Restricted Substances – Challenges Known and Unknown

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Need for Restrictions

Safety and health issues

- **Potential Carcinogens**
- **Toxic substances**
- **Potential Mutagens**

Environmental issues

- **Exposure in processing**
- **Disposal**

Restrictions and Trade

- **Opportunity for process re-engineering**
- **Corporate edge**
- **Commitment to Safety, Health and Environment**

Two decades of Eco-Restrictions

- Initial restrictions
    - PCP
    - Aryl amines
    - Cr(VI)
    - Formaldehyde

- Indian leather industry displayed resilience

- Quick response - alternatives emerged for most

Compliance Levels

Restricted substance	1996-1999	2006-2009
PCP	> 97%	Near 100%
Aryl Amines	> 97%	> 98%
Cr (VI)	~ 85%	~ 80%
Formaldehyde	~ 35%	> 75%

Penta Chloro Phenol

- **First restricted Substance**
- **Challenges for alternatives too**

CLRI pioneered extraction procedures

Arylamines

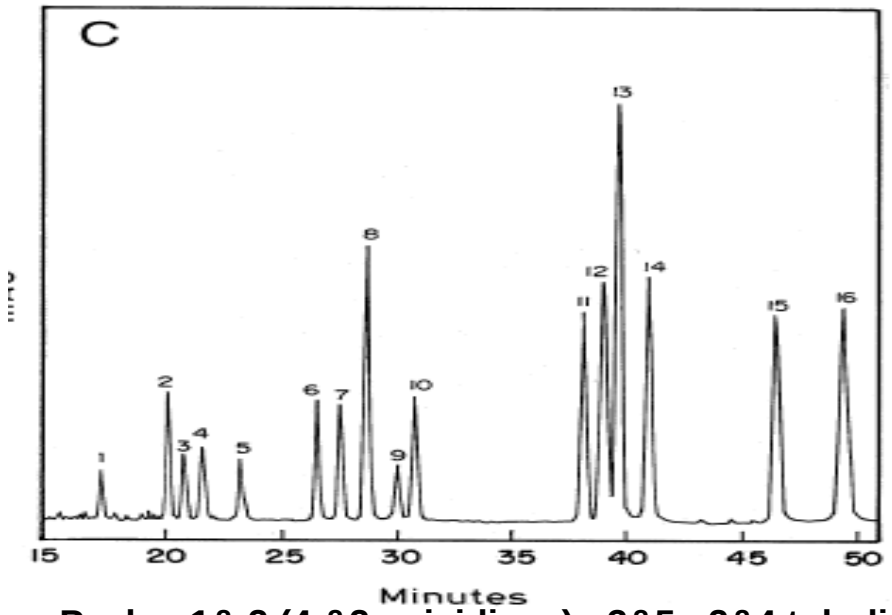
- **Additions continue**

  2,4-Xylidine (China only)
  2,6-Xylidine (China only)

- **Alternatives available**
- **Challenges from isomers**

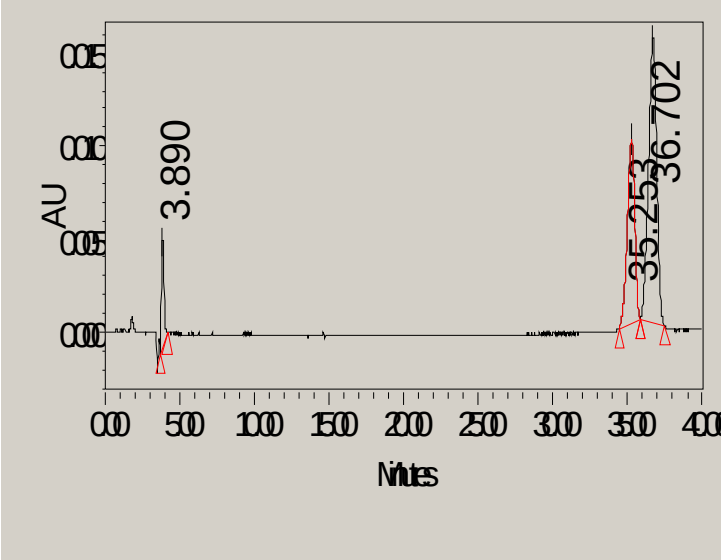
CLRI addressed testing challenges of arylamines

Isomer separation - CE



Peaks :1& 2 (4 &2 anisidines) ; 3&5 - 2&4 toludines) ;4&8 –(2&4chrysidines) ; 6&9-(2&4chloroanilines) ;7&10-(2,6 &2,4dimethyl anilines) ; 11&12-(246&245-trimethyl anilines) ;13&14-(1&2-naphthyl amines) ; 15&16-(2&4-aminobiphenyls).

Toludine – Structural isomers



35.25-OTD; 36.70-PTD

Hexavalent Chromium – Issue not yet resolved !?

