

REACH COMPLIANCE AMONG COMESA FOOTWEAR TANNERS AND SMES

November 2016



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- President of the Society of Leather Technologists & Chemists 2006 – 2008
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John Hubbard

- SATRA Technical Manager
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- SATRA Technology Centre (1996 – Present)
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- BSc (Hons) Colour Chemistry & Dyeing – University of Leeds 1990



Programme outline

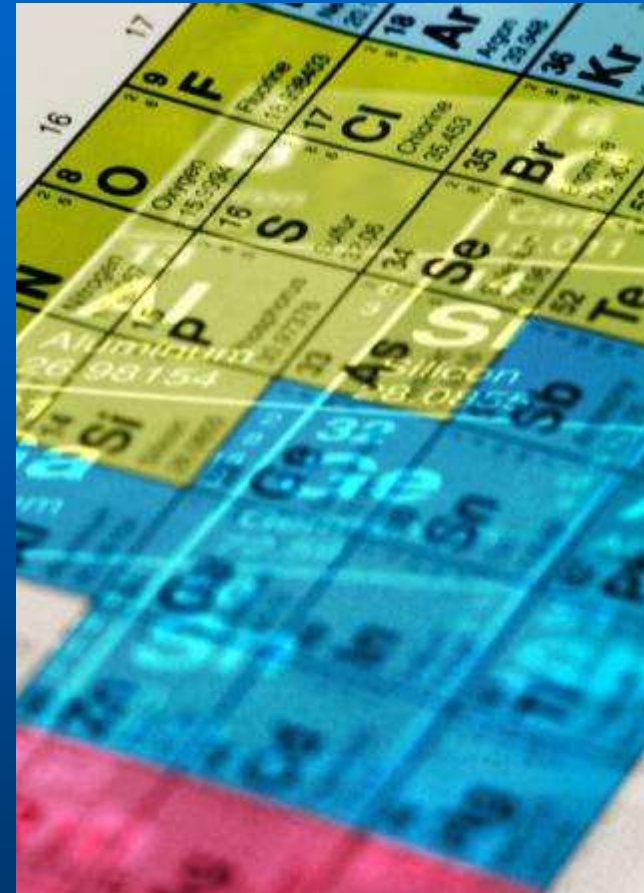
- REACH Introduction
- Requirements for articles and SVHCs
- Annex XVII Restricted Substances
- Testing for Restricted Substances



REACH Introduction

What is REACH?

- Registration, Evaluation, Authorisation (& restriction) of Chemicals
- Regulation (EC) No 1907/2006
- Entered into force 01 June 2007
- Final phase in dates 2018



Why REACH?

- Remove distinction between 'New' – post 1981 and Existing chemicals Prior to 1981
- To protect Human Health & Environment
- To impose restrictions on most harmful chemicals
- To improve communication throughout the supply chain



Who does REACH affect?

- Chemical Manufacturers
- Formulators and Suppliers of Preparations
- Downstream Users
- Suppliers of Articles



What is covered by REACH?

- All Chemicals supplied in quantities greater than 1 tonne per annum (tpa) into the European Union
- Whether use is industrial, professional or domestic



Where does REACH apply?

- European Union (EU)
- European Economic Area (EEA):
Iceland
Norway
Liechtenstein



Requirements for Substances and Preparations

Requirements for Substances and Preparations

- Each company supplying each chemical must register
- Registration is per substance not per product
- Must communicate with downstream users
- Authorisation will only cover recognised downstream uses



Who is responsible for registration?

