



# Welcome to Delegates

## Restriction of Hazardous Substances (RoHS) Key Features, Identification and Testing Methods and its Applicability in Indian Legislation

February 06, 2017

At

CII-Sohrabji Godrej Green Business Centre  
(CII-Godrej GBC)

Centre for Materials for Electronics Technology (C-MET)

Min. of Electronics and Information Technology (MeitY), Govt. of India

IDA Phase - III, Cherlapally,  
Hyderabad - 51

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## ✓ Ultra high purification of Metals

- High Purity Metals: Ga, In, Cd, Te, Zn for III-V compound semiconductors
- Refractory Metals: Ta, Nb, Hf
- **World Class RoHS testing facility**

## ✓ Processing Thick Film Materials

- Electronic Packaging
- Sensors
- Opto-Electronic Materials
- Advanced Nanomaterials

## ✓ High Tech Ceramic Processing

- Multilayer Ceramic Packaging
- Multilayer Actuators
- **Nanomaterials**



**HYDERABAD**



**PUNE**



**THRISSUR**



# Out line



- ❑ Legislative background
- ❑ What is it about
- ❑ Restricted elements and compounds
- ❑ Toxicity of hazardous substances
- ❑ Exemptions
- ❑ Characterization of RoHS elements
- ❑ Case studies at C-MET, Hyderabad
- ❑ Summary



# RoHS





- **Restriction of Hazardous Substances in Electrical and Electronic Equipment (RoHS)**
- **Directive (2002/95/EC)**
- **As of July 1, 2006, this directive bans lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) from all new electrical and electronic equipment sold to EU companies and manufactured in the EU.**





**Computer Hardware is Subject to RoHS Directive**  
**Automotive Hardware is Subject to ELV Directive**

# Why Important ?

## \$ Cost

-  Dutch Government blocked the shipment of 1.3M Sony Playstation system, 800K accessories - combined value of over US \$200M in 2001.
-  Cadmium in cables exceeds 0.01% limit by 3 – 20x.

## Health Fears

-  Media reported that over 100 workers in two Chinese battery factories ( Huizhou, Southern China ) were suspected to be contaminated by cadmium in July 2004.
-  Medical report states “ excessive levels of cadmium in blood” .

# What is the meaning of ?

- EU Directive 2002/95/EC of the European Parliament and of the council on the **R**estriction of the use of certain **H**azardous **S**ubstances ( RoHS ) in electrical and electronic equipment





# What is it about it



- Approximate the laws of the Member States
- Contribute to the protection of human health
- Environmental
- Disposal of **w**aste **e**lectrical and **e**lectronic **e**quipment

# Rationale for RoHS Directive

Land filling or illegal dumping of WEEE



Destruction of Ecosystem



## Ecological Destruction

- Air
- Water Quality
- Soil Pollution



RoHS/WEEE: Keeps to a Minimum of Environmental Destruction and Adverse Health Effect on Eco System

Effect on Food

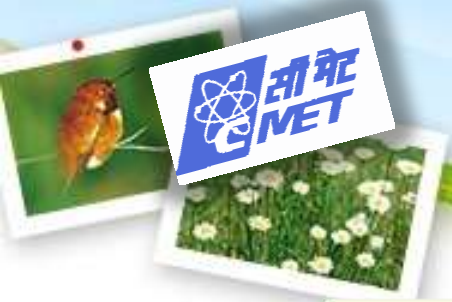


Adverse Health Effects





# Restricted substances & their permissible limit



Hexavalent Chromium  
1000 ppm

Lead  
1000 ppm

PBDE  
1000 ppm

PBB  
1000 ppm

Cadmium  
100 ppm

Mercury  
1000 ppm



# Categories of Electrical and Electronic Equipment (EEE) Covered by EU WEEE & RoHS

Large Household Appliances

Small Household Appliances

IT and Telecommunications Equipment

Lighting Equipment

Electrical and Electronic Tools (with the exception of large-scale stationary industrial tools)

Toys, Leisure and Sports Equipment

Medical Devices (with the exception of all implanted and infected products not covered by RoHS)

Monitoring & Control Instruments (Not covered by RoHS)

Automatic Dispensers



# Scope of RoHS Directive

## What is included: in general

- Applies to any product which is dependent on electric current or electromagnetic fields. Also, Includes all non-electronic parts of the product.
- Voltage rating of the product is less than 1000 V AC or 1500 V DC



# SCOPE OF ROHS DIRECTIVE

## What is NOT included:

- Spare parts for the repair, or the reuse, of electrical & electronic equipment put on market prior to July 1, 2006



- Military Equipment



- Medical Equipment



- Measurement and Control Equipment

- Large scale stationary industrial tools



# Summary on related directives

Directive Ref.	Date	Objective	Remarks
2002/95/EC	27Jan03	Restriction of the use of certain hazardous substances in electrical and electronic equipment ( <b>EEE</b> ) and to contribute to the protection of human health and the environmentally sound recovery and disposal of waste EEE.	6 banned materials included Pb, Hg, Cr6+, Cd and PBB / PBDE. Related consultation paper was issued to interested parties for review on 30/7/04. <ul style="list-style-type: none"> <li>• <i>Max. conc. value - 0.1%</i> by weight in homogeneous material for <i>Pb, Hg, Cr6+, PBB/ PBDE</i></li> <li>• <i>Max. conc. value - 0.01%</i> weight in homogenous material for <i>Cd</i>.</li> </ul>
2000/53/EC	18Sept00	Measures at the prevention of waste from vehicles and at the re-use, recycling and other forms of recovery of end-of life vehicles ( <b>ELV</b> ) and their components.	Related consultation papers issued on March 2003 and February 2004 , confirm the maximum concentration value limit to :- <ul style="list-style-type: none"> <li>• <i>0.1%</i> by weight per homogeneous material for <i>Pb, Cr6+ and Hg</i>.</li> <li>• <i>0.01%</i> for <i>Cd</i>, which are not intentionally</li> </ul>
94/62/EC 2004/12/EC (amendment)	20Dec94 2Nov04	Amending directive 94/62/EC, on <b>Packaging</b> and Packaging Waste is to prevent packaging waste by encouraging packaging re-use and recycling while at the same time avoid distortions in the internal market.	The targets defined are the following: <ul style="list-style-type: none"> <li>• <i>Recovery of minimum 60%</i> by weight of the packaging waste</li> <li>• <i>Recycling of at least 55%</i> and a maximum 80% by weight of the totally of packaging materials, with a material-specific minimum recycling rate for plastic of 22.5%</li> <li>• <i>Max. sum of concentration levels of Pb, Cd, Hg and Cr6+ -&gt; 100 ppm</i> by weight</li> </ul>



# Summary on related directives

Directive Ref.	Date	Objective	Remarks
91/338/EEC	18Jun91	Restriction on the use of <b>Cadmium pigment</b> (amending for the 10th time Directive 76/769/EEC)	The cadmium content (expressed as Cd metal) exceeds 0,01 % by mass is prohibited in the finished products or components of products manufactured from polymers or copolymers of vinyl chloride and stabilized by substances.
91/157/EEC 98/101/EC (amendment)	3Mar91 22Dec98	The recovery and controlled disposal of those spent <b>batteries</b> and accumulators containing dangerous substances.	Batteries and accumulators are prohibited with content: <ul style="list-style-type: none"> <li>• More than 25mg of mercury per cell, except alkaline manganese batteries,</li> <li>• More than 0.025% of cadmium by weight,</li> <li>• More than 0.4% of lead by weight,</li> <li>• Alkaline manganese batteries containing more than 0.025% of mercury by weight</li> </ul>
76/769/EEC	27Jul76	Approximation of the laws, regulations and administrative provisions of the Member states relating to restrictions on the marketing and use of certain dangerous substance and preparations	



# Offences and Penalties



## Penalties

### UK

Failing to comply the RoHS could result:

Summary Conviction : Max. £5,000

Indictment Conviction : **Unlimited Fine**

director, manager or similar officer of the corporate body, they could be regarded as having committed the offence as well as the corporate body

### **Defence:**

'due diligence' is available where a person can show he took all reasonable steps and exercised all due diligence to avoid committing an offence.

(include reference to an act or default or information given by a third party or that information in possession of the person making the claim)



# Loss in Failing Compliance



## Other invisible penalty

- ❁ **Lost market competitiveness and business chance**
- ❁ **Product cannot sell in Europe, US and China markets.**
- ❁ **Reputation Damage**





# RoHS Documents



- **On request to provide technical documentation or other information to enforcement authority**
- **Record should be kept at least 4 years**
- **Self-declaration**



# China RoHS Regulation



- China RoHS will apply to electronics manufactured in China for **sale domestically** as well as goods imported into China.
- It does not apply to electronics made in China for export and it does not apply to military electronics.
- Electronic products shall indicate the names and contents of toxic and harmful substances contained therein and the recyclability of such products.
- From January 2007, products shall not contain lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls (PBB), polybrominated diphenyl ethers (PBDE) and **other toxic and harmful substances**.
- **Packaging-material use-and-declaration requirement** stating that "nontoxic, harmless, readily degradable and recyclable materials shall be used as the packaging materials, and the materials ingredients of the packaging shall be clearly marked".



# Which materials are banned ?

( Directive 2002/95/EC )

- ***Lead (Pb)***
  - Used in virtually all solders and electronic components.
- ***Cadmium (Cd)***
  - Used in batteries (NiCd), plastic stabilizers, platings.
- ***Mercury (Hg)***
  - Used in some electrical components, batteries, pigments.
- ***Hexavalent chromium (Cr<sup>6+</sup>)***
  - Used in dyes, pigments, plating solutions, alloys.
- ***Polybrominated biphenyls (PBB) & Polybrominated diphenyl ethers (PBDE)***
  - Both PBB and PBDE are used as flame retardants in plastics

# Exceptions to RoHS

*(All exceptions will be reviewed every 4 years or less)*

## 1. Lead:

- in the glass of cathode ray tubes
- in certain steel (<0.35%), aluminum (<0.4%) and copper alloys (< 4%)
- in high melting temperature type solders
- in solders for servers and Storage Arrays (Until 2010)
- Lead in solders for network infrastructure equipment in electronic ceramic parts (i.e. piezoelectric components)

2. **Mercury:** in some lighting applications

3. **Cadmium:** Cd plating

4. **Hexavalent chromium** in refrigerators

5. Further exceptions are still under discussion.

# Issues in using Pb-free solders

➤ Replacement of lead in solders → costly material to replace, difficult to process, less reliability data

- **Lower solderability**

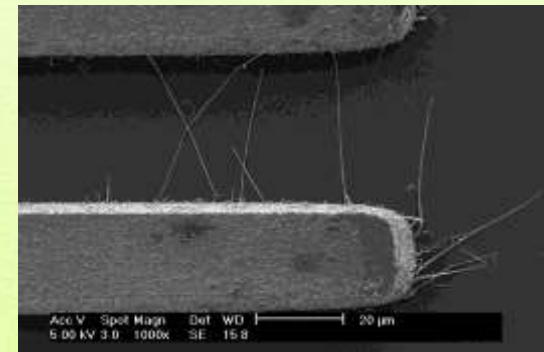
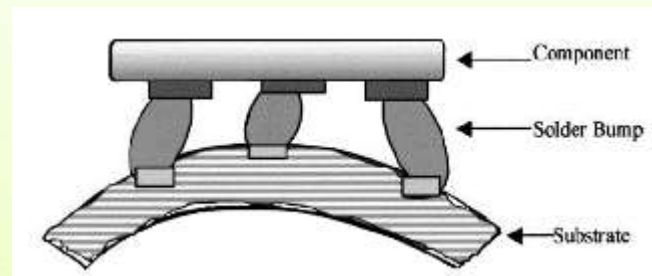
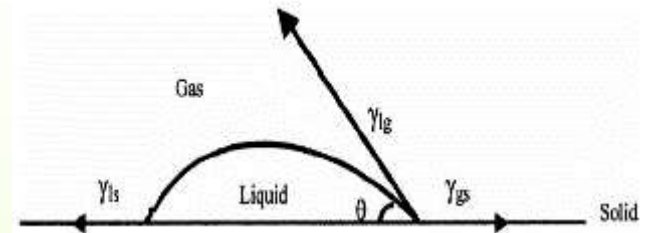
- Higher surface tension → cannot spread easily

- **Higher reflow profile**

- Increase board warpage.