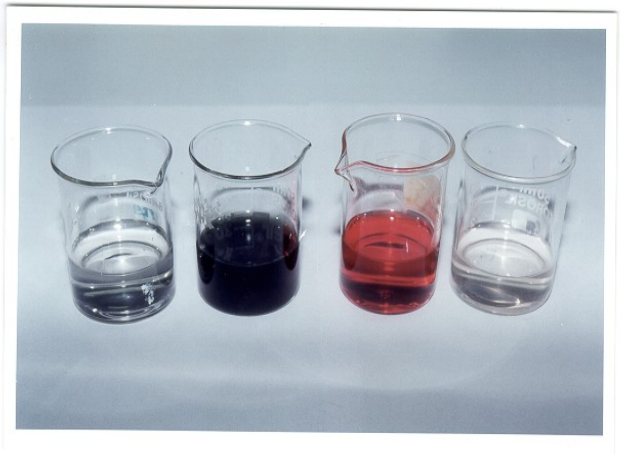
Problems posed by practices

- **Inadequate process control**
- **Sunlight exposure**
- **Finishing formulations**
- **Special treatments**

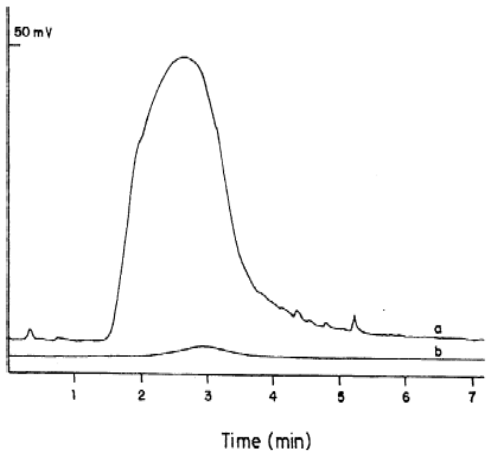
- **Challenges in determination in Cr (III) rich environment and in presence of large quantities of colorants**

Hexavalent Chromium– Testing Challenges

- **Inadequate official protocol**
- **C18 – Inefficient to handle dark colored extracts**
- **Florosil based robust procedures**
- **CLRI method found most accurate by EU lab (JALCA,102(3),2007)**



On line membrane dialysis : Robust procedure for Cr (VI)



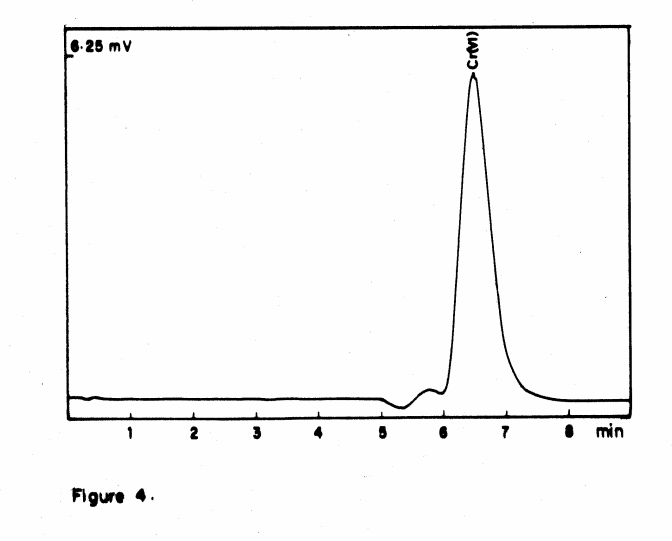


Figure 4.

Procedure validated with more than 7000 samples

Formaldehyde

- Varying levels of restrictions
- Conditions play prominent role
- Sources do mystify

- IUC26 : Formaldehyde in chemicals – Screening test

Lack of clarity in test protocals and requirements

- **Formaldehyde testing – Size reduction, Stirring speed**

- **Extractable Vs Soluble heavy metals**

- **Varying limits, challenging methods and instruments**

Newer Restrictions

- **During the second decade RSL has expanded exponentially**
- **By 2010 the list has crossed 200 Substances**
- **This poses tremendous technological and analytical challenge**

Reach related issues

- **REACH is a subset of total RSL – Relatively easy to manage**
- **REACH envisages screening for 30 SVHC**
- **Many substances tested indirectly**
- **Two more lists before June 2011**

SVHC in REACH : Potential Causes and Origin

Restricted Substances	Potential Causes and Origin
Anthracene	Impurity or un reacted substances of dyes, insecticides, curing agent in epoxy adhesives
Diaminodiphenylmethane	Azo dyes, curing agent in epoxy adhesives
Dibutylphthalate Bis(2- ethylhexyl)phthalate Benzyl butylphthalate Di iso butylphthalate	Plasticizers (top coats,polymeric and rubber soles), pigment pastes,residues in alcohols
Hexabromocyclododecane and all major Diasteroisomers	Flame retardants
Cobalt dichloride	drying agents including silica gel, * As Cobalt (cobalt naphthenate in top coats,sulphited fat liquors, pigments or metal complex dyes or as impurity in other inorganic pigments)

