

Programme Overview and Training Arrangement

项目概况和培训安排

TÜV Rheinland
March 2019



Learning objectives 学习目标:

1. Introduce the whole programme 介绍整个项目情况
2. Introduce the arrangement of the training and tutorship arrangement 介绍培训安排和辅导安排
3. To understand the trainee's expectations 知道被培训者的期望

Target Group 目标群:

- 1) At least 1 top management participated in both intro & advanced training 至少有1名高层管理人员同时参加了入门和高级培训
- 2) At least 9 or 5% of workers participated in both intro & advanced training 至少有9%或5%的工人参加了入门和高级培训
- 3) At least 2 internal training conducted for all workers contacted with chemicals with documented record 对所有接触化学品的员工至少进行2次内部培训，并记录在案
- 4) At least 3 trained workers are able to screen substance listed on RSL or MRSL using CAS No/ chemical name. 至少3名受过培训的工人能够使用CAS编号/化学名称筛选RSL或MRSL上列出的物质

Length: 时长

1 Hour 1小时

Training outcomes 培训成果

By the end of this training, you should be able to ...

培训结束后，您应该能够

- Understand the whole chemical management programme from chemical mapping, chemical testing, chemical training, and knowledge sharing
从化学绘图、化学测试、化学培训和知识共享中了解整个化学管理方案
- Understand the detailed arrangement of the training section
理解培训部分的详细安排
- Express your expectations for the coming training
表达你们对未来培训的期望

Overall objectives of the training 这个培训的整体目标

To know what is chemical management, why it is important and who should be involved
了解什么是化学管理，为什么它很重要，应该由谁参与

To understand the key elements and benefits of a chemical management system and how you implement it at your factory
了解化学品管理系统的关键要素和好处，以及如何在工厂实施该系统

To address critical issues in chemical management to improve worker health and safety, the business environment and the factory's chemical management performance
解决化学品管理中的关键问题，提高工人的健康和安全性、商业环境和工厂的化学品管理绩效。

To get a good understanding that you can pass on to your staff and coworkers
更好地理解你所需要传给员工的和同事的知识

The Shoe Industry Overview 鞋业概况

- The shoe industry is an important employer for many workers in China. 在中国，鞋业是很多工人的重要雇主。
- As the available income of Chinese people continues to rise, the consumer demanding for footwear products grows. 随着中国人可支配收入的持续增长，消费者对鞋类产品的需求也在增加。
- The value of footwear in Mainland China shows a 2% year-on-year increase. 中国大陆的鞋类价值同比增长2%。
- There are currently four major footwear industry clusters in China, predominantly located in the southeast coastal regions. 中国目前有四大鞋业集群，主要分布在东南沿海地区。
- The development partnership works with factories in the districts of Guangzhou and Wenzhou, which produce for the mainland market but also for international buyers and brands. 发展伙伴关系与广州和温州地区的工厂合作，这些工厂为中国大陆市场生产，也为国际买家和品牌生产。

But the shoe industry is also the big polluters on the planet, which generate **one-fifth** of the world's industrial water pollution and use **20,000 – 40,000** chemicals to make shoes. 但是制鞋工业也是地球上最大的污染源。它产生了世界五分之一的工业水污染，并使用20000-40000种化学物质制造鞋子。

The use of harmful chemicals in the shoe industry has consequences for **worker health** 在制鞋工业中使用有害化学物质会对工人健康产生影响

They can occur in workers along the life-cycle of shoes: workers in production and retail, in consumers, in waste handlers, in the community around production and waste handling. 它们可以伴随着鞋的生命周期发生在工人身上：生产和零售工人、消费者、废物处理者、生产和废物处理周围社区的工人

Harmful chemicals are linked to many diseases:

有害化学物质与许多疾病有关：

- Infertility, lower sperm quality, different types of cancer, neurological problems, asthma, allergies, skin problems, lung problems, heart diseases and other 不孕、精子质量低下、不同类型的癌症、神经系统问题、哮喘、过敏、皮肤问题、肺部问题、心脏病等
- Most diseases lead to death or severe ill-being. This has also negative consequences for the families, due to income loss, high medical cost etc. 大多数疾病会导致死亡或严重的疾病。这也给家庭带来了负面影响，如收入损失、高昂的医疗费用等。



The use of harmful chemicals in the shoe industry has consequences for **worker health** 在制鞋工业中使用有害化学物质会对工人健康产生影响

- Oral 经口
- Inhalation 经吸入
- Dermal 经皮肤



The use of harmful chemicals in the shoe industry has consequences for **the environment** 在制鞋工业中使用有害化学物质会对环境产生影响

- Water pollution 水污染
- Pollution of soil and farmland 土壤和农田污染
- Hazardous waste generation 有害废物产生



Water pollution 水污染

- Growing cotton needs a lot of water and often used pesticides are polluting soil and groundwater
种植棉花需要大量的水，经常使用的杀虫剂正在污染土壤和地下水。
- Effluents from textile production pollute freshwater resources and eventually the ocean
纺织生产废水污染淡水资源，最终污染海洋
- Used hazardous chemicals can even build up in the food chain
使用过的危险化学品甚至会在食物链中堆积起来



Pollution of soil and farmland 土壤和农田污染

- Hazardous chemicals in wastewater can pollute soil and farmland along rivers
废水中的有害化学物质会污染河流沿线的土壤和农田
- Sewage sludge containing hazardous chemicals is being applied to land as a soil supplement
含有有害化学物质的污水段塞被用作土壤补充物
- Contaminated soil can lead to contaminated food that is grown on these fields; therefore chemicals can enter the food chain
受污染的土壤会导致种植在这些农田上的受污染的食物；因此化学品可以进入食物链



Hazardous waste generation 有害废物产生

- Hazardous waste in the textile production has to be handled professionally
纺织生产中的危险废物必须经过专业处理
- It cannot be dumped
它不能倾倒
- The less hazardous chemicals are being used in production, the less hazardous waste is generated
生产中使用的化学品危险性越低, 产生的废物危险性就越低

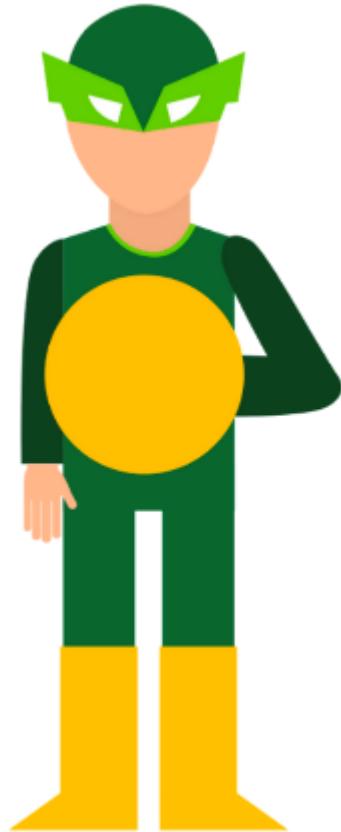




You are important! 你很重要!

Because it is up to you how **healthy and safe** you, your employees and neighbours stay and if you continue to live in a **safe environment**.

因为你、你的员工和邻居的**健康与安全**、你是否能够生活在**安全的环境中**，这些都取决于你。



What can you do to be an front-runner? 要成为一个领跑者, 你需要做些什么?

- Take part in our training
参加我们的培训
- Set up an Action Plan
制定行动计划
- Implement and Monitor improvements at your factory
在工厂内执行并监控改进

➤ Improve your chemical management performance 提高你的化学品管理表现

- Establish a holistic and comprehensive chemical management system in your factory
建立一个全面的化学品管理体系
- Enable you to trace your daily work of chemical management process
能够跟踪化学品管理过程中的日常工作
- Enable you to control and improve the quality of your products 能够控制和提高产品质量
- Improve your productivity 提高生产力


➤ Improve the working conditions and safety of your workers at the workplace 改善工作场所工人的工作条件和安全

- Improve worker satisfaction and loyalty 提高员工满意度和忠诚度
- Reduce your staff turnover 减少员工流动
- Reduce the risk of costs related to any accidents at the workplace
降低与工作场所任何事故相关的成本风险

➤ Improve your business environment inside and outside 改善内外部商业环境


- Keep sustainable and long-run development of your factory under more stringent environmental regulation in China
在中国更加严格的环境法规下，保持工厂的可持续和长期发展
- Improve your factory commitment and be a strong signal to the brands buying from you
提高你的工厂承诺，成为你购买品牌的有力信号
- Increase your competitive advantage in the domestic and global market
提高您在国内外市场的竞争优势

Benefits of a Chemical Management System 化学管理系统的好处

 Maintain a license to operate 保持经营许可


 Access to global market 进入全球市场


 Maintain a competitive advantage 保持竞争优势


 Minimise excessive or replicative chemical purchases/consolidate chemical purchasing 减少过量或重复化学品购买/整合化学品采购


 Reduction in costs by reducing waste/overages 通过减少浪费/过量来降低成本


 Enforce chemical managing knowledge by expert or certified trainer 由专家或认证培训师强化化学管理知识

 Reduce down time by creating a safer work environment 通过创建更安全的工作环境来减少停机时间

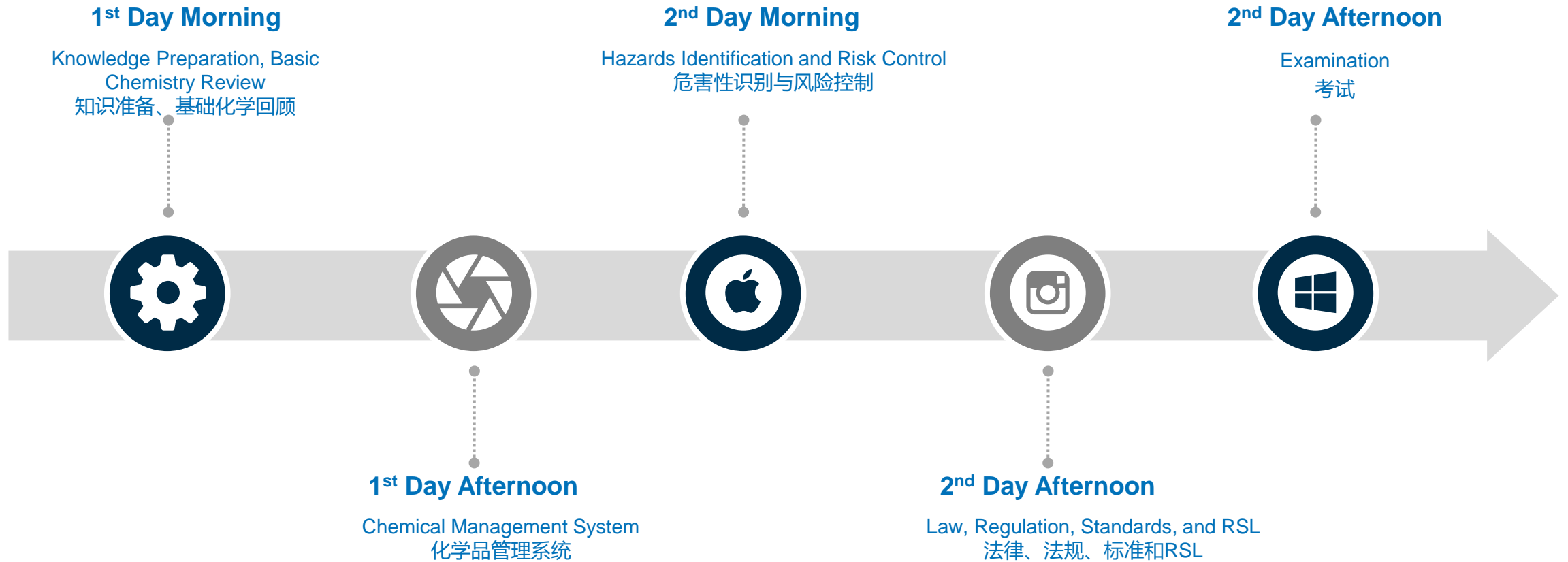
 Stop potential hazards before they become an issue 阻止潜在危险的发生

 Helps facilities ensure that RSL compliant materials are being produced; becomes invaluable in tracking down issues if they do arise 帮助设施确保生产符合RSL标准的材料;如果出现问题,就能提供非常有用的资料追溯根源

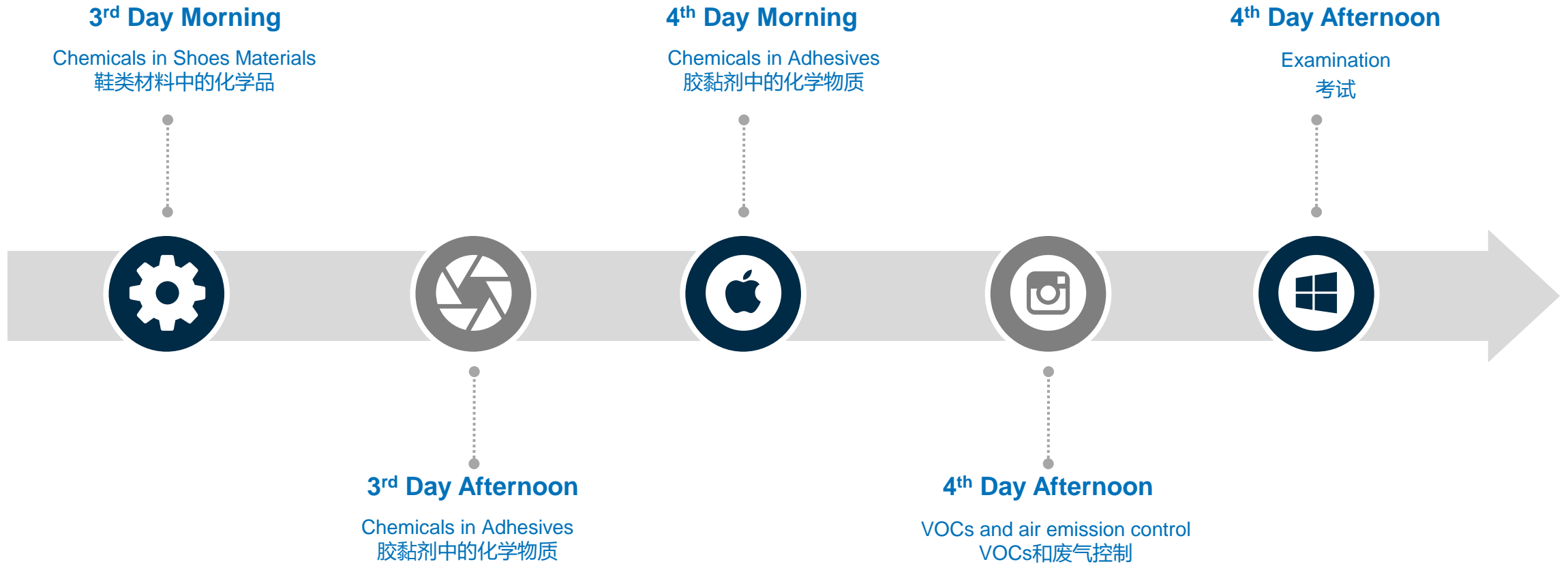
 Traceability of chemicals in the supply chain 供应链中化学品的可追溯性

 Reduction of chemicals can result in loading reduction in ETP 减少化学品会减少污水处理厂的负荷

Phase I Training – Introductory Training 第一阶段培训 – 基础培训



Phase I Training – Advanced Training 第一阶段培训 – 进阶培训



Phase I Training – Training Factory’s Trainers 第一阶段培训 – 培训工厂培训师

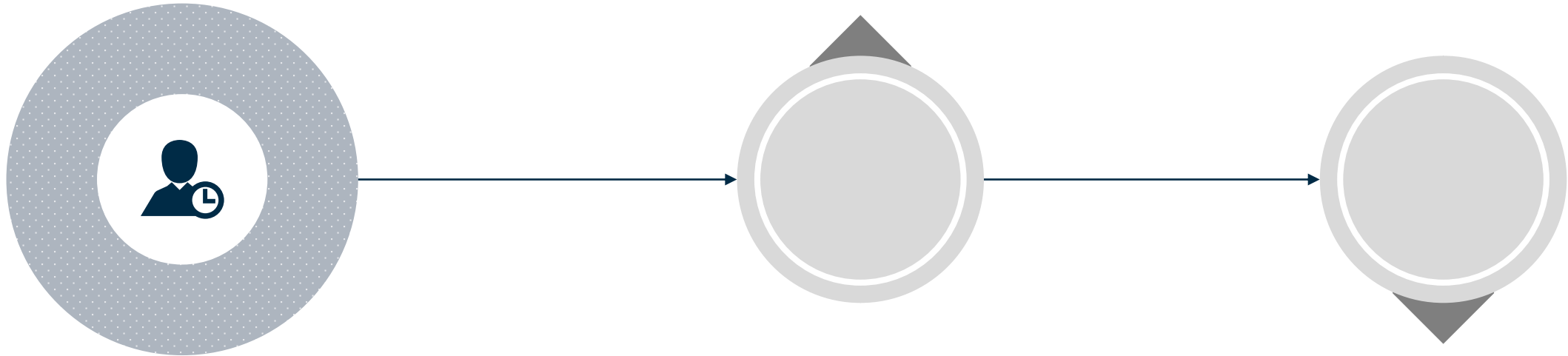
Soft Skills 软技能



Q&A on Techniques 技术答疑

Phase II Training 第二阶段培训

Internal Training roll-out to factories Part 1
工厂展开内部培训 – part I



Internal Training roll-out to factories Part II
工厂展开内部培训 – part II

The same people should go to basic training (part 1) and advanced training (part 2).

同样的人应该参加基础培训（第1部分）和高级培训（第2部分）。

Some workers, should be chosen to be the in-house expert trainers who will receive additional trainer training on soft skills.

一些工人（可能每个工厂2名）将被选为内部专家培训师，他们将接受额外的软技能培训。

Requirements on the Facility during training 培训中对工厂的要求

- Participate in training on time 准时参加培训
- Mute Cell Phone 手机静音
- Participate in interaction actively 积极参与互动
- In principle, trainee should attend the training throughout the course; if there is an emergency, trainee can leave with application. 原则上，应全程参加培训；若有紧急事务，需申请方可离开。

Activity 活动

Write down your expectations to our training courses.
写下您对我们培训课程的期望。

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Write down your expectations to our training courses.
写下您对我们培训课程的期望。

Module 5: Detox, ZDHC and MRSL
模块五：“去毒”、零排放、生产受限物质清单

TÜV Rheinland
August 2019

CONTENTS



Introduction of
Greenpeace's Detox
campaign
介绍绿色和平去毒运动

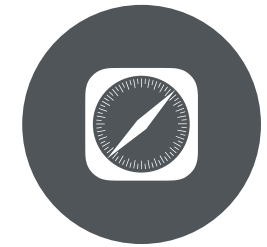


ZDHC Tools ZDHC工具

- ZDHC Chemical Management Guidance Manual ZDHC 化学品管理手册
- ZDHC MRSL ZDHC生产受限物质清单
- ZDHC Wastewater Guideline ZDHC废水指南



Introduction of Restricted Substances 受限物质介绍



Tools to choose safe
chemicals
选择安全化学品的工具

Learning objectives 学习目标:

1. To gain knowledge about Green Peace's DETOX campaign 了解绿色和平排毒运动
2. To gain knowledge about ZDHC and ZDHC's tools 了解ZDHC和ZDHC的工具
3. To learn about the hazardous chemicals listed on ZDHC's MRSL 了解ZDHC的MRSL中列出的危险化学品
4. To learn about customer's MRSL 了解客户的MRSL

Target Group 目标群:

5% of participating factory workers may include: 工厂5%的员工应包括:

- 1.High management: factory Board Chairman, Managing Director, General Manager 高层: 董事长、常务董事、总经理;
2. Department Manager in Quality, EHS, R&D, Manufacturing, Purchasing, IT, HR, Sales, and Admin 部门经理 (质量、EHS、研发、生产、采购、IT、人力资源、销售、行政)
3. All staff in quality department, lab, and EHS department 质量部门、实验室和EHS部门的所有员工
- 4.Shift leaders in each manufacturing line, in chemical warehouse 每条生产线、每个化学品仓库领班
- 5.All interested workers are welcome 所有感兴趣的员工
6. Minimum 10 people for each factory 每家工厂至少10人

Length 时长:

3 Hours 3小时

Training outcomes 培训成果

At the end of this training, the participants will be able to ...

培训结束后，您应该能够

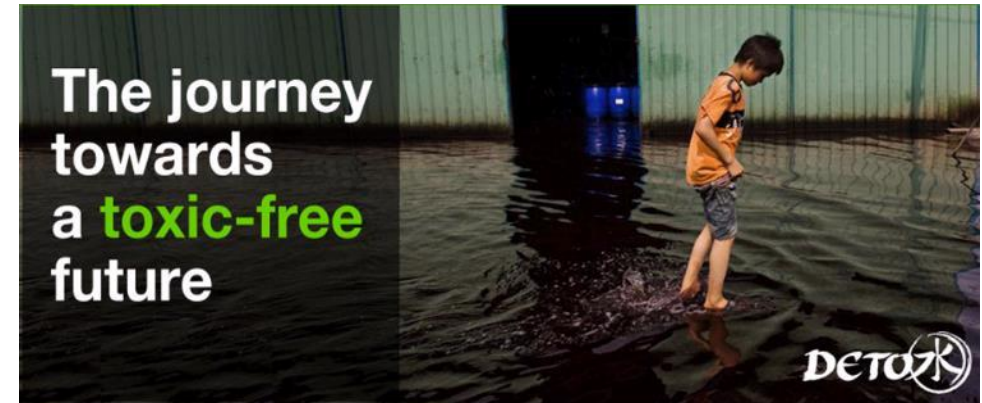
- Explain the relevance of Detox campaign and ZDHC to chemical management requirements
解释去毒活动和ZDHC与化学品管理要求的相关性
- Explain the difference between MRSL and RSL
能够解释MRSL和RSL之间的区别
- Identify the root source of substances listed on MRSL
能够了解MRSL所列物质的根源

Introduction of Greenpeace's Detox campaign 介绍绿色和平去毒运动

/01

Greenpeace – Detox Campaign 绿色和平-去毒运动

- Greenpeace is campaigning to stop industry poisoning waterways around the world with hazardous, persistent and hormone-disrupting chemicals.
绿色和平组织致力于阻止全球范围内的工业使用危害性、持久性和激素破坏性化学品时水”中毒”。
- Fieldworks and investigations in key manufacturing countries, along with testing of branded garments for traces of hazardous chemicals
在关键制造国家的实地工作和调查，以及对品牌服装进行有害化学品痕迹的检测。



An excerpt from Greenpeace's website.

