# MANAGING THE RISK OF CHEMICAL RESIDUES IN FINAL PRODUCTS

November 2017



Version 1.4

# THE PROBLEM

**What problems can occur when you lack an overview of chemicals purchased and used?**

Brainstorm as a group and take notes in your workbook, exercise (19-1).

# LEARNING OUTCOME & RESOURCES

## Learning Outcome

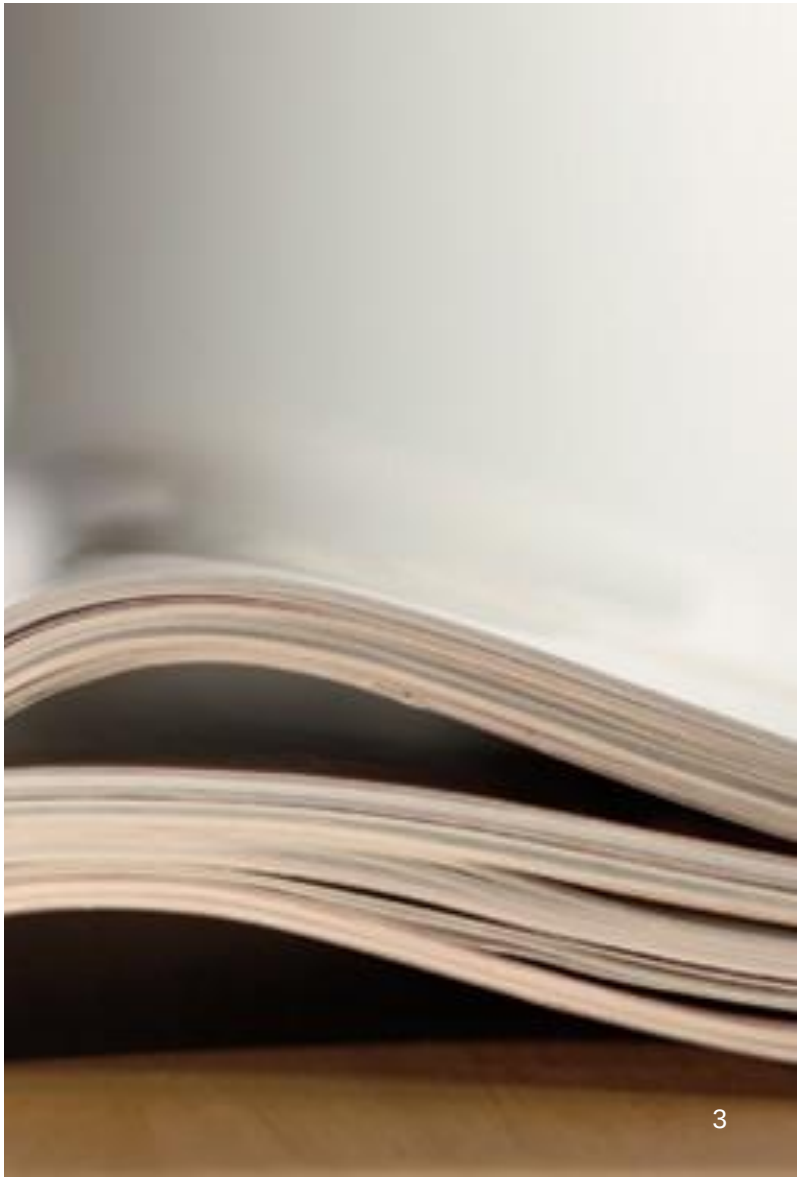
- Understand the implications and risks of using hazardous chemicals in production and the impact on your chemical testing result.
- Knowledge on how to conduct an alternative assessment.
- Knowledge to work on an Phase-out plan.

## Resources

- REMC Company Handbook.
- ZDHC Chemical Management Systems Guidance Manual.

## Workbook

Refer to complimentary excercises in your workbook.



# ZDHC REQUIREMENTS

**ZDHC 2.6.1 MRSL Compliant Formulations**

- Chemical Inventory with MRSL Compliant Formulations
- Phase out target dates and action plan for 11 priority chemical groups.

