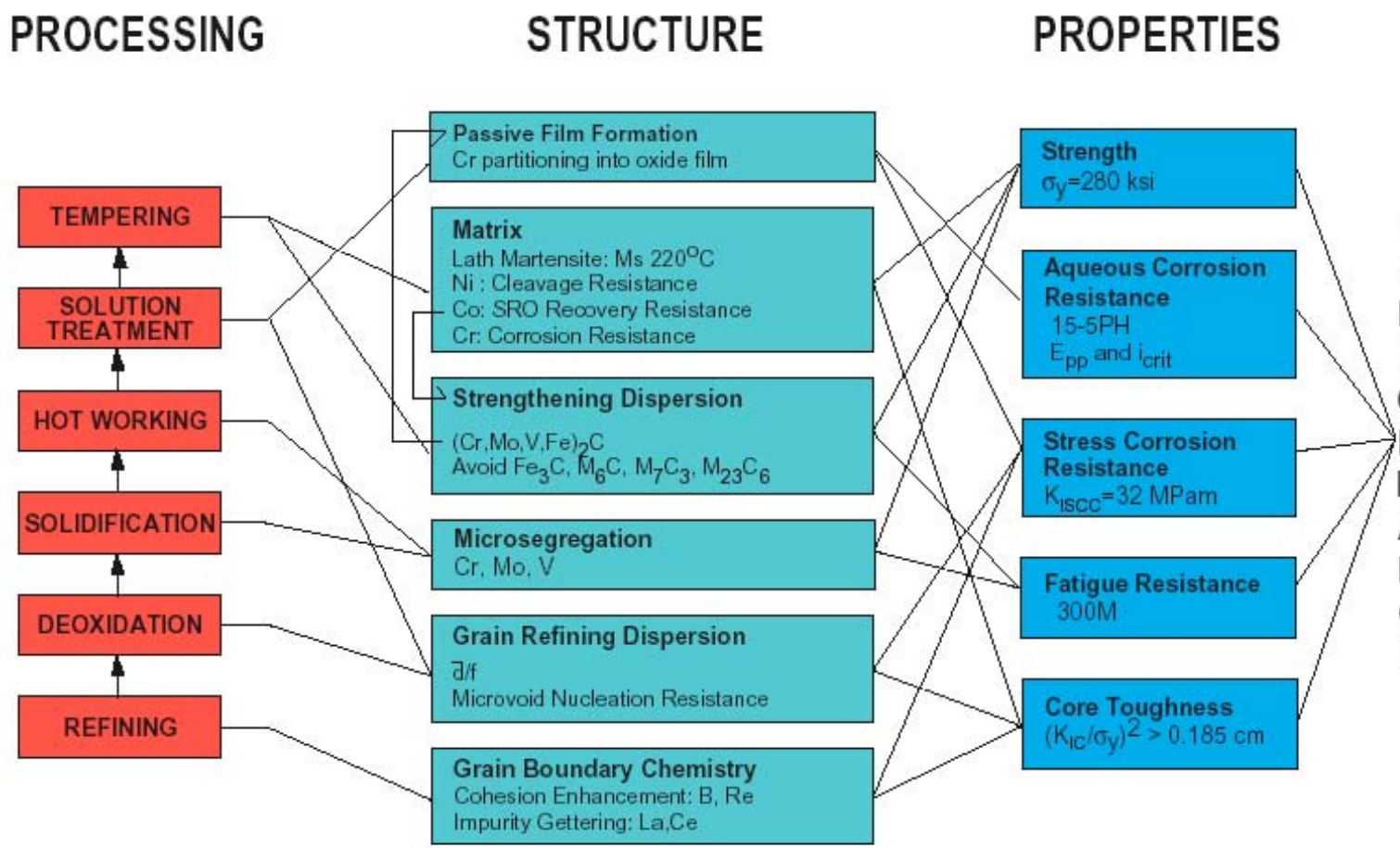
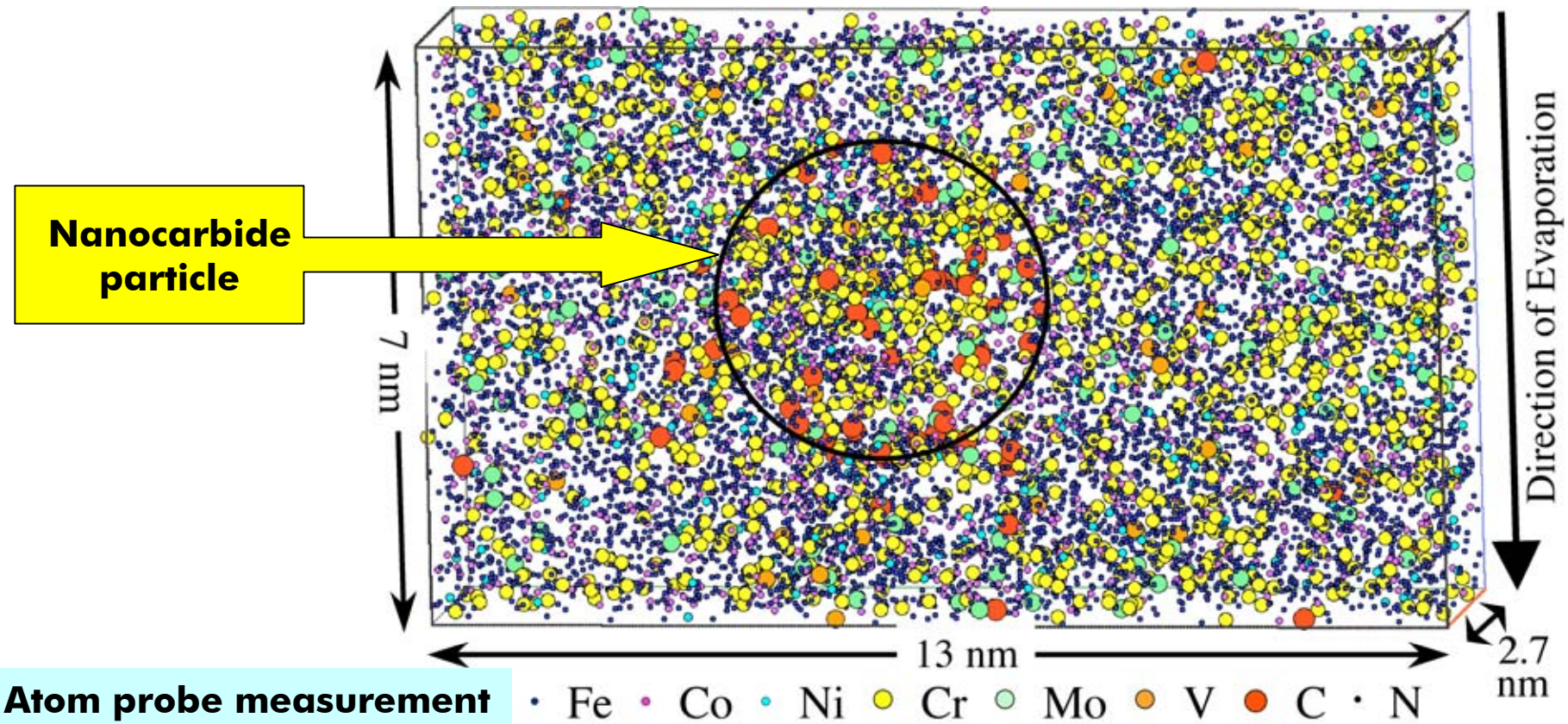
Materials by Design – (not Materials by Luck)