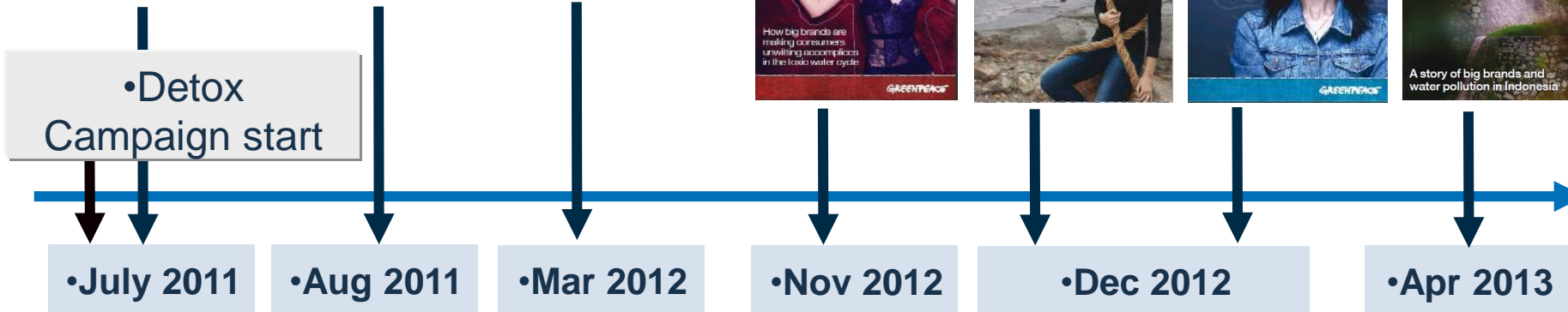
Greenpeace – Detox report

- First set of Detox reports is called “Dirty Laundry”. 第一版去毒报告为“时尚之毒”
- Afterwards, Greenpeace published another set of reports called “Toxic Threads” intensifying the message conveyed. 随后，绿色和平发表了新一版的报告“潮流。污流”加快了相关信息的传递

Dirty Laundry

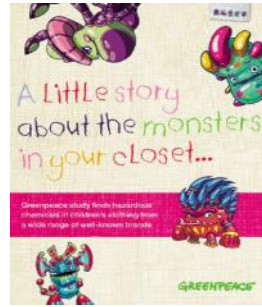


Toxic Threads



Greenpeace – Detox Reports 2014

- More reports about toxic chemicals used in textile industry were published in 2014 更多的相关报道
- Greenpeace also organized many demonstrations to get people's attention to Detox campaign 更多的社会活动



2014



GREENPEACE
绿色和平

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极净之境？——全氟化合物（PFCs）雪地污染调查

📅 2015年9月12日 👤 Yang Shen

绿色和平抽验来自全球10个偏远地区的雪及湖水样本，发现这些没有人类活动的地方，均受到环境激素“全氟化合物（PFCs）”的污染。其中来自斯洛伐克的高塔特拉山、意大利的锡比利尼山和瑞士的艾伯塔斯山的样本PFCs含量较高。PFCs是一类人造化学物质，不但会污染环境，部分PFCs更会影响人类的内分泌系列，甚至致癌。由于它具有防水防污的特性，因此受到户外品牌的青睐，常被应用于生产户外防水用品。绿色和平呼吁户外品牌尽快淘汰PFCs及其他有毒有害化学物质；同时各国政府亦应遵从预防性原则，全面限制PFCs这类化学物质。

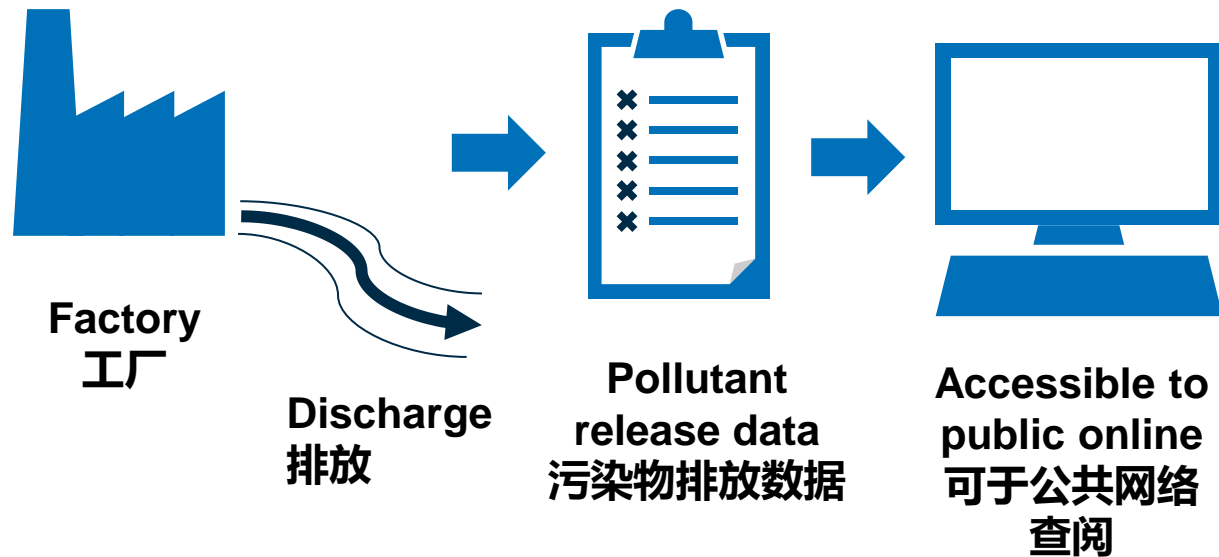
[点击下载>>极净之境？全氟化合物（PFCs）雪地污染调查摘要](#)

Greenpeace's Approach 绿色和平的方法

Demand public disclosure of discharge of hazardous chemicals from factories.
推动公开披露工厂排放危害化学品



Existing systems in US, EU and Japan:
PRTR- Pollutant Release and Transfer Register.
美国, 欧盟和日本的现有系统: PRTR-污染物排放和转移登记册



Greenpeace believes that everyone, especially those living close to factories, have the right to know what is being discharged. 绿色和平组织认为, 每个人, 特别是那些靠近工厂的人, 都有权知道正在排放的是什麼东西

Which Criteria are Greenpeace Assessing? 绿色和平按什么标准作评估

Detox 2020 Plan 去毒2020计划

Manufacturing Restricted Substances List (MRSL), to enable brands to eliminate all hazardous chemicals.

生产限用物质清单 (MRSL) , 使品牌能够消除所有危害化学品

PFC Elimination 排除全/多氟化碳

Commitment for the elimination of per/poly fluorinated chemicals (PFC) as a group. 承诺消除全/多氟化合物 (PFC)

Transparency 透明度

Publication of precise, relevant, up to date and locally accurate information on the use and discharge of hazardous chemicals.

发布精准, 相关, 最新和当地的有关使用和排放危害化学品的信息

Greenpeace aims to remove hazardous chemicals from the textile supply chain, engage consumers, whilst ultimately “**closing and slowing the loop**”. 绿色和平旨在从纺织供应链中去除有害化学物质, 吸引消费者, 同时最终向“**循环经济**”迈进。



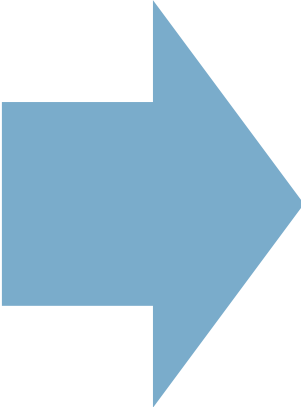
Zero Discharge of Hazardous Chemicals (ZDHC)

有害化学品零排 (ZDHC)

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Ø ZDHC



Brands Committed to 'Detox' as of October 2017

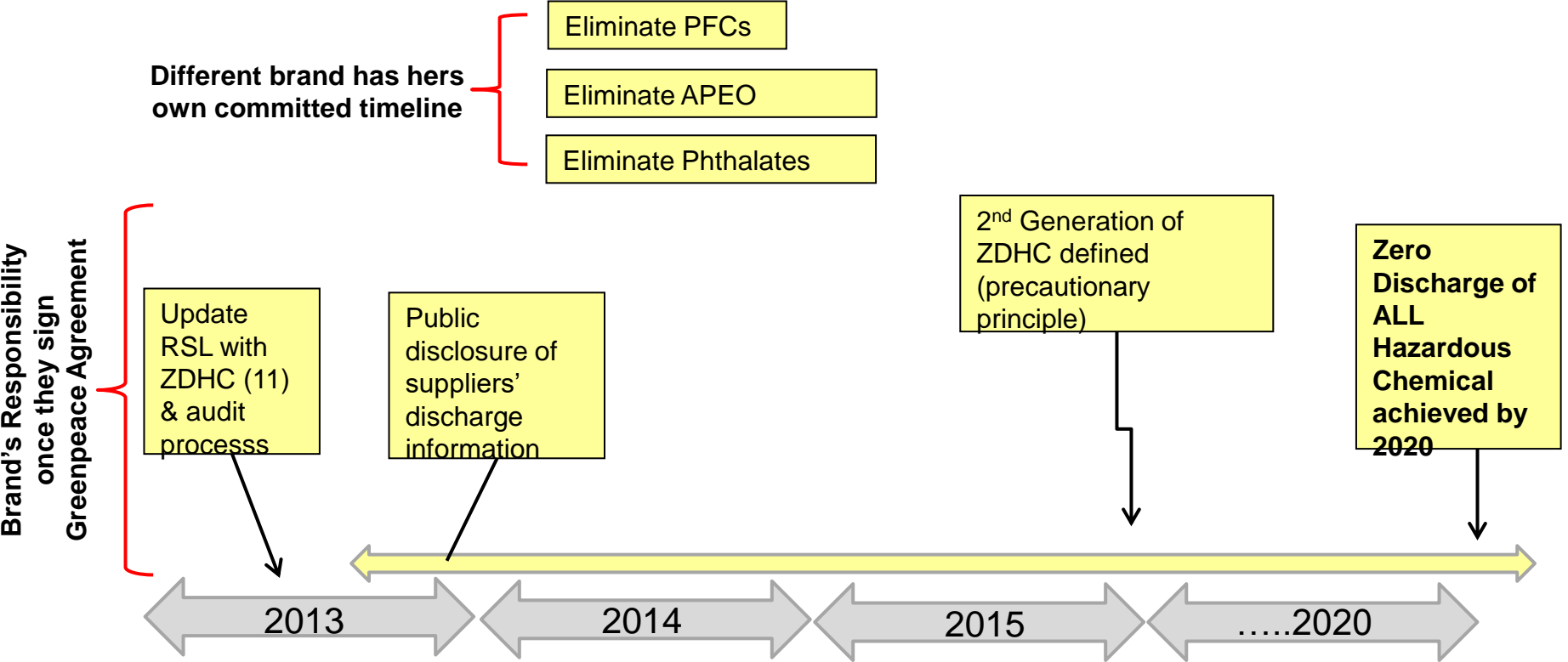
自2017年10月为止向“去毒”承诺的品牌

More than 44 international brands & retailers are committed to stop the usage of hazardous chemicals
 超过44个国际品牌和零售商承诺停止使用有害化学品



* Adopted the ZDHC MRSL

Timeline of General ZDHC Commitment



ZDHC Tools ZDHC工具



ZDHC TOOLS ZDHC工具

- Joint initiative established in 2011. 联合倡议于2011年成立
- Released a shared roadmap “to advance towards zero discharge of hazardous chemicals”. 发布了“推进有害化学品零排放”的共同路线图
- Geographical regions include: China, Bangladesh, India, but not exclusive. 地理区域包括：中国，孟加拉国，印度等
- Aims to create better tools and knowledge for the next step: Implementation. 旨在为下一步创造更好的工具和知识：实施
 - ✓ Have issued a publically available MRSL 已经公布了MRSL
 - ✓ Chemical Guidance Sheets 化学品指导表
 - ✓ Chemical Management System Guidance Manual 化学品管理系统指导手册
 - ✓ NEW Wastewater Guidelines 新的废水指南

Chemical companies issue ZDHC chemical positives lists: 发布了ZDHC化学正面清单的化学品公司

- ✓ DyStar, Hunstman, Rudolph GmbH, Tanatex, Transfar



ZDHC TOOLS ZDHC工具

ZDHC Chemical Management Guidance Manual:

https://www.roadmaptozero.com/fileadmin/layout/media/downloads/chin/CMS_ZH.pdf

ZDHC MRSL:

https://www.roadmaptozero.com/fileadmin/layout/media/downloads/MRSL_V1.1_ZH.pdf

ZDHC Wastewater Guideline:

https://www.roadmaptozero.com/fileadmin/layout/media/downloads/MRSL_V1.1_ZH.pdf



ZDHC Manufacturers Restricted Substances List (MRSL)

➤ MRSL Chapters

- Chapter 1: MRSL for Textiles and Synthetic Leather Processing
第一章：纺织品和人造革生产中的MRSL
- Chapter 2: MRSL for Natural leather Processing
第二章：天然皮革生产中的MRSL

➤ MRSL Groups

Group A: Raw Material and Finished Product Supplier Guidance
A类：原材料及成品供应商指南

Group B: Chemical Supplier Formulation Limit
B类：化工品配方中的限值

The full **ZDHC MRSL** is available at
www.roadmaptozero.com



Manufacturers Restricted Substances List (MRSL)

Chemical Substances Subject to Usage Ban 生产中禁止使用的化学物质

These include relevant substances from the original 11 priority chemical groups in the Joint Roadmap along with additional substances discussed with qualified experts from the ZDHC Technical Advisory Committee: ZDHC技术委员会专家给出了相关物质的建议，包括联合路线图中的11类优先物质及其他额外的物质。

- Alkylphenols/Alkylphenol Ethoxylates (AP/APEOs) 烷基酚/烷基酚聚氧乙烯醚
- Chlorobenzenes & Chlorotoluenes 氯化苯和氯化甲苯
- Chlorophenols 氯化酚
- Dyes, including Azo, Navy Blue Colourant, Carcinogenic and Disperse (Sensitising) Dyes 染料类，包括偶氮、海军蓝、致癌和致敏性分散染料
- Flame retardants 阻燃剂
- Glycols 乙二醇类物质
- Organotin Compounds 有机锡化合物
- Polycyclic Aromatic Hydrocarbons (PAHs) 多环芳香烃
- Perfluorinated and Polyfluorinated Chemicals (PFCs) 全氟及多氟化合物
- Phthalates 邻苯二甲酸酯类物质
- Heavy Metals 重金属
- Volatile Organic Compounds (VOCs) 可挥发的有机化合物

Quiz 小测试



Do you remember the
difference between RSL
and MRSL?

您还记得RSL和MRSL之间的
区别吗?

Manufacturing Restricted Substances List (MRSL) and Restricted Substances List (RSL)

The difference between the Manufacturing Restricted Substances List (MRSL) and Restricted Substances List (RSL) is:生产限制物质清单与限制物质清单的分别:

MRSL
Input Chemistry
输入化学



MRSL sets chemical limits for
chemical formulations
MRSL 设定化学限制于
化学制剂

RSL
Product Chemistry
成品化学



RSL sets limits for chemicals in
materials
RSL 设定化学限制于
物料

The MRSL is a valuable tool for procuring chemical formulations that will help suppliers meet sustainability targets.

MRSL是采购化学制剂的有用工具，可帮助供应商达到可持续发展目标

Introduction of Restricted Substances 受限物质介绍



Alkylphenols and Alkylphenol Ethoxylates

烷基酚和烷基酚聚氧乙烯醚

■ Alkylphenols (AP) & Alkylphenol Ethoxylates (APEO)

烷基酚和烷基酚聚氧乙烯醚

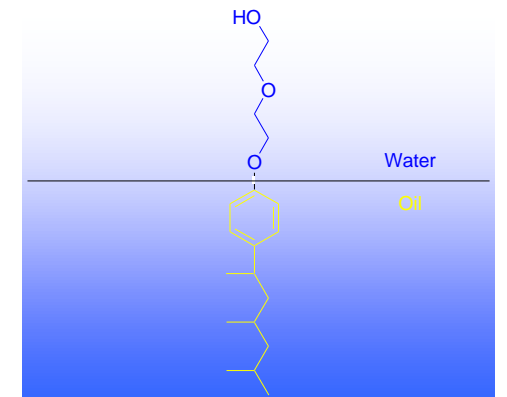
- AP: Nonylphenol (NP), Octylphenol (OP)
- APEO: Nonylphenol ethoxylate (NPEO), Octylphenol ethoxylate (OPEO)

■ Applications in textile and footwear industry 在纺织和制鞋行业的应用

- Good emulsifiers and wetting agents 好的乳化剂和润湿剂
- Use as industrial surfactants in manufacture of wool and metal, as emulsifiers for emulsion polymerization, in laboratory detergents, and pesticides
在加工羊毛和金属产品时用作工业表面活性剂，在乳液聚合中用作乳化剂，用作实验室清洗剂和杀虫剂
- Use as detergent auxiliaries in scouring and bleaching process
在煮练和漂白过程中用作洗涤助剂

■ Concerns in the market 市场的关注

- Bio-accumulates in aquatic organisms 水生生物的生物累积性
- Irritation - destructive to upper respiratory tract, eyes and skin
刺激 - 对上呼吸道，眼睛和皮肤有害



Alkylphenols and Alkylphenol Ethoxylates

烷基酚和烷基酚聚氧乙烯醚



ZDHC MRSL Recommended limit for chemical supplier commercial formulation

ZDHC MRSL对化学品供应商生产配方的推荐限值

AP: 250mg/kg (each), APEO: 500mg/kg (each)

Test Material Categories 测试样品类别

Plastics 塑料	Natural fibres 天然纤维	Synthetic fibres 合成纤维	Coating/ Printing 涂层/印花	Leather 皮革	Metal parts 金属部件
✓	✓	✓	✓	✓	

Legislation / Requirement 法规/要求

Test Item 测试项目	Methods 方法	Reference for Restriction 限值参考	Recommended Max. Limit 建议最大限值
Nonylphenol (NPs) & Nonylphenol Ethoxylates (NPEOs)	Textile: ISO/FDIS 18254 Leather: ISO 18218:2015	Entry 46 of Regulation (EC) No 552/2009 amending Annex XVII of REACH Regulation (EC) No 1907/2006	0.1% (each) in substance and mixture
		Proposed Restriction to Annex XVII of REACH Regulation under consultation	In textile clothing / Fabric accessories / Interior textile articles: NPEO: 100 mg/kg

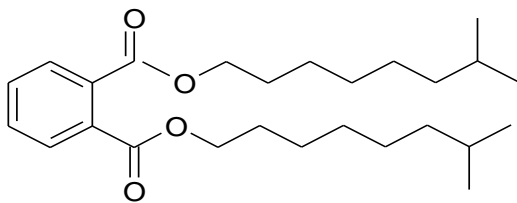
What are PHTHALATES? 什么是邻苯二甲酸酯?

Phthalates are a class of organic compounds added to plastics to increase flexibility. 邻苯二甲酸酯是一类加入到塑料中增加其柔韧性的有机化合物。

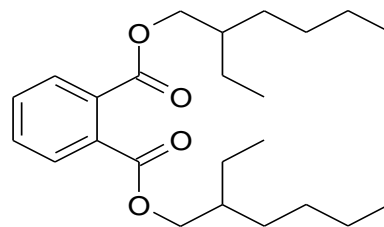
In textile and apparel products, phthalates may associated with flexible plastic components, trims and screen print. 在纺织品和服装产品中，邻苯二甲酸酯与有柔韧性的塑料、配件和丝印有关。

Previous literature showed that phthalates can migrate from a plastic into the body of a child sucks or chews on the plastic. They are suspected to be carcinogenic and to disturb the hormone system.

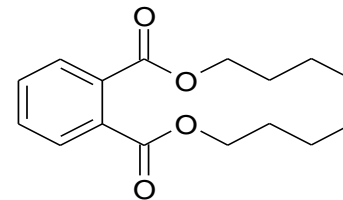
以前的文献表明邻苯二甲酸酯能够通过吮吸或者啃咬从一种塑料迁移到儿童体内。被怀疑是致癌的并破坏荷尔蒙系统。



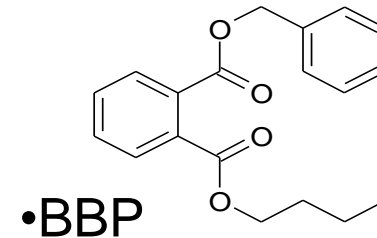
•DINP



•DEHP



•DBP



•BBP

Phthalates 邻苯二甲酸酯

■ What are phthalates? 什么是邻苯二甲酸酯

- Used as plasticisers in plastics (especially PVC)
用作塑料的增塑剂（尤其是PVC）
- Advantages to plastic: flexible, durable, longevity, low cost
对塑料的优点：弹性，耐用，增长产品寿命，低成本

■ Applications in textile and footwear industry 在纺织和制鞋行业的应用

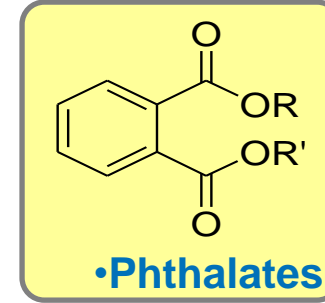
- Plasticizers in plastics such as PVC, Rubber, plasticized coating, plastisol prints
在塑料如PVC，橡胶，塑化的涂层，塑料溶胶中作为增塑剂

■ Concern in the market 市场的关注

- Bioaccumulative 生物累积性
- Endocrine disruptor 内分泌干扰物
- Carcinogenic listed 列出的致癌性

■ ZDHC MRSL Recommended limit for chemical supplier commercial formulation (ZDHC MRSL对化学品供应商生产配方的推荐限值)

- Sum of phthalates: 250mg/kg



Flame Retardants 阻燃剂

■ What is flame retardant? 什么是阻燃剂?

- Inhibit or resist the spread of fire 抑制或抵抗火势的蔓延
- Used in textiles to reduce their flammability 用于纺织品中以减低可燃性
- Naturally occurring substances such as asbestos 天然具有阻燃的物质，如石棉



■ Synthetic materials: usually halocarbons such as PBDEs, PCBs have been used in this capacity:

合成材料：卤烃如PBDEs和PCBs已被使用，由于它们的以下性质：

- Effective flame-retardant 有效地阻燃剂
- applied to prevent electronics, clothes and furniture from taking fire 用于避免电子产品，服装和家具起火



■ Where they can be found? 在哪些地方可被发现?

- Plastic - electronic products (mostly) 塑料 – 电子产品
- Textile - Home textile (e.g. curtains, beddings, etc), Pyjamas 纺织品 – 家纺（例如窗帘，寝具等），睡衣



Flame Retardants 阻燃剂

■ Concern in textile and footwear industry

纺织和制鞋行业的关注

- These flame retardants are suspected to be carcinogenic and mutagenic 疑似致癌性和致突变性的阻燃剂
- They are bioaccumulative in the biological tissues and along the food chain
这些物质在生物组织内具有生物累积性并沿着食物链传递

■ ZDHC MRSL Recommended limit for chemical supplier commercial formulation

ZDHC MRSL对化学品供应商生产配方的推荐限值

- Flame retardants: 250 mg/kg



Azo dyes (Aromatic Amines) 偶氮(芳香胺)

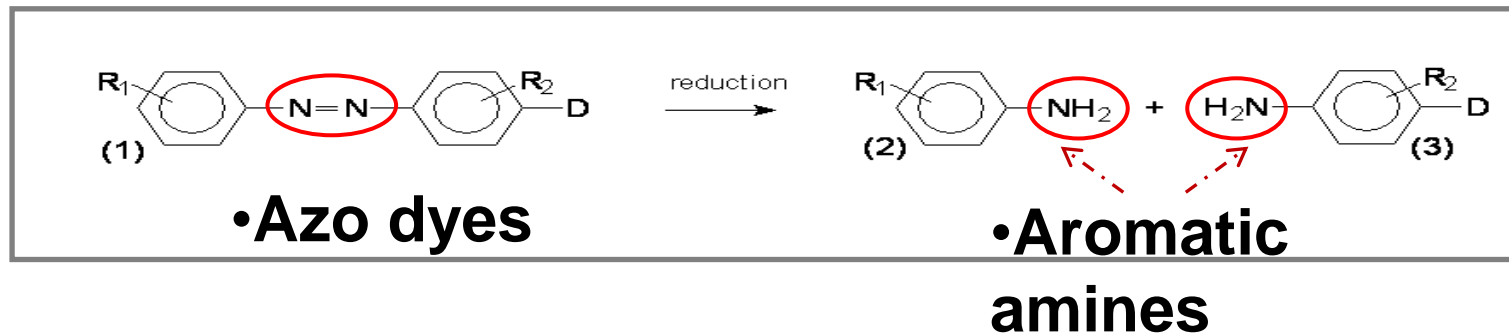
■ What are Azo Dyes? 什么是偶氮?

- Dyestuffs which contain at least one azo bond (-N=N-) 包含至少一个偶氮键 (-N=N-) 的染料
- Contribute to 60% - 70% of the dyes used nowadays 占到目前使用染料的60%-70%

■ Concern in textile and footwear industry 纺织和制鞋行业的关注

- Azo dyes may undergo *in vivo* reductive cleavage to **carcinogenic** aromatic amine

偶氮染料在活体内可能会裂解为致癌的芳香胺



- Only those produced aromatic amines which are listed/found to be carcinogenic or suspected carcinogen are concerned!

仅有能够产生列于限制表单内/致癌的，或疑似致癌芳香胺的偶氮染料才需要关注

Azo dyes (Aromatic Amines) 偶氮(芳香胺)

- **Main Routes of Human Exposure** 人类暴露的主要途径

Dermal absorption, oral ingestion, inhalation

皮肤吸收, 口服, 吸入

- **Legislation / Requirement** 法规/要求

Entry 43 of Annex XVII of REACH Regulation (EC) No 1907/2006

Limit: 30 mg/kg (each) (22 amines)

- **Recommend Test Material** 建议测试材料

Plastics 塑料	Natural fibres 天然纤维	Synthetic fibres 合成纤维	Coating/ Printing 涂层/印花	Leather 皮革	Metal parts 金属部件
	✓	✓	✓	✓	

- **ZDHC MRSL Recommended limit for chemical supplier commercial formulation**

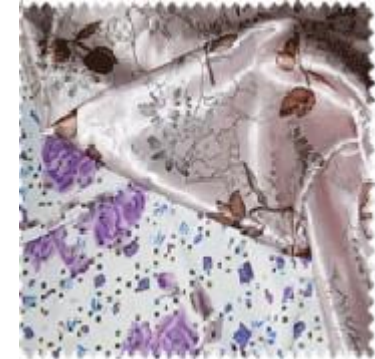
ZDHC MRSL对化学品供应商生产配方的推荐限值

Azo Dye: 200mg/kg (each)

Allergenic & Carcinogenic Disperse Dyes 致敏致癌分散染料

- These dyes are suspected to cause allergenic and carcinogenic reactions
这些染料有造成敏感和致癌的机会

- Disperse dyes are used for dyeing synthetic fibers(e.g. polyester, acetate, etc)
分散染料主要用作人造纤维的漂染，如聚酯纤维、醋酸酯



■ Test Material Categories 测试材料种类

Plastics 塑料	Natural fibres 天然纤维	Synthetic fibres 合成纤维	Coating/ Printing 涂层/印花	Leather 皮革	Metal parts 金属部件
		✓	✓		

■ Legislation / Requirement 法规/要求

Test Item 测试项目	Methods 方法	Reference for Restriction 限值参考	Recommended Max. Limit 建议最大限值
Disperse Dyes	DIN 54231 & 64 LFGB 82.02-10	German BfR recommendation	N.D (5mg/kg)

Organotin Compounds 有机锡

■ What are Organotin Compounds? 什么是有机锡?