**ZDHC 2.6.2 Alternatives Assessment**

- Best Practice Alternative Assessment

Reference: ZDHC Chemical Management Systems Guidance Manual

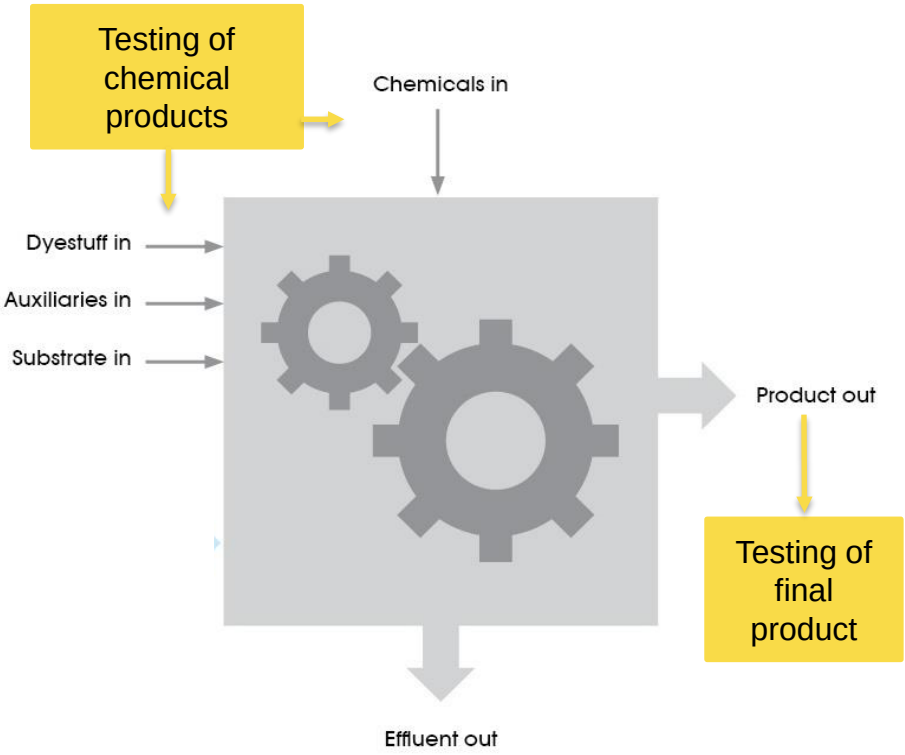
# TWO APPROACHES TO TESTING

**Option 1: Testing the chemical products before use in production (MRSL):**

Safest option to ensure no hazardous chemicals are used in production. Minimal risk of generation of hazardous chemicals during production from inappropriate application of chemicals.

**Option 2: Testing the final product after production (RSL):**

Compliance of the final product to ensure compliance with all requirements. In case the product fails at this stage it is difficult to identify the root-cause and financial loss is likely due to product not to be sold.



# RESTRICTIONS OF CHEMICALS IN FINAL PRODUCTS

**Restricted Substances List**

A guidance document to provide an inventory of maximum recommended levels of known hazardous substances in products.

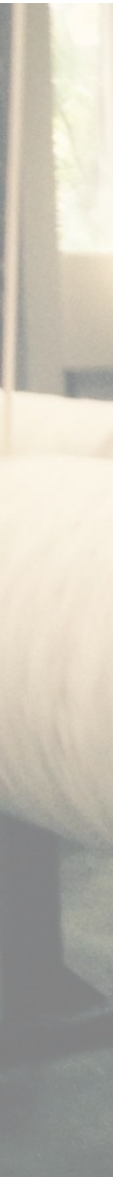
Typically encompasses: materials, parts, chemicals, components, packaging and other goods.

Enables suppliers to ensure compliance with all relevant legislations and regulations.

Ultimately, shall protect the of Health and Safety of Consumers and our Environment.

**Chemical testing to proof for compliance with RSL.**

# TYPES OF PROCESSES



**Type of risk depends upon the type of chemicals used in different processes.**

- Dye Houses (Continuous/Exhaust).
- Printing Houses (All over/Positional).
- Washing Laundry (Garment Dyeing/Washing).
- Effluent Treatment Plant (ETP)

## KNOW YOUR CHEMICALS

**Check all data and information**

- Source of the chemical and its possible impurities.
- Data available about the chemicals (SDS/ TDS/COA etc.).
- These criteria need to be looked at before any chemical is allowed inside the dye house, even for the lab trial.
- Remember that hazards and risks are not just limited to substances labelled as ‘hazardous'.