Nanocarbides in high strength stainless steel

3-D M_2C Precipitate in S53 Tempered 500°C 5 hrs



Atom probe measurement (QuesTek Innovations)

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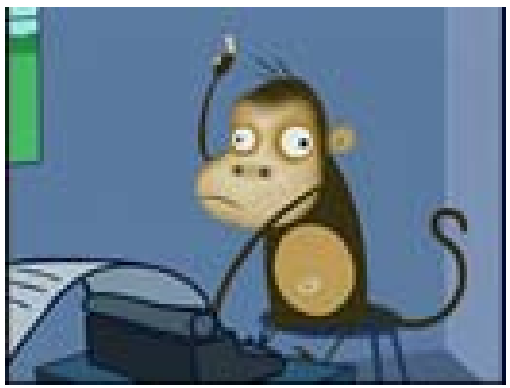
Why is computational design a better way?

- This approach does not set out to make "nanomaterials"
  - It employs nanomaterials as design elements only where they offer best performance
  - Avoids "cure in search of a disease" syndrome
  - Only cost-effective way to design complex new materials
    - Much lower development cost
    - Much faster time-to-market
- Some companies in this area
  - QuesTek Innovations (IL)
    - Alloys, composites
  - Nanomix (CA)
    - C-based materials, nanotubes
  - Accelrys (CA and UK)
    - Modeling software

Alternative approach for rapid development

- **Combinatorial chemistry**
  - **Rapidly make and test large numbers of chemistries on a single chip**
  - **"Edison on a chip"**
  - **Best for complex systems that are difficult to model**
    - **Drugs, catalysts**
- **Companies in this area**
  - **Symyx**



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Where are the business opportunities?

- High volume producers of nanomaterials
  - Technology capable of producing nanomaterials for <$20/kg (equivalent to C fiber)
    - Smectite clays are a good example
- Better yet - product manufacturers who can effectively use high volume production nanomaterials
  - Not because they are nano, but because they are better
  - Genuine market need
  - Product you cannot make any other way
- Companies that can take advantage of modern materials design tools to build-in nanomaterials
  - Market-driven products designed with computational and combinatorial methods
  - Much more acceptable costs, high performance, shorter time-to-market
  - Requires effective relationships between manufacturer and specialized materials design and development companies
- But only where nanomaterials provide a clear market advantage in performance or cost

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Coatings

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Functional coatings

- **Surface that differs from the underlying material**
  - **Wear, erosion, abrasion**
  - **Corrosion (Zn)**
  - **Friction (MoS_2)**
  - **Optical (glasses, CD)**
  - **Electronic, magnetic**
  - **Decorative (Cr)**
  - **Specialized military**
    - **low observable (aircraft)**
    - **anechoic (subs)**

(U.S. Air Force)

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Methods of putting down coatings

Vacuum deposition
Eyeglasses, drills, watchbands

- **Much less material needed**
  - **Get the advantages of nanomaterials without making the whole part of expensive material**
    - **Nanoparticle cost not as critical**

Thermal spray
Aircraft, industrial rolls

Electroplating
Chrome plate, Ni

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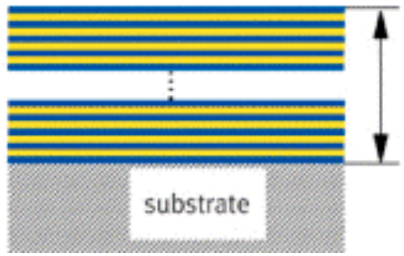
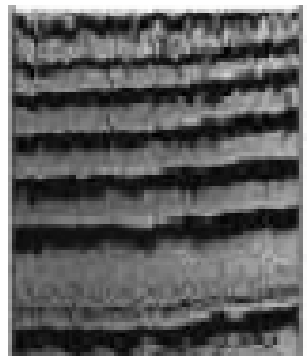
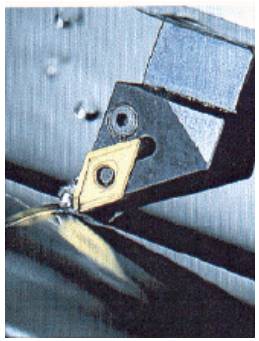
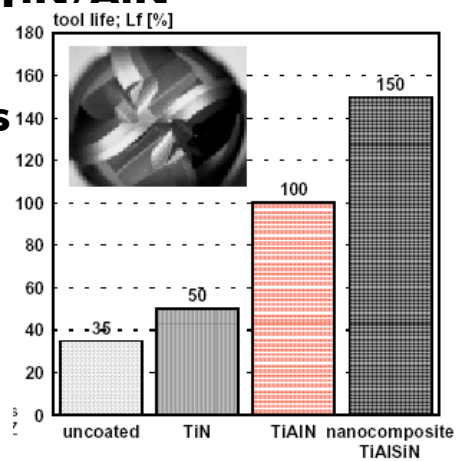
Where are nanocoatings used today?

