Electronic Materials

Environmental Legislation Affecting PWB Metallization Chemistries

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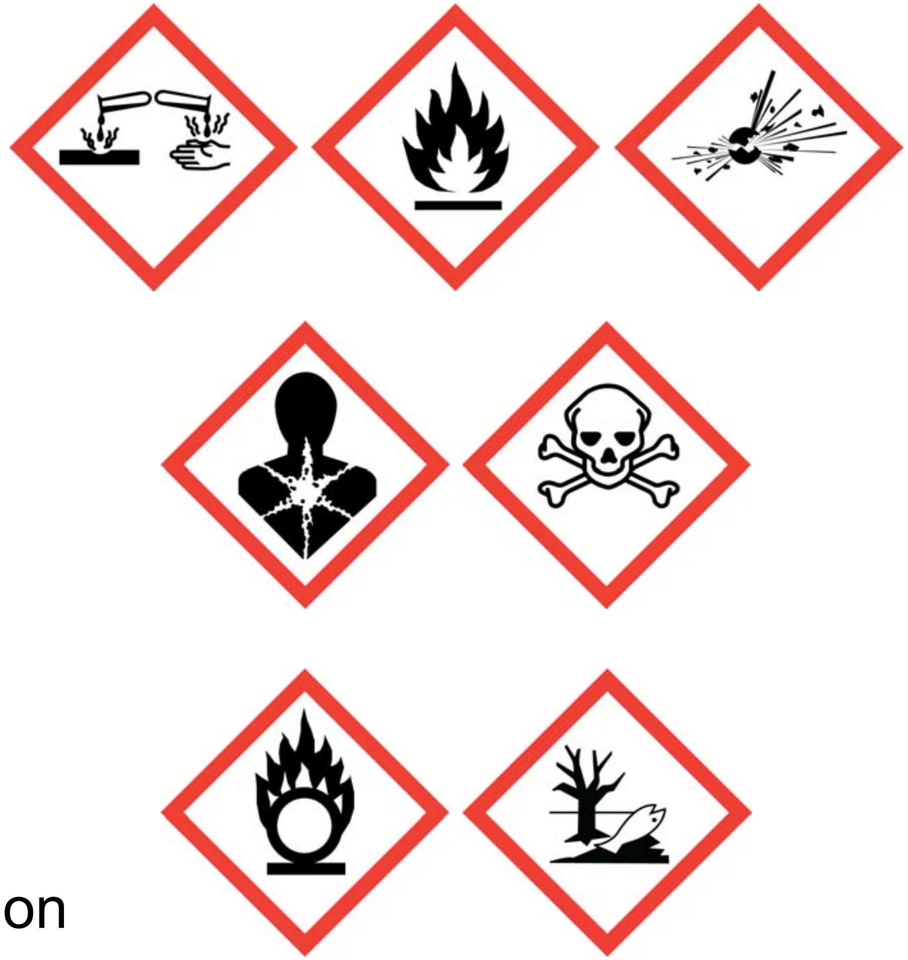
Presentation Outline

- Overview of Chemical Hazards and Risk Management
- Evolution of Legislative Approaches to Chemical Management
- Impacts on New Product Development Processes
- Impacts on Material Selection for PWB Metallization Processes
- Examples
- Summary

Overview of Chemical Hazards and Risk Management

Potentially Hazardous Impacts of Chemicals

- Corrosivity
- Reactivity
- Stability
- Irritation / Sensitization
- Toxicity
  - Acute
  - Chronic
- Mutagenicity
- Aquatic Toxicity
- Biodegradability
  - Biological Oxygen Demand
  - Persistence / Bioaccumulation
- Stratospheric chemistry impacts



Identification of Chemical Hazards

- Factors that aid rapid and certain identification of hazard
  - Immediate effects
  - Clearly visible impact
  - Direct effect of material on people or environment

  - Examples : Reactive materials, highly poisonous substances

- Factors that make identification of a hazard more difficult
  - Delayed effects
  - Impact on a small number of those exposed
  - Material interacts with people or environment indirectly