- **Tin Whisker**

- An elongated single crystal of pure tin
  - Potential failure risk by short circuits





# WEEE and RoHS

Waste Electrical and Electronic Equipment **WEEE** as set out in Directive 2002/96/EC of 27 January 2003

Reduce the load of electronic waste:

- heavy metals
- flame retardants

# Exemptions

- ❖ Exemptions from the substitution requirement should be permitted if substitution is not possible from the scientific and technical point of view.
- ❖ or if the negative environmental or health impacts caused by substitution are likely to outweigh the human and environmental benefits of the substitution

# Exemptions for Hg

- Mercury in compact fluorescent lamps not exceeding 5 mg per lamp.
- Mercury in straight fluorescent lamps for general purposes not exceeding:
  - halophosphate 10 mg
  - triphosphate with normal lifetime 5 mg
  - triphosphate with long lifetime 8 mg
- Mercury in straight fluorescent lamps for special purposes.











# Exemptions for Pb



- Lead in glass of cathode ray tubes, electronic components and fluorescent tubes.
- Lead as an alloying element in steel containing up to 0.35 % lead by weight, aluminium containing up to 0.4 % lead by weight and as a copper alloy containing up to 4 % lead by weight.
- Lead in high melting temperature type solders (i.e. tin-lead solder alloys containing more than 85 % lead).

# RoHS like regulations

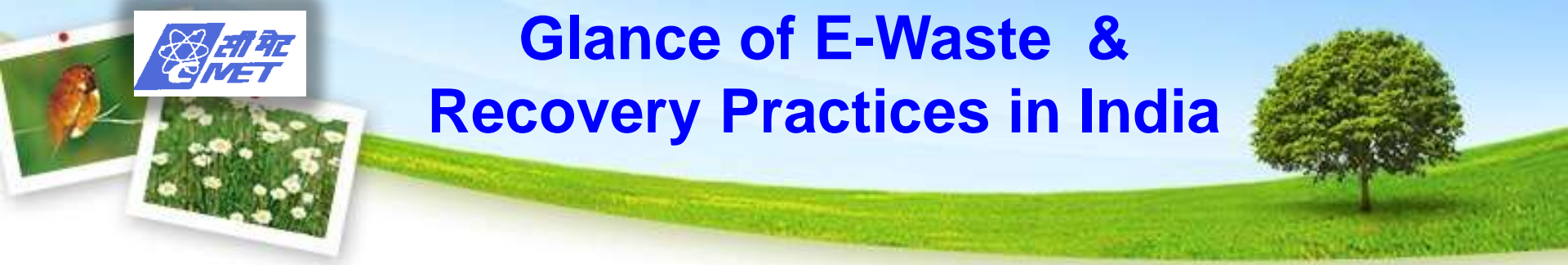
Country	Entry date for into force	Restricted substances	Product Scope
EU (incl. N, S) 	1.7.2006	Hg, Cd, Pb, CrVI, PBB, PBDE	defined product categories
USA/California  	1.1.2007	Hg, Cd, Pb, CrVI	only for larger displays, extension of the scope (beginning 2010) fallen through
China 	1.3.2007	like EU RoHS	EIPs (substance bans only for selected EIPs)
South Korea 	1.7.2008	like EU RoHS	all electronic products, automotive electronics
USA/New Jersey  	1.2.2009	like EU RoHS+PVC	only for larger displays and computers

# Hazardous practices of recovery of metals in un-organized sector



Total Au-recovery efficiency only  $\approx 25\%$ , while environmental & health damage is dramatic (Rochat, Keller, EMPA 2007)

# Glance of E-Waste & Recovery Practices in India





# Who is responsible ?



## → Producer

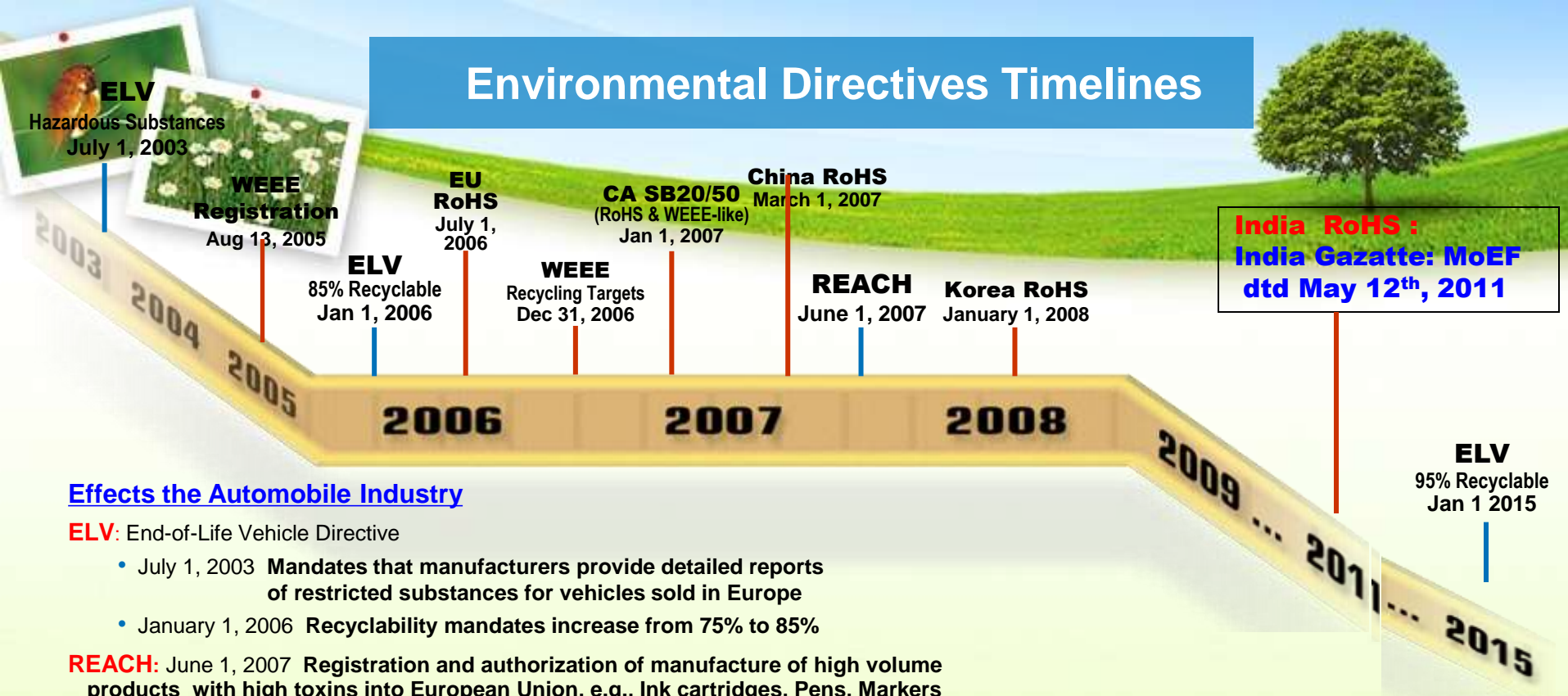
- Producers are required to keep appropriate records for a period up to 4 years after the use.

### Who is a producer ?

Any person / company who irrespective of selling technique used,

- Manufactures & sellers of EEE under his own brand
- Resales under their own brand, equipment produced by other suppliers
- Imports or exports of electrical & electronic equipment on a professional basis into member states.

# Environmental Directives Timelines



## Effects the Automobile Industry

**ELV:** End-of-Life Vehicle Directive

- July 1, 2003 Mandates that manufacturers provide detailed reports of restricted substances for vehicles sold in Europe
- January 1, 2006 Recyclability mandates increase from 75% to 85%

**REACH:** June 1, 2007 Registration and authorization of manufacture of high volume products with high toxins into European Union, e.g., Ink cartridges, Pens, Markers

## Effects the Electrical and Electronics Industries

**WEEE:** Waste Electrical and Electronic Equipment Directive

- Aug 13, 2005 Establishes producer responsibility for recycling and disposal of electrical goods
- Dec 31, 2006 EU country-specific recycling targets must be achieved

**EU RoHS:** Restriction of Hazardous Substances Directive

- July 1, 2006 No lead (lead-based solder), cadmium, mercury, hexavalent chromium and PBB/PBDE flame retardants

**California SB20/50:** Restriction of Hazardous Substances Directive


- January 1, 2007 Limited product scope, LCD, Printers

**China and Korea RoHS:** Restriction of Hazardous Substances Directive

- March 2007 and January 1, 2008 respectively: Labeling; No lead (lead-based solder), cadmium, mercury, hexavalent chromium, PBB/PBDE flame retardants

**India RoHS :**  
**India Gazette: MoEF**  
**Notification dtd May 12<sup>th</sup>, 2011**

(Chapter V: Reduction in the use of Hazardous substances in the electrical and electronics equipment)



**MoEF & CC, India, E-waste  
(Management)  
Rule - 2016**

**[PUBLISHED IN THE GAZETTE OF INDIA, EXTRAORDINARY PART-II, SECTION-3, SUB-SECTION (i)]**

**GOVERNMENT OF INDIA  
MINISTRY OF ENVIRONMENT, FOREST AND CLIMATE CHANGE**

**NOTIFICATION**

**New Delhi, the 23<sup>rd</sup> March , 2016**

- 1. Short title and commencement.** - (1) These rules may be called the E-Waste (Management) Rules, 2016.  
(2) They shall come into force from the 1<sup>st</sup> day of October, 2016.