- Compounds containing at least one tin-carbon bond
含有至少一个锡-碳键的化合物

Organotins 有机锡	Applications 应用
Tributyltin (TBT) Triphenyltin(TPHT)	<ul style="list-style-type: none">• Antifouling paints 抗污涂料• Industrial agricultural biocides 工业农业杀菌剂• Antifungal action in textile treatment and preservation 在纺织的处理和保存中具有抗菌作用
Dibutyltin (DBT) Diocetyl tin (DOT) Monobutyltin (MBT)	<ul style="list-style-type: none">• Plastic Stabilizer, Catalytic agents for PU 塑料稳定剂, 聚氨酯催化剂• Plastic additives 塑料添加剂



■ Concern in textile industry 纺织行业的关注

- Very toxic to marine and freshwater organisms
对海洋和淡水生物具有很强的毒性
- Damage liver & kidney system 损坏肝和肾脏系统
- Disrupt biochemical process such as blood forming mechanism and enzyme system
破坏生化过程, 例如血液的形成机制和酶系统

Organotin Compounds 有机锡

Recommended Test Materials 建议检测材料

Plastics 塑料	Natural fibres 天然纤维	Synthetic fibres 合成纤维	Coating/ Printing 涂层/印花	Leather 皮革	Metal parts 金属部件
✓	✓	✓	✓	✓	



Legislation / Requirement 法规/要求

Test Item 测试项目	Methods 方法	Reference for Restriction 限值参考	Max. Limit 最大限值
Tributyltin (TBT)	ISO 17353	Entries 20 of Regulation (EC) No 276-2010 amending Annex XVII of REACH Regulation (EC) No 1907/2006	≤ 0.1 % by weight of tin (sum)
Triphenyltin (TPHT)			
Tricyclohexyltin (TCyT)			
Trioctyltin (TOT)			≤ 0.1 % by weight of tin
Dibutyltin (DBT)			≤ 0.1 % by weight of tin
Dioctyltin (DOT)			≤ 0.1 % by weight of tin

ZDHC MRSL Recommended limit for chemical supplier commercial formulation ZDHC MRSL对化学品供应商生产配方的推荐限值

DBT: 20mg/kg, other organotins: 5mg/kg (each)

Perfluorinated Compound (PFC) 全氟化合物

■ Applications 应用

- Anti-dirt treatment in garments and carpet 服装和地毯的抗污处理
- Resistance to water, mechanical loads and intense heat 拒水，抗机械载荷和抗高温
- Anti-pollution agents in textile treatment baths 纺织品处理浴中的抗污剂
- Finishing on furnishings to prevent paste and glue migration from wallpaper to lining furniture 用作家具的整理剂，以避免糊剂或胶由墙纸迁移至家具内层

■ Where they can be found? 在哪里可以被发现?

- It is mostly found in functional wear and footwear
主要在功能性服装和鞋类被发现
- Requiring this coating for fashion consideration
要求涂层具有时尚性时

■ Concern in textile and footwear industry 在纺织和制鞋行业的关注

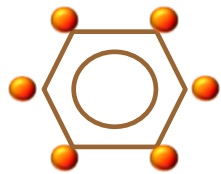
- Bioaccumulate in the fatty tissue of living organisms 在生物体的脂肪组织具有生物累积性
- Bioaccumulative & toxic to human as well as for the environment.
对人类和环境具有生物累积性



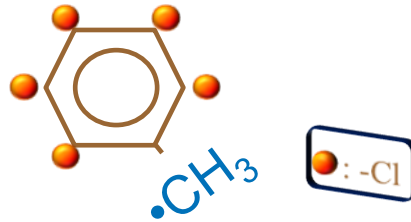
Chlorobenzenes / Chlorinated Organic Carrier (COC) 氯代有机载体

■ What is Chlorinated Organic Carrier (COC)? 什么是氯代有机载体?

- | Usually found in synthetic fibres 通常在合成纤维中被发现
- | Chlorinated aromatic structure 氯化芳香结构



•Chlorobenzene



•Chlorotoluene

■ Application in Textile & Footwear Industry 在纺织和制鞋行业的应用

- | Batch dyeing of synthetic fibres, particular polyester fibre, promote the absorption & diffusion of disperse dyes into the fibre at relative low temperature (Dyeing color more consistent)
合成纤维，尤其是聚酯纤维在间歇染色过程中，促进分散染料在较低的温度下在纤维上的吸收和扩散（染色更持久）

■ Concerns in Textile & Footwear 纺织和制鞋行业的关注

- | Irritant/allergenic properties 刺激性/致敏性
- | Carcinogenic 致癌性

Chlorophenol / Chlorinated Phenols (CPs) 氯苯酚

■ What are Chlorophenol / Chlorinated Phenols? 什么是氯苯酚?

- | Pentachlorophenol (PCP), Tetrachlorophenol (TeCP), Trichlorophenol (TriCP)
- | Dichlorophenol (DiCP), Monochlorophenol (MCP)

■ Application in Textile & Footwear Industry

纺织和制鞋行业的应用

- | Wood preservative 木材防腐剂
- | Preservative of fabric and leather 织物和皮革防腐剂
- | Anti-fouling paint (e.g. paint of print on garment)
抗污涂料（例如服装印花所用涂料）

■ Concerns in Textile & Footwear 纺织和制鞋行业的关注

- | Short term exposure lead to damage on central nervous system
短期暴露导致中枢神经系统的损伤
- | Long term exposure result in damage in reproductive system, liver and kidney, and may also be carcinogenic 长期暴露引起生殖系统，肝脏，肾脏的损伤，同时还可能就有致癌性



Short Chain Chloroparaffins (SCCP) 短链氯化石蜡

■ What is short chained chlorinated paraffin? 什么是短链氯化石蜡?

- Synthetic n-alkanes with varying degrees of chlorination, 合成的具有不同氯化程度的正构烷烃
- With 10 – 13 carbon is defined as short chained 带有10-13个碳原子的被定义为短链

■ Why they are concerned in textile and garment industry? 为什么它们在纺织和制鞋行业被关注?

- Highly toxic to aquatic organisms, 对水生生物具有高毒性
- Non-biodegradable, long-lasting in the environment 生物不可降解, 环境持久性
- Accumulate in the tissues of organisms 在生物组织内累积

■ Application in textile and footwear industry 在纺织和制鞋行业的应用

- Plasticizers in plastics and additives in paints 用于塑料的增塑剂和涂料添加剂
- Fatliquors or bulking agents in leather 皮革加脂剂和填充剂

■ ZDHC MRSL Recommended limit for chemical supplier commercial formulation ZDHC MRSL对化学品供应商生产配方的推荐限值:

50mg/kg



Heavy metal – Lead 重金属 – 铅

■ What is Lead? 什么是铅?

- A heavy metal which has been used in many applications
一种具有多方面应用的重金属

■ Applications in textile and footwear industry 在纺织和制鞋行业的应用

- Stabilizers / processing aids for PVC, other plastics and rubber,
metal items, leather PVC,
其他塑料和橡胶，金属和皮革的稳定剂/加工助剂
- Used as pigments (e.g. C.I. Pigment Red 104, C.I. Pigment
Yellow 34) 用作染料
- Used in glass / crystal to give higher refraction and reflection
用于玻璃/水晶以赋予更高的折射率和反射率

■ Concerns in the market 市场的关注

- Highly toxic and is bio-accumulative 高毒性和生物累积性
- Affect Central Nervous System 影响中枢神经系统



Heavy metal – Cadmium 重金属 – 镉

■ What is Cadmium? 什么是镉?

- Stabilizers and processing aids for plastics
用作塑料的稳定剂和加工助剂

■ Applications in textile and footwear industry 在纺织和制鞋行业的应用

- Cadmium plating for metals items 金属物品的镀镉
- Used as stabilizer in foam, plastics, rubbers / silicone, pigments
在泡沫，塑料，橡胶/硅树脂，颜料中作为稳定剂
- Garment: Printing, coating and plastic accessories found in textiles only as residues or impurities
服装：在纺织品的印花，涂层和塑料附件部位仅以残留物和杂质形式存在

■ Concerns in the market 市场的关注

- Chronic toxicity and bioaccumulative 慢性毒性和生物累积性

■ ZDHC MRSL Recommended limit for chemical supplier commercial formulation

ZDHC MRSL对化学品供应商生产配方的推荐限值

Cd: 20mg/kg (50mg/kg for pigment)



Heavy metal – Chromium 重金属 – 铬

■ What is Chromium? 什么是铬?



- Chromium (III) used in leather tanning 三价铬用于皮革鞣制
 - Over 80% of leather is tanned by Cr(III) tanning agents (wet blue) 超过80%的皮革采用的是含三价铬的鞣制剂（蓝湿革）
 - Cr(VI) is generated by oxidation of the unfixed Cr(III) tanning agents on leather 六价铬是由皮革上未固定的三价铬鞣制剂氧化而产生的
- Used on a large technical scale in garment. e.g. in dyestuff and as finished agent 在服装上也大规模使用，例如在染料中以及作为整理剂
- Used in chrome plating, leather tanning, dyes and pigments, etc 用于镀铬，皮革鞣制，染料和颜料等



■ Concern in textile industry 纺织行业的关注

- Chromium (VI) and certain Chromium (VI) compounds are known carcinogens. 六价铬和某些六价铬化合物被认为致癌
- Cr (VI) may also be corrosive to skin and can cause allergic reactions 六价铬可能对皮肤有腐蚀性并可能引起过敏反应

Heavy metal – Nickel 重金属 – 镍

■Where can be found? 在哪里可以被发现?

I Used on a large technical scale in garment. e.g. in dyestuff and as finished agent for making alloys with other metals

与其他金属制作合金

I Used in manufacture of stainless steel, nickel-plating
用于制作不锈钢，镀镍

I Used in anti-corrosion plating for metals
用于金属的抗腐蚀镀层

I Found in metal accessories : buttons, Zippers, Rivets
在金属附件：纽扣，拉链和柳钉中可被发现

■Concern in Textile Industry 纺织行业的关注

I Sensitizing agent can trigger dermatitis owing to prolonged contact
敏化剂，长期接触皮肤导致皮炎

Affect central nervous system (over 200 mg/day)

影响中枢神经系统（大于200mg/天）



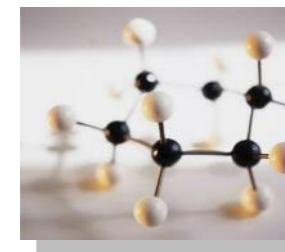
Volatile Organic Compounds (VOC) 挥发性有机化合物

■ What is VOC ? 什么是VOC?

- Organic compounds having a corresponding volatility which can evaporate under room temperature or particular condition of use. 具有类似的挥发性，能够在室温下或使用的特定条件下可以气化的有机化合物

■ Application in the textile and footwear industry 纺织和制鞋行业的应用

- Often used as solvents in printing, dyeing and surface finishing processes. 常用于印花，染色和表面处理过程的溶剂
- Used as solvents in adhesives in textile accessories and footwear production 在纺织附件和制鞋过程中使用的粘合剂中用作溶剂



■ Source of VOCs from footwear 鞋类的VOCs来源

- Textile and leather materials (mainly upper) 纺织品和皮革（主要为鞋面）
- Plastic materials (upper, outsole, coating, finishing, etc.) 塑料材料（鞋面，外底，涂层和整理等）
- Primers 引物: acetone, MEK, ethyl acetate, IPA, etc.
- Adhesives 粘合剂
 - » PU-based基于聚氨酯: acetone, butanone, MEK, ethyl acetate, etc.
 - » Neoprene-based基于氯丁橡胶: hexane, cyclohexane, heptane, ketones, etc.

■ ZDHC MRSL Recommended limit for chemical supplier commercial formulation

ZDHC MRSL对化学品供应商生产配方的推荐限值 50 mg/kg (benzene); Other VOCs: 500 mg/kg (each)

PAHs 多环芳香烃

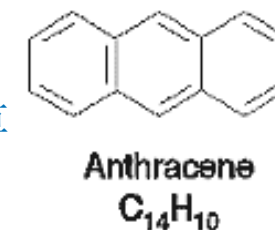
PAHs Polycyclic aromatic hydrocarbons 多环芳香烃化合物

- Persistent organic compound 不易被分解的有机化合物
- Bioaccumulative 可在生物食物链上累积
- Naturally occurred 自然产生
- Over 100 different substance 超过一百种的多环芳烃
- Pure PAHs is colourless, white or pale yellowish green solid 纯净形态的多环芳烃是呈无色，白色，或浅黄绿色固体状的



Common sources 主要来源

- Coal tar from petroleum refining process 石油精炼过程中残余的焦油
- Organic substances from incomplete burning of coal, oil, gas or tobacco 有机物的不完全燃烧，煤/油/气/烟草
- Presence in raw material to make rubber, plastics 存在于橡胶和塑胶的原材料
- Present in BBQ's food 发现存在于烧烤的食物里



Test Item 测试项目	Methods 方法	Reference for Restriction 限值参考	Recommended Max. Limit 建议最大限值
PAHs	ISO 16190	EC Regulation No. 1907/2006 annex XVII item no.50	Toy & Children articles:0.5mg/kg (Each of 8 PAHs); Others: 1mg/kg (Each of 8 PAHs)

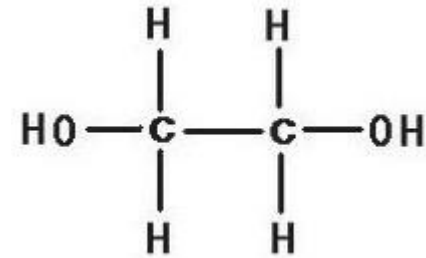
Glycols 乙二醇类

■ Common sources 主要来源

- In apparel and footwear, glycols have a wide range of uses including as solvents for finishing/cleaning, printing agents, and dissolving and diluting fats, oils and adhesives (e.g., in degreasing or cleaning operations).
在服装和鞋类工业中，乙二醇作为溶剂广泛使用于后整理 /清洗、印花试剂以及消脂剂和粘粘剂中（例：在脱脂或清洗操作中）
- Ethylene glycol is an important precursor to polyester fibers and resins
在聚酯纤维和树脂类生产过程中，乙二醇是一种重要的原料

■ Test Material Categories 测试材料种类

Plastics 塑料	Natural fibres 天然纤维	Synthetic fibres 合成纤维	Coating/ Printing 涂层/印花	Leather 皮革	Metal parts 金属部件
		✓	✓		



Activities 活动

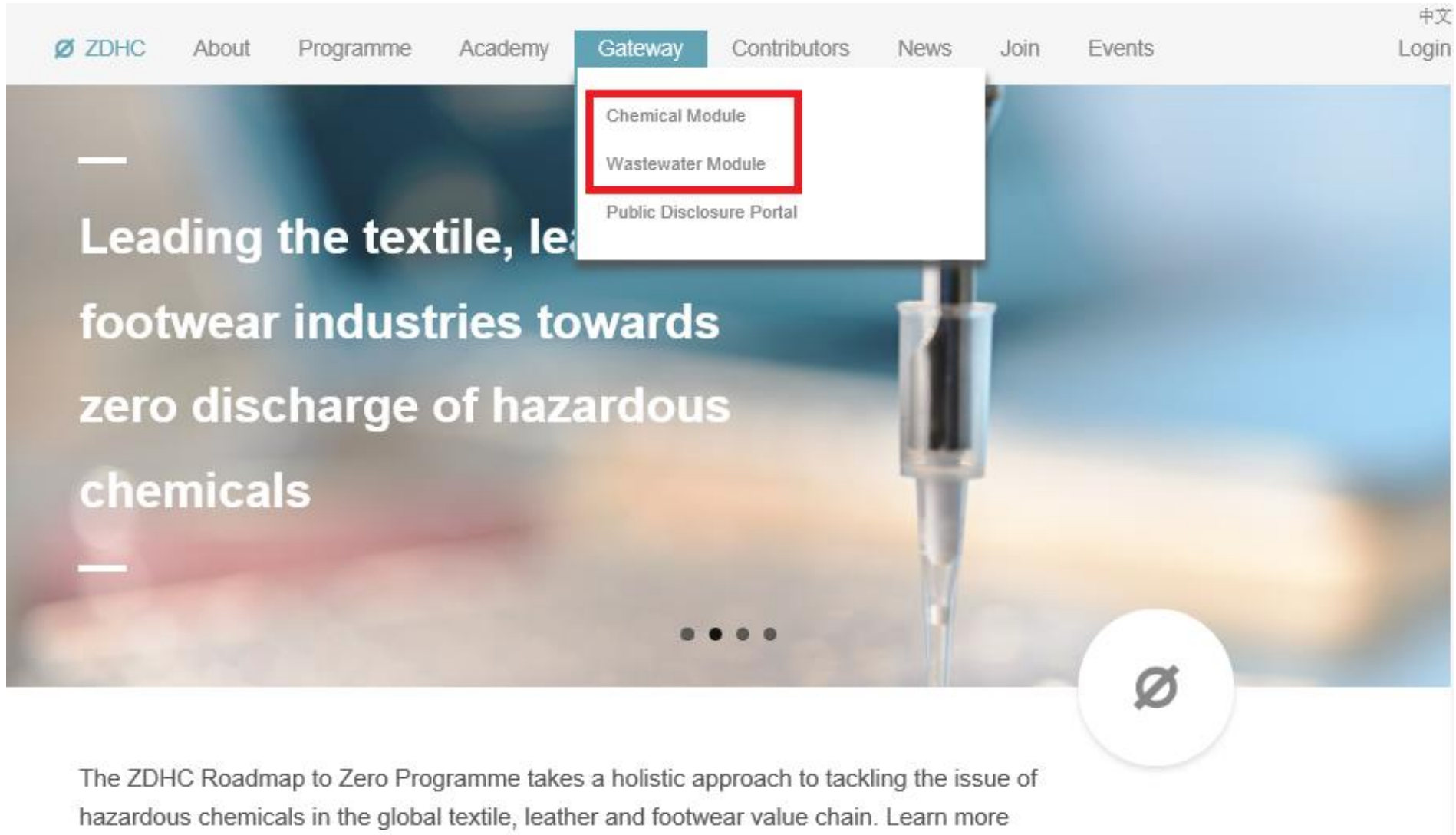
Does your customer has its own MRSL? Please compare ZDHC MRSL to find out the difference between them.

你的客户现在有自己的MRSL清单嘛？
请和ZDHC的MRSL比较，找出它们的不同之处。

Tools to choose safe chemicals 选择安全化学品的工具



ZDHC Gateway



The screenshot shows the ZDHC Gateway website. The navigation bar includes links for ZDHC, About, Programme, Academy, Gateway, Contributors, News, Join, Events, and Login. The Gateway dropdown menu is open, showing options for Chemical Module, Wastewater Module, and Public Disclosure Portal. The main content area features a large image of a laboratory pipette with the text: "Leading the textile, leather and footwear industries towards zero discharge of hazardous chemicals". Below the image, there is a circular icon with a diagonal slash and a paragraph of text: "The ZDHC Roadmap to Zero Programme takes a holistic approach to tackling the issue of hazardous chemicals in the global textile, leather and footwear value chain. Learn more".

ZDHC About Programme Academy Gateway Contributors News Join Events Login

Chemical Module
Wastewater Module
Public Disclosure Portal

Leading the textile, leather and footwear industries towards zero discharge of hazardous chemicals

The ZDHC Roadmap to Zero Programme takes a holistic approach to tackling the issue of hazardous chemicals in the global textile, leather and footwear value chain. Learn more

CHEMSEC – TOOLS CHEMSEC –工具



Marketplace: Marketplace for alternatives to hazardous chemicals. 危险化学品的替代



SIN (Substitute it Now!) List: Global database of chemicals likely to be banned or restricted in the near future. 可能在近期内被禁止或限制的化学品全球数据库



SIN Producers List: Searchable database of companies that are producing or importing the most hazardous chemicals in Europe and USA. 可搜索在欧洲和美国生产或进口危险化学品最多的公司的数据库



SINimilarity: Compares if a substance is similar to a substance on the SIN List. 一个物质与 SIN List 比较是否相似的物质



SUBSPORT: Information on alternative substances and tools and guidance for substance evaluation and substitution management. 有关替代物质和工具的信息以及物质评估和替代管理指南



Chemical Management Guide for Textiles: Guide to evaluate and prioritise your chemicals. 评估和优先考虑化学品的指南

Activity 活动

To make sure that your purchased chemicals are compliant with your customer's MRSL and your finished shoes are compliant with your customer's RSL, what do you need to do?
为了确保购买的化学品符合客户的MRSL，并且您的成品鞋符合客户的RSL，您需要做什么？

Module 6: VOCs and air emission control
模块六: VOCs和废气控制

TÜV Rheinland
March, 2019



Contents 目录

01

Air Pollution 大气污染物

- Pollution types and classification
污染物类型和分类
- Air Emission from footwear Industry
鞋类行业的大气污染物排放

02

VOCs 可挥发性有机物

- Introduction of VOCs
VOCs介绍
- Assessment model of VOCs risk
VOCs风险评估工具
- VOCs Treatment Technologies
VOCs治理技术

03

Substitution of chemicals containing VOCs 含有挥发性有机物化学品的替代

- Critical Thinking 批判性思维
- Six Steps to Substitution 替代的六步骤

04

Sustainable Alternatives 可持续的替代方案

- VOCs control from source
源头控制

Learning objectives 学习目标:

1. To learn how to define VOCs substance 学习如何定义挥发性有机化合物物质
2. To learn typical VOCs substance in footwear industry 了解制鞋工业中典型的挥发性有机化合物物质
3. To gain knowledge of regulations on VOCs 了解挥发性有机化合物法规
4. To learn VOCs control technology and its treatment mechanism 了解VOCs控制技术及其处理机理
5. To learn the procedures to do chemical substitution 学习化学品替代的程序

Target Group 目标群:

5% of participating factory workers may include: 工厂5%的员工应包括:

- 1.High management: factory Board Chairman, Managing Director, General Manager 高层: 董事长、常务董事、总经理;
2. Department Manager in Quality, EHS, R&D, Manufacturing, Purchasing, IT, HR, Sales, and Admin 部门经理 (质量、EHS、研发、生产、采购、IT、人力资源、销售、行政)
3. All staff in quality department, lab, and EHS department 质量部门、实验室和EHS部门的所有员工
- 4.Shift leaders in each manufacturing line, in chemical warehouse 每条生产线、每个化学品仓库领班
- 5.All interested workers are welcomed 所有感兴趣的员工
6. Minimum10 people for each factory 每家工厂至少10人

Length 时长:

3 Hours 3小时

Training outcomes 培训成果

At the end of this training, the participants will be able to ...
培训结束后，您应该能够

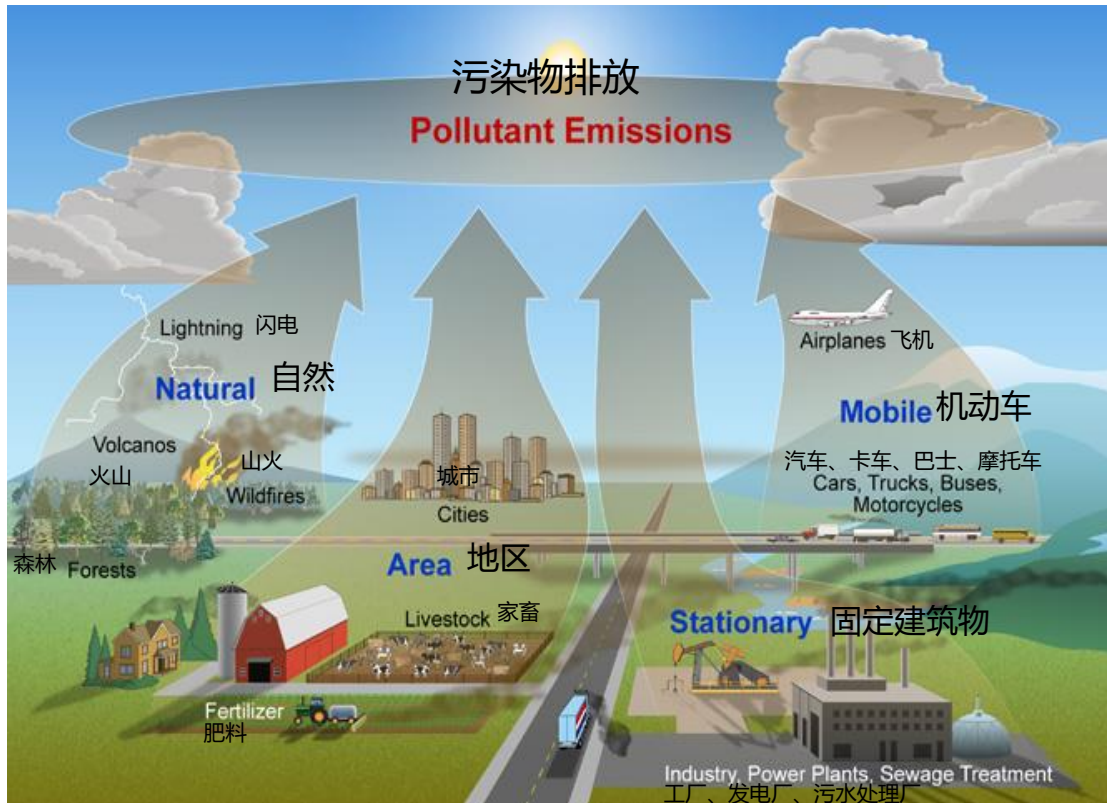
- Identify typical VOC substance 能够识别典型的挥发性有机化合物物质
- Find root cause if VOCs were detected 如果检测到挥发性有机化合物，能够找到根本原因
- Select and implement long-term and short-term control measures (in line with requirements of SDS and regulations) 选择和实施长期和短期控制措施（符合SDS和法规要求）
- Identify and prioritise chemicals in the factory's chemical inventory for substitution 识别并优先处理工厂化学库存中的化学物质，以备替换