# RISKS FROM DYES

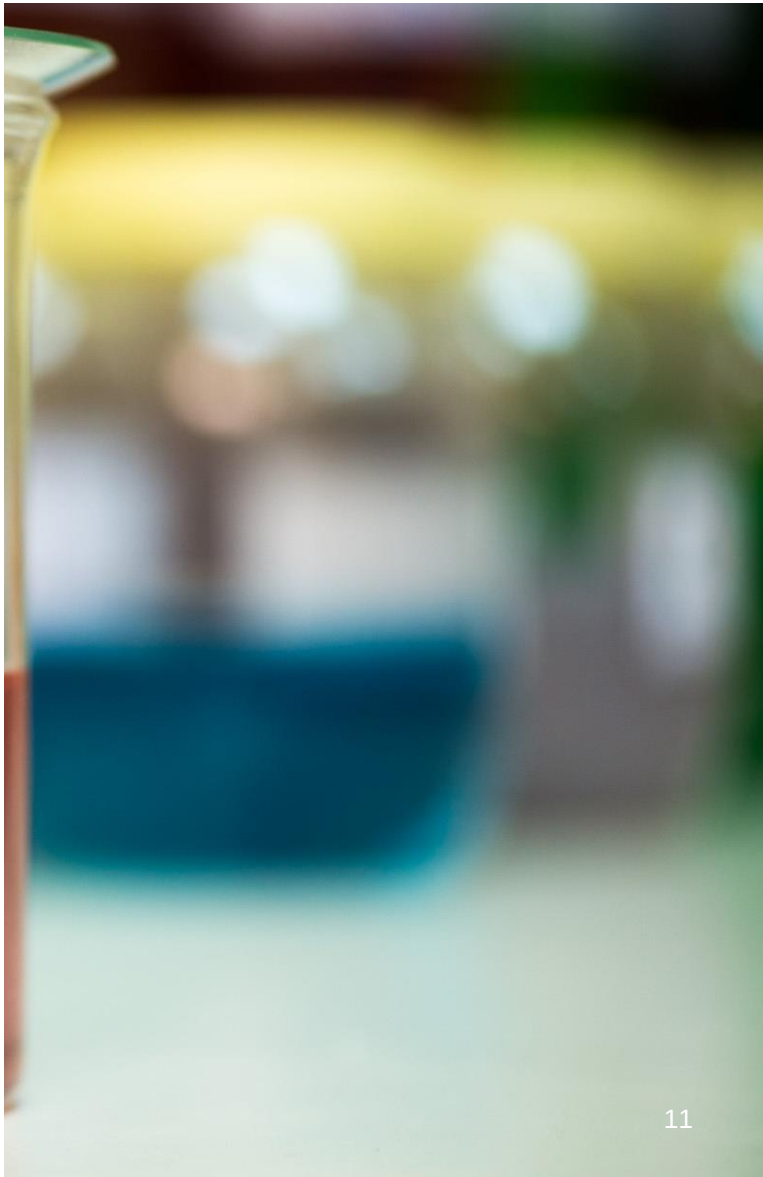
| Vat Dye | Direct | Acid | Reactive | Disperse | Pigments | Basic |
|---|---|---|---|---|---|---|
| Are based on anthraquinone molecule require more synthetic steps than acid, basic, direct, disperse and reactive dye classes. | | | **Some dyes may give rise to AOX, Nitrogen content and phosphorous content which may pose risk to aquatic life.** | | | |
| Multiple chemical reactions increase consumption of raw materials, resulting in having higher ratio of raw. | **Risk of carcinogenic aromatic amines as part of synthetic raw material or bi products formed during synthesis due to side reactions.** | | | | | |
| **solvents such as … are hazardous chemicals with the potential of severe environmental contamination.** | | | | | | |
| Most of raw materials used in manufacture of vat dyes are hazardous since they are ignitable, corrosive, or toxic.<br><br>Most common solvents are all hazardous and include: nitrobenzene, naphthalene and chlorinated solvents chlorobenzene, 1, 2-dichlorobenzene (ODCB), and 1, 2, 4- trichlorobenzene. | | | Biocides and Fungicides used in formulations which are hazardous. | | Solvents like glycols | Synthesized using hazardous raw materials - considered under SVHC e.g. Mechler's Ketone. |
| **Heavy metal catalysts and reagents used in key intermediates (raw material impurities) and synthesis of pigments could pose risk of high heavy metal content** | | | | | | |
| Heavy metal catalysts and reagents used in key intermediate steps, such as mercury, arsenic, copper, chromium, are primarily found in wastewater as soluble salts, and can contaminate both soil and groundwater if improperly treated or disposed of. | | e.g. (Cr, Co, etc.) | e.g. copper, Zinc, cadmium as impurity in zinc salt etc.,) | | e.g. fluro pigments | Metal salts used during synthesis (Lead acetate, Lead peroxide, Chromium salts and Zinc salts) give rise to high heavy metal residue. |
| Nitrobenzene is used as a solvent in few Vat colours whose residues can lead to formation of few carcinogenic amines such as Aniline and other aniline derivatives during processing stages (when subjected to reduction and oxidation atmospheres). | **APEOs could be present due to wetting agents used during diazotization and Coupling reactions.** | | | | | |
| Harmful chemicals such as PAH, Dioxins and Furans can be present in some of Vat dyes due to raw material impurities. | **In some dyes, presence of PAH due to impurities of raw materials could be present.** | | | | | |
| | **Presence of SCCPs in some dyes from de-dusting oil used in preparation.** | | | | | |

# RISKS FROM SPINNING/WEAVING/WARPING/SIZING ADDITIVES

- Antimony compounds are used as catalysts in polyester synthesis and partly remain in the fibers.
- Alkylphenol Ethoxylates (APEO) may be present in spinning oil / lubricant.
- APEOs/APEs may be present in some sizing agent.