**CHAPTER V**

**REDUCTION IN THE USE OF HAZARDOUS SUBSTANCES IN THE MANUFACTURE OF ELECTRICAL AND ELECTRONIC EQUIPMENT AND THEIR COMPONENTS OR CONSUMABLES OR PARTS OR SPARES**

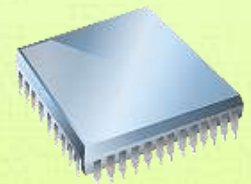
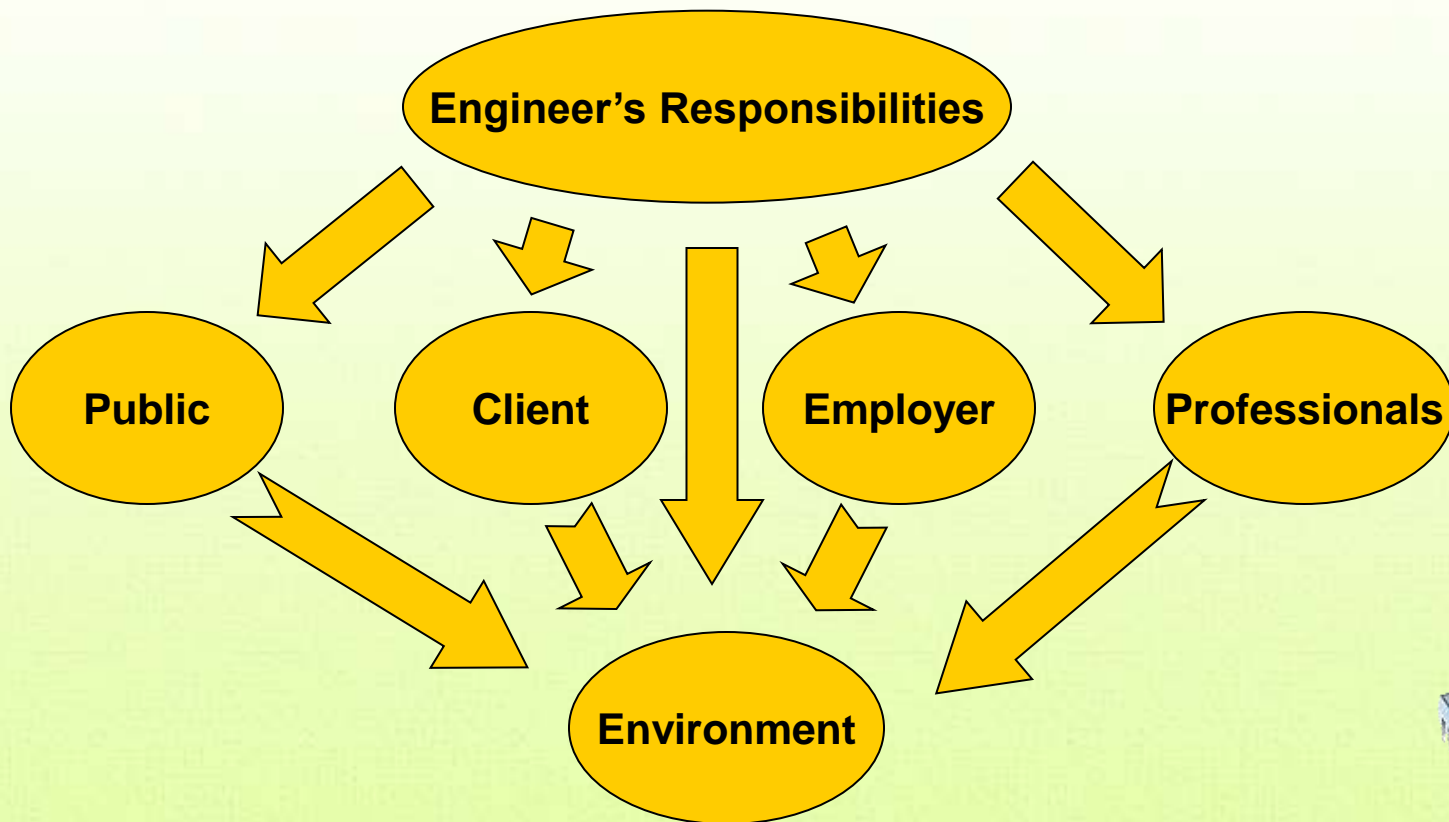
- 16. Reduction in the use of hazardous substances in the manufacture of electrical and electronic equipment and their components or consumables or parts or spares.** - (1) Every producer of electrical and electronic equipment and their components or consumables or parts or spares listed in Schedule I shall ensure that, new Electrical and Electronic Equipment and their components or consumables or parts or spares do not contain Lead, Mercury, Cadmium, Hexavalent Chromium, polybrominated biphenyls and polybrominated diphenyl ethers beyond a maximum concentration value of 0.1% by weight in homogenous materials for lead, mercury, hexavalent chromium, polybrominated biphenyls and polybrominated diphenyl ethers and of 0.01% by weight in homogenous materials for cadmium.  
(2) Components or consumables or parts or spares required for the electrical and electronic equipment placed in the market prior to 1<sup>st</sup> May, 2014 may be exempted from the provisions of sub-rule (1) of rule 16 provided Reduction of Hazardous Substances compliant parts and spares are not available.  
(3) The applications listed in Schedule II shall be exempted from provisions of sub-rule (1) of rule 16.



# ETHICS OF EEE MANUFACTURES

- **Ethics**

Application of moral principles and professional standards to situations encountered by professionals in the practice of manufacturing of EEE products.





# Compliance Strategy

## Supply Chain



# The toxicity of hazardous substances



# Where can we find the banned substances? $\text{Cr}^{6+}$



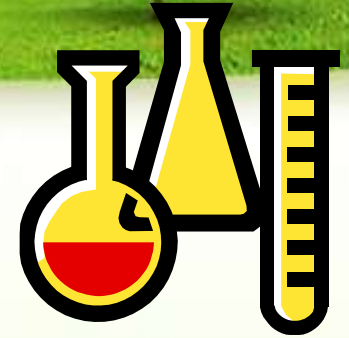
## *Hexavalent Chromium ( $\text{Cr}^{6+}$ )*

*$\text{Cr}^{6+}$  is generally produced by industrial processes, and used in industries such as :-*

- Pigments, catalysis, plating and tanning
- Parts with a metal frame  
( e.g. Motor, Transformers, etc. )
- Screws, nuts, some parts / areas that are chromate treated  
( e.g. AC adaptor, variable resistor, driver unit, etc.)



# Chromium Exists as Several Chemical Species



- Most common oxidation states: 0, +3, +6
  - 0: Elemental Chromium (Cr)
  - +3: Trivalent Chromium, Species:  $\text{Cr}^{3+}$ ,  $\text{Cr}_2\text{O}_3$
  - +6: Hexavalent Chromium, Species:  $\text{Cr}^{6+}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^-$
- Cr(VI) is much more toxic, stable and mobile than Cr(III)
- Cr(VI) is a known human carcinogen, Cr(VI) is also a respiratory tract irritant.
- Hexavalent chromium ( $\text{Cr}^{6+}$ ) exists in alkaline, strongly oxidizing environments
- Trivalent chromium ( $\text{Cr}^{3+}$ ) exists in moderately oxidizing and reduced environments

# ***Is Chrome a Carcinogen or Necessary Element?***



- Chrome III is an essential nutrient for maintaining blood glucose levels



- Chrome VI is classified as a known human carcinogen





# Why use *hexavalent chromium* ( $Cr^{6+}$ )



Used as a surface finish because of:

- low coefficient of friction
- High hardness, excellent corrosion resistance, high heat resistance
- Anti-galling properties (sliding on the surface without pressure )



# Routes of Exposure

- Inhalation of dusts, mists, or fumes created during processes involving the use of Cr(VI) compounds or hot processes that cause the formation of Cr(VI)
- Eye or skin contact with powder, dusts or liquids containing Cr(VI) with skin absorption possible
- Ingestion through contamination of food and drink.

# Major Health Effects



- Lung cancer
- Nasal septum ulcerations and perforations
- Asthma
- Skin ulcers
- Allergic and irritant contact dermatitis





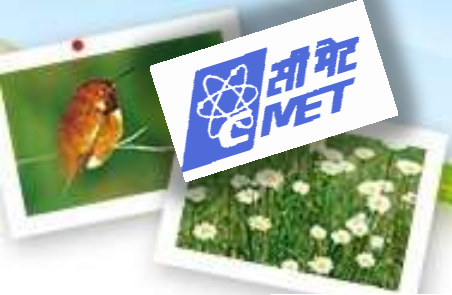


## The differences between $Cr^{3+}$ and $Cr^{6+}$ in terms of plating

The major disadvantage of the current process of chrome plating is that it requires the use of chromic acid-based electrolytes comprising  $Cr^{6+}$ .

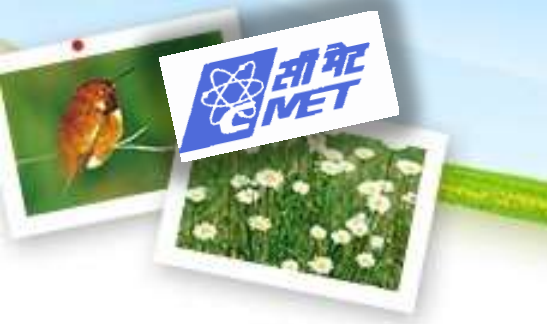
Consideration	$Cr^{3+}$	$Cr^{6+}$
Ease of burning	Very hard	Easy
Ease of rinsing	Easy	Not easy
Skin contact	Mild effect, similar to nickel	Strong acid burn and ulceration
Waste treatment	Easy	Not easy
Mistiness	Similar to nickel	Heavy and toxic
Color of deposit	Metallic white to pewter	Blue-white, "chrome" color

# E.g. for Cr<sup>6+</sup> components



Cr<sup>6+</sup>





**Cr<sup>6+</sup>**

Hexavalent Chromium (Chromium 6) Primary Route of Entry

 Inhalation	 Skin Absorption	 Ingestion
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# Can $\text{Cr}^{6+}$ be replaced in plating process ?

- using trivalent chromium plating baths ( but with inferior performance and poorer corrosion resistance )
- Nickel or Nickel and cobalt alloys
- Other techniques used for plating such as:
  - **Electroless plating**
    - Nickel  $\rightarrow$  replacement for chromium
    - metal ions in a dilute aqueous solution are deposited onto a substrate by means of a continuous chemical reaction.
  - Chemical vapor Deposition ( CVD ), surface hardening, thermal spraying, physical vapor deposition, etc.
  - **Organic Polymer Films**
    - Such as polyacrylate, polyethylene waxes, etc.