Air Pollution 大气污染物

01

Air pollutant 大气污染物

An air pollutant is a material in the air that can have adverse effects on humans and the ecosystem, which can be of **natural origin** or **man-made**. 大气污染物是指由于人类活动或自然过程排入大气的并对环境或人产生有害影响的那些物质。



Air pollutant 大气污染物

Pollutants are classified as primary or secondary. Primary pollutants are usually produced from pollutant sources directly. Secondary pollutants are not emitted directly. Rather, they form in the air when primary pollutants react or interact. 污染物可分为一次污染物和二次污染物。一次污染物是指直接从污染源排放的污染物质，二次污染物则是由一次污染物经过化学反应或光化学反应形成的与一次污染物的物理化学性质完全不同的新的污染物。

Category 类别	Primary pollutant 一次污染物	Secondary pollutant 二次污染物
Sulfur-containing compounds 含硫化合物	SO ₂ , H ₂ S	SO ₃ , H ₂ SO ₄ , MSO ₄
Nitrogen-containing compounds 含氮化合物	NO, NH ₃	NO ₂ , HNO ₃ , MNO ₃
Carbon oxides 碳的氧化物	CO, CO ₂	
Hydrocarbon (Carbon Hydroxide compounds) 碳氢化合物 (碳氢氧化合物)	C ₂ ~C ₅ H _n	Aldehyde, Ketone, Peroxynitrate (PAN) 醛, 酮, 过氧乙酰硝酸酯
Halogen-containing compounds 含卤素化合物	HF, HCl	
Particulates 颗粒物	PM2.5, PM10	

Pollutants Effects on human beings 对人体的影响

Pollutants 污染物	Effects of human being 对人的作用
Sulphur dioxide 二氧化硫	Irritates respiratory system and causes bronchitis 刺激呼吸系统，引起支气管炎
Aldehydes 乙醛	Irritates all parts of respiratory system 刺激整个呼吸系统
Chlorine 氯气	Causes lung irritation and also irritation in eyes 引起肺部过敏，和眼睛刺激
Carbon dioxide 二氧化碳	Deprives body cells of oxygen and cause unconsciousness by CO combining with hemoglobin 剥夺体细胞中的氧气，一氧化碳与血红蛋白结合造成意识丧失
Carbon Monoxide (CO) 一氧化碳	Headaches, reduced mental alertness, heart attack, cardiovascular diseases, impaired fetal development, death. 头痛、减少神经敏感性、心肌梗塞、心血管疾病、影响胎儿发育、死亡
Nitrogen Dioxide (NO ₂) 二氧化氮	Susceptibility to respiratory infections, irritation of the lung and respiratory symptoms (e.g., cough, chest pain, difficulty breathing). 易于呼吸感染、刺激肺部、呼吸疾病症状 (如咳嗽、胸痛、呼吸困难)
Particulate Matter (PM) 颗粒物	Eye irritation, asthma, bronchitis, lung damage, cancer, heavy metal poisoning, cardiovascular effects. 眼部刺激、哮喘、支气管炎、肺部损伤、癌症、重金属中毒、心血管影响
VOC 可挥发有机物	Health effects include eye, nose, and throat irritation; headaches, loss of coordination, nausea; and damage to the liver, kidney, and central nervous system, some are suspected or known to cause cancer in humans 健康影响包括眼、鼻、和喉咙刺激，头痛、丧失协调性、恶心，损害肝脏、肾脏和中心神经系统，并可能导致某些癌症

Pollutants Impact on Environment 对环境的影响

- Greenhouse effect 温室效应
- Particulate contamination 颗粒物污染
- Increased UV radiation (Ozone Depletion)
紫外线辐射增高 (臭氧层被消耗)
- Acid rain 酸雨
- Increased ground level ozone
concentration
地面臭氧浓度增高
- Increased levels of nitrogen oxides
氮氧化物的浓度增高



Current Standards on Air Pollutant in Footwear Industry 鞋类行业现有大气排放标准

Integrated emission standard of air pollutants – GB16297-1996

大气污染物综合排放标准 – GB1629-1996

Emission Limits of Air Pollutants from Existing Pollution Sources 现有污染源大气污染物排放限值:

Number 序号	Pollutants 污染物	Maximum permissible emission concentration 最高允许排放浓度 mg/m ³	Concentration Limit of Fugitive Emission: 无组织排放监控浓度限值 mg/m ³
1	SO ₂ 二氧化硫	700	0.5
2	Nitrogen oxide 氮氧化物	420	0.15
3	Particulate 颗粒物	/	/
	Carbon black dust and dye dust 炭黑尘、染料尘	22	Invisible to the naked eye 肉眼不可见
	Glass wool dust, quartz dust, slag wool dust 玻璃棉尘、石英粉尘、矿渣棉尘	80	2.0
	Other 其他	150	5.0
4	Benzene 苯	17	0.5
5	Toluene 甲苯	60	3
6	Xylene 二甲苯	90	1.5
7	Aniline 苯胺类	25	0.5
8	Non-methane Hydrocarbon 非甲烷总烃	150	5.0
9

Current Standards on Air Pollutant in Footwear Industry 鞋类行业现有大气排放标准

Integrated emission standard of air pollutants – GB16297-1996

大气污染物综合排放标准 – GB1629-1996

Emission Limits of Air Pollutants from New Pollution Sources 新污染源大气污染物排放限值:

Number 序号	Pollutants 污染物	Maximum permissible emission concentration 最高允许排放浓度 mg/m ³	Concentration Limit of Fugitive Emission: 无组织排放监控浓度限值 mg/m ³
1	SO ₂ 二氧化硫	550	0.4
2	Nitrogen oxide 氮氧化物	240	0.12
3	Particulate 颗粒物	/	/
	Carbon black dust and dye dust 炭黑尘、染料尘	18	Invisible to the naked eye 肉眼不可见
	Glass wool dust, quartz dust, slag wool dust 玻璃棉尘、石英粉尘、矿渣棉尘	60	1.0
	Other 其他	120	1.0
4	Benzene 苯	12	0.4
5	Toluene 甲苯	40	2.4
6	Xylene 二甲苯	70	1.2
7	Aniline 苯胺类	20	0.4
8	Non-methane Hydrocarbon 非甲烷总烃	120	4.0
9

Current Standards on Air Pollutant in Footwear Industry 鞋类行业现有大气排放标准

Zhejiang Province - Emission standard of air pollutants for shoe-making industry – DB33

浙江省 - 制鞋工业大气污染物排放标准 – DB33

For new enterprises: 对于新建企业:

Number 编号	Pollutant 污染物	Applicability 适用条件	Discharge limit (mg/m3) 排放限值	Monitoring position 监控位置
1	Particulate 颗粒物	All enterprise 所有企业	30	Workshop or Facility exhaust funnel 车间或生产设施排气筒
2	Benzene 苯		1	
3	Benzene series 苯系物		20	
4	Odor Concentration 臭气浓度		1000	
5	VOCs 挥发性有机物		80	
6	Ammonia 氨	Enterprise referring to Ammonia 涉氨企业	20	

Existing Enterprises implement current standards before 2019.11.15. Afterwards, should implement according to above standard.

现有企业2019年11月15日前仍执行现行标准，自2019年11月15日起执行上表规定的大气污染物排放限值。

Current Standards on Air Pollutant in Footwear Industry 鞋类行业现有大气排放标准

Guangdong Province - Emission standard of volatile organic compounds for shoe-making industry

广东省 - 制鞋行业挥发性有机化合物排放标准 – DB44/817-2010

For organized emission 有组织排放:

Pollutant 污染物	maximum acceptable emission concentration (mg/m ³) 最高允许排放浓度		maximum acceptable emission rate (kg/h) 最高允许排放速率	
	I time frame	II time frame	I time frame	II time frame
Benzene 苯	1	1	0.4	0.4
Total of Toluene and xylene 甲苯与二甲苯合计	30	15	1.9	1.5
Total VOCs 总VOCs	80	40	3.4	2.6

For fugitive emission 无组织排放:

Pollutant 污染物	Acceptable emission concentration (mg/m ³) 浓度限值
Benzene 苯	0.1
Toluene 甲苯	0.6
Xylene 二甲苯	0.2
Total VOCs 总VOCs	2.0

Current Standards on Air Pollutant in Footwear Industry 鞋类行业现有大气排放标准

Fujian Province - Comprehensive Emission Standard for Industrial Volatile Organic Compounds – Draft 福建省 – 工业企业大气挥发性有机物排放标准

For organized emission 有组织排放:

Number 编号	Pollutant 污染物		maximum acceptable emission rate 最高允许排放速率kg/h			
			15m	20m	30m	40m
1	Benzene 苯	3	0.3	0.7	1.8	3.2
2	Toluene 甲苯	20	0.6	1.2	3.2	5.8
3	Xylene 二甲苯	40	0.6	1.2	3.2	5.8
4	Non-methane Hydrocarbon 非甲烷总烃	100	1.8	3.6	9.6	17.4

For fugitive emission 无组织排放:

Pollutant 污染物	Acceptable emission concentration (mg/m ³) 浓度限值
Benzene 苯	0.2
Toluene 甲苯	1.2
Xylene 二甲苯	0.6
Non-methane Hydrocarbon 非甲烷总烃	4.0

Current Standards on Air Pollutant in Footwear Industry 鞋类行业现有大气排放标准

Emission Standards for Air Pollutants in Leather Products and Shoes Industry - Draft

皮革制品和制鞋工业大气污染物排放标准 – 意见稿

For organized emission 有组织排放:

Number 编号	Pollutant 污染物	Manufacturing process 生产工艺	Discharge limit (mg/m3) 排放限值	Monitoring position 监控位置
1	Particulate 颗粒物	Planing, grinding, polishing and other processes 刨磨、磨皮、抛光等工序	30	Workshop or Facility exhaust funnel 车间或生产设施排气筒
2	Benzene 苯	Adhesion, drying, painting, mixing, injection moulding and other processes 贴合、烘干、涂饰、调胶、注塑等工序	1	
3	Total of Benzene and xylene 甲苯与二甲苯合计		20	
4	1,2 - dichloroethane 1, 2 - 二氯乙烷		2	
5	TVOCs 总挥发性有机物		60	
6	NMHC 非甲烷总烃		40	Exhaust cylinder for fitting and drying process 贴合、烘干工序排气筒

Current Standards on Air Pollutant in Footwear Industry 鞋类行业现有大气排放标准

Emission Standards for Air Pollutants in Leather Products and Shoes Industry - Draft

皮革制品和制鞋工业大气污染物排放标准 – 意见稿

Control requirements for fugitive emissions 无组织排放控制要求：

- Materials containing VOCs such as adhesives, treatment agents and cleaning agents for leather products and shoemaking enterprises should be stored in sealed containers. Waste adhesives barrels or organic solvent barrels should be sealed for storage before being handed over to recycling facilities 皮革制品和制鞋企业胶黏剂、处理剂、清洗剂等含VOCs 的物料应储存于密闭容器中。废弃的胶黏剂桶或有机溶剂桶等在移交回收处理机构前，应密封储存；
- Operating units such as fitting, drying, mixing, painting and injection moulding shall adopt closed gas collecting system or local gas collecting system, and the VOCs generated in the process shall be imported into the exhaust gas collecting system and/or treatment facilities through the closed exhaust system. The emission of air pollutants shall comply with the requirements of organized emission 贴合、烘干、调胶、涂饰、注塑等操作单元应采用围闭式集气系统或局部集气系统，将工艺过程产生的VOCs 经由密闭排气系统导入废气收集系统和（或）处理设施，其大气污染物排放应符合有组织排放的规定；
- Production process equipment, exhaust gas collection system and treatment equipment should run synchronously. If the waste gas collection system or treatment equipment fails, the corresponding production process equipment shall be stopped and put into operation together after the completion of the overhaul 生产工艺设备、废气收集系统以及处理设备应同步运行。废气收集系统或处理设备故障，应停止运转对应的生产工艺设备，待检修完毕后共同投入使用；

ACTIVITY 活动

What actions have you taken in your facility so far to reduce your environmental impact? 至今你采取过哪些行动来减少环境影响?

What worked well? 哪些做得好?

What did not work so well? 哪些做得不好?

Best Practices Air Emission 废气排放良好示例

Height of chimneys 烟囱高度:

Chimneys height should not be less than 30 meters and release the pollutants not in the vicinity of living organism. 烟囱高度不应低于30米，排放的污染物不得靠近生物体。

Gravitational and inertial separator 重力和惯性分离器：

These are working on gravitational and inertial concepts of collecting, filtering etc. of the particulate matter. For example settling chambers, dynamic separator and wet cyclones and multiple cyclones. 他们研究收集、过滤等微粒物质的引力和惯性概念。例如沉降室、动态分离器和湿旋风分离器以及多个旋风分离器。

Filters 过滤器：

Woven or sintered metal beds of fibres, metal turning, fibrous mats and aggregate bed filter, paper filters and fabric filters are used for the filtration of particulate matter like dust, lint and fumes. 纤维编织或烧结金属床、金属车削、纤维垫和集料床过滤器、纸过滤器和织物过滤器用于过滤灰尘、棉绒和烟雾等颗粒物

Options to Reduce Air Pollution 减少空气污染的选项

- Decreasing emissions of organic solvents by changing to water-based products. 通过转变为水基产品来减少有机溶剂的排放
- Using scrubbers to collect particulate matter. 使用洗涤器收集颗粒物
- Optimising boiler operations to reduce the emissions of nitrous and sulphur oxides. 优化锅炉运行以减少氧化亚氮和硫的排放
- Pre-screening chemicals using the material safety data sheets to ensure that chemicals are not toxic. 使用材料安全数据表对化学品进行预筛选，以确保化学品无毒
- Identifying sources of air pollution and quantifying emissions. 确定空气污染源并量化排放
- Designing and manufacturing products that do not produce toxic or hazardous air pollutants. 设计和制造不产生有毒有害空气污染物的产品
- Avoiding fugitive air emissions from chemical spills through improved work. 通过改进工作，避免化学品泄漏造成的无组织空气排放



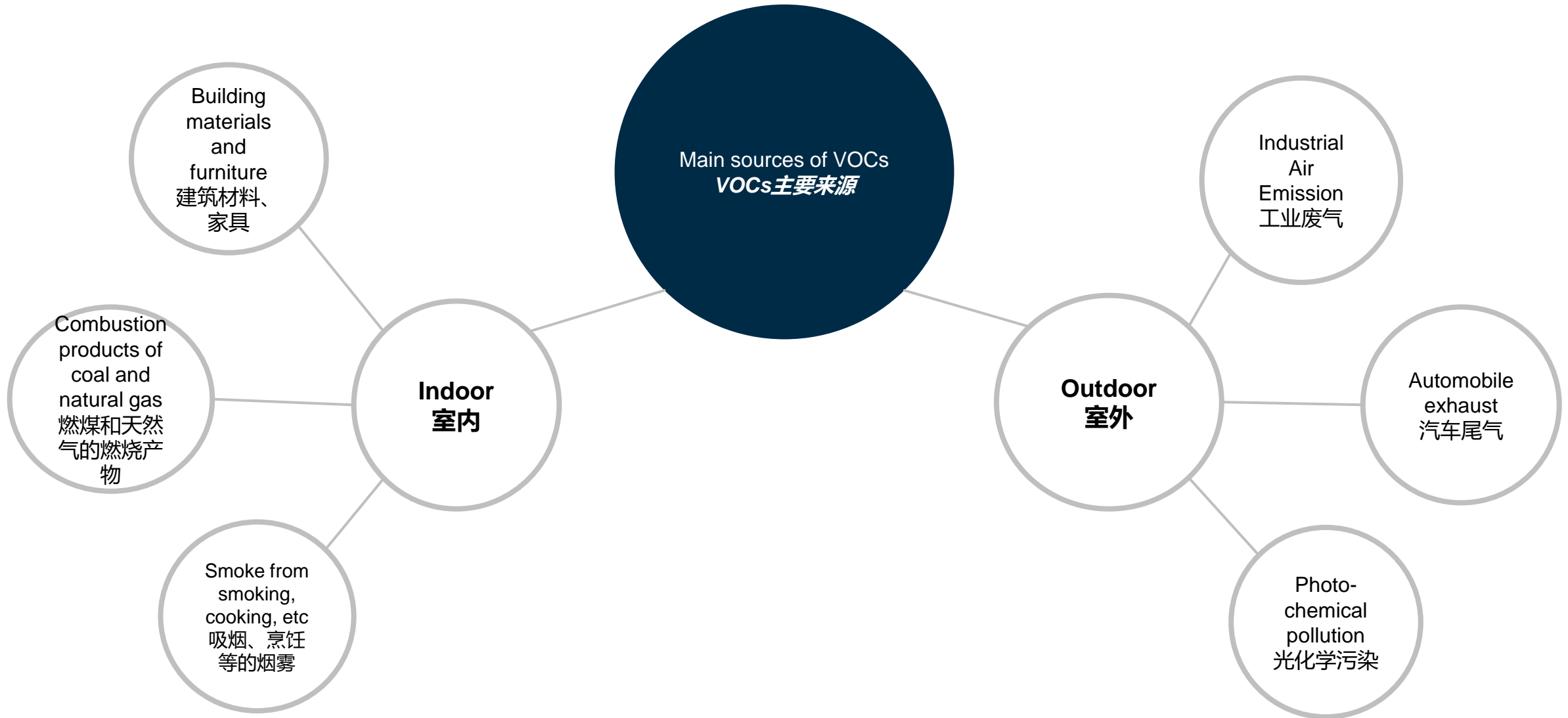
VOCs 可挥发性有机物

02

Definition of VOCs 可挥发性有机物的定义

- Volatile Organic Compounds, commonly referred to as VOCs, are abbreviations for the first letter of the three words Volatile Organic Compounds. Total VOCs are sometimes represented by TVOC.
挥发性有机物，常用VOCs表示，它是Volatile Organic Compounds三个词第一个字母的缩写，总挥发性有机物有时也用TVOC来表示。
- According to WHO definition, VOCs is a class of organic compounds with boiling point between 50 and 250 degree, saturated vapor pressure over 133.32 Pa at room temperature, and existing in the air as vapor at room temperature
按照世界卫生组织的定义沸点在50°C-250°C的化合物，室温下饱和蒸汽压超过133.32Pa，在常温下以蒸汽形式存在于空气中的一类有机物。
- EPA defines it as any carbon-containing compound participating in atmospheric photochemistry except CO, CO₂, H₂CO₃, metal carbides, metal carbonates and ammonium carbonate
美国环境保护局对其的定义是除CO、CO₂、H₂CO₃、金属碳化物、金属碳酸盐和碳酸铵外，任何参加大气光化学反应的含碳化合物。

Main sources of VOCs 可挥发性有机物的主要来源



List of VOCs 可挥发有机物一览表

- Fossil fuels
化石燃料
- Benzene 苯
- Methylene chloride
二氯甲烷
- Perchloroethylene
全氯乙烯
- Methylene chloride
二氯甲烷
- Perchloroethylene
全氯乙烯
- Formaldehyde 甲醛
- Tetrahydrofuran
四氢呋喃
- Cyclohexane
环己烷
- Methyl Ethyl Ketone (MEK) 甲乙酮
- Toluene, Acetone, Hexane
甲苯、丙酮、己烷
- 1,1,1-Trichloroethane
1,1,1-三氯乙烷
- Methyl-Iso-Butyl Ketone (MIBK)
甲基异丁基酮



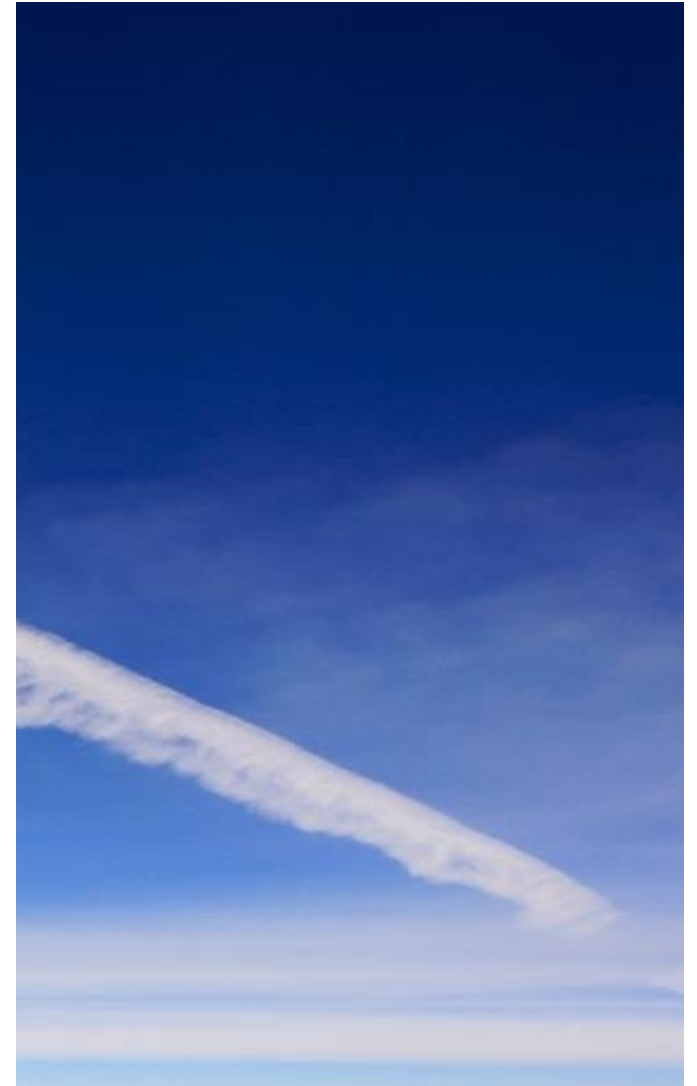
Effect of VOCs 可挥发性有机物的影响

Respiratory, allergic, or immune effects in infants or children are associated with man-made VOCs and other indoor or outdoor air pollutants. 人造 VOCs 和其它室内机室外空气污染可能影响婴儿和儿童的呼吸系统、过敏、以及免疫系统。

Styrene and limonene, can react with nitrogen oxides or with ozone to produce new oxidation products and secondary aerosols, which can cause sensory irritation symptoms. Unspecified VOCs are creating smog. 苯乙烯和柠檬烯可能与氮氧化物或臭氧反应生成新的氧化物和二级溶胶，可能引起感觉刺激症状。不少不明的 VOCs 造成雾霾。

Some organics can cause cancer in animals; some are suspected or known to cause cancer in humans. 某些有机物可能造成动物癌症；某些则被怀疑或已知引起人类癌症。

Key signs or symptoms associated with exposure to VOCs include conjunctival irritation, nose and throat discomfort, headache, allergic skin reaction, dyspnea, declines in serum cholinesterase levels, nausea, vomiting, nose bleeding, fatigue, dizziness. 暴露在 VOCs 下的关键标志包括粘膜刺激、鼻腔和喉咙不适、头痛、皮肤刺激、呼吸困难、血清胆碱酯酶水平下降、恶心、呕吐、流鼻血、疲乏、头晕。



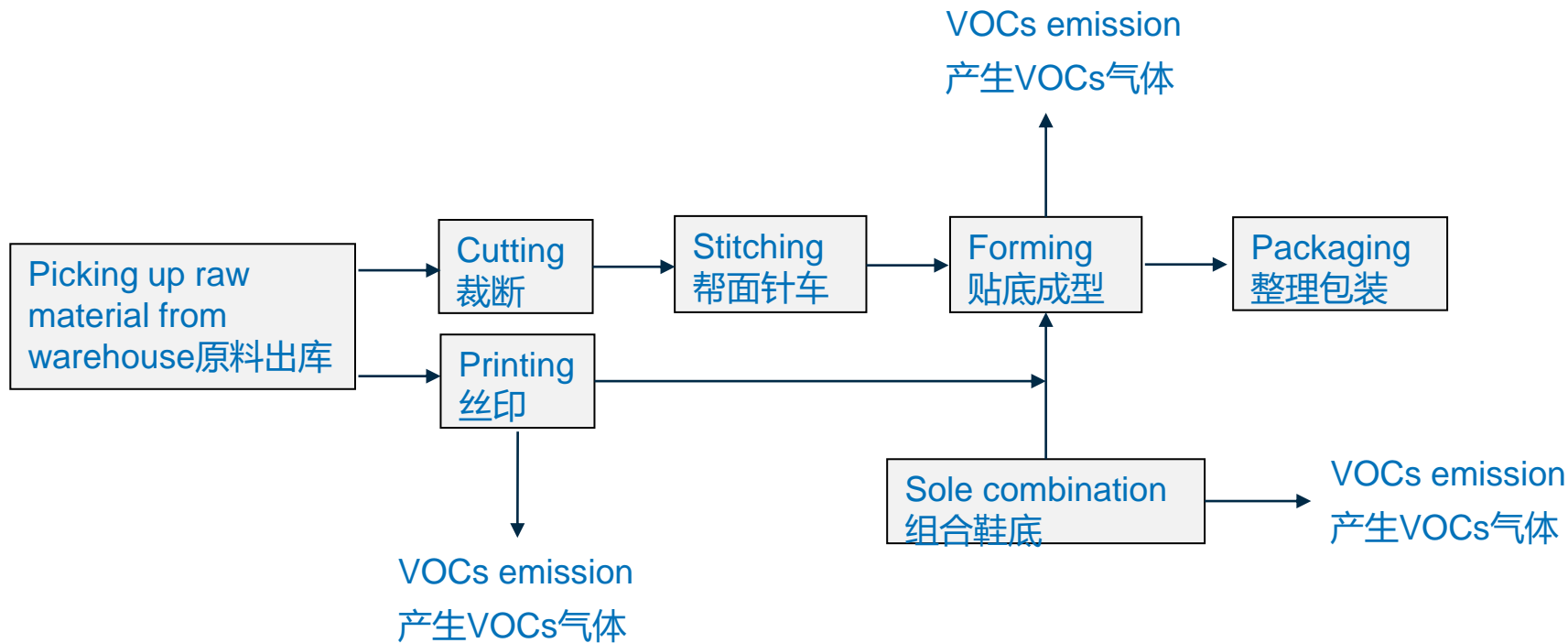
Quiz 小测试



Do you know where emissions of VOCs to air may occur in your factory?
你知道你的工厂哪些地方会发生VOCs污染?