- Chemical Manufacturer (if in EU)
- Chemical Importer who first brings product into EU (may be multiple organisations)
- Only Representative (Sole agent for manufacturers outside the EU)



Registration

PHASE IN DATES

Nov 2010

CMR > 1 tpa,

R50/R53 > 100 tpa,

All substances >1000 tpa

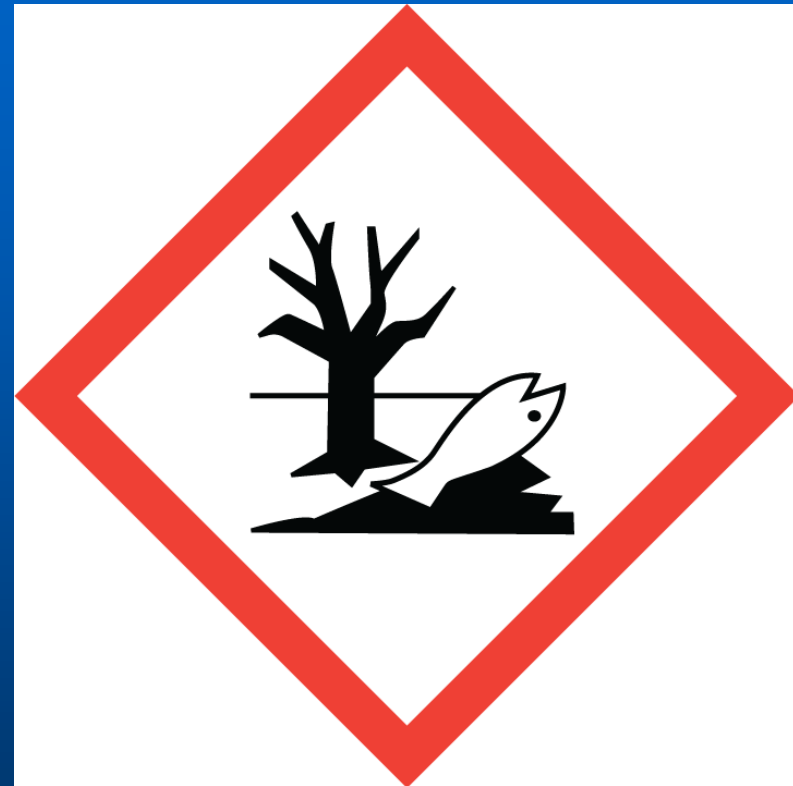
May 2013

100-1000 tpa

Nov 2018

10-100 tpa

1-10 tpa



Candidate List Substances in Articles

Definition of an article in REACH

- “an object which during production is given a special shape, surface or design which determines its function to a greater degree than its chemical composition”
- Consumer goods will fall into this category
- Liquid products will normally be classified as preparations (mixtures)



Why Substances in Articles?

- Original proposals only restricted chemical use and production in the EU and had no requirements for product coming into the EU from outside
- Requirements for articles resulted from lobbying by the EU chemical industry



Candidate List

- Substances of Very High Concern (SVHCs) will be placed in this category during the evaluation process
- Current SVHC list (June 2016) includes 169 Chemicals – ECHA target to complete list by 2020
- Threshold limit 0.1% on weight of article or separate component
- Above threshold limit obligations apply



SVHC Obligations

1. Respond to customer requests within 45 days
2. If one or more SVHC is present above 0.1% but less than 1 tonne of the SVHC is imported per annum – inform supply chain and provide information for safe use of product (or information on exposure prevention)



Sunset Dates

- 31 SVHCs have been assigned “sunset dates” and added to Annex XIV (the authorisation list)
- As a result, 4 phthalate plasticisers are now banned from use in manufacturing within EU / EEA
- Exemptions can be applied for based on socio-economic benefit
- The authorisation list chemicals will not automatically be restricted in consumer products – this will require additional legislation



Managing SVHCs

- What materials are used in my products (composition)?
- Are any treatments applied to my product?
- What information does my supplier have about the chemicals used in the product?
- Create a matrix of information and identify any gaps



Targeted testing for SVHCs and interpreting test results

SVHC Testing

- 169 chemicals on the candidate list
- Not practical / economic to test for all 169!
- Not all SVHCs relevant to consumer products
- Some have very specific uses for example in explosives / road surfaces
- Advisable to target testing at those chemicals most likely to be present in your product range



Efficient Testing

Remember articles which contain substances on the candidate list above 0.1% must provide sufficient information

- 0.1% is a high concentration in analytical terms (1000ppm)
- 0.1% is based on the weight of each component
- Combining similar materials is possible
- Screening testing is an effective testing tool.