# Where can we find the banned substance ? **Cd**



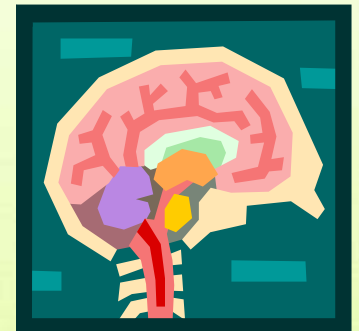
## *Cadmium (Cd)*

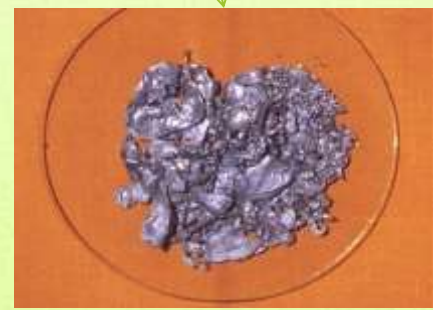
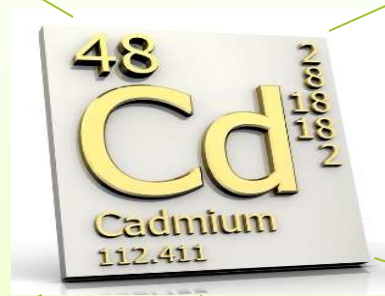
- a natural-occurring element in the earth's crust - often found in combination with other elements, e.g oxygen (cadmium oxide,  $\text{CdO}$ ), chlorine (cadmium chloride,  $\text{CdCl}_2$ ), or sulfur ( cadmium sulfide,  $\text{CdS}$  )
- not corrode easily, when used as a sacrificial coating (dual qualities of lubricating at minimal thickness and superior sacrificial corrosion protector).
- used in products such as rechargeable batteries (NiCd), plastic stabilizers, electroplating coatings, metal coating, pigments, electrical contact alloys for relays and switch, etc.

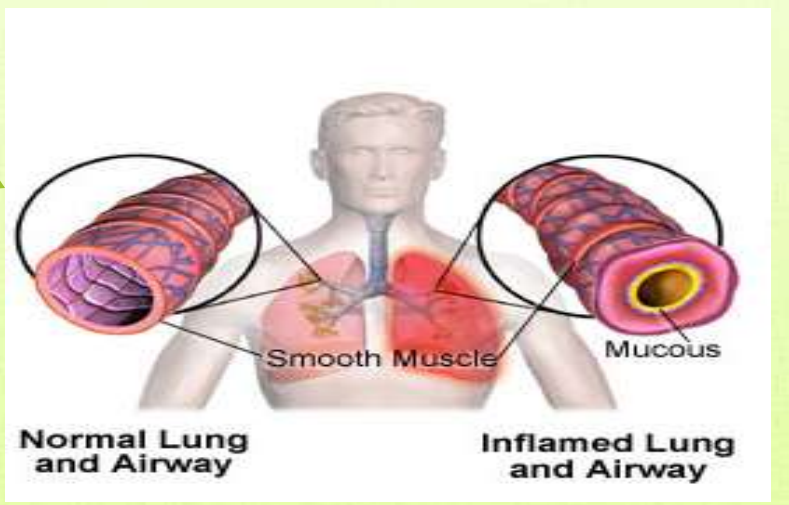
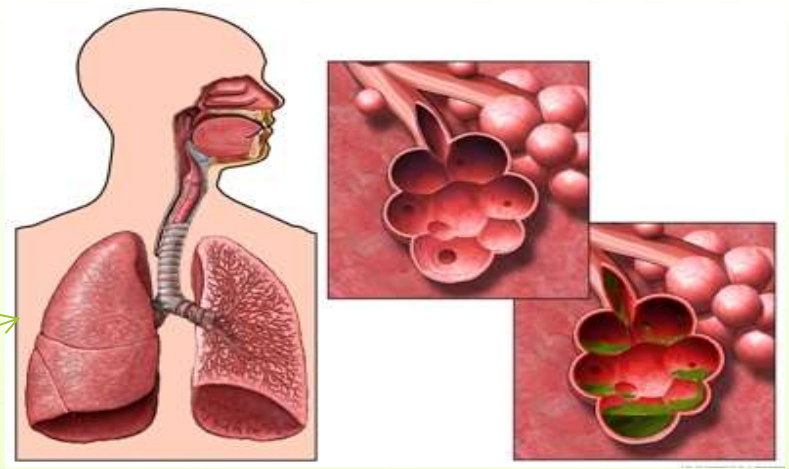
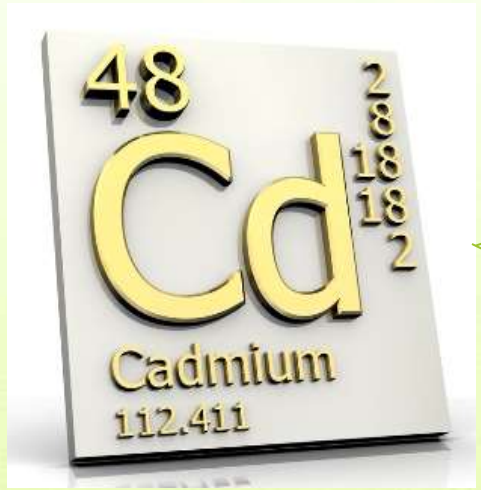
# Cadmium ( Cd ) - Human health issues



- CdO is a cancer-causing agent– especially prostate and kidney cancer in humans (*carcinogen*).
- **CdO fumes:**
  - toxic to the respiratory system (destroy epithelium layer)
  - high exposure results in severe bronchial and pulmonary irritation.
  - also hamper the development and function of immune system, reproductive organs and nervous system











# Any alternative material to replace Cd in electroplating ?

## *Aluminum Ion Vapour Deposition System ( AIVD )*

- used in place of cadmium in the electroplating industry.
- advantages include:
  - no hazardous materials (HM) required and generated
  - prevents employee exposure to HM
  - eliminates the need for environmental permits
  - prevents corrosion better than Cd coatings in acidic environments
  - the coatings stand up to higher temperatures than Cd
  - allows for thicker coatings and a more uniform coating



# Any alternative material to replace Cd ?

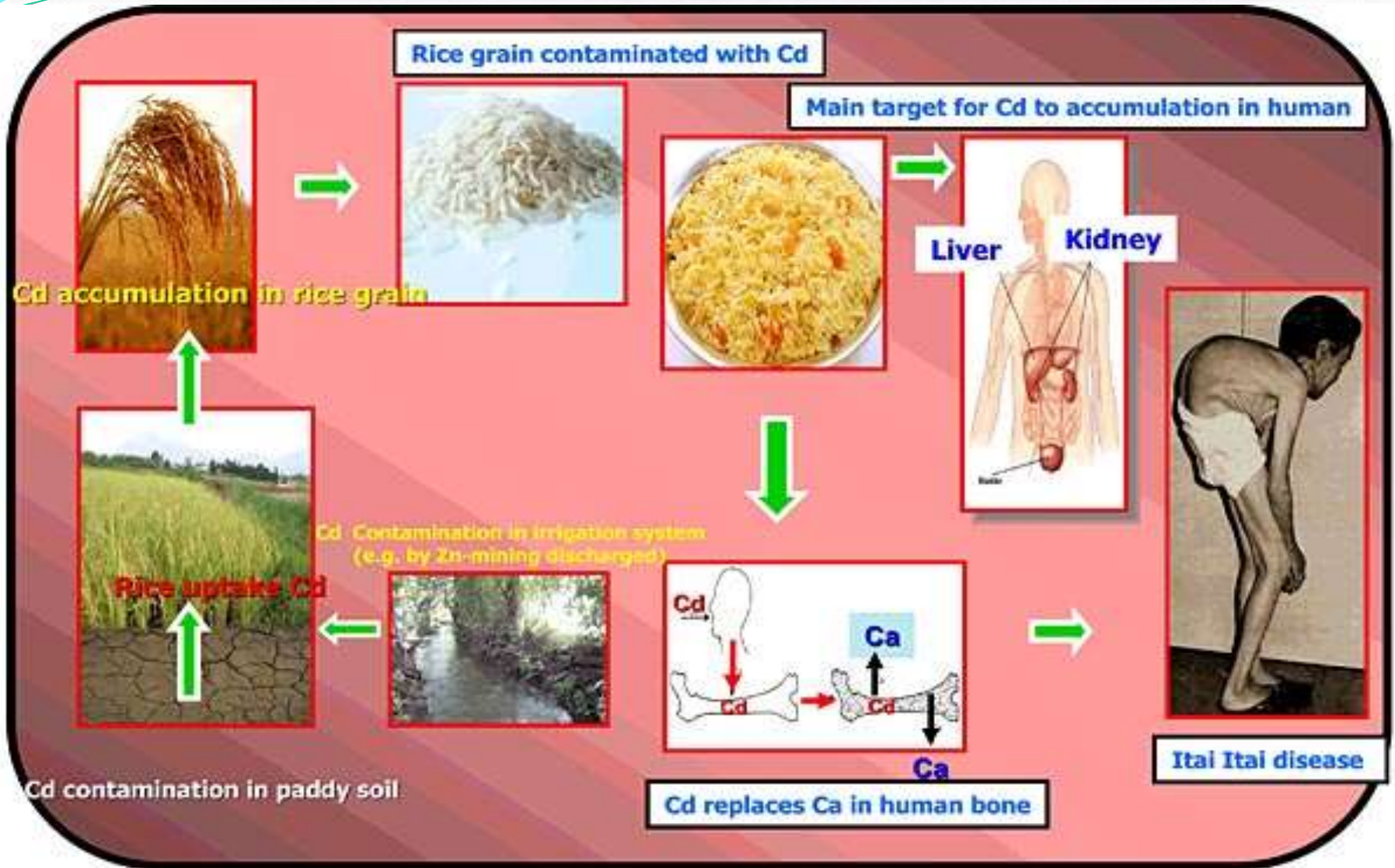


*Zinc-based replacement in electroplating industry such as:*

- **Zinc-Nickel alkaline plating bath:**
  - good corrosion resistance properties
  - uniform thickness during coating process
  - better wear resistance but lack of lubrication
- **Zinc-Cobalt acidic plating bath:**
  - its plating bath has higher cathode efficiency
  - higher plating speed
  - but variable current density



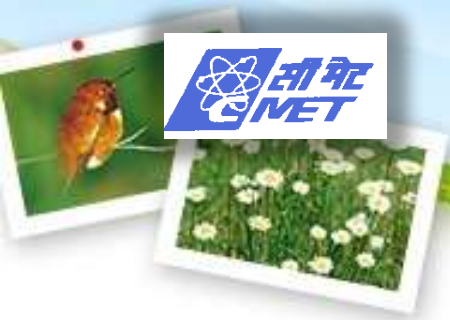
# Possible Cd intake to Human body



# Where can we find the banned substance? Hg



- Mercury : metal in liquid form in room temperature. Do not oxidize at room temperature.
- Very small amount of Hg can do a significant damage to the environment. For example, 1gm of Hg per year is enough to contaminate all the fish in lake with a surface area of 8 hectares.
- Metallic mercury – use in producing chlorine gas and caustic soda and commonly apply to use in thermometer, dental fillings, batteries.
- In electronics industry → thermal indicators, relays, sensors, fluorescent lamp, switches, sensors, etc.