# RISKS FROM PRE-TREATMENT CHEMICALS

- Certain halogenated solvents can be used in textile processing as a scouring solvent or carrier solvent for preparations.
- Halogenated solvents are also used as spot cleaners.
- APEOs are primarily used as detergents in the textile wet processing industry.



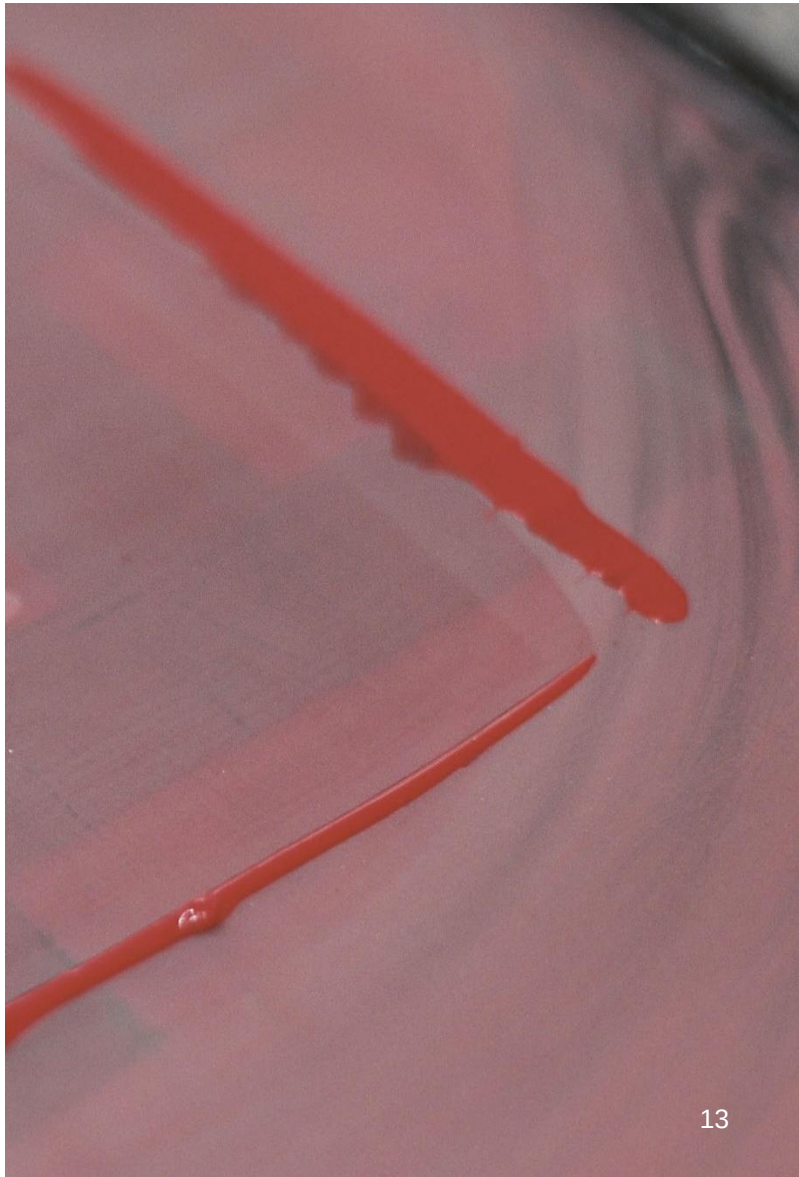
# RISKS FROM DYEING CHEMICALS

- Chlorobenzenes are mainly used as intermediates in the synthesis of other chemicals and may be present as impurities in chemical formulations (for example, dyestuffs and biocides).
- Chlorobenzenes can be used as dyeing carriers or levelling agents for dyeing, printing and coating.
- APEO in small quantities as emulsifiers or wetting agents in few dyestuffs and pigment preparations.
- Some copper compounds improve the light fastness of polyamide-based carpets, while chromium compounds can be used as oxidants in sulphur and vat dyeing processes, or as mordents in the after-chroming of certain wool dyes.
- Fixer used in dyeing posses the risk of formaldehyde.