VOCs in footwear industry 挥发性有机物

Process of shoes - making 制鞋工艺流程



VOCs in footwear industry 挥发性有机物

Average concentration of VOCs in raw material in footwear industry 制鞋行业原辅材料VOCs平均含量

For reference only (仅作参考)

Number 序号	Raw material name 原辅材料名称	Range of VOCs concentration(%) VOCs含量范围	Average concentration of VOCs (%) VOCs平均含量
1	Water-based adhesive 水性胶黏剂	< 1%	< 1%
2	PU胶	66-90	83
3	黄胶	50-85	73
4	粉胶	80-92	86.5
5	生胶	84-95	87.5
6	白胶	0	0
7	Oil-based treatment agent 油性处理剂	50-100	93
8	Water-based treatment agent 水性处理剂	<2	<2
9	Oil-based hardener 油性硬化剂	65-99	80
10	Water-based hardener 水性硬化剂	10-25	17

VOCs in footwear industry 挥发性有机物

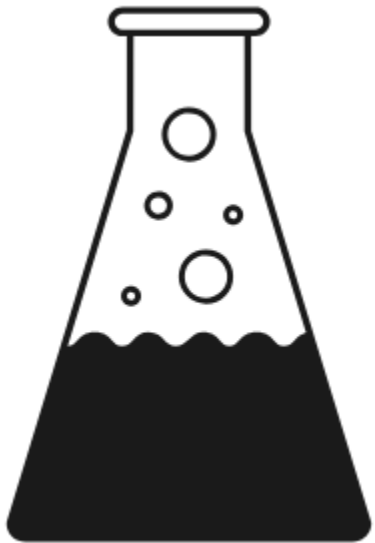
Components of VOCs in raw material in footwear industry 制鞋行业含VOCs原辅料成分

For reference only (仅作参考)

Number 序号	Raw material name 原辅材料名称		Main components 主要成分
1	Adhesive 胶黏剂	黄胶、粉胶、万能胶、喷胶、PU胶、水性胶, 白胶、生胶、热熔胶	丙酮、甲苯、丁酮、乙酸乙酯、乙酸丁酯、环己烷、甲基环己烷、乙酸甲酯、碳酸二甲酯、正己烷
2	Treatment agent 处理剂	橡胶处理剂、PU处理剂、TPR处理剂、EVA处理剂、ABS处理剂、油皮处理剂、PVC处理剂、UV处理剂、水性处理剂	丙酮、丁酮、环己酮、乙酸乙酯、乙酸甲酯、乙酸丁酯、甲苯、环己烷、甲基环己烷
3	Cleaning agent 清洗剂	白电油、天那水、甲苯、快干、清洁剂	甲苯、丁酮、己烷、三氯乙烷、二氯甲烷、丙酮、环己烷
4	Hardener 硬化剂	油性硬化剂、水性硬化剂	乙酸乙酯、聚异氰酸酯、二氯甲烷、乙酸丁酯、丙酮
5	港宝水	甲苯、快干、二氯甲烷、天那水	甲苯、快干、二氯甲烷、天那水

Assessment model of VOCs risk VOCs风险评估工具

Model Explanation



Assumption: the proportions of the chemicals remain the same during evaporation

Considered: TVOC value in the chemical mixture
Detected chemicals which are listed in Chinese Work Safety Standard

Question: if the proportions remain the same, how likely can it happen that the substances will exceed the legal work safety limits after evaporation?

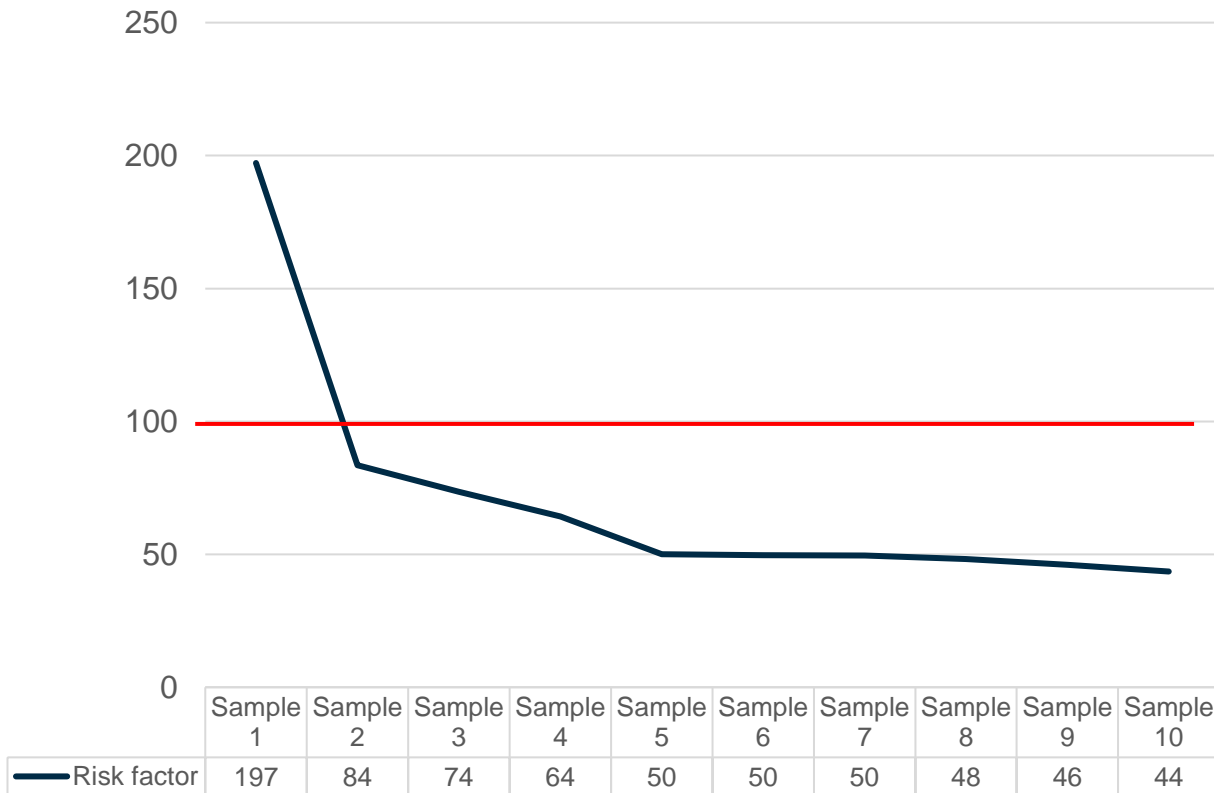
TVOC in the factory: the value is always the highest value measured in the factory

Calculation: Percentage of chemical in the mixture has been applied to the highest detected TVOC in the breathing air

$$\frac{\left[\frac{C_{\text{substance in the mixture}}}{C_{\text{TVOC in the mixture}}} \cdot \text{MAX TVOC}_{\text{air}} \right]}{C_{\text{substance Chinese working standard}}} \cdot 100\% = \text{Risk Factor}$$

Worst top 10 chemicals

Risk factor

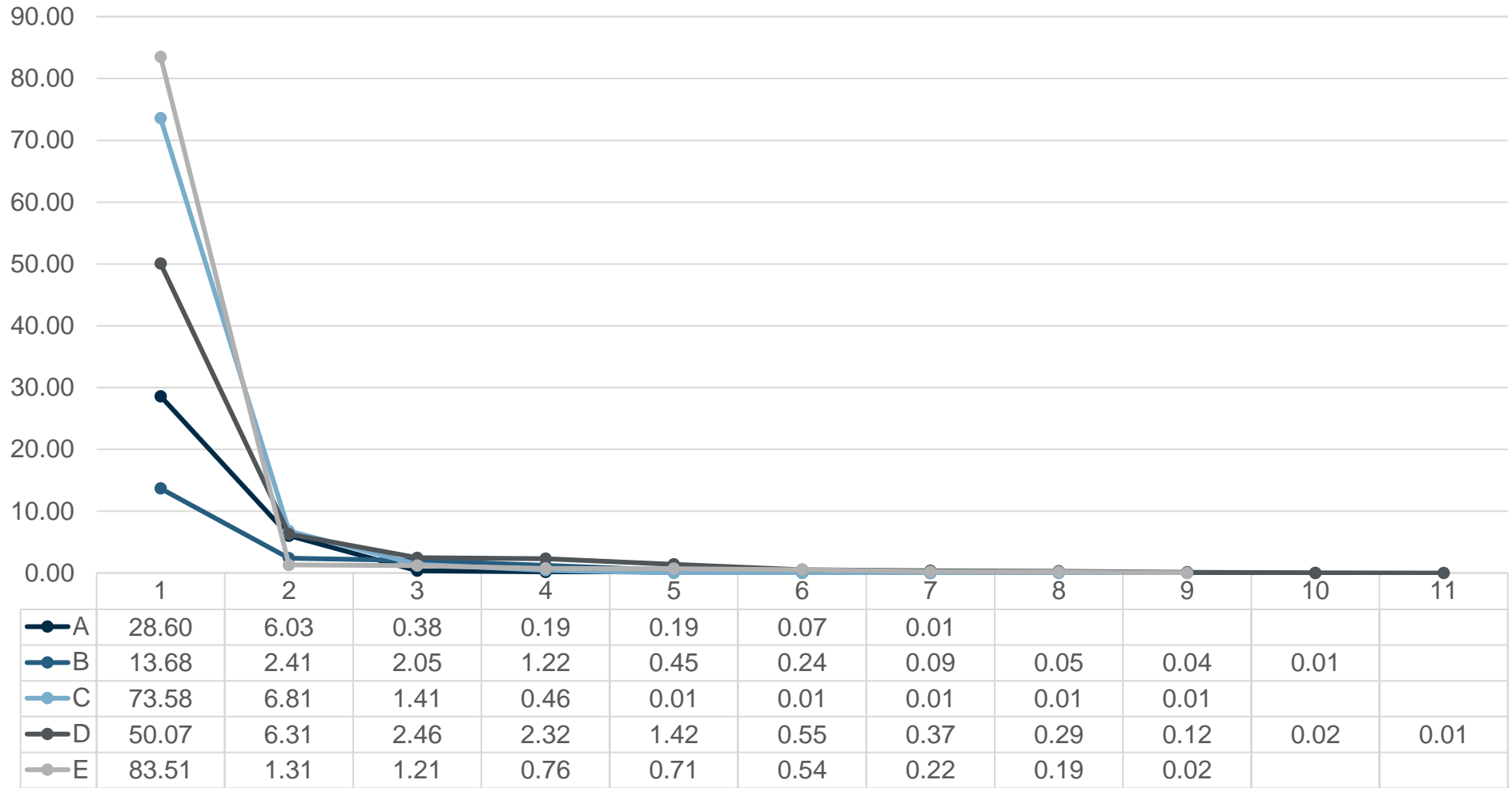


Risk factor: calculated factor which shows, how high the level of restricted substance can raise compared to the limit value which is defined in Chinese work safety standard.

Red line: 100%, shows the limit value of a critical substance

Chemical Nr.	Factory name	Critical substance
1	Factory 11	Benzene
2	Factory 3	Toluene
3	Factory 3	Toluene
4	Factory 4	Xylene
5	Factory 3	Toluene
6	Factory 10	Toluene
7	Factory 10	Cyclohexanone
8	Factory 10	Toluene
9	Factory 10	N,N-Dimethylformamide
10	Factory 11	Ethyl Acetate

Examples – Factory 3



Safety rating

- Chemical B
- Chemical A
- Chemical D
- Chemical C
- Chemical E

VOCs treatment technologies

VOCs治理技术

Activity 活动

Which technology is your facility using now to control VOCs? What is advantage and disadvantage of this technology? 你的工厂现在使用哪种技术控制VOC? 该技术有什么优缺点?

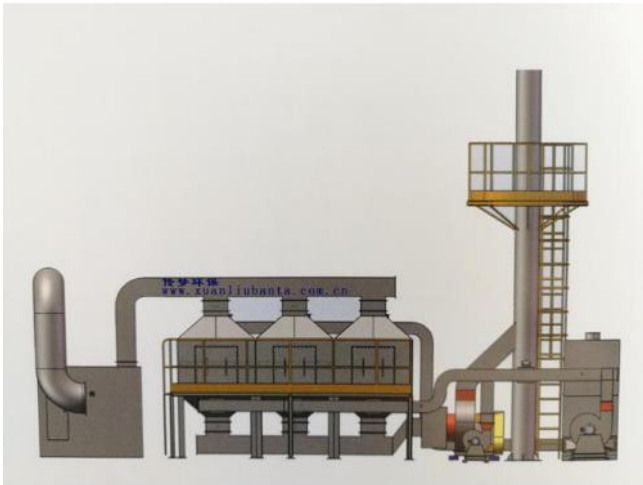
VOCs treatment technologies VOCs治理技术

Adsorption-Catalytic Combustion 吸附浓缩-催化燃烧法

Principle 原理:

Low concentration VOCs exhaust gas is converted into high concentration VOCs exhaust gas after adsorption and desorption by adsorber, and then discharged to environment after treatment by catalytic combustion device. Thermal energy generated can be recovered and utilized. It can be used to treat VOCs exhaust gas with high air volume and low concentration.

低浓度VOCs废气经吸附器吸附-脱附后变为高浓度VOCs废气，再经催化燃烧装置处理后达标排放，产生的热能可回收利用。可用于处理大风量、低浓度的VOCs废气。



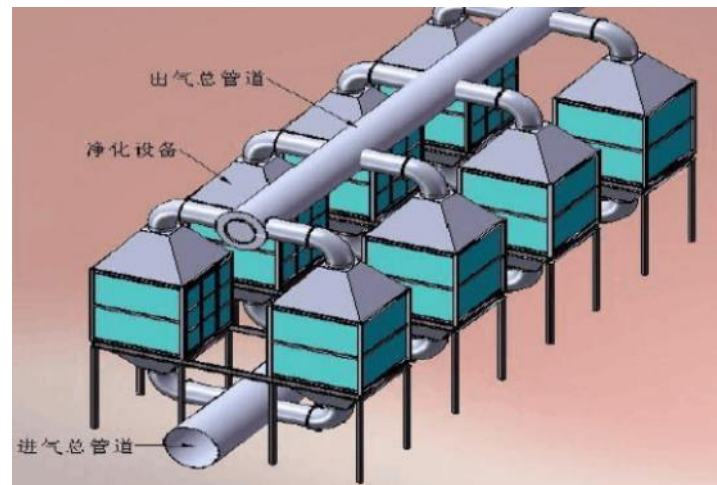
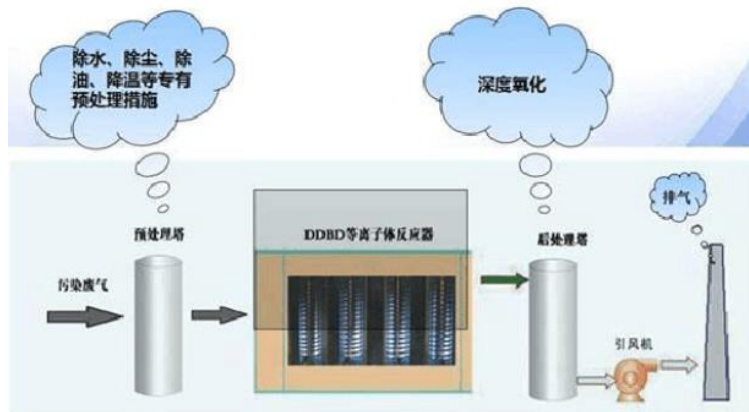
VOCs treatment technologies VOCs治理技术

Low-temperature plasma method 低温等离子体法

Principle 原理:

Low-temperature plasma method is to obtain low-temperature plasma by high-voltage discharge, which produces a large number of active particles such as high-energy electrons, ions and free radicals, which can interact with various HC pollutants and convert them into harmless or low-harmful substances such as CO_2 and H_2O , so that the exhaust gas can be purified.

低温等离子体法是通过高压放电，获得低温等离子体，即产生大量高能电子、离子和自由基等活性粒子可与各种HC污染物发生作用，转化为 CO_2 和 H_2O 等无害或低害物质，从而使废气得到净化。



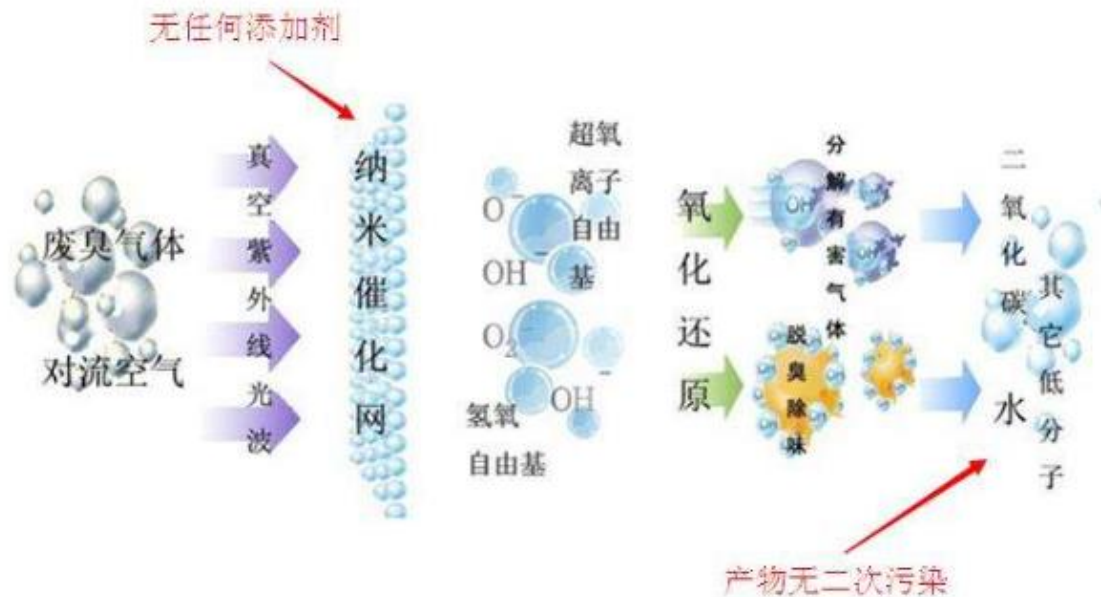
VOCs treatment technologies VOCs治理技术

Photocatalytic oxidation 光催化氧化法

Principle 原理:

Photocatalytic oxidation mainly uses vacuum ultraviolet light produced by artificial ultraviolet lamp to activate photocatalytic materials and oxidize VOCs adsorbed on the surface of catalysts.

光催化氧化法主要是利用人工紫外线灯管产生的真空紫外光来活化光催化材料，氧化吸附在催化剂表面的VOCs



VOCs treatment technologies VOCs治理技术

Adsorption 吸附法

Adsorption is a method of enriching gaseous pollutants onto adsorbents by using the selective adsorption characteristics of adsorbents (such as activated carbon, activated carbon fibers, molecular sieves, etc.). It is suitable for the purification of low concentration organic waste gas.

吸附法是利用吸附剂（如活性炭、活性炭纤维、分子筛等）对废气中各组分选择性吸附的特点，将气态污染物富集到吸附剂上后再进行后续处理的方法，适用于低浓度有机废气的净化。

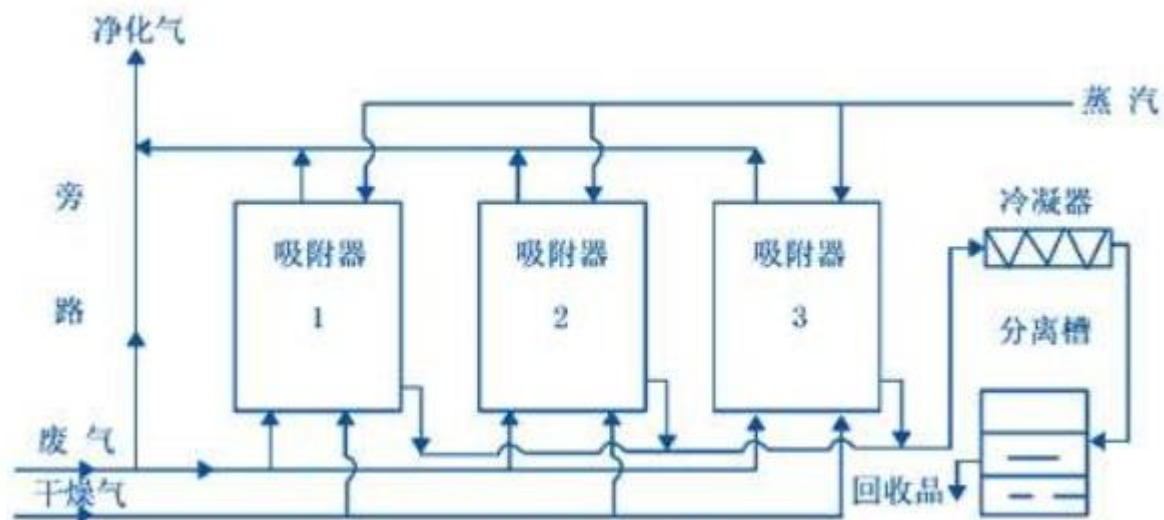


图 1 二氯甲烷废气治理工艺流程简图



VOCs treatment technologies VOCs治理技术

Comparison of VOCs treatment technologies VOCs治理技术比较

For reference only (仅作参考)

Technology 治理技术	Adsorption-Catalytic Combustion 吸附浓缩-催化燃烧法	Low-temperature plasma method 低温等离子体法	Photocatalytic oxidation 光催化氧化法	Adsorption 吸附法
Primary cost 初次投入成本 (万元)	30-60	50-60	30-50	30-50
Annual operation cost 年运行费用 (万元)	10-15	25-35	15-25	80-100
Treatment efficiency(%) (可达治理效率)	more than 95%	50-90%	50-95%	50-90%
Problems: 存在的问题:	1. Applicable for organic waste gas with low concentration and high air volume 适用于低浓度大风量的有机废气 2. There are some potential safety hazards. 存在一定安全隐患。	1. Treatment efficiency fluctuates widely. 治理效率波动范围较大 2. Possible secondary VOCs pollution exists. 可能存在二次污染。	1. Affected by pollutant composition, the treatment efficiency fluctuates widely. 受污染物成分影响, 治理效率波动范围较大 2. Catalyst may deactivate. 催化剂易失活	1. It is necessary to replace adsorbent in time, otherwise the treatment efficiency will be reduced. 需要及时更换吸附剂, 否则治理效率降低; 2. Hazardous Waste is generated by Adsorption 吸附后产生危险废物。