  - For example : Carcinogen, atmospheric ozone destruction

Persistent Organic Pollutants

- **Persistent**
  - If a material is so stable that it resists environmental breakdown, residence time in the environment can be extremely long (months or even years)
- **Bioaccumulative**
  - If the material is soluble in animal (fatty) tissues, continued exposure will lead to increasing concentrations
- Materials with these characteristics are of particular concern, as their negative effects are very hard to reverse
- Classes that are of particular concern
  - Persistent Bioaccumulative Toxic (PBT), e.g. DDT Pesticide
  - Very Persistent, very Bioaccumulative vPvB
  - Very Persistent, Environmentally Hazardous, e.g. O_3 depletion

Known Hazard versus Precautionary Principle

- The complex interactions of chemicals with human health and the environment are now better understood
- Some materials that had previously been considered safe have been found to have unexpected long term environmental or human health impacts
- Assumption that existing or new materials are safe has now changed to a situation where comprehensive analysis and testing data is required to demonstrate an acceptable hazard profile
- Precautionary Principle

  "…where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation"

  Principle #15 of the Declaration of the United Nations Conference on Environment and Development Rio de Janeiro June 1992

Evolution of Legislative Approaches to Chemical Management

Evolution of Regulatory Controls

Control of Substances with Immediate Impacts

↓

Control of Substances with Delayed Impacts

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Registration of Chemicals and Control of Newly Introduced Materials

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Regulation of Environmentally Hazardous Substances

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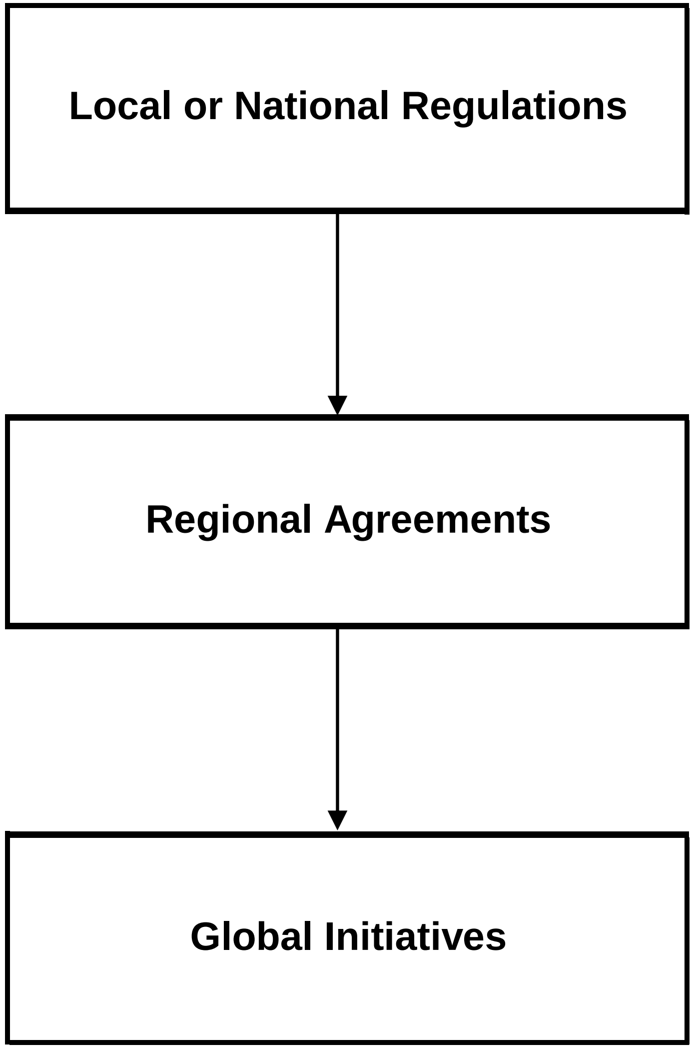
Comprehensive Assessment of Chemical Hazards and Requirement to Justify Usage

1970 - 1980

2000

2009

Shift from National to Global Regulatory Controls



Global Regulatory Trends

- Due to the global nature of problems caused by persistent organic pollutants (POPs), such as ecosystem degradation and ozone depletion, these issues were the first to be handled through global agreements
- Regional materials restrictions that affect the ability of manufacturing economies to export products (WEEE / RoHS) have been quickly adopted by other countries
- A new global standard for product hazard labeling (GHS System) represents another case where international trade is an important driver