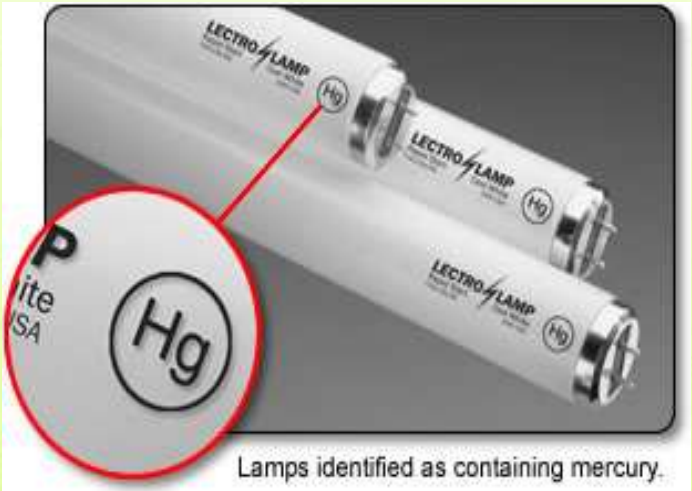
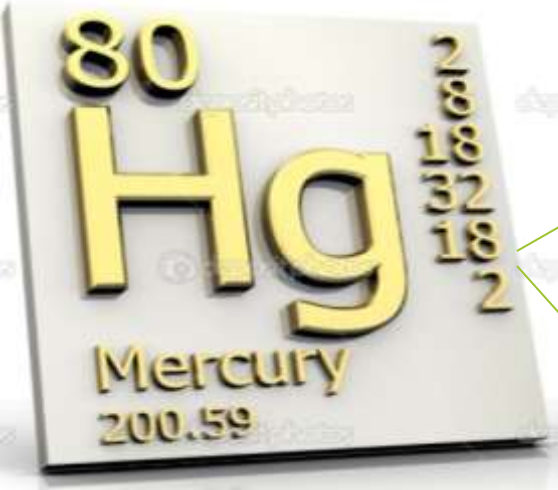


# Quantitative Exemptions of Hg

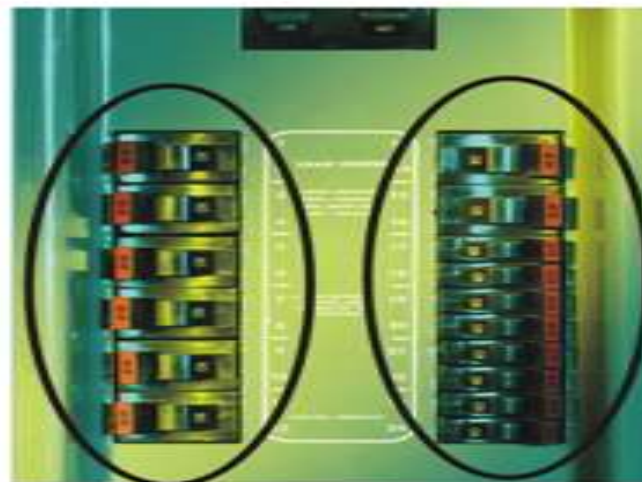
As per the Directive exemptions :

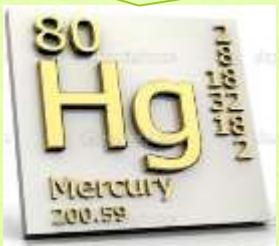
- *Mercury in compact fluorescent lamps  $\leq 5\text{mg}$  per lamp.*
- *Mercury in straight fluorescent lamps purpose not exceeding :*
  - *halophosphate*  $10\text{mg}$
  - *triphosphate with normal lifetime*  $5\text{mg}$
  - *triphosphate with long lifetime*  $8\text{mg}$
- *Mercury in straight fluorescent lamps for special purposes*

The amount of mercury used in the fluorescent lamps may affect the lifetime of the product i.e. % of weight of Hg decrease  $\rightarrow$  the lifetime of the product may also decrease.



# Occurrence of Hg









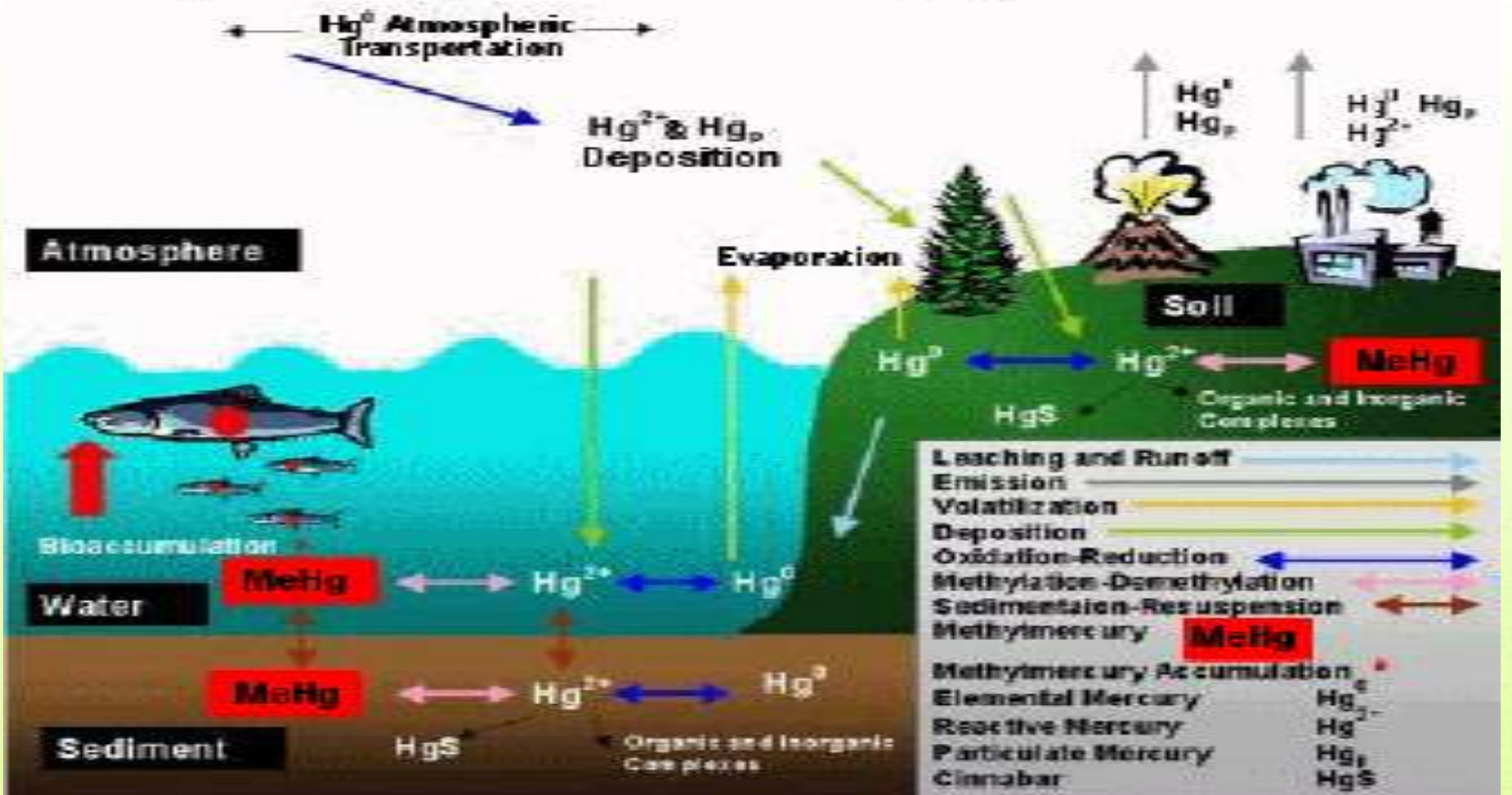
# Any alternative of Hg ?



- *No viable replacements for Hg-fluorescent lamp yet.*
- *Sodium vapor lamps:*
  - *Ne and Ar gas + Na Vapor. Na vapor emits yellow light – make all the objects more or less yellow.*
- *Sulfur lamps:*
  - *Matching the sun light but again harmful because of S.*
- *For some mercury wetted relays, may prefer to use gold plated or silver plated ( AgNi / AgSnO ) contacts as alternative.*



# Conceptual Biogeochemical Mercury Cycle





**WARNING**

This Area Contains A  
Chemical Known To  
The State Of  
California To Cause  
Birth Defects Or Other  
Reproductive Harm.

**HAZARDOUS AREA**

THE FISH, FROGS AND SOILS  
IN THIS AREA  
CONTAIN MERCURY AND OTHER  
TOXIC CHEMICALS

DO NOT EAT THE FISH

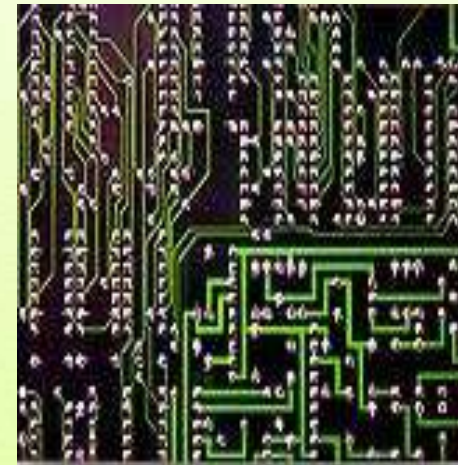


# Where can we find the banned substance? **Pb**



## *Pb-Sn Alloy*

- most commonly used in solders;
- Terminations, PCB coatings, component lead finishes, & cable (PVC).





# Pb - Based Components







# *Pb - free coating*



## **Component lead coating:**

- Electroplated tin,
- Electroless Nickel/Immersion Gold,
- Immersion Silver,
- Electrolytic Gold,
- Palladium/nickel - used on some semiconductor lead frames, good wetting properties but higher price

## **Surface finish on the solder bond pad of PCB/BGA substrate:**

- Organic Solderability Preservatives (OSP)
  - lower cost
  - thin coating, thus easily damaged
- Nickel/gold
  - good alternative
  - expensive



# Pros & Cons



- Lead-free solders have a higher melting point requiring higher process temperatures
- Lead-free solders are significantly harder, which can increase the likelihood of cracks instead of plastic deformation, which is typical for lead-containing solders
- Energy consumption
- Costs to upgrade to technology standard



# Where can we find the banned substances ?

## *Polybrominated Biphenyls (PBBs) and Polybrominated Diphenyl Ethers ( PBDEs)*

Commonly used in flame retardants ( FR ) in a variety of plastics → to meet stringent global fire safety standards ( e.g. UL94 – V0 )

- TV / Display Cabinets
- PCB – epoxy resin
- Wire / cable insulation and connectors



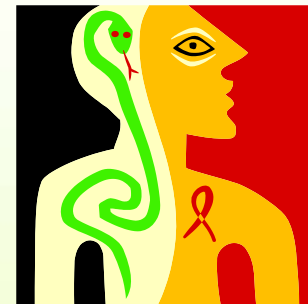
Mostly with Polystyrene, Terephthalates, Polyamides, Polycarbonates, Polypropylene.