Substitution of chemicals containing VOCs 含有挥发性有机物化学品的替代

03

Critical Thinking and Problem Solving 批判性思维和解决问题

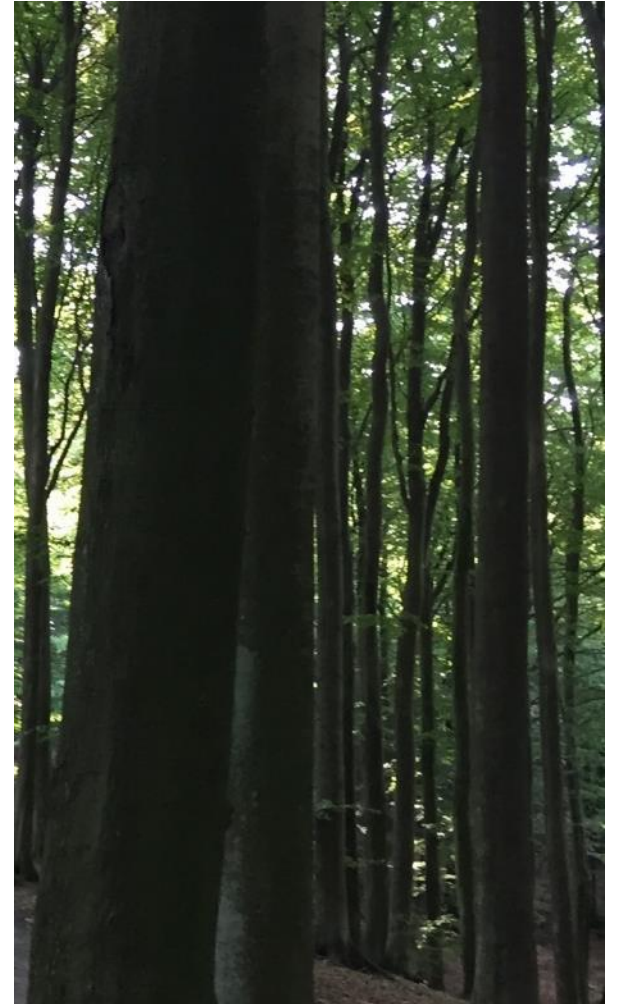
- Critical thinking is the **objective analysis of facts** to form a judgment
批判性思维是**基于事实的目标分析**以形成判断
- It is **aimed at achieving the best possible outcome** in any situation. It must involve gathering and evaluating information from as many different sources as possible
目的在于任何情况下都能**达到最可能的结果**，必须要求收集和分析来自尽可能多渠道的信息
- It is **based on the analysis of facts** rather than opinions.
基于对事实而不是观点的分析
 - **Facts** are information that is usually not debateable.
事实即无可争论的信息
 - **Opinions** are subjective, value judgements based on isolated items (e.g. own experience, history) and can be debateable.
观点是主观的、基于孤立项（如个人的经验、历史）的价值判断，并且是可能商榷的。



Critical Thinking and Problem Solving 批判性思维和解决问题

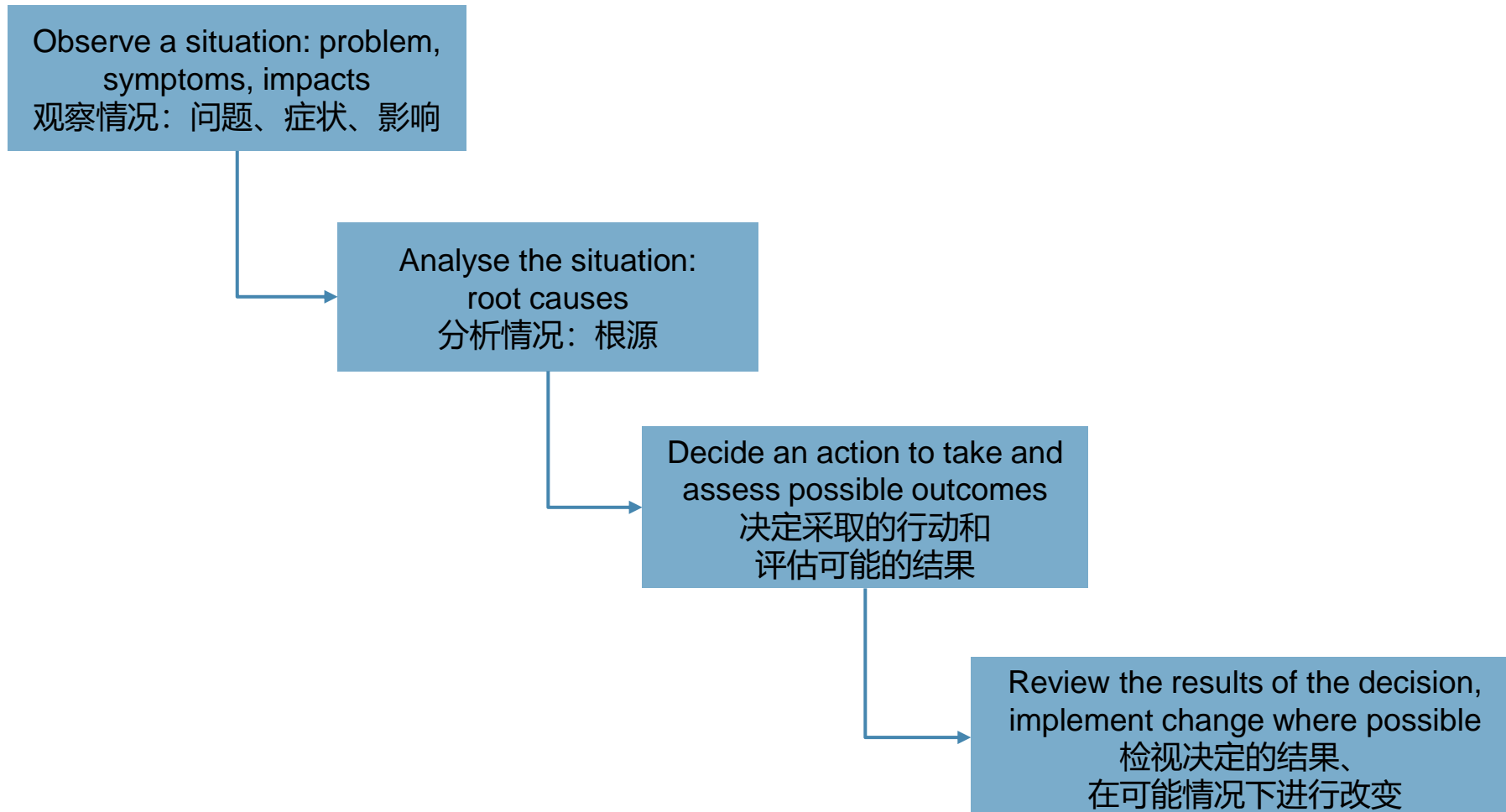
Benefits of Critical Thinking 批判性思维的好处

- It helps with **effective communication** and **problem-solving abilities**
帮助**有效沟通和解决问题的能力**
- It helps to **reflect in one's own beliefs**. Provides the **tools for the process of self-evaluation**
有助于**反应自身的看法**，提供**进行自我评估的工具**
- It helps to **evaluate new ideas**, **selecting the best ones** and **modifying them if necessary**
帮助**评估新思路、选择最佳、必要时进行修改**
- It promotes the **ability to deal with changes quickly and effectively**
提高**快速和有效地应对变化的能力**



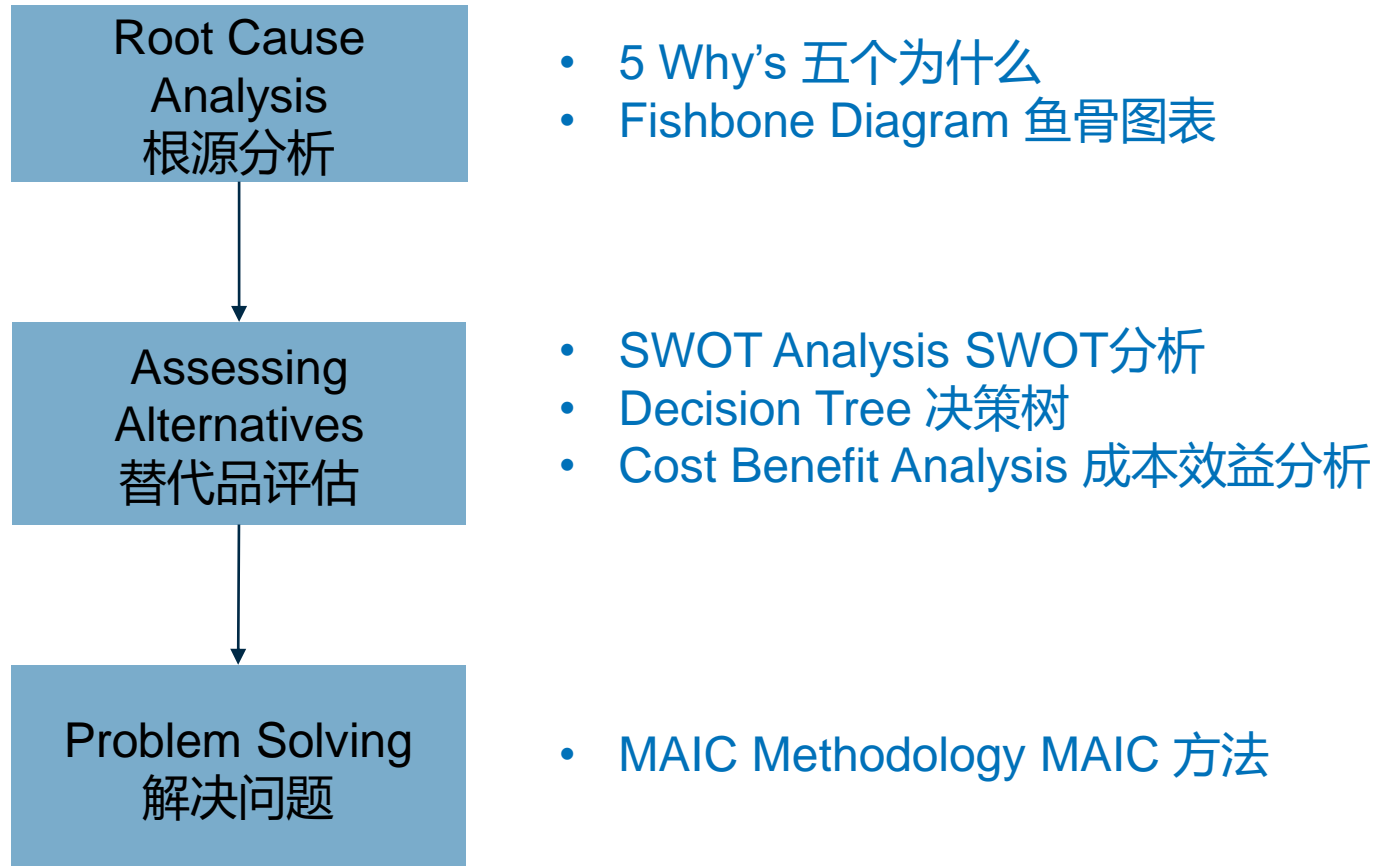
Critical Thinking and Problem Solving 批判性思维和解决问题

How To Apply Critical Thinking 如何应用批判性思维

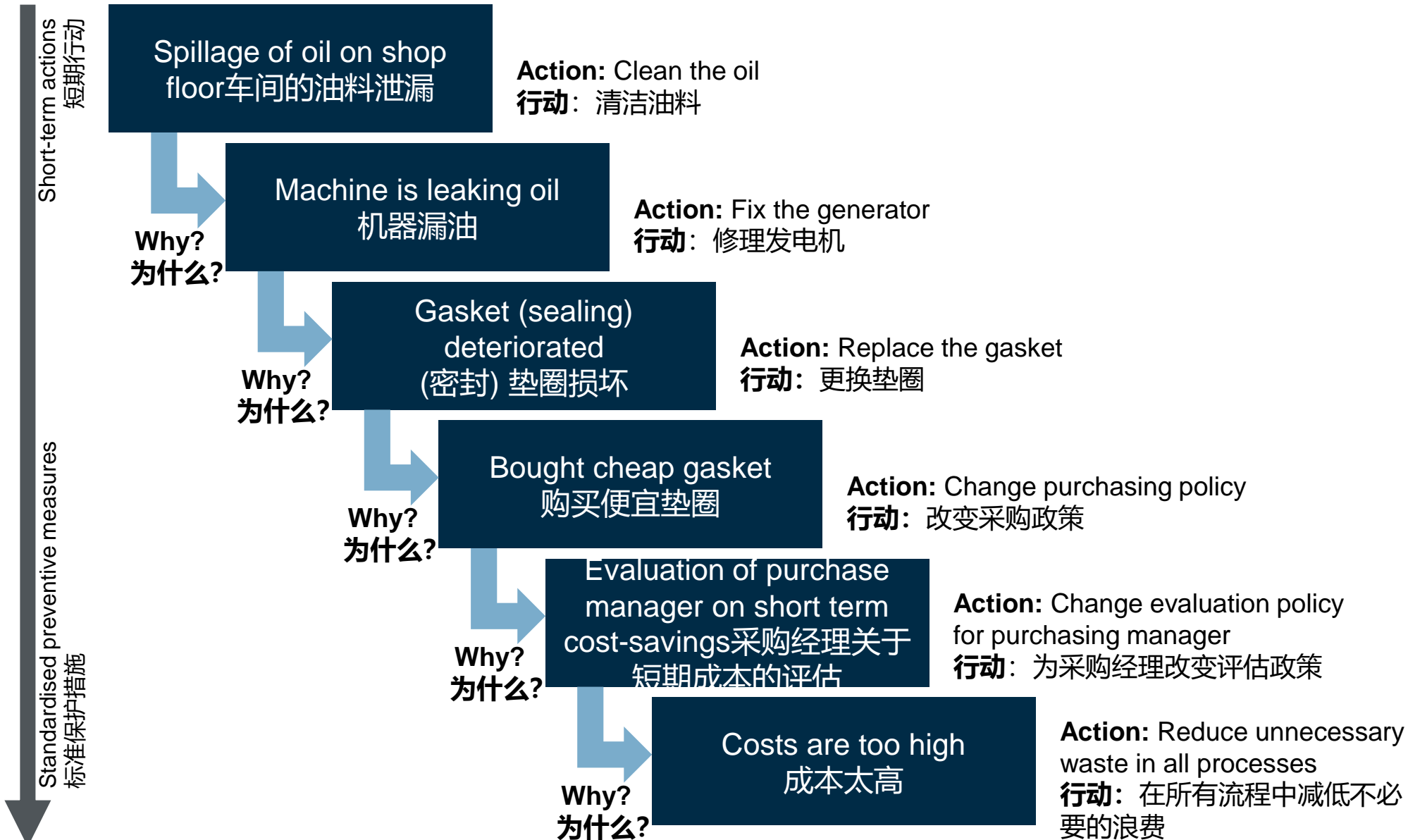


Critical Thinking and Problem Solving 批判性思维和解决问题

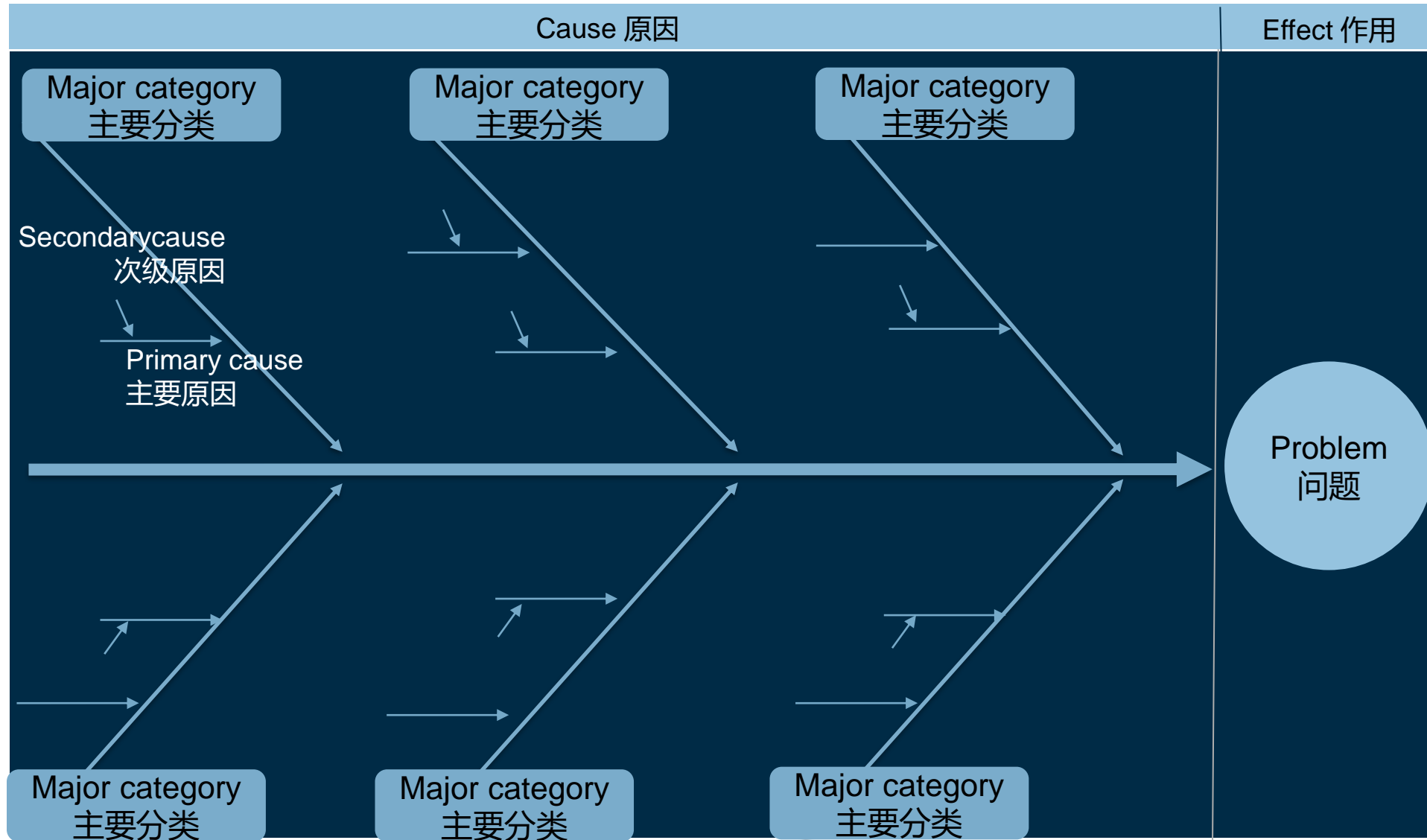
Critical Thinking Methodologies 批判性思维的方法



Finding the Root Cause – 5 Whys 寻找根源：五个为什么



Finding the Root Cause – Fishbone 寻找根源: 鱼骨图表



Evaluating Alternatives - SWOT Analysis 评估替代选择 – SWOT分析

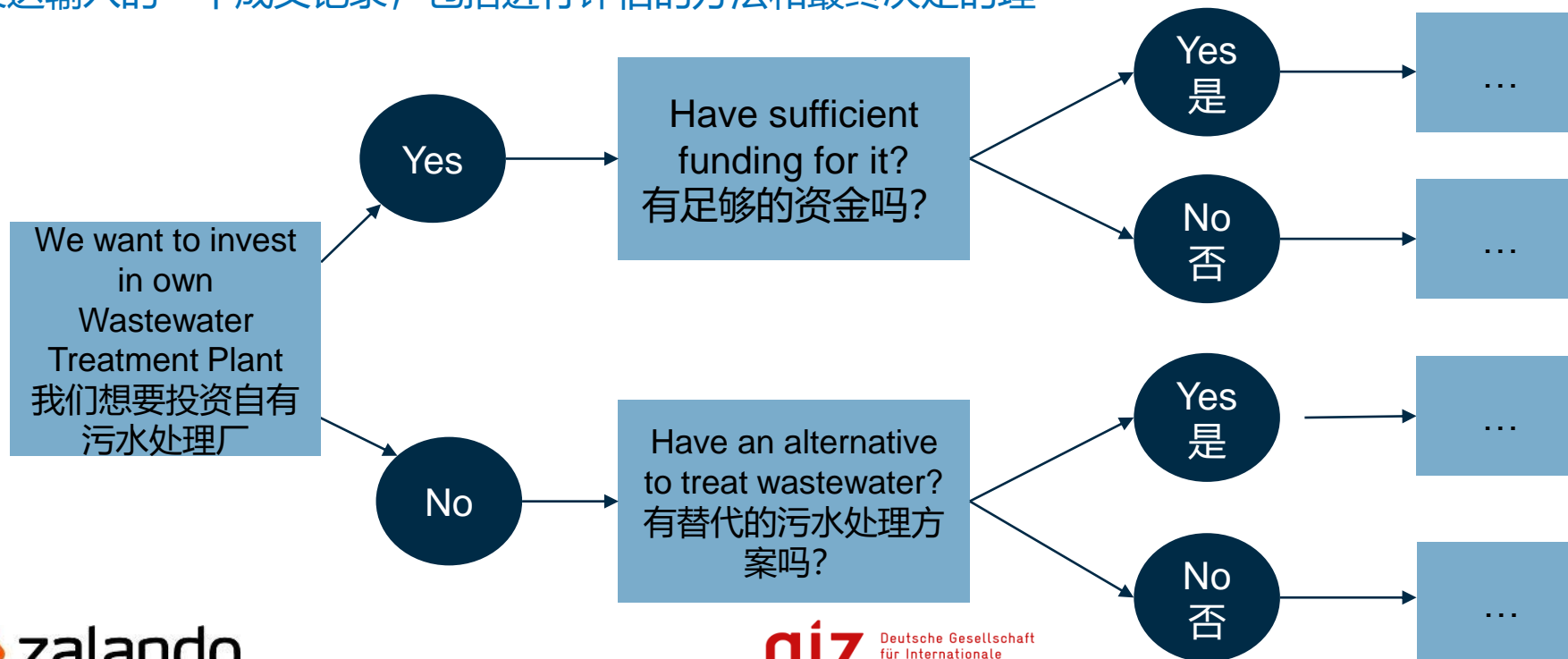
A basic, analytical framework that assesses what a 'solution' can and cannot do, for factors both internal (the strengths and weaknesses), as well as external (the potential opportunities and threats).

一种简单解析的框架来评估一种解决方法可行或不可行，内部因素（优势和弱点）以及外部因素（潜在机会和风险）



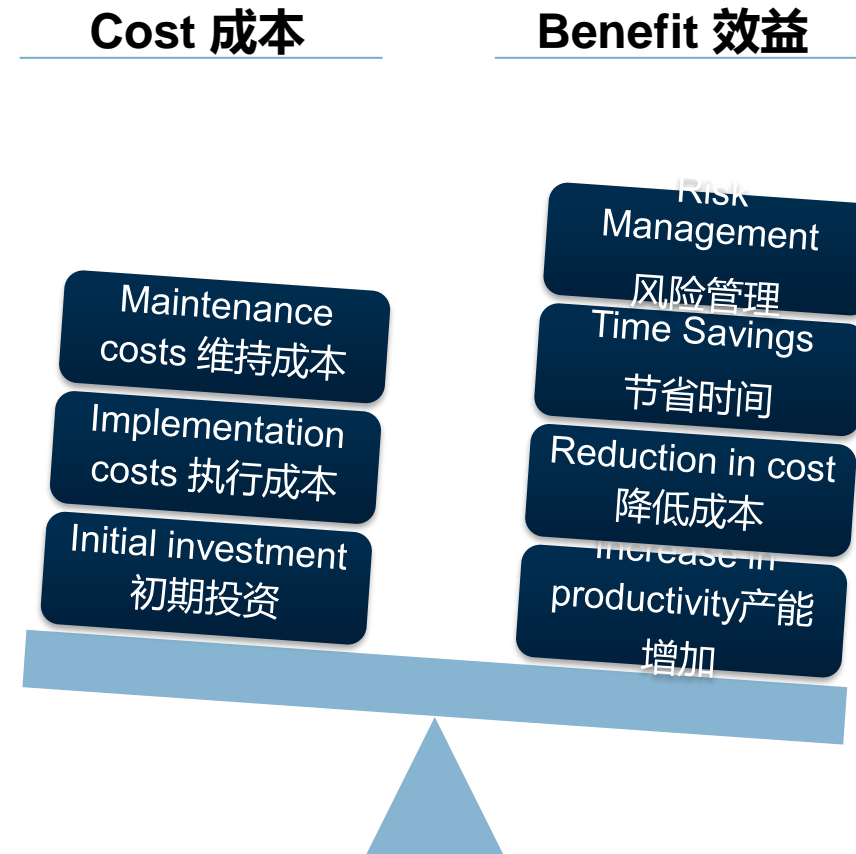
Evaluating Alternatives – Decision Tree 评估替代分析 – 决策树

- Graphical representation of possible solutions to a decision based on certain conditions. 图解表达可能的方法以基于一定条件来决策
- Allows you to approach the problem in a structured and systematic way to arrive at a logical conclusion. 处理问题的方式，以一个结构性的系统的方法来达成逻辑结论
- Represents a documented record of the inputs that were available, the way you performed your evaluation and the reasons for the final decision. 表达输入的一个成文记录，包括进行评估的方法和最终决定的理



Evaluating Alternatives – Cost Benefit Analysis 评估替代分析 – 成本效益分析

- Quick and simple technique that you can use for non-critical financial decisions.
能用于非关键金融决策的快速和简单的技术
- Straightforward tool for deciding whether to pursue a project.
决策是否进行某个项目的明了工具
- You can include financial and intangible items into your analysis.
在分析中包括金融和其它无形因素
- Where decisions are mission-critical, or large sums of money are involved, this approach lacks complexity.
如决策是关键任务或涉及大笔资金，这方法缺少考虑复杂性



Six Steps to Substitution 替代的六步骤

Step 1 – Define the Problem 识别问题



- Describe hazards and useful properties of these chemicals.
描述这些化学品的危害性和有用的性能
- Ask your suppliers and/or use *reliable sources* to check hazards.
询问供应商和/或使用其它可靠资源, 了解危害性
- Describe the function of the substance and the operational parameters (pH, temperature, etc), quantity, equipment.
描述物质的功能和操作参数 (pH值、温度等)、数量、设备

Six Steps to Substitution 替代的六步骤

Step 2 – Set Substitution Criteria 建立替代标准



- Set criteria to eliminate alternatives that are not safer or not safe enough.
设立淘汰不安全或不够安全的化学品的标准