Picture from: ec.europa.eu

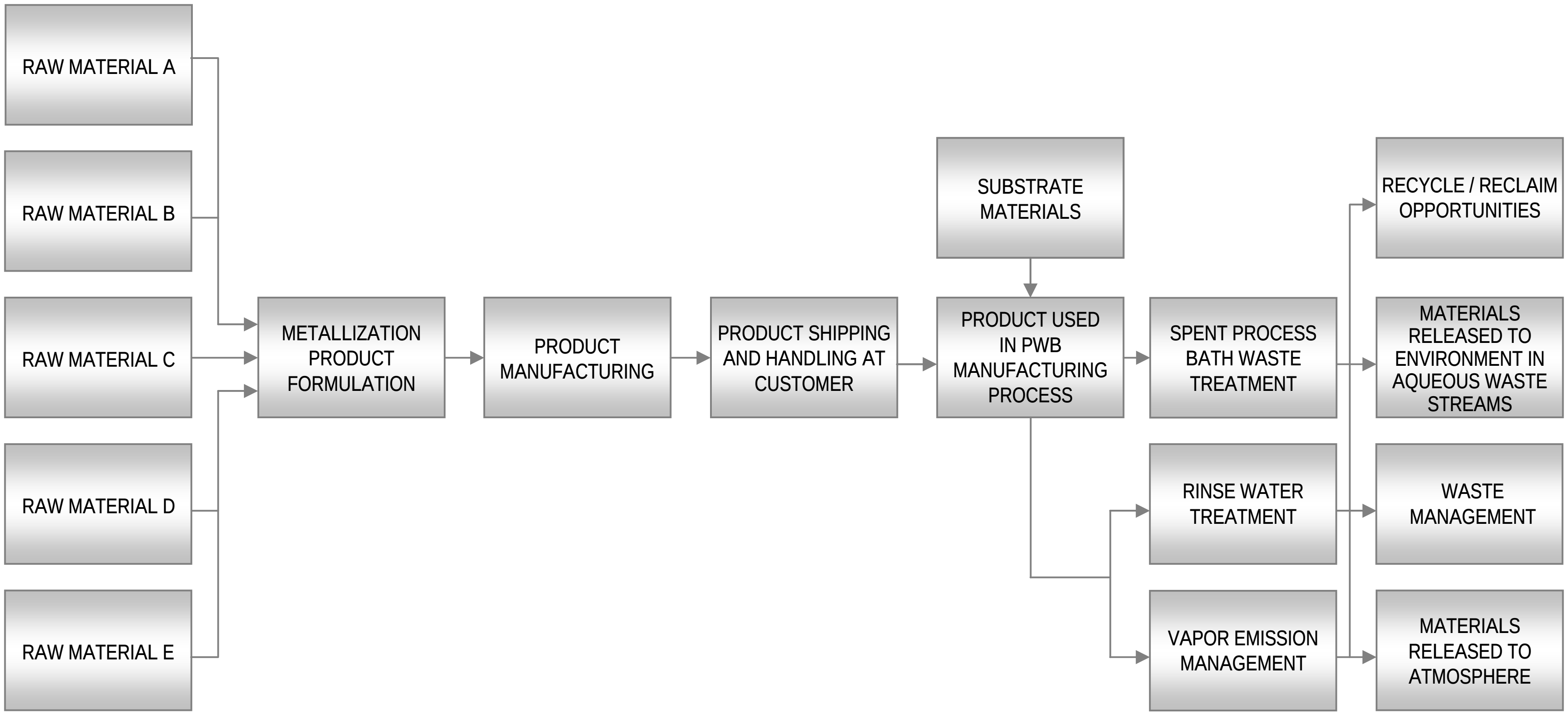
Global Regulatory Trends

- An emerging trend is for local regulatory approaches to move more quickly to other countries (for example, REACh style chemical assessments). Risk assessment approaches based on hazard data are being replaced by approaches based on the Precautionary Principle

- Public awareness of environmental issues is increasing and Non Governmental Organizations (NGOs) such as Greenpeace have been able to put substantial pressure on OEMS by publishing environmental "scorecards"