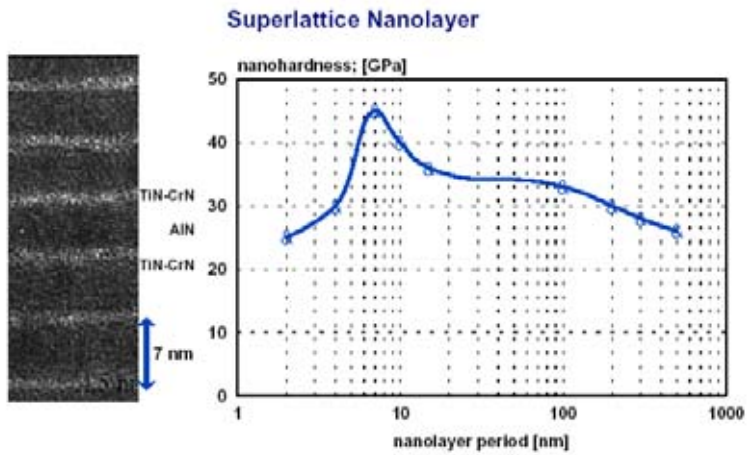
- **Nanolayered coatings for cutting tools**
  - **Superhard, tough**
  - **Less wear**
  - **Less setup time**
  - **Manufacturers**
    - **Balzers Futura Nano TiAlN**
    - **Sumitomo ZX TiN/AlN**
    - **Bekaert Dylyn**
    - **Various others**











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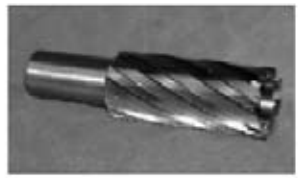
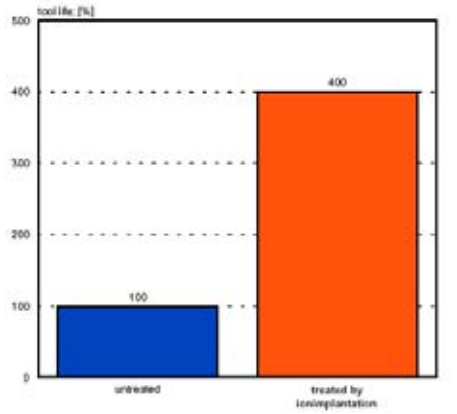
A word of caution on cutting tools

- Superhard sounds good, but does not mean much to the market
- Wear life increases of 2-4x may not be worth much either
  - the tool market rarely pays more than 20% extra for anything
  - cf Ion Implantation
    - pushed for many years
    - good improvements some applications
    - never made a real dent in the market





Source: Trion, Jyllinge, DK

- Simple coatings still dominate market
- However, the tool market could get excited about something that gave truly unique capability
  - e.g. interrupted cutting dry machining for steels

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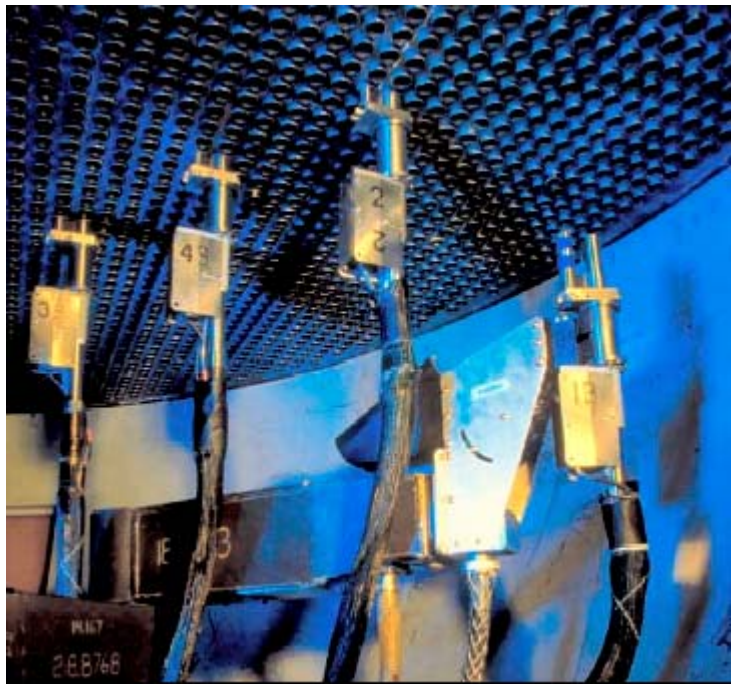
Nanophase electroplate