## Background information



- Brominated flame retardant ( BFR ) has been the largest market group because of
  - low cost
  - high performance efficiency



- It will react and form polybrominated dibenzo-p-dioxins (PBDD) and polybrominated dibenzofurans (PBDF) after its reaction to put down fire. Both are carcinogenic elements

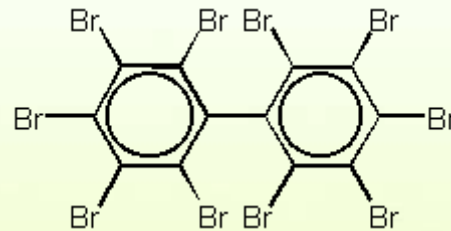


# Background information about the PBB and PBDE

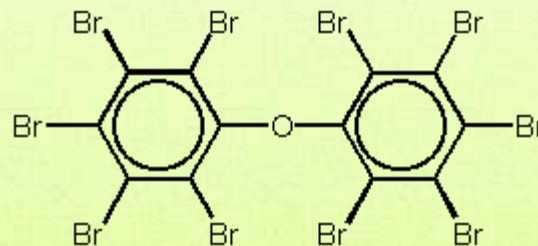


Chemical structure of the monomer:

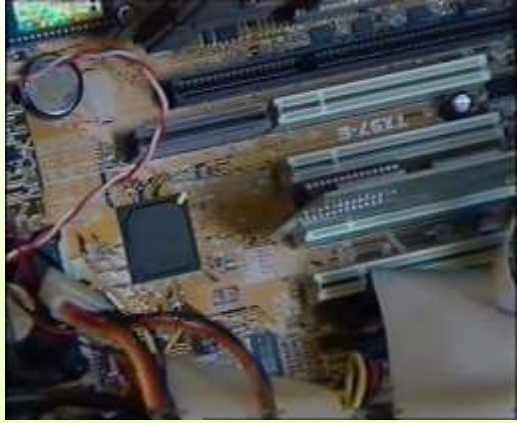
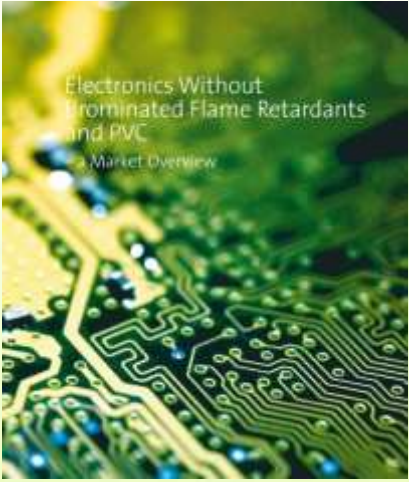
Deca-bromo-biphenyl is a monomer of PBB



Deca-bromo-diphenyl-ether is a monomer of PBDE



# PBB, PBDE used Components





# Occurrence of PBB and PBDE



PBB

PBDE



The diagram illustrates the human heart and its chemical components. At the top, a cross-section of the heart shows the four chambers: the right and left atria and ventricles. Below the heart, two chemical structures are shown, representing nucleic acid bases. The structure on the left is a purine base, and the structure on the right is a pyrimidine base. At the bottom, a DNA double helix is depicted, with the text "DNA with bases" written below it. The diagram is set against a light yellow background.

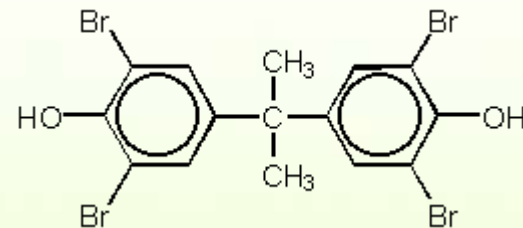


# Alternatives for PBB & PBDE



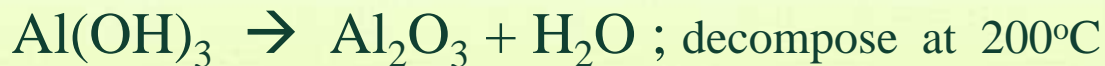
- *Tetra-bromobisphenol A (TBBPA)*

- commonly used both as a reactive flame retardant or as an additive flame retardant in PWB.



- *Non-halogenated flame retardants*

- Al(OH)<sub>3</sub> and other hydroxides: Currently the most widely used flame retardant.



water vapor cool the substrate during heating and also dilute the gas phases





## Non halogenated flame retardant – cont.

- Zinc Borate ( $\text{ZnBO}_3$ ):
  - act by endothermic reactions and by the formation of a glassy coating protecting the substrate.
- Antimony Oxide ( $\text{Sb}_2\text{O}_3$ ):
  - Works together with a halogen-containing compound
- Common disadvantages:
  - Difficult to incorporate
  - Require high loading to be effective

# Summary

- ❑ **No exact or drop-in replacement !**
- ❑ **Several alternative materials have been recommended for each of the banned materials**
- ❑ **There is not yet much field data available for the new materials!!**
- ❑ **Most of the cases, the alternative materials are costly and inferior in performance**
- ❑ **More R & D is needed in near future**





# NABL Accreditation to CMET



## NABL

**National Accreditation Board for Testing and Calibration Laboratories**  
Department of Science & Technology, India

### CERTIFICATE OF ACCREDITATION

**CENTRE FOR MATERIALS FOR ELECTRONICS TECHNOLOGY (C-MET), ANALYTICAL DIVISION**

has been assessed and accredited in accordance with the standard

**ISO/IEC 17025:2005**

"General Requirements for the Competence of Testing & Calibration Laboratories"

for its facilities at

IDA Phase-III, Cherlapally, HCL (Post), Hyderabad

in the discipline of

**CHEMICAL TESTING**

(To see the scope of accreditation of this laboratory, you may also visit NABL website [www.nabl-india.org](http://www.nabl-india.org))

Certificate Number T-1780  
Issue Date 28/06/2012



Valid Until 27/06/2014

This certificate remains valid for the Scope of Accreditation as specified in the annexure subject to continued satisfactory compliance to the above standard & the additional requirements of NABL.

Signed for and on behalf of NABL

*Anuja*  
Anuja Anand  
Convener

*Anil Relia*  
Anil Relia  
Director

*Dr. T. Ramasami*  
Dr. T. Ramasami  
Chairman



## रा.प्र.प्र.बो.

**राष्ट्रीय परीक्षण और अंशशोधन प्रयोगशाला प्रत्यायन बोर्ड**  
विज्ञान एवं प्रौद्योगिकी विभाग, भारत

### प्रत्यायन प्रमाण-पत्र

सेन्टर फॉर मेटिरियल्स फॉर इलेक्ट्रॉनिक्स टेक्नोलॉजी (सी-मेट), एनालिटिकल डिविजन

का मूल्यांकन और प्रत्यायन निम्न मानक के अनुसार

**आई.एस.ओ./आई.ई.सी. 17025:2005**

"परीक्षण एवं अंशशोधन प्रयोगशालाओं की सक्षमता की सामान्य आवश्यकताएँ"

**हैदराबाद**

में स्थित इसकी सुविधाओं के लिए

**रासायनिक परीक्षण**

के विषय क्षेत्र में किया गया।

(इस प्रयोगशाला के प्रमाणन के विषय क्षेत्र की जानकारी एवं ए.पी.पी.ए.सी. वेबसाइट [www.nabl-india.org](http://www.nabl-india.org) से भी प्राप्त कर सकते हैं।)

प्रमाण-पत्र संख्या P-1780  
जारी करने की तिथि 28/06/2012



विद्यता की तिथि 27/06/2014

यह प्रमाण-पत्र उपर्युक्त मानक तथा राष्ट्रीय परीक्षण और अंशशोधन प्रयोगशाला प्रत्यायन बोर्ड की अतिरिक्त अपेक्षाओं का निरंतर संतोषप्रद अनुपालन किए जाने पर अनुबंध में निर्दिष्टानुसार प्रत्यायन के क्षेत्र के लिए वैध रहेगा।

रा.प्र.प्र.बो. की ओर से हस्ताक्षरित

*Anuja*  
अनुजा आनंद  
संयोजक

*Anil Relia*  
अनिल रेलिया  
निदेशक

*Dr. T. Ramasami*  
डा. टी. रामसामी  
आयुक्त



# RoHS testing procedures



IEC 62321 technical  
procedures for the Determination  
of Levels of Regulated Substances in  
Electrotechnical Products



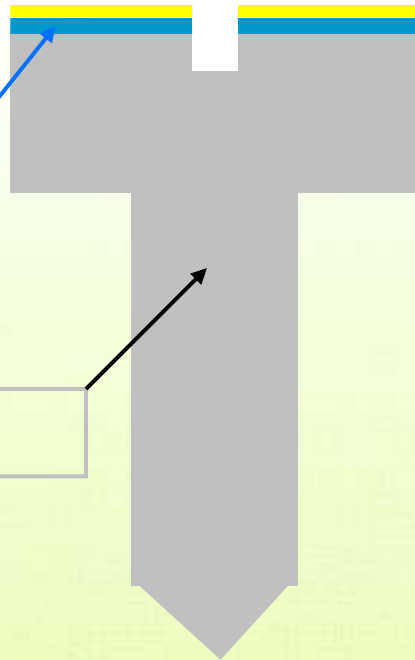
# Homogeneous material definition – analysis of coatings



Cr6

Zinc

Steel



- Definition of homogeneous materials explains concentration limit
  - It is NOT an analysis instruction
- Removal of Cr6 coating by abrasion is possible so this is a homogeneous material
  - But - very difficult to remove enough material for analysis
- However - it is possible to analyse coating in-situ by chemical extraction method



# Testing methods



- Screening:  
XRF (X-ray Fluorescence)
- Non destructive
- Fast
- Needs reference material
- Calibration



# Testing methods



## 🌿 Wet chemistry

ICP-MS (Inductively Coupled Plasma Mass Spectrometry)

ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy)

CV-AAS (Cold Vapor Atomic Absorption Spectrometry)

AAS (Atomic Absorption Spectrometry)