Targeted SVHC Testing

Common screening groups:

- Phthalates on flexible PVCs
- Metal screening using ICP
- Organic Compounds using GC-MS
- Specialist testing where real suspicions exist.



Phthalates

- Esters derived from phthalic acid
- Used to make materials flexible especially PVC
- They may be added in the order of 30-50% by weight to increase the polymer's flexibility
- Not all phthalates are restricted
- Testing - solvent extraction followed by GC-MS



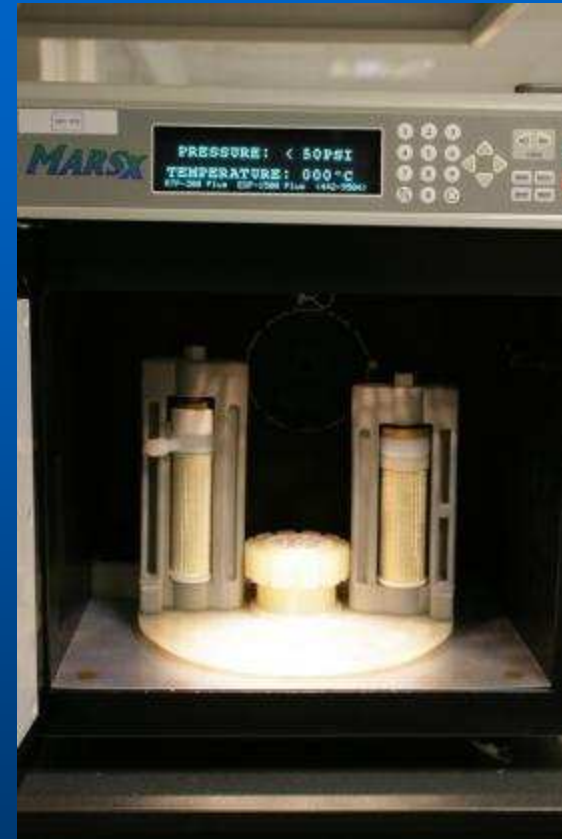
SVHC Phthalate Plasticisers

Benzyl butyl phthalate (BBP)	85-68-7
Bis (2 ethyl(hexyl) phthalate (DEHP)	117-81-7
Dibutyl phthalate (DBP)	84-74-2
Diisobutyl phthalate (DIBP)	84-69-5
1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich (DIHP)	71888-89-6
1,2-Benzenedicarboxylic acid, di-C7-11-branched and linear alkyl esters (DHNUP)	68515-42-4
Bis(2-methoxyethyl) phthalate (DMEP)	117-82-8
1,2-Benzenedicarboxylic acid, dipentylester, branched and linear	84777-06-0
Diisopentylphthalate (DIPP)	605-50-5
N-pentyl-isopentylphthalate	776297-69-9
Dipentyl phthalate (DPP)	131-18-0
Dihexyl Phthalate (DHP or DnHP)	84-75-3
1,2-Benzenedicarboxylic acid, dihexyl ester	68515-50-4



Metal Screening

- High proportion of chemicals on the candidate list contain metals
- These metals can be screened for using XRF or microwave digestions followed by ICP analysis
- Many of the chemicals contain combinations of metals eg *Lead chromate* contains both lead and chromium



Metal Screening

Metals included in the SATRA screening test:

Tin – Sn

Lead – Pb

Cobalt – Co

Chromium – Cr

Arsenic – As

Potassium – K

Zirconium – Zr

Sodium – Na

Boron – B

Zinc – Zn

Strontium – Sr

Barium - Ba

Titanium – Ti

Cadmium – Cd



GC-MS Screening

- Solvent extraction followed by GC-MS for semi volatile organic compounds
- Used for Anthracene and TCEP screening



GC-MS Headspace Screening

- GC-MS headspace analysis can be used to screen for volatile organic compounds
- Such as 2-ethoxyethanol, trichloroethylene and 1,2-dichloroethane
- These may have been used as cleaning solvents, contaminants in adhesives or a specific function e.g. musk xylene is a fragrance



Specialist testing

- Chromium VI in leathers where high levels of chromium is detected.
- Where water, stain resistant or flame retardant treatments are known to have been added.
- Chloro-alkanes in leather oils.