* Testing limitation

SVHC in REACH : Potential Causes and Origin

Restricted Substance	Potential Causes and Origin
Diarsenic pentaoxide, Diarsenic trioxide	Fungicides,insecticides and also as impurity in inorganic pigments. As impurity with antimony flame retardants
Sodium dichromate	Preservatives, pigments or metal complex dyes or as impurity in inorganic pigments, in Chromium tanning salts
5-tert-butyl-2,4,6-trinitro-m-xylene (musk xylene)	insecticides spray formulations
Alkanes,C10-C13,chloro (short chain chlorinated paraffins)	Sulphochlorinated fat liquors, flame retardant components
Bis (tri butyltin) Oxide	Preservatives

SVHC in REACH : Potential Causes and Origin

Restricted Substances	Potential Causes and Origin
Lead hydrogen arsenate	Lead : insecticides and as impurity in inorganic pigments Arsenic : Fungicides, insecticides, impurity in flame retardants, as impurity in inorganic pigments
Triethyl arsenate	Preservatives, impurity in flame retardants, as impurity in inorganic pigments
Acrylamide	Syntans , pigment pastes, as residues in treated water
2,4-DI NITRO TOLUENE	Azo dyes
Lead Chromate/lead chromate molybdate sulphate Red/ Lead sulfo chromate yellow	insecticides and inorganic pigments

SVHC in REACH : Potential Causes and Origin

Restricted Substances	Potential Causes and Origin
Tris(2-chloroethyl)phosphate	Flame retardants and plasticizers. (Top-coats and polymeric/synthetic lining and sole materials), also in packaging materials.

- Unlike in chemicals, analysis of specific substances in articles pose challenge

- In-house procedures adopted

Additional RS : Potential Causes and Origin

Restricted Substance	Potential Causes and Origin
Soluble heavy metals (Cr,Al,Ti,Zr)	Tanning agents
Aldehydes (Glutaraldehyde, Glyoxal)	Syntans,Top coats,Synthetic linings
Naphthalene	Syntans,Pesticides
Poly aromatic hydrocarbons	Syntans,Flame retardants, Pesticides
Phenols	Syntans

Additional RS : Potential Causes and Origin

Restricted Substances	Potential Causes and Origin
Lead	Pigments,leaching from reactors
Soluble heavy metals Arsenic,Antimony,Mercury,Cadmium, Copper,Nickel,Barium,Selenium,Cobalt,Chromium	Pigments,Pesticides,Metal fittings
Alkyl Phenol Ethoxylates Nonyl phenol, Octyl phenol	Degreasing agents,fat liquors
VOC	Degreasing agents,fat liquors,Top coats,Synthetic linings,Sole,Flame retardants
Chlorinated Aliphatic Compounds	Degreasing agents,fat liquors

Additional RS : Potential Causes and Origin

Restricted Substances	Potential Causes and Origin
Per Fluoro Octane Sulfonates	Fat liquors,Top coats,Water proofing agents
Organo tins	Top coats, Preservatives
Di methyl Formamides	Preservatives
Dioxins	Pesticides
Pesticides (33 compounds)	Vegetable tanning extracts

Additional RS : Potential Causes and Origin

Restricted Substances	Potential Causes and Origin
Disperse dyes	Synthetic fabrics
Decabromo diphenyl ether	Flame retardants
Tris (2,3-dibromopropyl) phosphate	Flame retardants
Bis (2,3-dibromopropyl) phosphate	Flame retardants
Tris (1-aziridinyl)-phosphine oxide	Flame retardants

Additional RS : Potential Causes and Origin

Restricted Substances	Potential Causes and Origin
Poly Brominated Biphenyls (PBBs) Poly Chlorinated Biphenyls (PCBs) Poly Chlorinated Terphenyls	Flame retardants
PVC	Soles

Speciality Chemicals : Boon or Bane

Restricted Substances predominant in

- **Syntans**
- **Synthetic Fatliquors**
- **Top coats**
- **Flame retardants**
- **Water proofing agents**
- **Packing materials (DMFU,PVC,PCP)**

Challenges in testing restricted substances

- **APEO – Unsure extraction procedures**
- **HBDD in Flame retardants – Poor sensitivity**
- **PCBs – Presence of 209 isomers**
- **Chloroparaffins can pose threat to instruments**

Mystifying Analytes

- **Formaldehyde - In PU dispersions**
- **Lead - In Fatliquors**
- **Nickel - In Compact Finish**
- **PCP - In Dyes**

CHALLENGES - Summed up

- **Fast changing – ever increasing RSL**
- **Absence of test protocols – derived not specific**
- **Origin of restricted substances do mystify**
- **Non-availability of expertise for quick response**
- **Inadequate information**

Challenges Contd…

- Unique extraction procedures
- Time consuming protocols
- Polluting test procedures
- Economics challenged

NEEDED CHANGES

- **Screening of inputs**
- **Periodical review and revisit of processes**
- **Normalization of extraction procedures and development of realistic protocols**
- **Development of Greener and Integrated protocols**