# RISKS FROM PRINTING CHEMICALS (1/2)

- Phthalates commonly added to plastics to make them soft, increase flexibility, prevent cracking and facilitate moulding by decreasing its melting temperature which may found in plastisol prints or screen-printing.

- PCP and TeCP can also be used as preservatives in print pastes based on biologically unstable thickening agents and sizing liquors based on starch.



# RISKS FROM PRINTING CHEMICALS (2/2)

- Halogenated solvents are used in printing inks and paints.
- Organotins are often used as a heat stabiliser in PVC or as catalysts in the production of polymeric materials (e.g. polyurethane (PU), polyester or self-crosslinking silicone polymers).
- APEO in small quantities as emulsifiers or wetting agents in few dyestuffs and pigment preparations.
- Fixer, thickeners and binders posses the risk of containing formaldehyde.

**What is smart testing?**

## SMART TESTING

**Analyse possible risks to test most risky parameters only.**

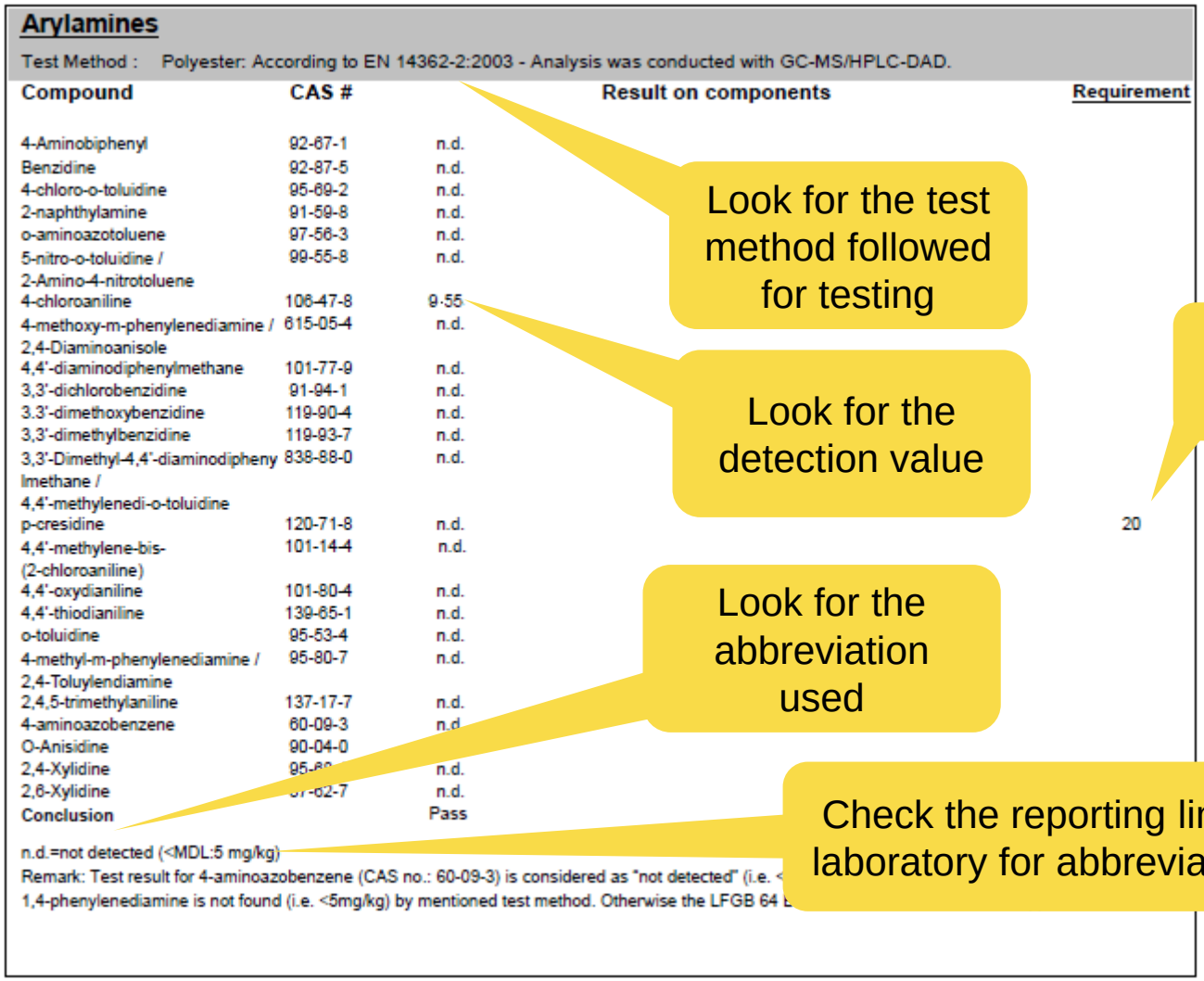
**Examples:**

- Dyestuff and pigments need to be tested only for Arylamine.
- Fixers for dyeing and printing need to be tested for formaldehyde.
- Detergent, wetting agent and dispersing agents need to be tested alkyl phenol ethoxylate.