- **Babcock and Wilcox Electrosleeve nanophase Ni coating**
  - **Used for reclamation of IDs of boiler tubes in power stations**
  - **Framatone Technologies**
  - **Nanophase electroplating technology development by Integran**
    - **buildup**
    - **wear**
    - **corrosion**



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Nanocoatings under development

- Thermal spray nanocomposite coatings
  - Alumina/titania thermal sprays
    - Hard/wear-resistant + ductile/crack resistant
    - Developed for Navy
    - Powder from Inframat
  - Polymer/nano-ceramic composite
    - Nylon or polycarbonate + nano-silica
    - Improved scratch-resistance
    - Various developers
    - Note: these do not have to be thermal spray
- Good potential for nano-fillers in polymer coatings
  - scratch-resistance
  - corrosion resistance
- Does something you cannot do another way
  - keeps it clear

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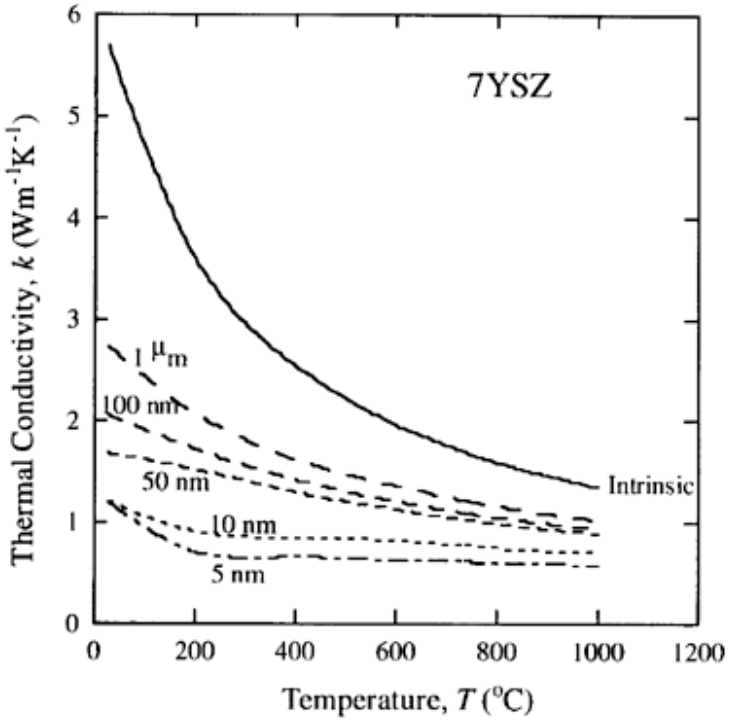
Another potential nanophase coating

- **Nanophase thermal barriers**
  - **Significantly lower thermal conductivity**
  - **Thinner, lower weight, better fatigue likely**
  - **Gas turbine engine blades and hot section walls**



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Best potential applications for functional nanocoatings

- **Look for the things you cannot do any other way**
  - **scratch-resistant + gas and corrosion-resistant + clear coatings**
    - **may be able to engineer for exceptional corrosion resistance**
  - **hard + ductile coatings for wear resistance**
    - **high stress components**
  - **thermal barriers**
    - **turbine engines (aircraft and power)**

Corrosion is a multi-billion dollar issue throughout the economy

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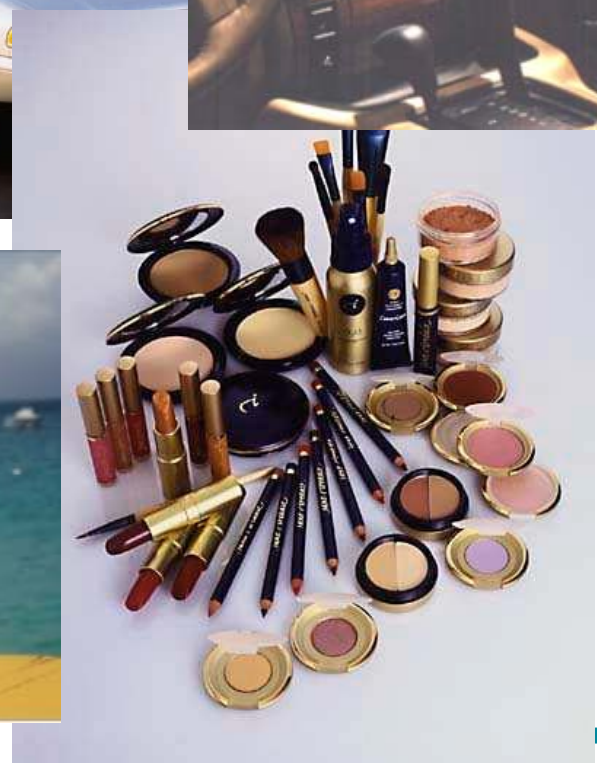
Consumer coatings