The Future?

- Further chemicals to be added to the SVHC List
- SVHCs will become authorised - (Annex XIV)
- Substances may then be added to Annex XVII by further legislative acts
- SIN lists are lobbying documents not proposals



Annex XVII

Restrictions on the manufacture,
placing on the market and use of
certain dangerous substances,
preparations and articles

Key Differences between Candidate List & Annex XVII

- Annex XVII is **mandatory** and all organisations should be able to demonstrate compliance
- Candidate List obligations are not a ban on SVHCs in articles



Annex XVII

- All requirements of Marketing and Use Directive were incorporated into ANNEX XVII of REACH during May 09.
- Maximum permitted levels are different for each entry and expressed on the material not the article
- Brands / retailers should base their restricted substances list on these requirements
- ANNEX XVII will increase as member states make proposals on SVHC's.



Annex XVII - Requirements

- Limits based on authorisation to ensure safe use
- May be product, material or process specific
- May prohibit use in the supply chain or residues in final materials



Annex XVII

The current revision of annex XVII includes restrictions on 62 unique substances / entries.

<https://echa.europa.eu/addressing-chemicals-of-concern/restrictions/substances-restricted-under-reach>

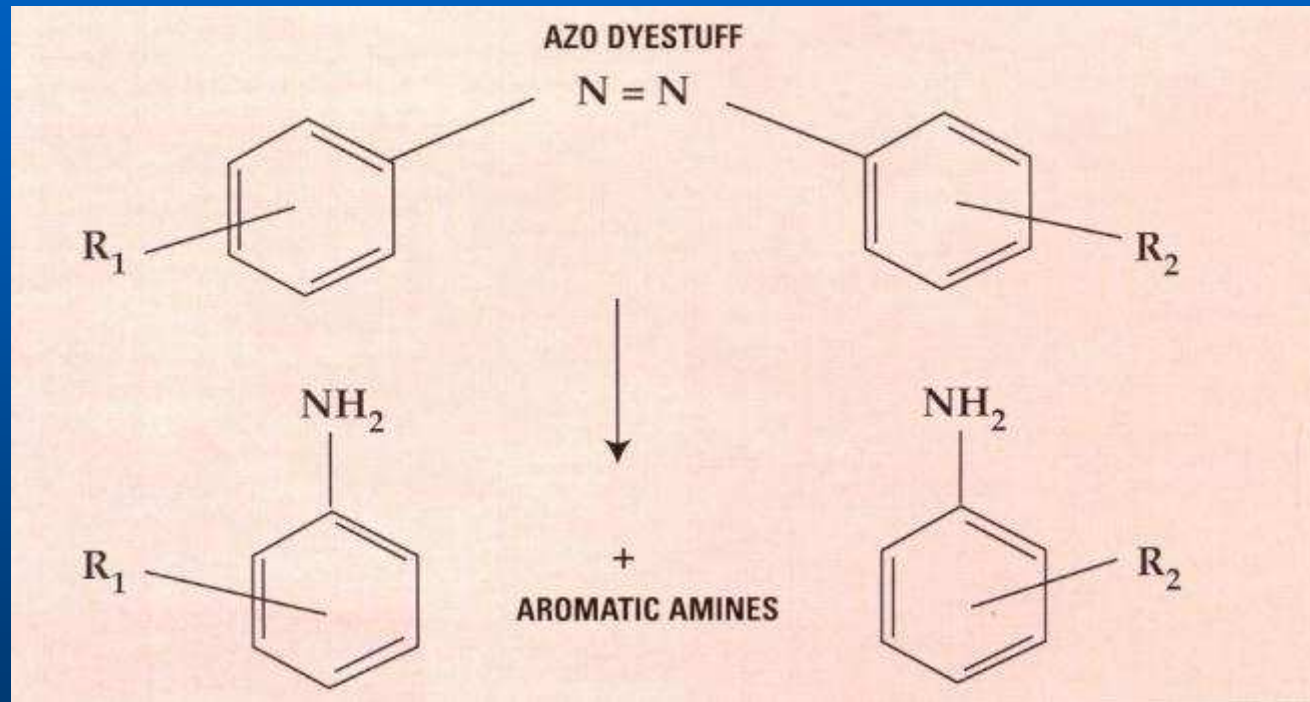


ANNEX XVII - Key Chemicals in Consumer Products

- Azo dyes
- Pentachlorophenol
- Chromium VI
- Nickel
- Dimethyl fumarate
- **Penta/Octa BDE**
- NP/NPEO
- **PFOS**
- Cadmium
- Lead
- Phthalates
- Organotins
- PAHs



Azo Dyes



Azo Dyes

- EU restriction introduced in 2002
- 22 restricted Aromatic Amines - **carcinogens**
- REACH Annex XVII entry number 43
- Maximum permitted level 30ppm
- Applicable to dyed leather & textiles in direct and prolonged contact with the skin
- No need to test white or undyed materials or polymers



Azo Dyes

- 4-amino bi phenyl
- Benzidine
- 4-chloro-o-toluidine
- 2-Naphthylamine
- o-aminoazotoluene
- 5-nitro-o-toluidine
- 4-Chloroaniline
- 4-Methoxy-m-phenylenediamine
- 4,4'-methylenedianiline
- 3,3'-dichlorobenzidine
- 3,3'-dimethoxybenzidine
- 3,3'-dimethylbenzidine
- 4,4'-methylenedi-o-toluidine
- 6-methoxy-m-toluidine
- 2-chloroaniline
- 4,4'-oxydianiline
- 4,4'-thiodianiline
- o-toluidine
- 4-methyl-m-phenylenediamine
- 2,4,5-trimethylaniline
- o-anisidine
- 4-aminoazobenzene

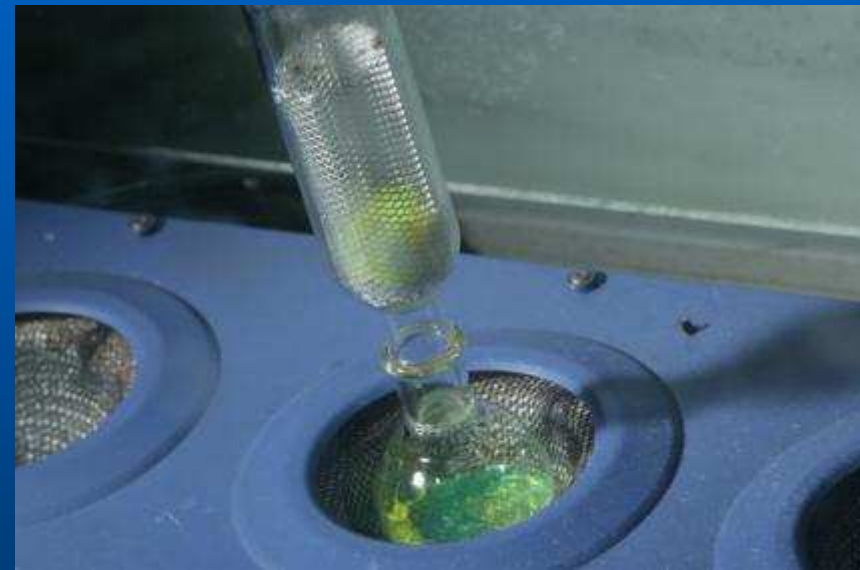


Azo Dyes - Testing

Test methods:

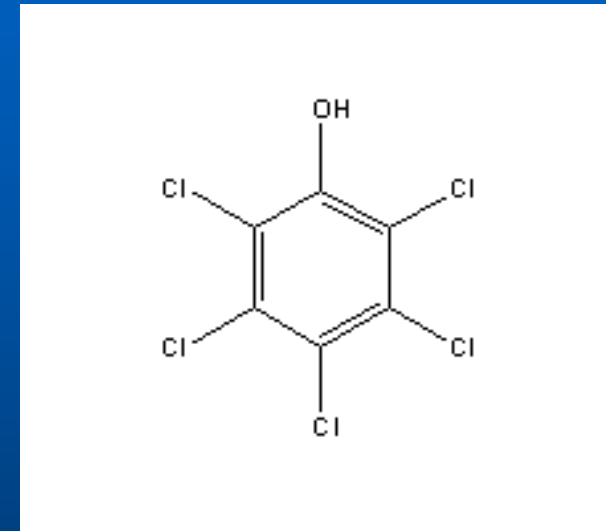
- EN 14362-1
(natural textiles, synthetic textiles)
- EN 14362-3
(4-aminoazobenzene)
- ISO 17234-1 (leather)
- ISO 17234-2
(4-aminoazobenzene)

All use GC-MS with HPLC
as second confirmatory
technique



Pentachlorophenol (PCP)

- Fungicide used historically in leathers and wood
- Fatal if inhaled, toxic if swallowed and toxic in contact with the skin
- Very toxic by inhalation and to aquatic organisms
- Accumulates in the environment
- REACH Annex XVII entry number 22
- Requirement <1000ppm
- Restricted in Germany < 5ppm



PCP – Testing

- ISO 17070
(steam distillation extraction)
- SATRA TM 342
(acetone extraction)



Chromium VI

Might be present in chromium tanned leather as chromium sulphate (Cr III) tanning salts present in low percentage levels

Also called extractable hexavalent chromium (Cr VI)



Chromium VI

- Skin irritant
- Carcinogen by inhalation & ingestion
- Environmental hazard
- Zero tolerance in German consumer products
- Restricted in toys (EN 71-3, <math><0.02\text{mg/kg}</math> in category III materials)



Chromium VI

- Included in innocuousness assessment for protective clothing & gloves containing leather
- Originally Annex XVII entry 47 applied only to cements
- However, Regulation 301/2014 extended entry 47 from 1st May 2015



Regulation 301/2014

- *5. Leather articles coming into contact with the skin shall not be placed on the market where they contain chromium VI in concentrations equal to or greater than 3 mg/kg (0,0003 % by weight) of the total dry weight of the leather.*
- *6. Articles containing leather parts coming into contact with the skin shall not be placed on the market where any of those leather parts contains chromium VI in concentrations equal to or greater than 3 mg/kg (0,0003 % by weight) of the total dry weight of that leather part.*
- *7. Paragraphs 5 and 6 shall not apply to the placing on the market of second-hand articles which were in end-use in the Union before 1 May 2015.*



Testing for Chromium VI

- ISO 17075:2007 – extraction in phosphate buffer, UV-Vis detection after reaction with DPC
- Method will shortly be replaced by ISO 17075-1 and ISO 17075-2 (currently at final voting stage)

Key changes:

- Cut leather (not ground),
- Part 2 uses ion exchange chromatography – fewer interferences
- Part 2 will take precedent



IULTCS Guidelines for Cr VI free leather

- 1. Always use premium chrome tanning salts
- 2. No use of oxidation agents (i.e. bleaching) on leather after tanning
- 3. Finish the wet end processing at (low) pH conditions (3.5 - 4)
- 4. Carry out a final washing
- 5. Avoid the use of excess ammonia prior to the dying process