**Benefits:**

Maximum compliance at minimum possible cost.

# INTERPRETING A CHEMICAL TESTING REPORT FROM THE LABARATORY



**Arylamines**

Test Method : Polyester: According to EN 14362-2:2003 - Analysis was conducted with GC-MS/HPLC-DAD.

| Compound | CAS # | Result on components | Requirement |
|---|---|---|---|
| 4-Aminobiphenyl | 92-67-1 | n.d. | |
| Benzidine | 92-87-5 | n.d. | |
| 4-chloro-o-toluidine | 95-69-2 | n.d. | |
| 2-naphthylamine | 91-59-8 | n.d. | |
| o-aminoazotoluene | 97-56-3 | n.d. | |
| 5-nitro-o-toluidine / 2-Amino-4-nitrotoluene | 99-55-8 | n.d. | |
| 4-chloroaniline | 106-47-8 | 9·55 | |
| 4-methoxy-m-phenylenediamine / 2,4-Diaminoanisole | 615-05-4 | n.d. | |
| 4,4'-diaminodiphenylmethane | 101-77-9 | n.d. | |
| 3,3'-dichlorobenzidine | 91-94-1 | n.d. | |
| 3.3'-dimethoxybenzidine | 119-90-4 | n.d. | |
| 3,3'-dimethylbenzidine | 119-93-7 | n.d. | |
| 3,3'-Dimethyl-4,4'-diaminodipheny lmethane / 4,4'-methylenedi-o-toluidine | 838-88-0 | n.d. | |
| p-cresidine | 120-71-8 | n.d. | 20 |
| 4,4'-methylene-bis-(2-chloroaniline) | 101-14-4 | n.d. | |
| 4,4'-oxydianiline | 101-80-4 | n.d. | |
| 4,4'-thiodianiline | 139-65-1 | n.d. | |
| o-toluidine | 95-53-4 | n.d. | |
| 4-methyl-m-phenylenediamine / 2,4-Toluylendiamine | 95-80-7 | n.d. | |
| 2,4,5-trimethylaniline | 137-17-7 | n.d. | |
| 4-aminoazobenzene | 60-09-3 | n.d | |
| O-Anisidine | 90-04-0 | | |
| 2,4-Xylidine | 95-68 | n.d. | |
| 2,6-Xylidine | 87-62-7 | n.d. | |
| **Conclusion** | | Pass | |

n.d.=not detected (<MDL:5 mg/kg)

Remark: Test result for 4-aminoazobenzene (CAS no.: 60-09-3) is considered as "not detected" (i.e. <
1,4-phenylenediamine is not found (i.e. <5mg/kg) by mentioned test method. Otherwise the LFGB 64 L

Look for the test method followed for testing

Look for the detection value

Required Limit

Look for the abbreviation used

Check the reporting limit of the laboratory for abbreviation used

# IDENTIFYING OPPORTUNITIES FOR SUBSTITUTION OF CHEMICALS FROM TESTING RESULTS - EXAMPLE

## 1) PRODUCT TYPE AND FAILURE

Printed T-shirt tested positive for phthalate.

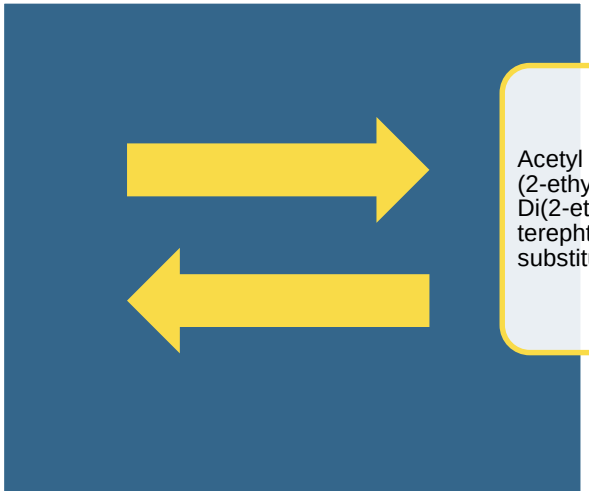
## 2) ROOT CAUSE


The plastisol print paste contained phthalate based Plasticizers.