Impacts on New Product Development Processes

Regulatory Impacts on Product Development and Usage

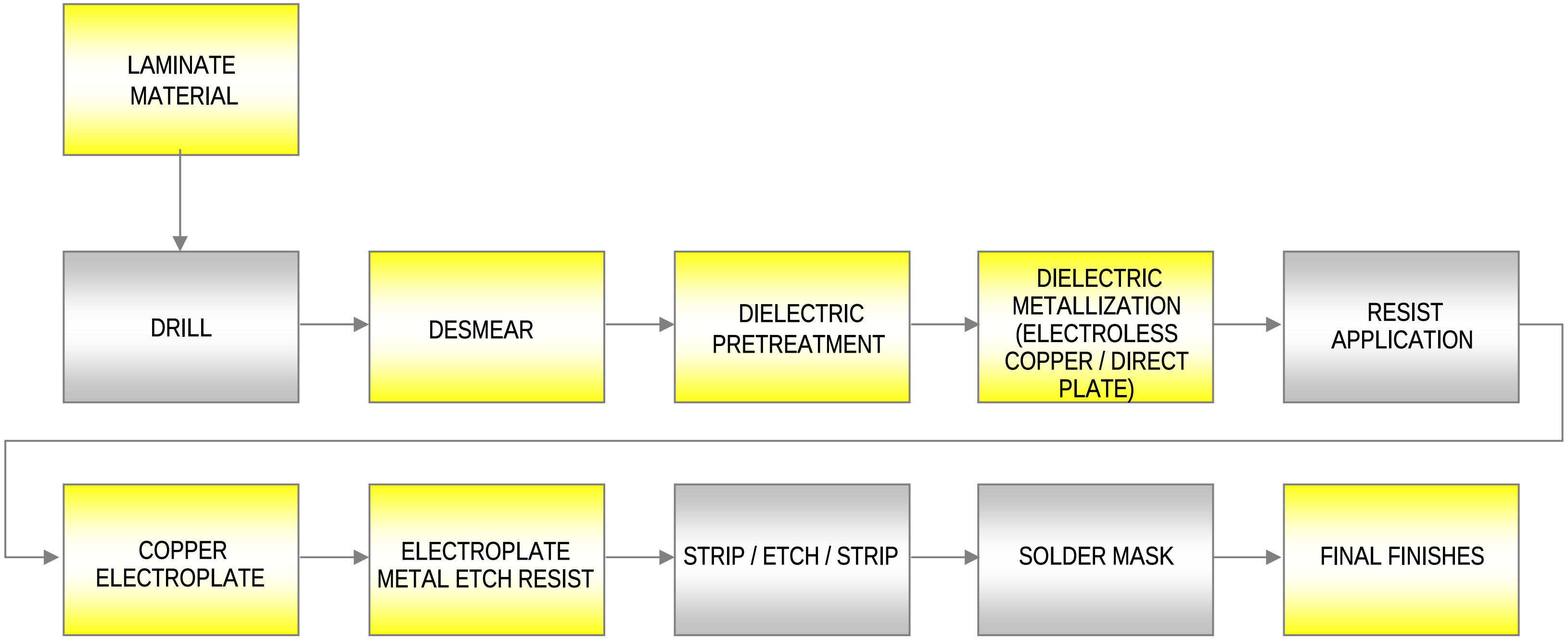


EXAMPLES OF APPLICABLE GOVERNMENT REGULATIONS

CHEMICAL REGISTRATION	AIR EMISSION STANDARDS	PRODUCT LABELLING		AIR EMISSION STANDARDS	HAZARDOUS WASTE REGULATIONS
MATERIAL USAGE OR RELEASE RESTRICTIONS OR BANS	WATER DISCHARGE STANDARDS	HAZARD COMMUNICATION	HAZARD COMMUNICATION		WATER DISCHARGE STANDARDS
ACUTE TOXICITY	EXPOSURE STANDARDS	SHIPPING REGULATIONS	EXPOSURE STANDARDS		SHIPPING REGULATIONS

Impacts on Material Selection for PWB Metallization Processes

Circuit Board Metallization Process Flow



Surfactants

- Widely different environmental regulations affect certain surfactants
  - Nonylphenol Ethoxylates (NPE) – environmental endocrine disruptors classified as reproductive hazards, which have been banned or restricted in a number of regions
  - Biodegradability – Problems with effects of poorly biodegradable surfactants led Europe to introduce the EU Detergent Regulation in 2005, requiring surfactants in cleaning formulations to be very biodegradable
  - Persistent Organic Pollutants - Some types of fluorinated surfactants (for example, PFOS – perfluorooctanesulfonates) are extremely resistant to degradation, resulting in extremely long environmental lifetimes. These materials are to be phased out under the Stockholm Treaty on POPs.