- **Decorative coatings**
  - **Look around – how many coatings do you see?**
  - **Paints**
  - **Inks**
- **Temporary coatings**
  - **Cosmetics**
  - **Razor blade lubricants**
  - **Sunscreen, insect repellant**



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Where are consumer nanocoatings used today?

- **Cosmetics, sunscreen, etc.**
  - **"Temporary coatings"**
    - **Incorporate oxides**
      - **nano TiO_2, ZnO, Al_2O_3**
    - **Liquid-carrying globules**
      - **nano-vesicles**
  - **A great deal of talk, few identifiable products**
    - **Sunscreens in use (including "nanopants")**
    - **Limited, but growing, usage in cosmetics**
      - **lipsticks, creams, hair products**
  - **Why nanoparticles?**
    - **Light scattering**
      - **particles <100nm are invisible**
    - **Dispersion and charge control**

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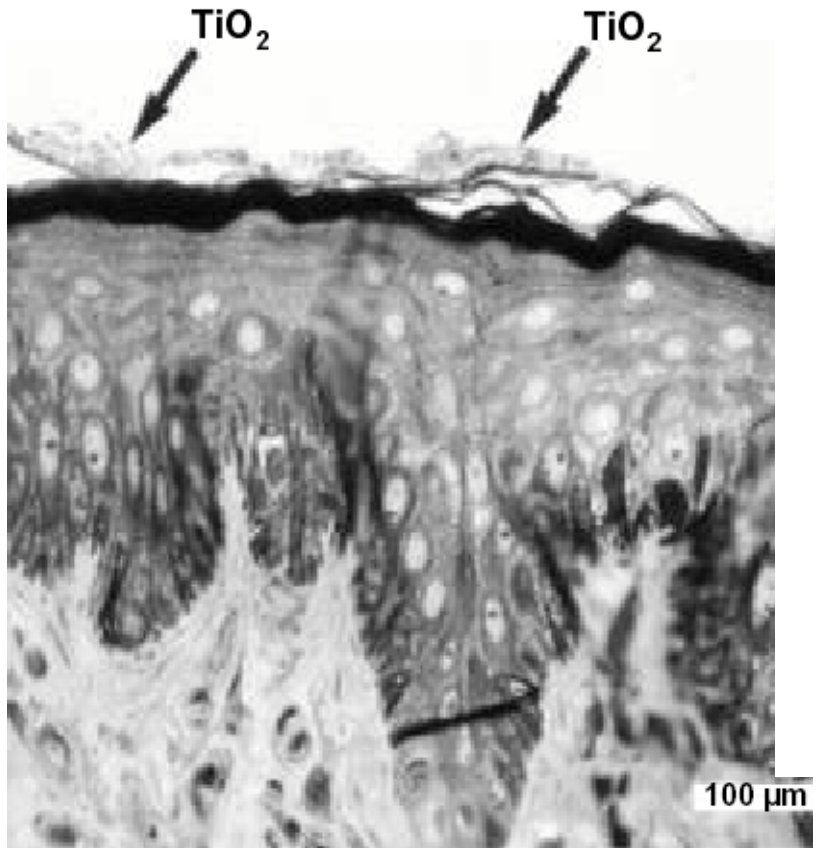
Nanoparticles in sunscreens

- **Nanopowders**
  - for sunscreen, wide spectrum reflectance
  - no light scattering (clear, not white)
  - high surface coverage (large surface area)
  - good dispersion
  - safe
    - well below 2.5μm particle size
    - does not penetrate skin
- **Producers include**
  - BASF (TiO_2 on textiles)
  - Sachtleben (Germany)