🌿 Destructive, digestion

🌿 Time vs precision

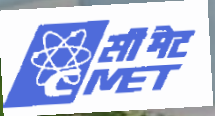
🌿 Calibration



# Non-destructive and Destructive







# Energy Dispersive X-Ray Fluorescence Spectrometer (ED-XRF)

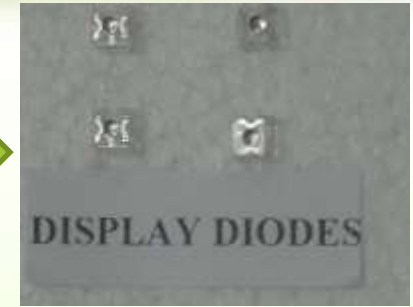




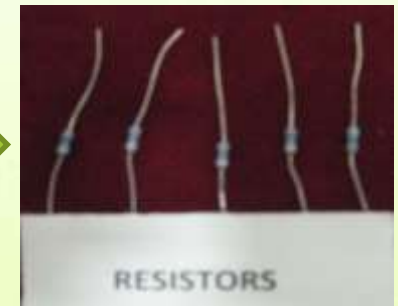
# Showcase of some of the samples tested for RoHS compliance



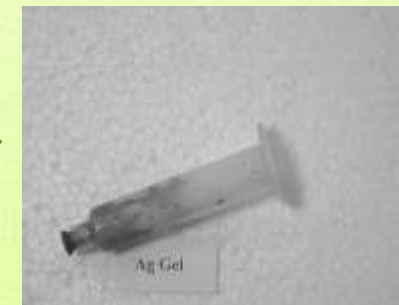
← **Active Components- Diodes** →



← **Passive Components- R&C** →



← **Silver Paste & Epoxy Resin** →





# Showcase of some of the samples tested for RoHS compliance



← Plastic computer Keyboard



Magnetic data storage tapes →



← Blue epoxy powder



Lead based PVC granules →



← Epoxy tape



PVC sheath of wires →



## A CASE STUDY OF COUNTERFEIT MOBILE PHONES IN INDIA



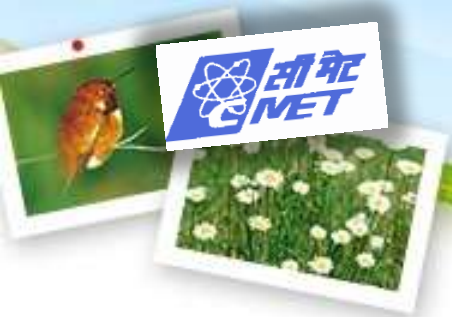
# Counterfeit phones RoHS compliance testing (C-MET Study)

Do Non-RoHS Complaint Phones  
Potentially Pose a Health or Create  
Environmental Hazards?

# EXAMPLE OF TOXICITY FROM MOBILE PHONES



- There are about 900 million mobiles in India and are growing @10% per annum.
- There are 90 million mobiles (~10% of 900 million) gets outdated every six months
- Average mobile phone weight is 150 g
- Nearly 15g of toxic elements like Cd, Pb, Cr<sup>+6</sup>, PBB and PBDE.
- Therefore,  $15 \times 90 \times 10^6$  gms = 1350 tones of toxicity is generated every six months.

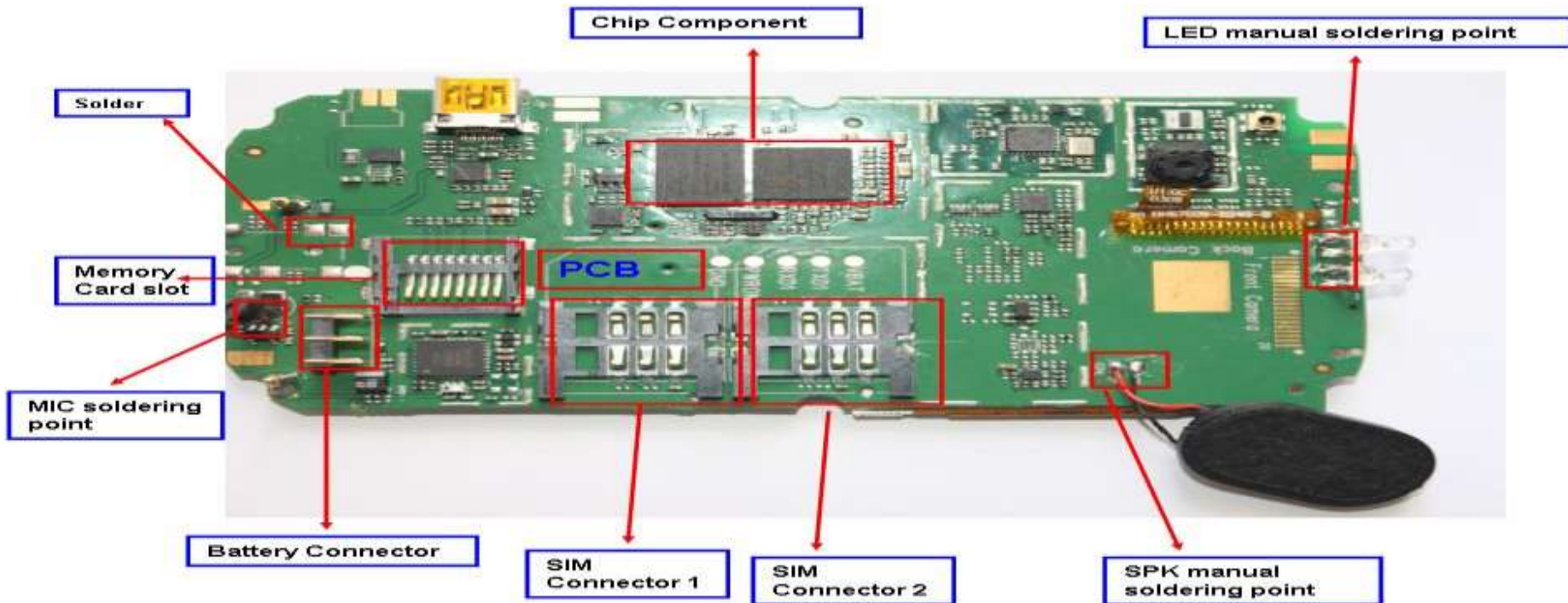


# Testing Methodology



Internal parts of cell phone

External parts of the cell phone





Mobile Name		XXXX				
S. No.	Position	Concentration (All in ppm)				
		Cd	Hg	Pb	Br	Cr
1	Back Cover	0	0	0	32.7	26
2	Key Pad	0	0	0	0	48
3	SIM 1	0	0	400.9	3031	0
4	SIM 2	0	0	2566	2031.3	1148
5	Memory Card Slot	95	0	28240	0	0
6	PCB	0	0	493	648	0
7	Chip Component	0	0	17824	3664	0
8	Battery Connector	42	0	4578	2456	0
9	LED soldering point	0	0	2235	0	0
10	Speaker	93	0	22790	0	0



Mobile Name		XXXX				
Sl. No.	Position	Concentration (All in ppm)				
		Cd	Hg	Pb	Br	Cr
1	Back Cover	0	0	0	0	20
2	Key Pad	0	0	0	0	35.8
3	SIM 1	0	0	0	1230	0
4	SIM 2	48	0	0	2751	0
5	Memory Card Slot	0	0	36	2023.4	0
6	PCB	54	0	155	3496	0
7	Chip Component	70	0	0	0	0
8	Battery Connector	0	0	69.3	2249	188
9	LED soldering point	0	0	0	3138	0
10	Speaker soldering point	0	0	97	0	0
11	MIC soldering point	0	0	0	2764	0

Mobile Name		XXXX				
Sl. No.	Position	Concentration (All in ppm)				
		Cd	Hg	Pb	Br	Cr
1	Back Cover	0	0	0	516.1	31.9
2	Key Pad	0	0	0	0	20.9
3	SIM 1	30	0	17.6	760.7	0
4	SIM 2	87	0	43.9	3524	0
5	Memory Card Slot	136	0	425	0	590
6	PCB	0	0	210	2587	1340
7	Chip Component	0	0	73	3688	0
8	Battery Connector	0	0	19.4	762	0
9	LED soldering point	0	0	3753	0	0
10	Speaker soldering point	0	0	3440	3446	0
11	MIC soldering point	0	0	1902	0	0

Mobile Name		XXXX				
Sl. No.	Position	Concentration (All in ppm)				
		Cd	Hg	Pb	Br	Cr
1	Back Cover	0	0	5.6	309.8	0
2	Key Pad	0	0	0	0	41.1
3	SIM 1	0	0	7137	2187.4	0
4	SIM 2	0	0	4180	3595	0
5	Memory Card Slot	0	0	77.5	3686	0
6	PCB	0	0	78	0	0
7	Chip Component	44.6	0	1933	2939	0
8	Battery Connector	0	0	377	0	0
9	soldering point	61	0	28110	0	0
10	Speaker soldering point	0	0	829	2405	0
11	MIC soldering point	0	0	2027	3560	0

Mobile Name		XXXX				
Sl. No.	Position	Concentration (All in ppm)				
		Cd	Hg	Pb	Br	Cr
1	Back Cover	0	0	0	2.98	0
2	Key Pad	0	0	0	0	0
3	SIM 1	0	0	0	268.1	0
4	SIM 2	0	0	0	170.4	0
5	Memory Card Slot	66	0	0	3478	0
6	PCB	0	0	51	0	0
7	Chip Component	74	0	842	2196	0
8	Battery Connector	76	0	155	0	173
9	LED soldering point	0	0	0	2633	0
10	Speaker soldering point	90	0	255	0	0
11	MIC soldering point	-	-	-	-	-

Mobile Name		XXXX				
Sl. No.	Position	Concentration (All in ppm)				
		Cd	Hg	Pb	Br	Cr
1	Back Cover	0	0	0	0	23.3
2	Key Pad	0	0	0	3	0
3	SIM 1	0	0	0	487	0
4	SIM 2	-	-	-	-	-
5	Memory Card Slot	-	-	-	-	-
6	PCB	0	0	0	421	0
7	Chip Component	0	0	1716	568	0
8	Battery Connector	153	0	517	203	0
9	LED soldering point	-	-	-	-	-
10	Speaker soldering point	-	-	-	-	-
11	MIC soldering point	-	-	-	-	-

Mobile Name		XXXX				
Sl. No.	Position	Concentration (All in ppm)				
		Cd	Hg	Pb	Br	Cr
1	Back Cover	0	0	0	619.5	0
2	Key Pad	0	0	0	0	36.7
3	SIM 1	0	0	0	2629	0
4	SIM 2	0	0	0	0	0
5	Memory Card Slot	84	0	287	0	0
6	PCB	40	0	14.3	3372	0
7	Chip Component	0	0	1241	0	0
8	Battery Connector	0	0	0	1119.8	0
9	LED soldering point	0	0	122	0	0
10	Speaker soldering point	0	0	0	2070	222
11	MIC soldering point	0	0	44	0	0