## 3) ACTION

Search for a plastisol print paste which didn‘t contain phthalate as a plasticizer or a water based printing paste.

## 4) SUBSTITUTION



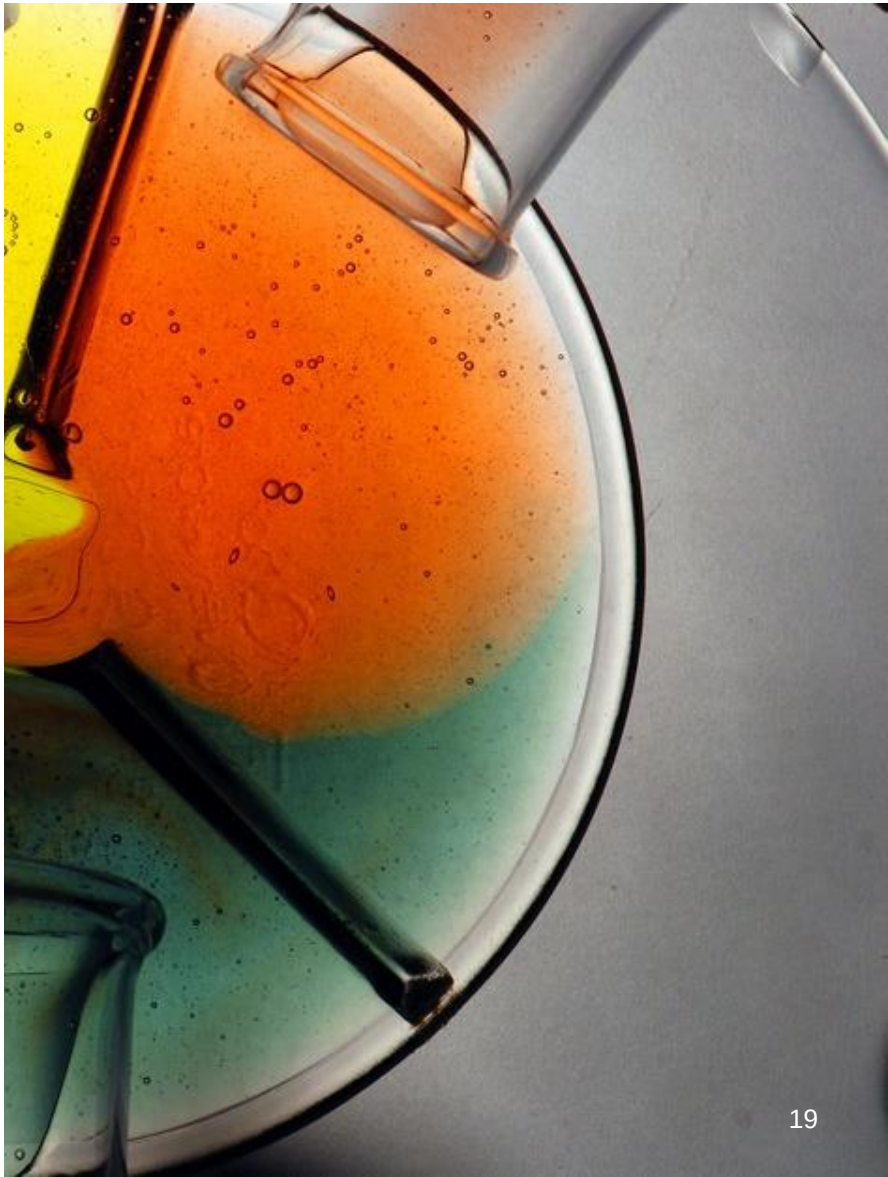
Acetyl tributyl citrate, (2-ethylhexyl) adipate, Di(2-ethylhexyl) terephthalate used as substitute.

# ALTERNATIVE ASSESSMENT

Establish, document and implement a process for assessing alternatives for chemicals that are found to have significant hazards, risks or discharges and set an annual goal for the number of alternatives it will assess.

**The process for assessing alternatives should include:**

- The development of action plans.
- Assigned responsibilities.
- Timeframes for actions.
- An estimate of resources needed (e.g., financial, human) to conduct the assessment.