Surfactants

- Nonylphenol Ethoxylates
  - Widely used in the past, due their excellent surfactant properties, in cleaner formulations and also present as additives in some electroplating baths.
  - A variety of biodegradable alternatives are available, which provide equivalent product performance.

- PFOS
  - High chemical resistance of these materials allowed them to be used in highly oxidizing solutions such as alkaline permanganate
  - Optimization of desmear processes allows elimination of PFOS use without any loss in overall process performance

Solvents

- Major concerns with solvents are physical hazards, such as flammability, and toxicity
- Primary application of solvents in PWB metallization processes is in the solvent swell step of the desmear process
- Some ethylene based glycol ethers have reproductive hazards,
- N-methyl pyrrolidone (NMP), which may also be used in solvent swell applications, has recently been listed by its suppliers as a reproductive hazard
- Solvent swell formulations based on safer solvents, such as glycol ethers based on propylene glycol, are widely available

Chelates / Buffers

- Chelates and buffers are used in many PWB metallization processes, including cleaning steps and electroless, immersion and electrolytic plating baths.
- Chelates and buffers may have a number of potentially adverse environmental effects
  - Solubilization of toxic metals
  - Poor biodegradability
  - Provision of nutrients for algal growth
  - High BOD / COD

Chelates / Buffers

- Strong, poorly biodegradable chelates, such as EDTA, are used in many cleaning formulations
- EDTA is used as the chelate in the majority of high performance electroless copper formulations
  - Several European countries have banned use of EDTA, but these regulations do not affect other chelates with similar properties
  - Analysis of the hazards of strong chelates is complex, as they also reduce the toxicity of metal ions, compared to the unchelated forms
- While a number of alternate biodegradable materials are available, their chelation properties are somewhat weaker than EDTA, leading to some reduction in electroless copper product performance

Chelates / Buffers

- Problems with degradation of water quality in Mainland China, particularly due to high levels of algal growth, have led to increased restrictions on wastewater discharge
- Algae typically contain a carbon : nitrogen : phosphorus ratio of about 100 : 16 : 1 (known as the Redfield weight ratio) and reduction in concentrations of either phosphorus or nitrogen-containing nutrients can limit growth
- Alternatives to products containing chelates and buffers such as phosphonates and phosphates are available

Metals

- Driven by the desire to reduce use of hazardous materials, the RoHS Directive limited the maximum acceptable levels of several toxic heavy metals in finished products
- This affected both plated deposits and solder alloys
- Within PWB metallization processes, use of tin-lead electrodeposits as etch resists had already been largely replaced with pure tin before the new regulations
- Use of lead as a stabilizing additive in electroless nickel systems, leads to co-deposition, but levels well below the RoHS limit can be easily maintained
- Alternative electroless nickel formulations which do not use lead as an additive are available, with properties that are generally comparable, but have not yet replaced earlier formulations

Formaldehyde

- Formaldehyde is a strong reducing agent, whose vapors are flammable
- Since 2006, it has been classified as a human carcinogen by IARC
- As a human carcinogen, the REACh chemical assessment process is likely to apply restrictions on its use in Europe
- It is the most commonly used reducing agent in electroless copper plating baths and is also used as a starting material for many resins and adhesives
- Formaldehyde is highly biodegradable
- Low residual levels of formaldehyde can be present in some adhesives and resins used in electronic devices
- Some OEMs have begun to require elimination of formaldehyde from their products

Formaldehyde in Electroless Copper Formulations

- During material handling and process operations, it is critical to prevent worker exposure to formaldehyde solutions and vapors
- Use of well designed process equipment and ventilation is essential
- While both vertical and horizontal process equipment is available for electroless copper processing, use of horizontal lines simplifies prevention of formaldehyde exposure