Mobile Name		XXXX				
Sl. No.	Position	Concentration (All in ppm)				
		Cd	Hg	Pb	Br	Cr
1	Back Cover	0	317	0	387	0
2	Key Pad	0	0	0	0	27.6
3	SIM 1	0	0	2968	1225	0
4	SIM 2	0	0	4185	3323	532
5	Memory Card Slot	0	0	1290	2761	0
6	PCB	0	0	859	203.9	0
7	Chip Component	0	0	7067	0	0
8	Battery Connector	0	0	2863	1791	220
9	LED soldering point	-	-	-	-	-
10	Speaker soldering point	47	0	22311	2861	0
11	MIC soldering point	55	0	18454	1503.9	0

Mobile Name		XXXX				
Sl. No.	Position	Concentration (All in ppm)				
		Cd	Hg	Pb	Br	Cr
1	Back Cover	0	0	0	2.51	0
2	Key Pad	0	0	0	0	27.9
3	SIM 1	0	0	0	3551	0
4	SIM 2	0	0	9.8	369.7	0
5	Memory Card Slot	0	0	59630	0	0
6	PCB	0	0	36240	0	0
7	Chip Component	0	0	4629	0	0
8	Battery Connector	48	0	12396	3600	0
9	LED soldering point	0	0	4679	3676	0
10	Speaker soldering point	0	0	33930	0	0
11	MIC soldering point	-	-	-	-	-



Mobile Name		XXXX				
Sl. No.	Position	Concentration (All in ppm)				
		Cd	Hg	Pb	Br	Cr
1	Back Cover	0	0	0	3.35	0
2	Key Pad	0	0	0	0	975
3	SIM 1	0	0	0	2281	0
4	SIM 2	0	0	208	3203	0
5	Memory Card Slot	0	0	59	1778.7	0
6	PCB	109	0	0	3662	1450
7	Chip Component	113	0	1390	798.4	0
8	Battery Connector	0	0	0	350	0
9	LED soldering point	0	0	34	3687	0
10	Speaker soldering point	0	0	0	96	0
11	MIC soldering point	0	0	48	0	0



# What we need to do ?



- Identify restricted substances in homogeneous materials, get the test reports, verify & document the same. – All state holders
- Look for alternate materials / process where ever restricted substances exceed the limits. – All researchers
- Strengthen the IS procedures in India through BIS – All researchers and analytical laboratories .

## New norms mandate manufacturers to keep hazardous substances below a specified limit



Union Minister of State for Information Technology and Communications Killi Kruparani at the Centre for Materials for Electronics Technology (C-MET) in Hyderabad on Saturday. — PHOTO: K. RAMESH BABU

### Special Correspondent

**HYDERABAD:** Adding another feather to its cap, the city will house the first-of-its-kind laboratory to analyse and quantify the content of hazardous substances in electrical and electronic goods.

The facility Restriction of Hazardous Substances (RoHS) of the Centre for Materials for Electronics Technology (C-MET) has been set up in line with the stipulations and guidelines to be followed by manufacturers of e-waste.

Inaugurated by Union Minister of State for Information Technology and Communications Killi Kruparani on Saturday, the Restriction of Hazardous Substances (RoHS) had been designed to meet international standards on e-waste management which, in turn, would give fil-

lip to hardware exports from the country.

### Only such facility

Dr. Kruparani said although there were over dozen laboratories operational across the country, the RoHS certification would carry weight as it was the only such facility in the public sector. Exporters securing the C-MET certification would have better access to export markets than their counterparts without certification.

The industry was facing the challenge of reduction of hazardous substances as there was absence of provision for certification as also compulsory registration.

The facility would help Indian manufacturers gear up to the May 2014 deadline set by the Union Ministry of Environment and Forests to achieve substantial reduction

in hazardous substances including lead, cadmium and mercury forming part of the printed circuit boards of electronic equipment.

The new norms, according to C-MET executive director D.P. Amalnerkar, would mandate manufacturers to keep hazardous substances below a specified limit failing which they would not be allowed to be marketed.

"It will, however, take some time for the industry to achieve compliance. But there has to be a beginning," he said.

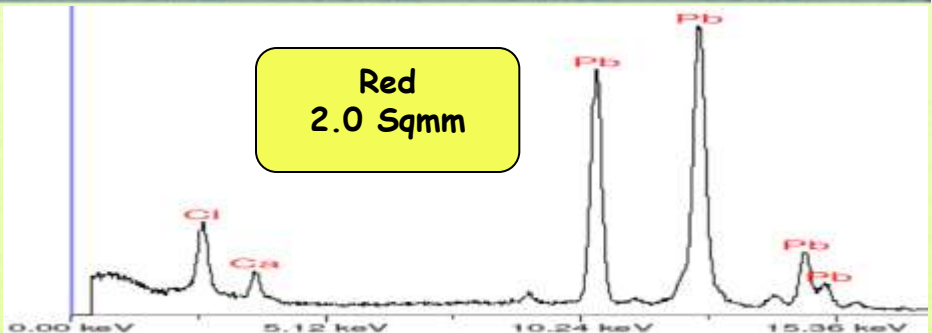
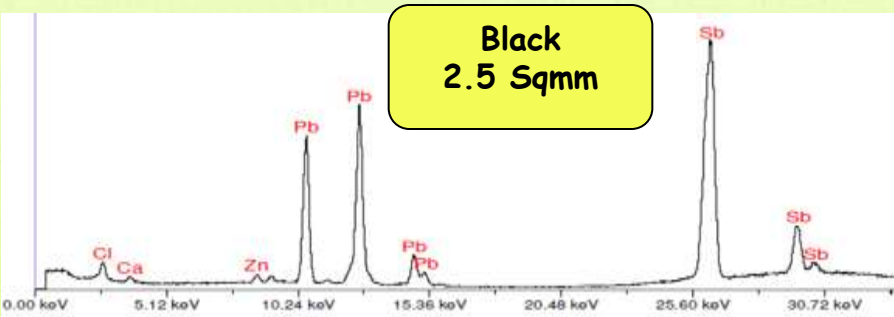
Department of IT and Electronics group coordinator Debashish Datta, who explained about the hazardous substances, said no electronic product with more than 100 mg of Cadmium and 1,000 mg of other hazardous substances would be allowed in the country.

# Evaluation of Pb levels in various gauge and coloured electrical cables using different characterization techniques -A case study



Pb concentration in various gauge and coloured electrical cables using different characterization techniques

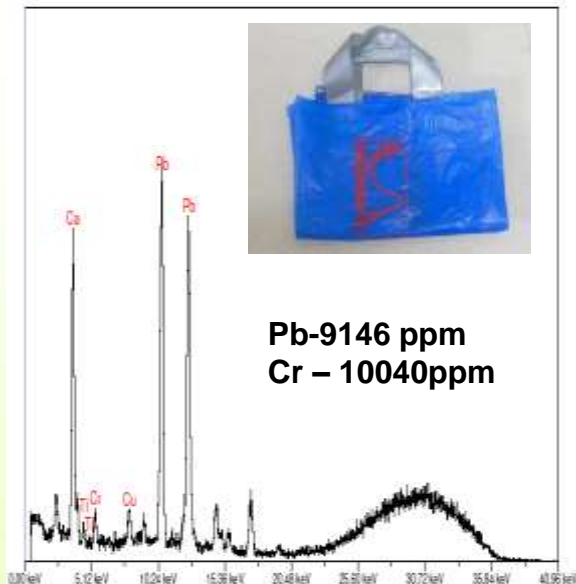
Sample	EDXRF (ppm)	ICP-OES (ppm) (Agilent)	% Recovery	AAS (ppm)	% Recovery	ICP-OES (ppm) (Thermo)	% Recovery	ICP-MS
Green (1sqmm)	1028	1123	94	1554	116	1264	105	1445
Yellow (1sq mm)	1875	1649	84	2015	92	1808	92	1639
Red (2Sqmm)	10419	9077	96	10484	75			6575
Blue (2Sqmm)	1259	1240	93	1453	114	1479	83	1560
Blue (1Sqmm)	1090	912	89	1176	104	1058	84	1167
Black (2.5sqmm)	31005	23099	92	25270	90			15192
Black (1sqmm)	985	1121	82	1338	107	1275	80	1075



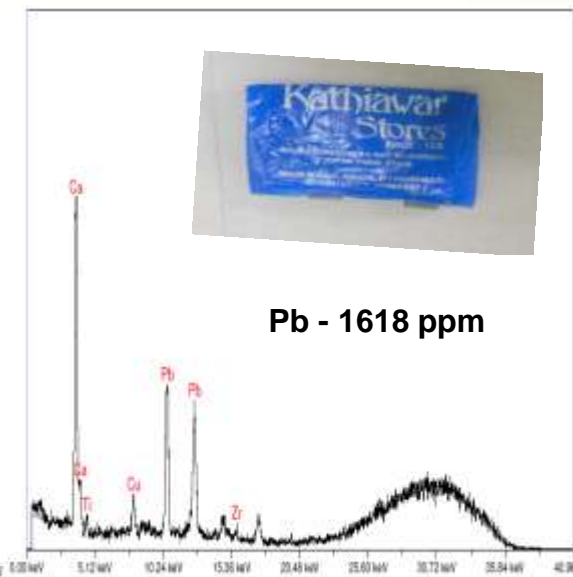
# Evaluation of Hazardous Substances in various carry bags - A case study



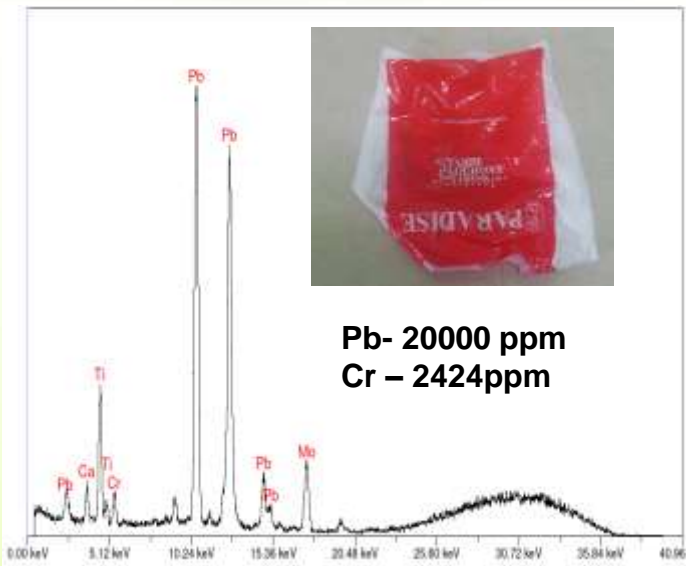
**Pb-9146 ppm  
Cr - 10040ppm**



**Pb - 1618 ppm**



**Pb- 20000 ppm  
Cr - 2424ppm**



Thank you very much  
for your kind attention