Reference: ZDHC Chemical Management Systems Guidance Manual

# CHEMICAL CONTROL ACTION PLANS (1/4)

| STEP 1: GATHER EXISTING INFORMATION |
| --- |
| Gather the information you have collected and developed on hazards, control measures, possible risk reduction actions, and legal obligations related to the control of chemicals and costs. |
| **STEP 2: DECIDE HOW MANY CHEMICAL CONTROL ACTION PLANS YOU WILL NEED** |
| Distinguish between one-off actions and periodic actions. |
| Decide if it will be more useful to create one or more than one plan. (for example, you may want to have separate plans for (i) all high priority/immediate one-off actions, (ii) normal priority one-off actions, and (iii) periodic/repetitive actions such as the ones related to maintenance, monitoring or reporting/legal obligations) |
| In most organizations, obtaining senior management endorsement for one single chemical control action plan will be easier. It will also be easier to follow-up one single plan. |

Reference: UNEP Responsible Production

# CHEMICAL CONTROL ACTION PLANS (2/4)

| STEP 3: CREATE YOUR CHEMICAL CONTROL ACTION PLAN(S) |
|---|
| Plan(s) should contain the following elements: |
| • a list of the 'hot spots' you identified (refer to the notes you made during the walkthroughs) |
| • a description of the measures that you propose for dealing with each hazard |
| • a definition of clear and realistic objectives and targets that you want to achieve with this measure, indicating the anticipated improvement or benefit in terms of optimising chemical use, reducing health risks for workers, reducing environmental damage, improving product quality |
| • a description of the specific activities to be undertaken to achieve the desired improvement or benefit |
| • the expected costs associated with implementation of the action, taking into account investment costs, maintenance/periodical costs, labour costs |
| • the person who is responsible for taking action and monitoring the results |
| • the time period within which action should be completed |
| • the expected results (indicates the eventual benefits achieved vis-à-vis cost savings, risk reduction, etc.) |

# CHEMICAL CONTROL ACTION PLANS (3/4)

| STEP 4: REVIEW YOUR PLAN FOR CONSISTENCY AND EFFECTIVENESS |
| --- |
| Have you reviewed your plan carefully before trying to seek endorsement from senior management? |
| Have you discussed draft plans with all the people that may be involved, particularly the ones that you believe should be responsible for each assigned action? In particular, try to get their pre-agreement on the deadlines you will be proposing to your senior management. |
| Have you consulted the people who are directly involved in handling chemicals about the proposed actions in order to understand the implications for changing procedures? |
| Have you thought about possible consequences – both positive and negative – before implementing action? |
| Have you checked that the proposed actions are sufficient to meet the stated objectives and targets? |
| Have you verified that the actions to be undertaken are clearly understood by those who will be involved? |
| Have you assigned clear responsibilities for each action? Give the responsibility for taking action to specific individuals. If no individual is responsible, nothing will happen! |
| Have you made sure that those designated as responsible have the needed expertise and authority to carry out the proposed action? |
| Have you been specific about who must do what and how? |
| Have you established a realistic time-frame for who should do what by when? |
| Have you made provisions in your plan so that all workers affected by changes to the current way of doing things will have an opportunity to be properly informed and trained in the new procedures? |

# CHEMICAL CONTROL ACTION PLANS (4/4)

| STEP 5: GET ENDORSEMENT |
| --- |
| Present the agreed plans to your senior management, clearly explaining the expected benefits from implementing the actions proposed. |
| Prepare yourself beforehand and be ready to provide justification for each proposed action. Be particularly attentive to possible questions like: |
| • Why should we implement this action now and not next year? |
| • Can we partially implement this action and still obtain the expected results? |
| • Are you sure of the expected range of costs? |
| • Did you take into account idle time? And warehouse cost? |
| • How many suppliers did you consult? |
| • Will there be any overtime hours involved? |
| • You will need to involve one of our permanent contractors/suppliers to implement this action. Are you taking their assistance for granted? Have you checked what extra costs will be involved? |
| • Have you discussed the feasibility of this action with this person? |
| • Why have you proposed him/her for the job? |
| • Why are you proposing this action to start 6 months from now? We are presently non-complying. What are the costs of non-compliance with this obligation (contractual, reputational, legal) vis-à-vis the investment and operational costs of this action now? Have you taken into account potential fines, or loss of customers/orders? |
| • Other:_____ (list possible questions you may be asked) |

Reference: UNEP Responsible Production

## ACTIVITY

## DISCUSSION

Take notes.
Workbook, exercise (19-2).

Note down which chemical failures you have experienced and link to the 11 priority hazardous chemical groups.

**Discuss:**

- What substitutes have you found?
- Which challenges remain?
- What is your approach to testing?

# Open To Questions

# SUMMARY

Every participant to feedback with one key learning from the session.

Take notes in your workbook, exercise (19-3).