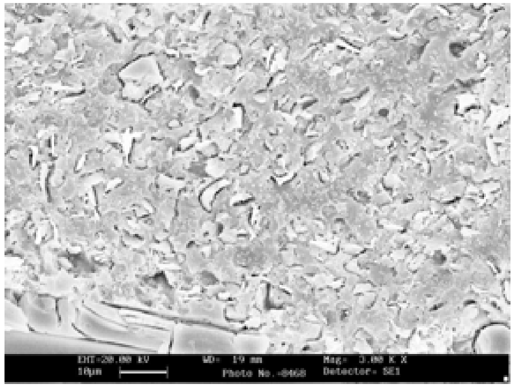
Examples

Impacts on Laminates

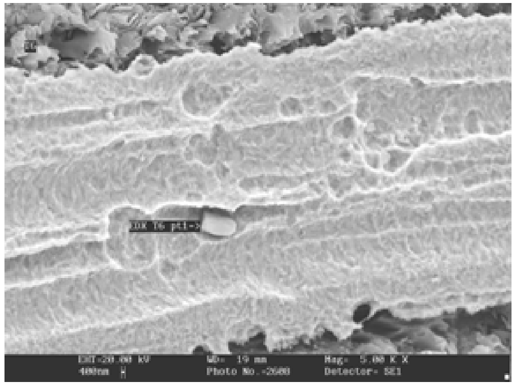
- The RoHS Directive has had both indirect and direct effects on laminate material performance requirements and composition
  - Introduction of new solder alloys requiring higher assembly temperatures
  - Higher assembly temperatures require laminates with higher T_g / T_d and lower thermal expansion
  - T_g / T_d can be increased by increasing resin cross-linking and thermal expansion lowered by addition of inorganic fillers
- While several types of brominated flame retardants were restricted by RoHS, these did not include the types used in epoxy based laminate materials
  - Consumer concern about the potential risks of environmental contamination from improper disposal of electronic wastes has driven introduction of Halogen-Free materials (HFR)
  - Addition of inorganic fillers to HFR materials can also improve their flame retardancy

Impacts on Dielectric Metallization Processes

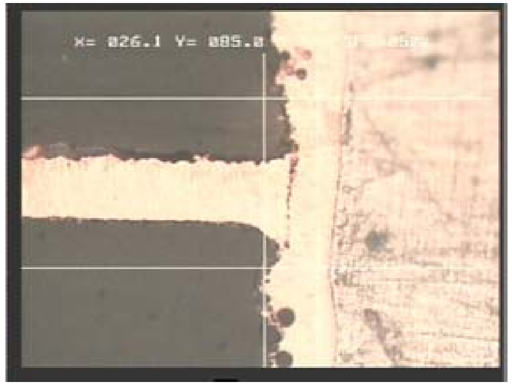
- Increased resin cross-linking makes chemical attack more difficult, requiring use of more aggressive process conditions to ensure removal of drill smear from copper interconnect surfaces
- Addition of fillers may lead to difficulties achieving complete metallization coverage and reduced adhesion to the dielectric surfaces, due to the presence of weakly attached fillers on the plated surface
- Filler materials may also become embedded in innerlayer surfaces, leading to increased levels of interconnect defects ICDs



Filler-containing Dielectric



Filler embedded in innerlayer



Filler related ICD

Characteristics of Alternate Cleaner Formulations

	New Cleaner	Cleaner A	Cleaner C
Chemical Oxygen Demand (ppm)	~4000	~13000	~41000
EU Detergent Registration (NPE Free)	Yes	No	Yes
Biodegradable Components	Yes	No	No
Phosphorus-Free	Yes	Yes	Yes
RoHS Compliant	Yes	Yes	Yes
Free of Strong Chelates	Yes	Yes	Yes

Performance Comparison of Cleaner Formulations

		New Cleaner	Cleaner A	Cleaner C
Cleaning Performance	Oil	★★★★★	★★★★	★★★★★
	Fingerprints	★★★★	★★★	★★
	Soldermask Residue	★★★★★	★★	★★★
	Copper Oxidation	★★★★	★★★★★	★★
Ease of Rinsing		★★★★★	★★★★	★★★
Soldermask Attack (ENIG Process)		★★★★	★★★	★★★★

Summary

- Successful development of new metallization products and processes requires a thorough understanding of environmental regulations and the balance between the hazard profiles and performance of different formulations and processes
- Alternative formulations with improved environmental characteristics and equal or better performance are generally available
- The trend from national / regional to global regulations is likely to continue, with a strong emphasis on elimination of persistent, bioaccumulative, toxic (PBT) materials

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