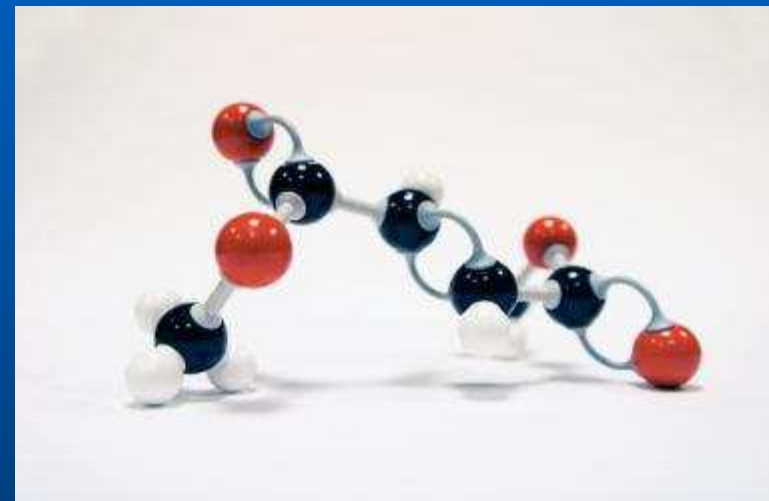
IULTCS Guidelines for Cr VI free leather

- 6. Use high performance softening chemicals (no unsaturated lipids or waxes)
- 7. Avoid the use of chromate pigments (yellow and orange inorganic pigments)
- 8. Use between 1 and 3% vegetable tannin extract as this provides antioxidant protection
- 9. Use of synthetic antioxidants where it is not possible to apply vegetable agents



Dimethyl fumarate (DMFu)

- Biocide that has been used to control mould growth
- Implicated in contact dermatitis and respiratory problems in furniture and footwear
- Sensitising chemical – adverse reactions at very low concentrations
- Present in packaging as sachets or pouches
- Use was forbidden in Europe (outside Biocidal Products Directive – BPD)



Dimethyl Fumarate (DMFu)

- Initial emergency ban (2009/251/EC)
- Annex XVII entry number 61 (Regulation 412/2012) – May 2012
- Requirement <0.1 mg/kg in articles
- Test methods:
SATRA DD09/02
pr EN TS 16186



Alkyl Phenol and Alkyl Phenol Ethoxylates (APE / APEOs)

- Wetting agents and detergents in textiles and leather processes (dyeing)
- Persistent environmental pollutants
- Skin and respiratory irritant
- Nonyl phenol (NP) is toxic to aquatic organisms and is a hormonal substance (endocrine disruptor)



Alkyl Phenol and Alkyl Phenol Ethoxylates (APE / APEOs)

- Restrictions were introduced on Nonyl phenol and NPE in 2005 on their use within the supply chain
- Maximum allowed limit 1000ppm in mixtures
- 2012 environmental group report highlighted NP and NPEO in many branded products
- Annex XVII Entry number 46 applies to mixtures, however Regulation (EU) No 2016/26 applies from 3rd February 2021



Regulation (EU) No 2016/26

- NPE restricted to $< 0.01\%$ by weight of the textile article or textile part
- Applies to textile articles that can reasonably be expected to be washed during their lifetime
- Definition of textile – at least 80% textile fibres by weight



Testing for APE & APEOs

EN ISO 18218 parts 1 and 2

- Part 1 – direct Method (using HPLC-MS-MS)
- Part 2 – indirect method (using HPLC-DAD or GC-MS after converting NPE and OPE to NP or OP)



Organotin Compounds

- Can be used as PVC stabilisers and anti-Microbial treatments
- Residues from production processes (catalyst for PU)
- Anti-fouling compounds – original problems observed with marine life



Organotin Compounds

- Measured as ppb level (parts per billion – $\mu\text{g}/\text{kg}$)
- Typical RSL requirements:
 - < 50ppb for tributyl tin (TBT)
 - < 200ppb for total organotins (DBT, MBT)
- Japan Law 112 (1973)
- Annex XVII entry number 20 (276/2010) applies to articles and has much higher levels



Organotin Restrictions

Tri-butyl tin (TBT)

Restricted since 01 July 2010

Tri-phenyl tin (TPhT)

DBT restricted since Jan 2012

Di-butyl tin (DBT)

(Derogation on some products until 2015)

Di-octyl tin (DOT)

DOT restricted since Jan 2012 in specific items (including footwear)

All restricted to

< 0.1% (1000ppm)