Sachtleben

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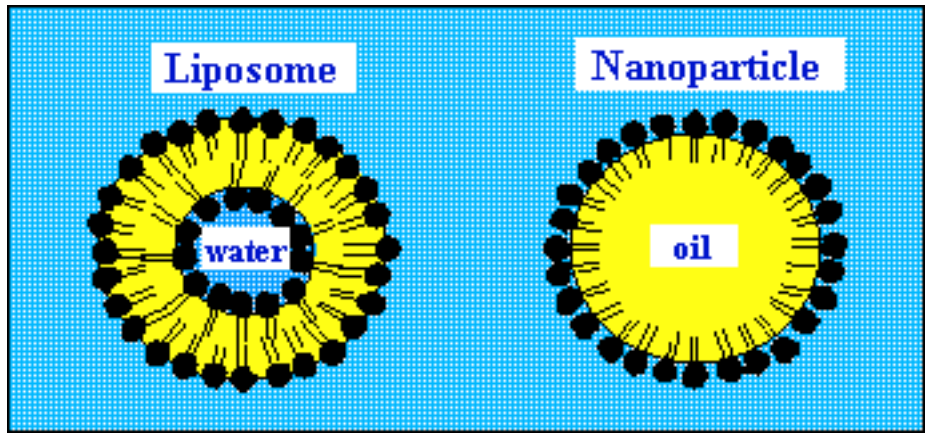
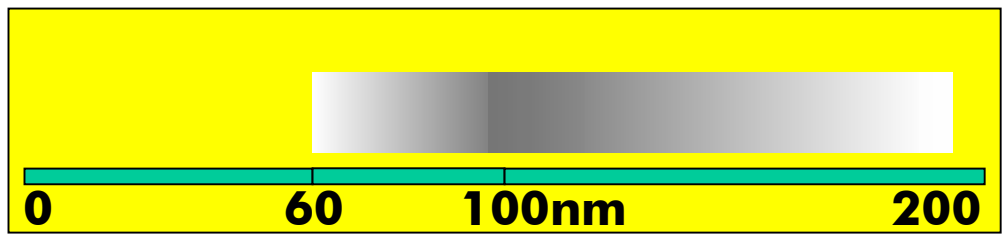
Nanoparticles in cosmetics

- **Lipid nanoparticles carry oil, which can incorporate Tretinoin, Retinol, Vitamin E, UV-Filters, Fragrance**
  - **<60nm transparent**
  - **Good dispersion**
  - **Affinity to skin, releasing active agents**
  - **Do not feel greasy**
  - **Can make +ve charge to remain on hair**
- **L'Oreal, Mibelle AG (Switzerland)**
  - **Microsomes transport through skin**





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Drivers and barriers - coatings

Drivers

- Unique combinations of properties
  - hardness + toughness
- Transparency
  - Packaging
  - Clear coats
  - Cosmetics
- Unique capabilities
  - Gas, liquid impermeability
    - packaging
    - corrosion?
  - Very low thermal conductance

Barriers

- Cost sensitive
  - Strong barrier, even in aerospace/military
- Hard coatings must offer unique capability
  - Not just less wear
  - Things like lubricant-free interrupted cutting

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Market potential

- **Cosmetics probably offers best market potential**
  - **"Temporary coatings"**
  - **Titania particles**
  - **Lipid nanoparticles**
- **Functional coatings**
  - **Clear coats**
    - **various deposition methods**
    - **various markets, including eyeglasses**
  - **Barrier and corrosion coatings**

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Where is the money to be made?

- Companies in the nano-area with very good chemistry capabilities venturing with large cosmetics, paint makers
- Companies able to apply computational methods and/or combinatorial chemistry
  - Cost-effective product development
  - Minimal time-to-market
- Large-scale production capable technologies for clear-coats (licensing)
- Are there good solutions for corrosion?

Serve market needs, not technology needs!

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Conclusions

- Long time scales
- Cost is critical
- Change the materials paradigm to develop structural materials efficiently and reduce time-to-market
  - Designing materials with built-in nanophases the most cost-effective way to produce them
- Real market linkage - teaming between materials development company and user
  - Man shall not live by nano alone! Only performance and cost sell
- Functional coatings are great but the best short term opportunities are in consumer coatings
  - Clear coats could be another big winner

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