Six Steps to Substitution 替代的六步骤

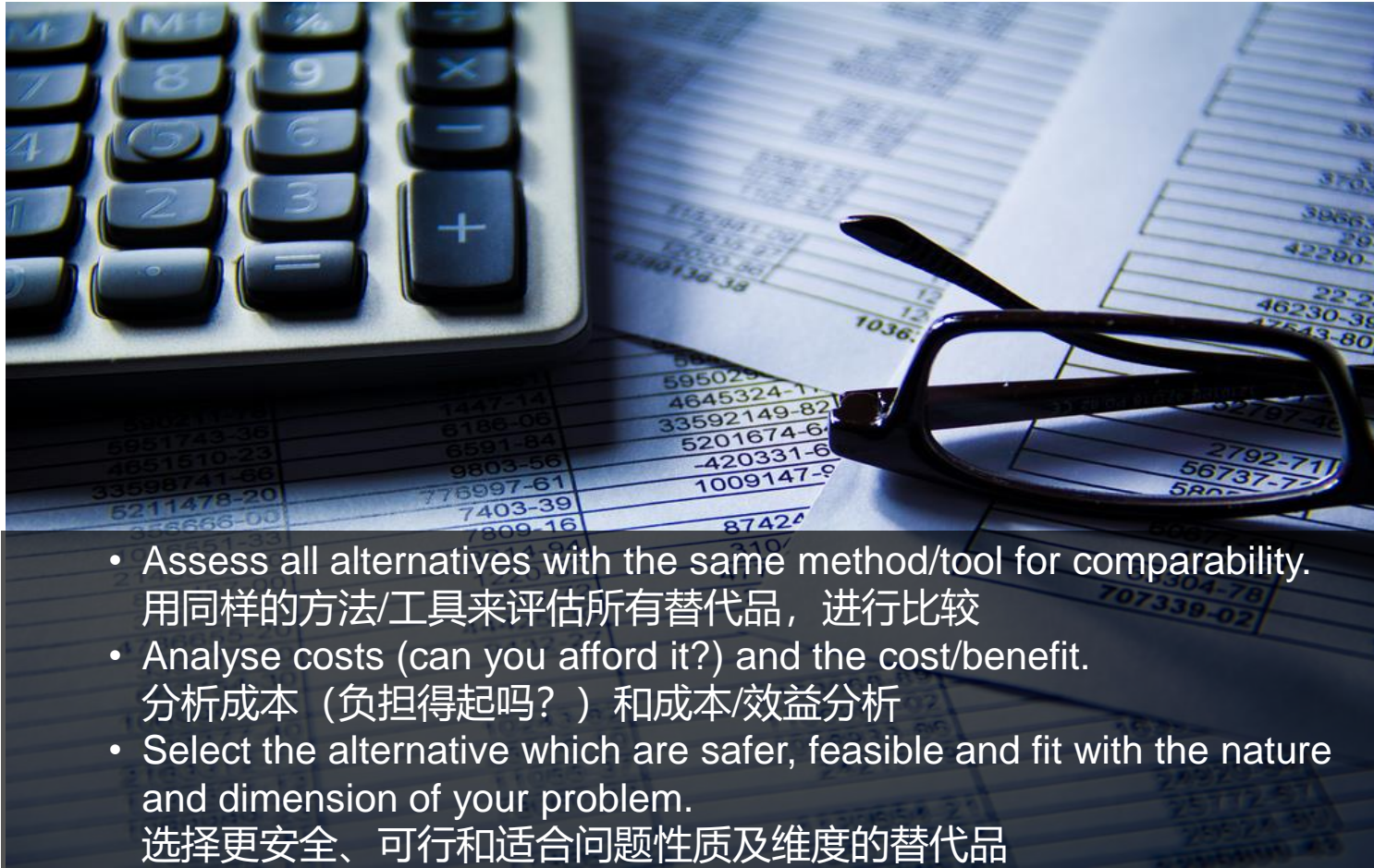
Step 3 – Search for Alternatives 寻找替代品



- Search within your own company. 在公司内部寻找
- Search on internet, ask authorities, professional associations, NGOs, trade unions.
在互联网上寻找，寻问主管部门、专业协会、非官方组织、贸易协会
- Look for *alternatives* already tested and implemented, this may lower the innovation costs and risks. 找寻已经测试和使用过的替代品，可能降低创新成本和风险
- You may also ask your supplier for safer alternatives. But first, search within your own company. 也可咨询供应商更安全的替代品。首先，在公司内部寻找

Six Steps to Substitution 替代的六步骤

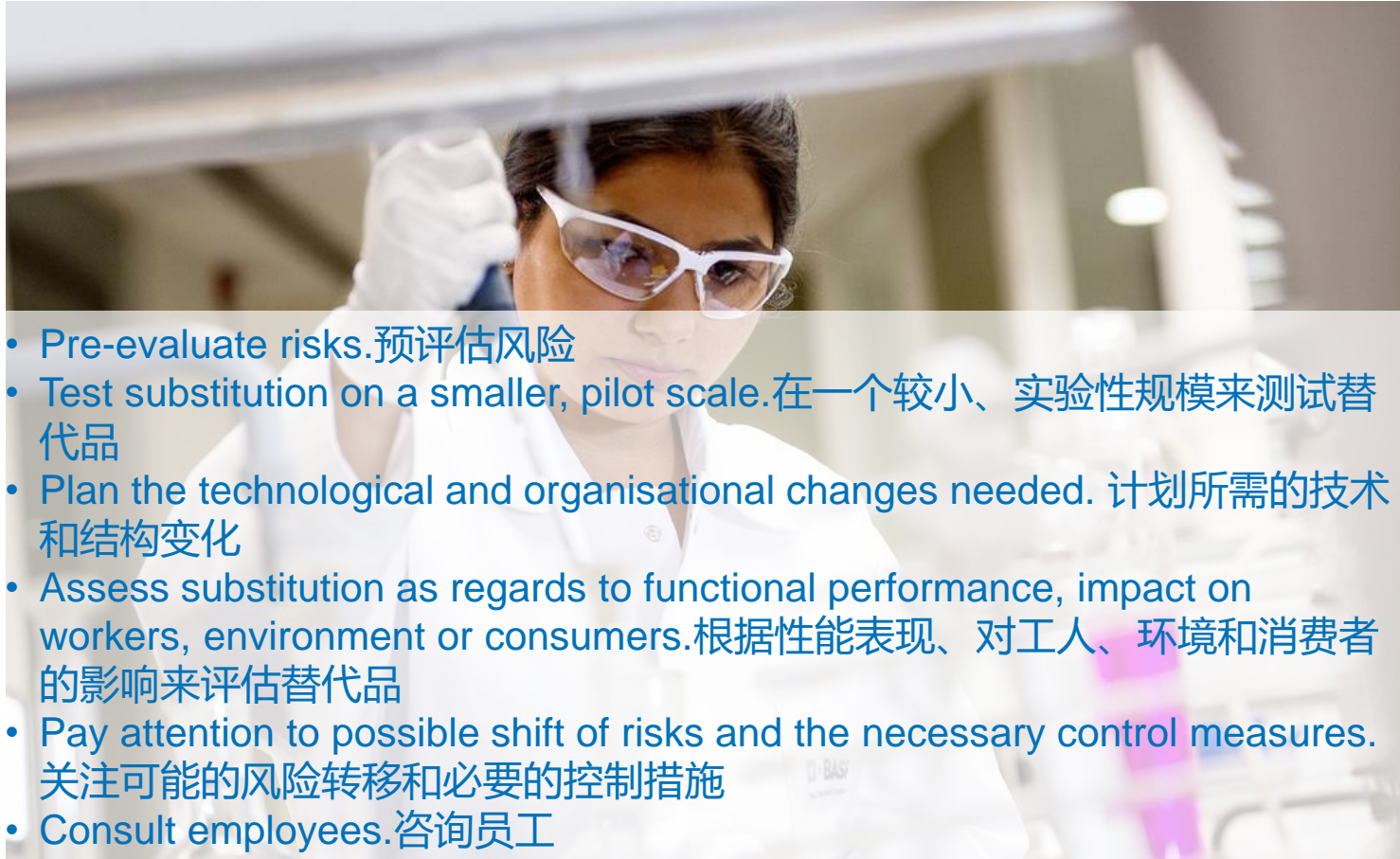
Step 4 – Access and Compare Alternatives 评估和比较替代品



- Assess all alternatives with the same method/tool for comparability.
用同样的方法/工具来评估所有替代品，进行比较
- Analyse costs (can you afford it?) and the cost/benefit.
分析成本（负担得起吗？）和成本/效益分析
- Select the alternative which are safer, feasible and fit with the nature and dimension of your problem.
选择更安全、可行和适合问题性质及维度的替代品

Six Steps to Substitution 替代的六步骤

Step 5 – Conduct Pilot Experiment 进行中试



- Pre-evaluate risks. 预评估风险
- Test substitution on a smaller, pilot scale. 在一个较小、实验性规模来测试替代品
- Plan the technological and organisational changes needed. 计划所需的技术和结构变化
- Assess substitution as regards to functional performance, impact on workers, environment or consumers. 根据性能表现、对工人、环境和消费者的影响来评估替代品
- Pay attention to possible shift of risks and the necessary control measures. 关注可能的风险转移和必要的控制措施
- Consult employees. 咨询员工

Six Steps to Substitution 替代的六步骤

Step 6 – Implement and Improve 执行和改进



- Think what other measures would be needed when implementing substitution at full capacity. 在进行工业规模的替代时，考虑是否需要其它措施
- Update your supply chain and inform your downstream users. 更新供应链、通知下游使用者
- Collect extended feedback from workers and clients. 收集工人和客户的广泛的反馈
- Identify points to improve. 识别改进点
- Promote your achievements. 推广所得的成效

Sustainable Alternatives 可持续的替代方案

04

Sustainable Alternatives 可持续的替代方案

VOCs control from sources 源头控制

- Choose the LEAST hazardous chemical suitable for use 选择危害性最小的化学品
- Strictly control chemical's use from pre-treatment to post-treatment
从预处理到后处理严格控制化学品使用
- Obtain the most updated SDS for every chemical 获取每种化学品的SDS
- Obtain an assessment and approval from environment, health and safety (EHS) personnel
获取EHS的评估和批准
- Ask for a RSL/MRSL Confirmation or Guarantee Letter
要求提供RSL/MRSL符合性声明或保证书
- Check the labels for all chemical containers (packages) comply with the legal requirements
检查化学品容器标签是否与法规要求一致

Activity 活动

Combined with the contents of the previous chapters, please summarize the methods to substitute or reduce VOCs in products and exhaust gases.

结合前面章节所学内容，请总结出替代或者降低产品和废气中VOCs含量的方法。

Measures for VOCs substitution and VOCs reduction

挥发性有机化合物替代和减少措施

- The substitution of solvent-based adhesives
溶剂型胶粘剂的替代
- Process change – Injection moulding may be used instead of gluing sole parts, which can avoid the need for adhesive together
工艺变更-可以使用注塑代替粘合鞋底，这样可以完全避免粘合的需要
- Improving the handling of solvent and adhesives, upgrading equipment and changes to adhesive application techniques
改进溶剂和粘合剂的处理，改进设备，改变粘合剂应用技术

Measures for VOCs substitution and VOCs reduction

挥发性有机化合物替代和减少措施

Objectives 目标	Description 描述
VOC-free systems 无VOCs系统	Water-based adhesives 水性胶
	Hot melt adhesives 热熔胶
	Solvent-free printing 无溶剂印刷
	Water-based coating and finishing 水性涂层和整理
VOC-reduced system 减少VOCs系统	Use of low solvent finishing pastes 使用低溶剂整理剂
Process Improvements 流程改进	Improved material handling and good housekeeping 改善物料处理和良好的内务管理
	Adhesive-free sole assembly 无粘胶鞋底组合
Abatement Technologies 减排技术	Adsorption 吸附
	VOC destruction VOC破坏

Module 7: Chemicals in Shoes Materials

模块七：鞋类材料中的化学品

TÜV Rheinland
March 2019



CONTENTS

目录



Man-made Leather 人造革

Chemical Application in Man-made Leather Industry
化学品在人工革中的应用



Leather 皮革

Chemical Application in Leather Industry
化学品在皮革行业的应用



Fabric 面料

Chemical Application in Textile Industry
化学品在纺织行业的应用

Learning objectives 学习目标:

1. To have a comprehensive understanding of the major shoe material are produced 对所生产的主要鞋材有全面的了解
2. To learn about which chemicals are used in the shoe material manufacturing process 了解鞋材制造过程中使用的化学品
3. To learn hazardous chemical's source from shoes material aspect 从鞋材方面了解危险化学品的来源
4. To introduce the advancement of the water-based PU technology 介绍水性聚氨酯技术的进展

Target Group 目标群:

5% of participating factory workers may include: 工厂5%的员工应包括:

- 1.High management: factory Board Chairman, Managing Director, General Manager 高层: 董事长、常务董事、总经理;
2. Department Manager in Quality, EHS, R&D, Manufacturing, Purchasing, IT, HR, Sales, and Admin 部门经理 (质量、EHS、研发、生产、采购、IT、人力资源、销售、行政)
3. All staff in quality department, lab, and EHS department 质量部门、实验室和EHS部门的所有员工
- 4.Shift leaders in each manufacturing line, in chemical warehouse 每条生产线、每个化学品仓库领班
- 5.All interested workers are welcomed 所有感兴趣的员工
6. Minimum 10 people for each factory 每家工厂至少10人

Length: 时长

3 Hours 3小时

Training outcomes 培训成果

At the end of this training, the participants will be able to ...

培训结束后，您应该能够

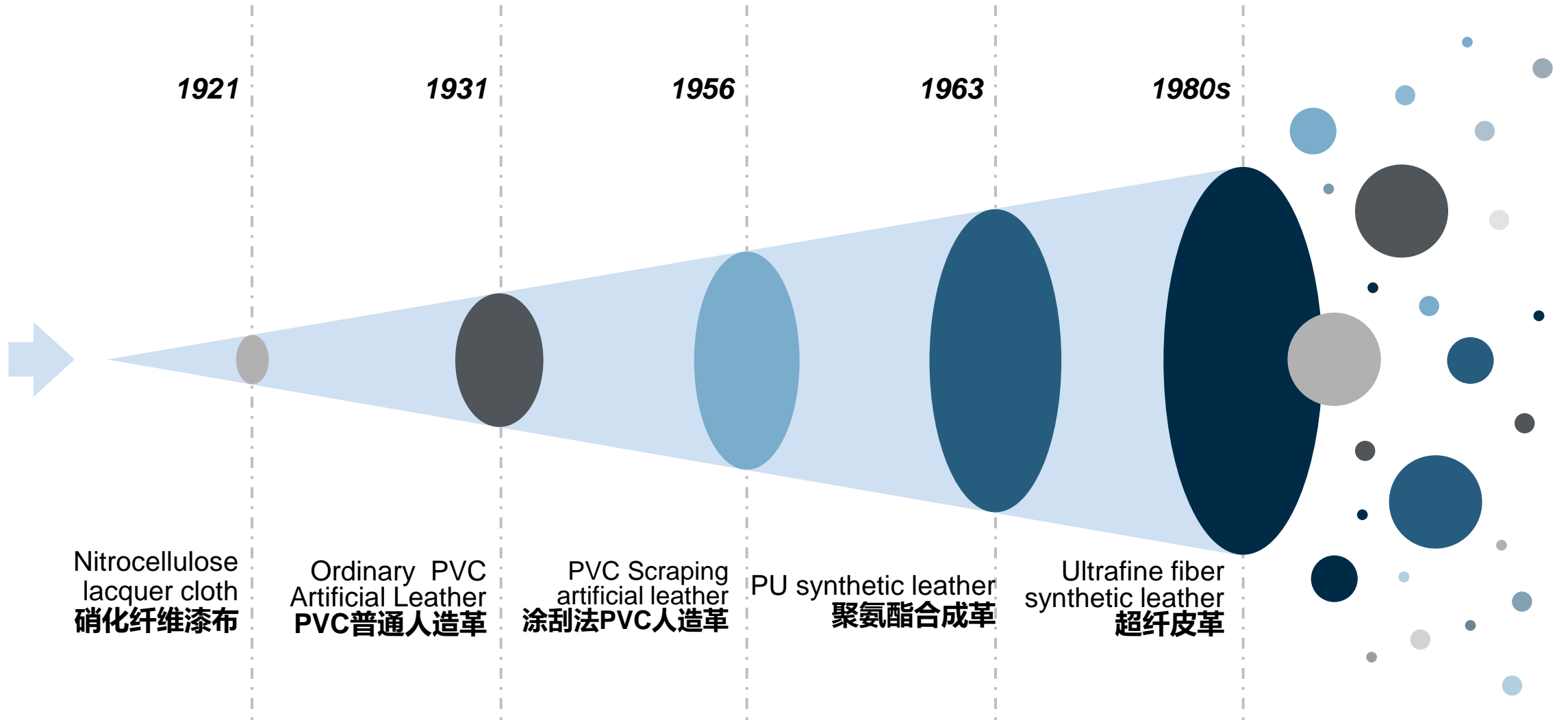
- Describe the general manufacturing process of the natural leather, synthetic leather, and textile
描述天然革、合成革和纺织品的一般制造工艺
- Have a basic understand about chemicals used in shoe's material manufacturing process
对鞋材制造过程中使用的化学品有基本了解
- Identify some root cause of the hazardous chemicals
确定危险化学品的一些根本原因
- Understand the development of water-based PU materials
了解水性聚氨酯材料的发展

Chemical Application in Man-made Leather Industry

化学品在人工革中的应用



Development History of Man-made Leather 人工革的发展史



Artificial and Synthetic Leather 人造革和合成革

Artificial leather is a kind of plastic product which looks and feels like leather. The Artificial leather is usually made from non-woven fabrics and coated with synthetic resins and various plastics, while the synthetic leather is made from non-woven fabrics and coated with synthetic resins.

人造革是一种外观、手感似皮革并可代替其使用的塑料制品。通常以织物为底基，涂覆合成树脂及各种塑料添加制成；合成革则是以非织物为底基，涂覆合成树脂制成。

In China, We traditionally consider that
在我国，人们传统上将：

Artificial leather made from PVC resin and traditional fabric as base is PVC artificial leather.
用PVC树脂为原料、传统织物为底基而生产的人造革为PVC人造革（简称人造革）；

Artificial leather made from PU resin and traditional fabric as base is called PU artificial leather.
用PU树脂为原料、传统织物为底基而生产的人造革称为PU人造革（简称PU革）；

Synthetic leather made from PU resin and non-woven fabric as base is PU synthetic leather.
用PU树脂与无纺布为原材料的人造革称为PU合成革（简称合成革）。

Artificial and Synthetic Leather 人造革和合成革

At present, it is customary to distinguish artificial leather according to the types of surface resin:

目前，人们习惯按造面树脂的种类对人工革加以区分：

- Artificial leather coated with polyvinyl chloride (PVC) resin is called PVC artificial leather
将以聚氯乙烯（PVC）树脂作为涂层生产的人工革称为PVC人造革（简称人造革）；
- Artificial leather coated with polyurethane (PU) resin is called PU synthetic leather
将以聚氨酯（PU）树脂为涂层的人工革称作PU合成革（简称合成革）；
- Artificial leather with PVC resin as its base and PU resin as its surface is called semi-PU
将以PVC树脂为底层，PU树脂为面层的人工革称作半PU；
- Ultrafine fiber synthetic leather: Non-woven fabrics with three-dimensional network structure, which are made from superfine fibers by carding, needling or spunlace, form leather imitation products under wet polyurethane soaking, weight reduction, grinding, dyeing and finishing.
超细纤维合成革：将超细纤维通过梳理、针刺或水刺制成具有三维网络结构的无纺布，再聚氨酯湿法含浸、减量、磨皮、染整等工艺最终形成的仿革产品。

Microstructure of leather and Man-made leather 皮革和人工革的微观组织构造



图 1-1 天然皮革的微观组织构造



图 1-2 人造革的微观组织构造



图 1-3 合成革的微观组织构造



图 1-4 超纤革的微观组织构造

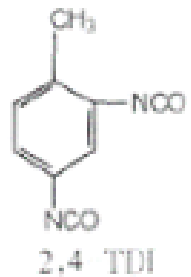
PU Synthetic Leather PU合成革

Polyurethane 聚氨酯

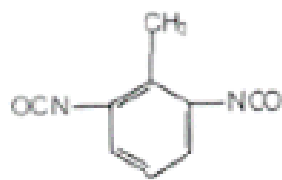
Definition of Polyurethane 聚氨酯的定义

It is a polymer containing duplicate carbamate (-NHCOO-) in the main chain formed by the step-by-step polymerization of di (or more) isocyanates with di (or more) monoalcohols.

聚氨酯全称为聚氨基甲酸酯。它是由二（或多）异氰酸酯与二（或多）元醇通过逐步聚合反应生成的主链上含有重复氨基甲酸酯 (-NHCOO-) 的聚合物。



2,4 TDI



2,6-TDI



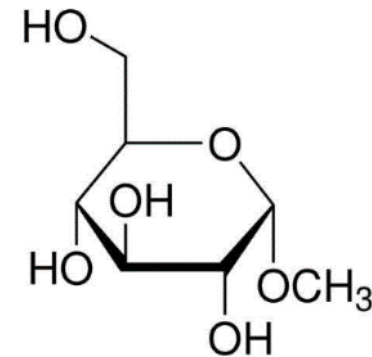
HDI



IPDI



MDI



PU Synthetic Leather PU合成革

Polyurethane 聚氨酯

TDI: High vapor pressure, volatility and toxicity; serious yellowing of products

蒸气压大，易挥发，毒性大；生成的制品黄变性严重

MDI: Low vapor pressure, less pollution to the environment, but also belongs to "yellow isocyanate", and the yellowing is larger than TDI

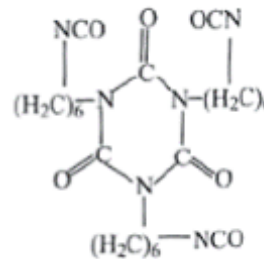
蒸汽压低，对环境污染小，但也属于“黄变性异氰酸酯”，且比TDI的黄变性更大

HDI: High vapor pressure, high toxicity, strong tear-inducing effect, commonly used after modification

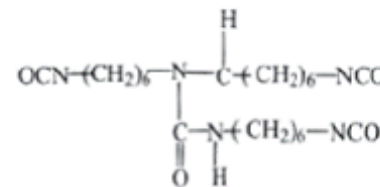
蒸气压高，毒性大，有强烈的催泪作用，一般改性后使用

IPDI: Yellowing resistance, aging resistance, heat resistance, good elasticity and high price

耐黄变、耐老化、耐热、弹性良好、价格高



HDI三聚体



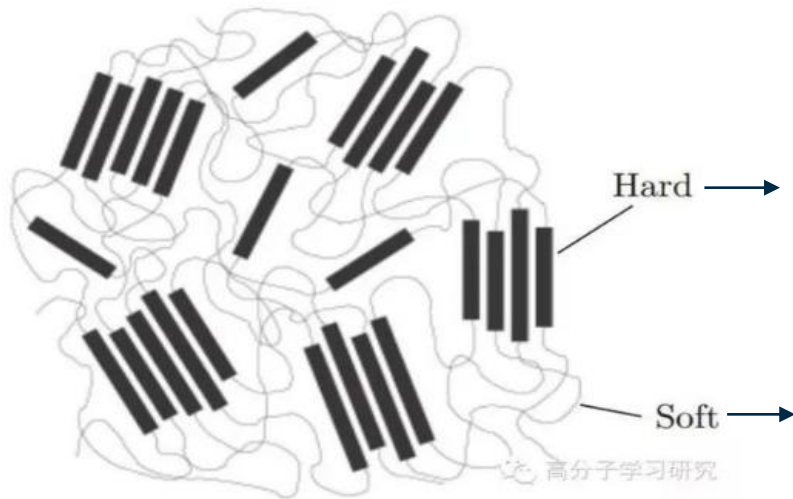
HDI缩二脲

PU Synthetic Leather PU合成革

Polyurethane 聚氨酯

Due to the variety of monomers and controllable reaction conditions, polyurethane can be synthesized with various properties and structures. It can be used to manufacture coatings, plastics, rubber, fibers, foam plastics and adhesives, etc.