Organotin Compounds - testing

- SATRA TM 277
- EN ISO TS 16179

Ultrasonic extraction,
derivation with sodium
tetraethyl borate followed by
GC-MS analysis

Also EN 71-3:2013
+A1:2014 limits for toys
(<12 mg/kg organic tin in
category III materials)



Regulation (EU) No 1272/2013

Polycyclic Aromatic Hydrocarbons (PAHs)

- May be present in rubbers and plastics
- Possible contaminants in extender oils and carbon black pigment
- Restricted to $< 1\text{mg/kg}$ where contact with skin or oral cavity since December 2015, (entry number 50)



PAHs – Regulation (EU) No 1272/2013

Articles shall not be placed on the market for supply to the general public, if any of their rubber or plastic components that come into direct as well as prolonged or short-term repetitive contact with the human skin or the oral cavity, under normal or reasonably foreseeable conditions of use, contain more than 1 mg/kg (0,0001 % by weight of this component) of any of the listed PAHs.

Such articles include amongst others:

- sport equipment such as bicycles, golf clubs, racquets
- household utensils, trolleys, walking frames
- tools for domestic use
- clothing, footwear, gloves and sportswear
- watch-straps, wrist-bands, masks, head-bands



Annex XVII - Summary

- Requirements of Annex XVII were transposed from the old Marketing & Use Directive
- These requirements are mandatory for affected materials / mixtures
- Generally lower requirements than 0.1%
- Advisable to base restricted substances lists on these requirements



Strategy To Demonstrate Restricted Substances Compliance

- Testing programme across product range
- Test products from different suppliers
- Cover large volume products first
- Learn from results
- Relationship with test laboratory(ies)



Suggested Testing Strategies

- Test for Annex XVII restricted substances and SVHCs separately
- Split into two groups for SVHC testing:
 - Basic: Relevant substances that might be present over 0.1%
 - Additional: Relevant substances unlikely to be present over 0.1%



Leathers - Restricted Substances

- Mandatory
 - Azo dyes
 - PCP
 - Organotins
 - Chromium VI
- Recommended
 - Formaldehyde
 - Heavy Metals



Leathers – SVHCs

- Basic testing
 - Metal screening and chromium VI (tanning salts)
 - Chlorinated paraffins
- Additional testing
 - Organic compounds GC-MS screening (solvent contaminants)



Understanding Test Reports

- Who?
 - Accredited laboratory (ISO 17025)
- How?
 - Recognised methods (ISO, EN, BS, ASTM, SATRA) or Full description of procedure
- What?
 - Result
 - Units
 - Limit of detection
- When?
 - How recent was the testing?
- Requirement?
 - Pass/Fail



Conversion of units

- 1 % = 10,000 ppm (parts per million)
- 0.1% = 1,000 ppm
- 0.01% = 100 ppm

- 1 mg/kg = 1 ppm
- 1 µg/kg = 1 ppb (parts per billion)
- 1 ppm = 1,000 ppb



Analytical Techniques

- **GC-MS**

(Gas Chromatography –
Mass Spectrometry)

- **ICP**

(Inductive Coupled Plasma)
spectrometry

- **HPLC**

(High Performance Liquid
Chromatography)

- **UV-Vis**

(UV/Visible Spectrometry)



Testing Summary

- It is commercially difficult to test every material for every substance
- Identify a programme which covers a range of products and formulations
- If raw materials change - test again.



Testing Summary

- Test most popular products first
- Possibility of combining samples for some tests
- Brand RSLs may require more demanding tests.



REACH – The Future

- December 2016 – new SVHCs to be added?
- 2018 – Final registration dates for chemicals
- 2020 – ECHA target to complete SVHC List



Questions and Answers

Conclusions

- All consumer products supplied into EU (+EEA) will need to comply with substances in articles requirements of REACH
- Primary responsibility lies with the importer for goods manufactured outside of the EU
- Brands push request for information up the supply chain
- Testing may be required to demonstrate compliance



Opportunity



- Brands looking for supply solutions
- Region is rich in raw material
- Compliance with REACH makes it easy to do business



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Thank-you for Listening