由于合成聚氨酯的单体品种多，反应条件可控，可以制备各种性能和结构的产品，可用于制造涂料、塑料、橡胶、纤维、泡沫塑料和粘合剂等多种材料



Hard → 异氰酸酯 + 短链醇

Soft → 异氰酸酯 + 长链醇

The types of soft segment and hard segment affect the degree of hardness and strength of materials
软段和硬段种类影响着材料的软硬程度、强度等性能

PU Synthetic Leather Manufacturing Process PU合成革生产过程

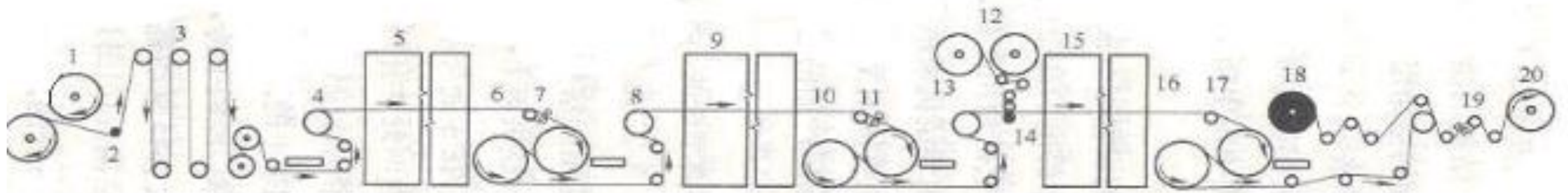
Dry process 干法

Dry-process: a kind of multi-layer complex composed of multi-layer film and cloth obtained by drying solvent PU solution. 干法PU合成革是把溶剂型PU溶液烘干后得到的多层薄膜与基布结合而构成的一种多层复合体。



PU Synthetic Leather Manufacturing Process PU合成革生产过程

Dry process 干法



转移涂层联合机

- 1—离型纸退卷机 2—压纸辊 3—储存器 4—第一涂头 5—第一烘箱 6、10、16—冷却辊 7、11、17、19—气动基材导辊
8—第二涂头 9—第二烘箱 12—基布退卷机 13—第三涂头 14—贴合辊 15—第三烘箱 18—涂层织物卷绕机
20—离型纸卷绕机 D.R.—主动的拖动辊 A.R.—可调节辊

PU Synthetic Leather Manufacturing Process PU合成革生产过程

Dry process 干法

- **Coating slurry in dry method is mainly composed of resin, solvent, colorant and additives.**
干法涂层浆料主要由树脂、溶剂、着色剂和助剂四大部分组成。
- Selection of solvent 溶剂的选择
Solvent is usually composed of two kinds of solvent (solvent 1: solvent 2 = 3:1) .
Solvent 1: 二甲基甲酰胺 DMFa
Solvent 2: Acetone, ethyl acetate, methyl ethyl ketone, methyl acetate, methyl acetal, toluene, etc
丙酮、醋酸乙酯、甲乙酮、醋酸甲酯、甲缩醛、甲苯等

PU Synthetic Leather Manufacturing Process PU合成革生产过程

Dry process 干法

Example of slurry receipt of surface layer 表层浆料配方举例：

Slurry receipt of surface layer 表层浆料配方		
材料名称	用量/份	材料的作用
高模量树脂 (含固量30%)	100	成膜剂
手感剂	0~8	手感
抗磨剂	0~3	提高耐磨性
流平剂	0.2~1.5	流平
色浆	0~25	着色剂
二甲基甲酰胺 DMFa	60~100	溶剂

PU Synthetic Leather Manufacturing Process PU合成革生产过程

Dry process 干法

Example of slurry receipt of top layer 面层浆料配方举例：

Slurry receipt of top Slurry 面层浆料配方		
材料名称	用量/份	材料的作用
高模量树脂	0~50	成膜剂
中模量树脂	50~100	成膜剂
低模量树脂	0~50	成膜剂
色浆	5~30	着色剂
二甲基甲酰胺 DMFa	35~80	溶剂
甲乙酮	15~60	溶剂

PU Synthetic Leather Manufacturing Process PU合成革生产过程

Dry process 干法

Example of slurry receipt of bottom layer 底层浆料配方举例：

Slurry receipt of bottom Slurry 底层浆料配方		
材料名称	用量/份	材料的作用
黏合树脂	100	成膜剂
二甲基甲酰胺 DMFa	0~100	溶剂
甲乙酮	20~30	溶剂
甲苯	0~10	溶剂
促进剂	0~6	促进剂
交联剂	0~14	交联剂

PU Synthetic Leather Manufacturing Process PU合成革生产过程

Wet-process 湿法

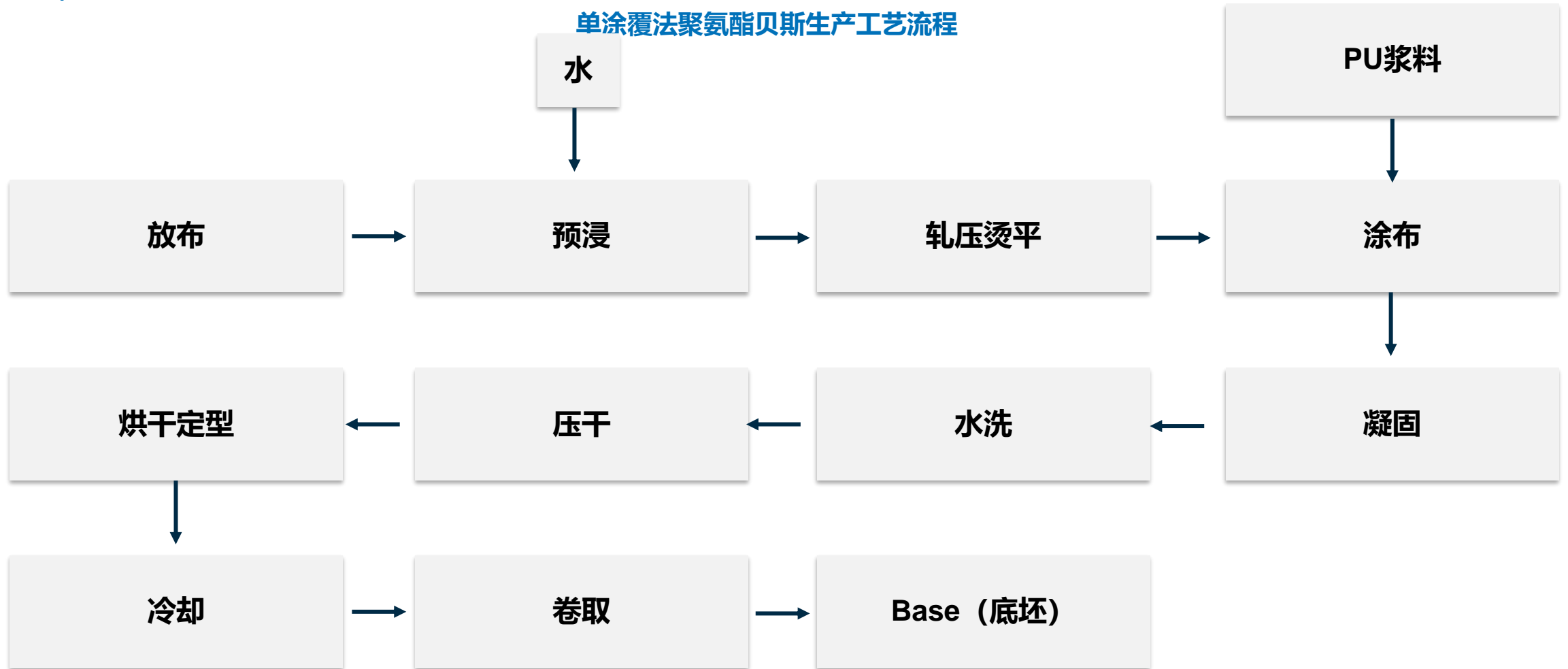
- Solvent-based polyurethane slurry is usually used to coat or impregnate the base cloth, and then enters the “H₂O-DMF” coagulation bath to make the polyurethane coagulate and form a coating or filler with microporous structure
一般采用溶剂型湿法聚氨酯浆料，涂布在基布表面或者浸渍基布，然后进入“H₂O-DMF”凝固浴，使聚氨酯湿法凝固而形成具有微孔结构的涂层或填充体
- Wet process can be divided into wet impregnation and wet coating. But in most cases, they are used in combination
湿法工艺分为湿法浸渍和湿法涂层两种方式。但绝大多数情况下，是两种方式结合起来使用。
- A base cloth impregnated with polyurethane or coated with polyurethane microporous coatings is called a bass (semi-finished product). 浸渍过聚氨酯或带有聚氨酯微孔涂层的基布称为贝斯（半成品）
- Base can become polyurethane synthetic leather only after dry veneering or surface printing, embossing and grinding etc. 贝斯经过干法贴面，或者经过表面印刷、压花、磨皮等工艺后，才能成为聚氨酯合成革。

Manufacturing method of PU synthetic leather PU合成革生产方法

Wet process 湿法

Single coating(wet): PU base manufacturing process flow chart

单涂覆法聚氨酯贝斯生产工艺流程

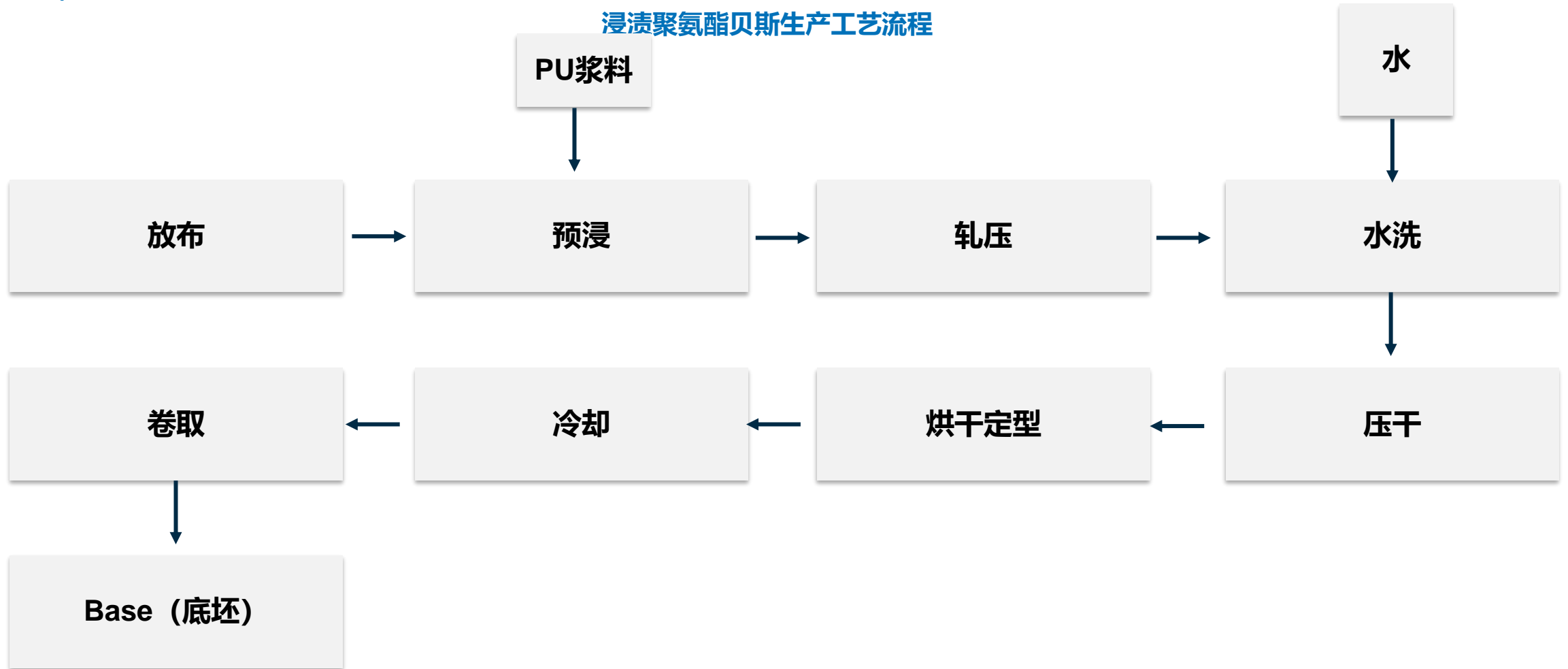


Manufacturing method of PU synthetic leather PU合成革生产方法

Wet process 湿法

Soaking(wet): PU base manufacturing process flow chart

浸渍聚氨酯基生产工艺流程

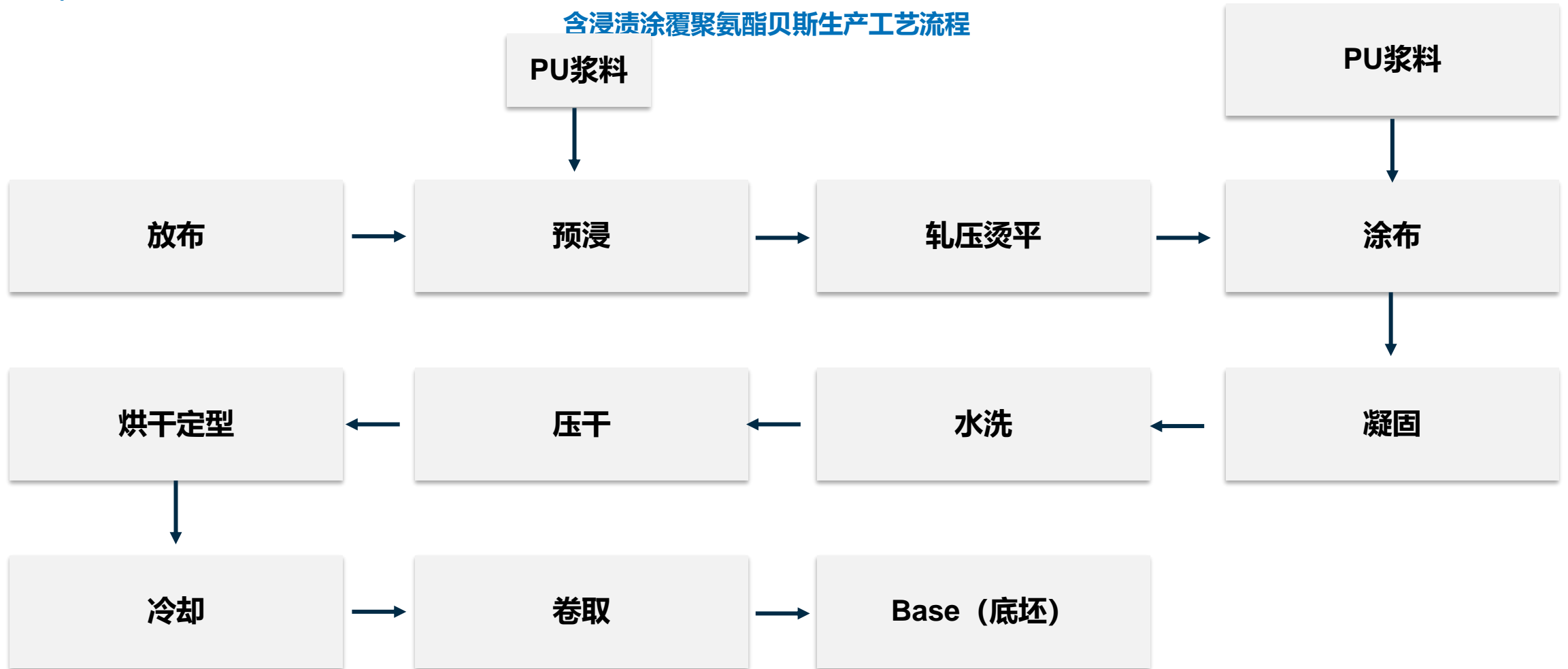


Manufacturing method of PU synthetic leather PU合成革生产方法

Wet process 湿法

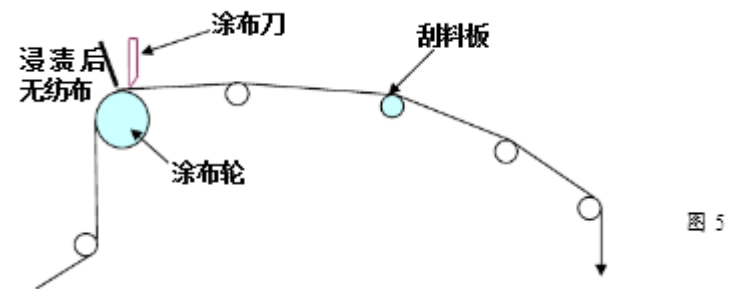
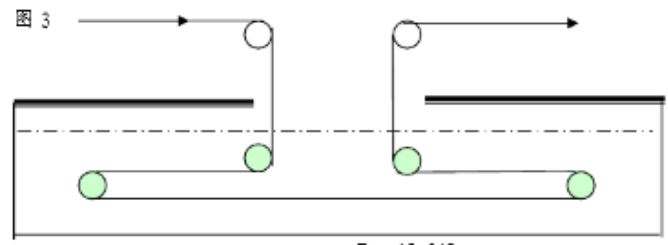
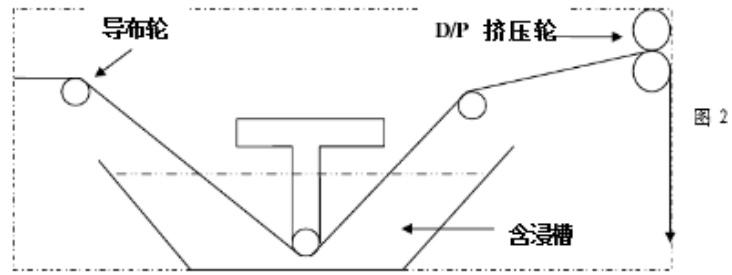
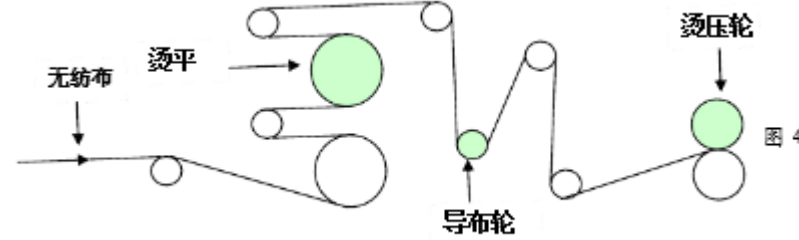
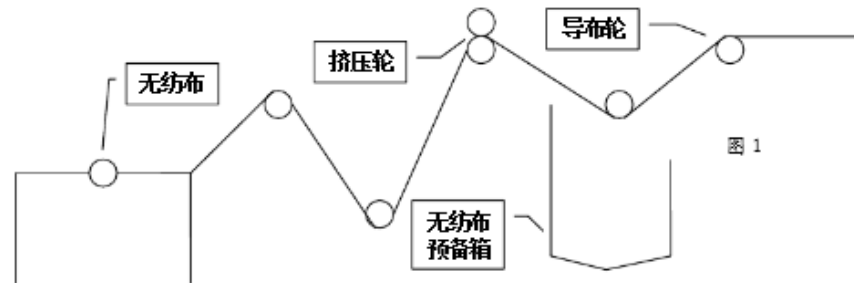
Soaking and coating(wet): PU base manufacturing process flow chart

含浸渍涂覆聚氨酯基生产工艺流程



Manufacturing method of PU synthetic leather PU合成革生产方法

Wet process 湿法



Manufacturing method of PU synthetic leather PU合成革生产方法

Raw material for PU Synthetic leather PU in wet process 湿法PU合成革原材料

- Base cloth 基布: Woven fabric for artificial leather, Non-woven fabric for synthetic leather
- Resin 树脂: PU
- Lignin powder 木质粉: Using a certain amount of wood powder can not only reduce the cost of products, but also play a skeleton role in the solidification process 使用一定量的木质粉, 既能降低产品成本, 又能在凝固过程中起到骨架的作用
- Anionic surfactant 阴离子表面活性剂: It mainly accelerates the exchange rate of DMF and water and improves the solidification rate. At the same time, the cell is compacted. Anionic surfactants can form spherical cell structure. 主要起加快DMF与水的交换速度, 提高凝固速度的作用。同时, 使泡孔细密化。阴离子表面活性剂可生成球形泡孔结构。
- Non ionic surfactant 非离子表面活性剂: Because of its hydrophobicity, it can postpone the solidification speed of the surface, so it can make the internal DMF exchange with water more quickly and fully. Non ionic surfactants can form acicular pore structure. 由于具有疏水性, 可推迟表面的凝固速度, 因此可使内部的DMF与水更快更充分地交换。非离子表面活性剂可生成针状的泡孔结构
- DMFa 二甲基甲酰胺 : Work as solvent 作为溶剂

Manufacturing method of PU synthetic leather PU合成革生产方法

Wet process 湿法

Basic receipt of impregnating slurry 湿法浸渍浆料的基本配方:

原料名称	材料用量/(质量分数)
湿法聚氨酯树脂	100
DMFa	150~400
非离子凝固调节剂	0.5~1.5
阴离子凝固调节剂	0~1.5
填料 (木质粉)	0~10
着色剂	0~3

Manufacturing method of PU synthetic leather PU合成革生产方法

Wet process 湿法

Basic receipt of coating slurry 湿法涂层浆料的基本配方:

原料名称	材料用量/%(质量分数)
聚氨酯树脂 (成膜剂)	100
DMF(溶剂)	35~150
阴离子凝固调节剂	0.5~2.5
非离子凝固调节剂	0.5~1.5
消泡剂	0.1~0.5
流平剂	0.5~1.0
填料	0~60
色浆	0~15

Manufacturing method of PU synthetic leather PU合成革生产方法

Wet process 湿法

Basic receipt of impregnating and coating slurry 湿法浸渍涂层浆料的基本配方:

原料名称	浸渍浆料配方	涂层浆料配方
聚氨酯树脂 (成膜剂)	100	100
DMFa (溶剂)	400~800	40~120
阴离子凝固调节剂	0~1.5	0.5~2.5
非离子凝固调节剂	0.5~1.5	0.5~1.5
消泡剂	0~0.5	0.1~0.5
流平剂	-	0.5~1.0
填料	-	15~40
色浆	0~15	0~15

Water-based PU Synthetic Leather 水性聚氨酯合成革

- Water-based polyurethane is polyurethane with water as dispersing medium
水性聚氨酯是以水作为分散介质的聚氨酯
- The core of water-based polyurethane synthetic leather is the introduction of hydrophilic groups
水性聚氨酯合成革的核心是亲水基团的引入
- The properties of water-based polyurethane mainly depend on the composition of hard and soft segments and the types of ions
水性聚氨酯的性能主要取决于软硬链段的组成和离子的种类
- Advantage 优点:
Environment friendly 环保
- Disadvantage 缺点:
Poor water resistance and high cost 耐水性差、成本高
Film forming time is longer than solvent-based PU 成膜时间比溶剂型PU长

Water-based PU Synthetic Leather 水性聚氨酯合成革

Water-based PU Slurry receipt of surface layer 表层水性聚氨酯浆料配方

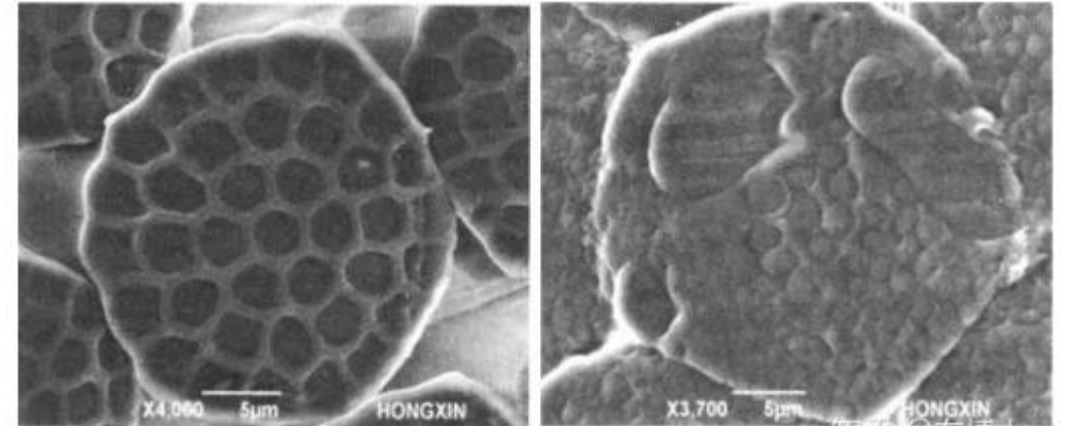
材料名称	用量、份	材料的作用
硬性聚氨酯	70	成膜剂
中硬聚氨酯	30	成膜剂
水性色浆	12~18	着色剂
助剥离剂	0~3	提高涂层的剥离效果
增稠剂	0.5~1	调节树脂粘度
手感剂	0~0.5	调节表面的手感

Water-based PU Slurry receipt of top layer 面层水性聚氨酯浆料配方

材料名称	用量、份	材料的作用
中硬聚氨酯	100	成膜剂
水性色浆	12~18	着色剂
增稠剂	0.5~1	调节黏度

Ultrafine fiber synthetic leather 超细纤维

- Formed by embedding one polymer in a very fine form (island phase) in another polymer (marine phase). Because the dispersed fibers are island-like in the cross-section of the fibers and the continuous matrix is sea-like, they are called Marine-island fibers. 由一种聚合物以极细的形式(岛相)包埋在另一聚合物(海相)之中形成的。因分散相原纤在纤维截面中呈岛屿状态,而连续相基质呈现出海的状态,因此被形象地称之为海岛纤维。
- The island components of marine-island fibers are generally polyester (PET) or polyamide (PA); the sea components can be polyethylene (PE), polyamide (PA or PA66), polypropylene (PP), polyvinyl alcohol (PVA), polystyrene (PS), acrylate copolymer or modified polyester, etc. 海岛纤维的岛组分一般采用聚酯(PET)或聚酰胺(PA);海的组分可以是聚乙烯(PE)、聚酰胺(PA或PA66)、聚丙烯(PP)、聚乙烯醇(PVA)、聚苯乙烯(PS)以及丙烯酸酯共聚物或改性聚酯等。



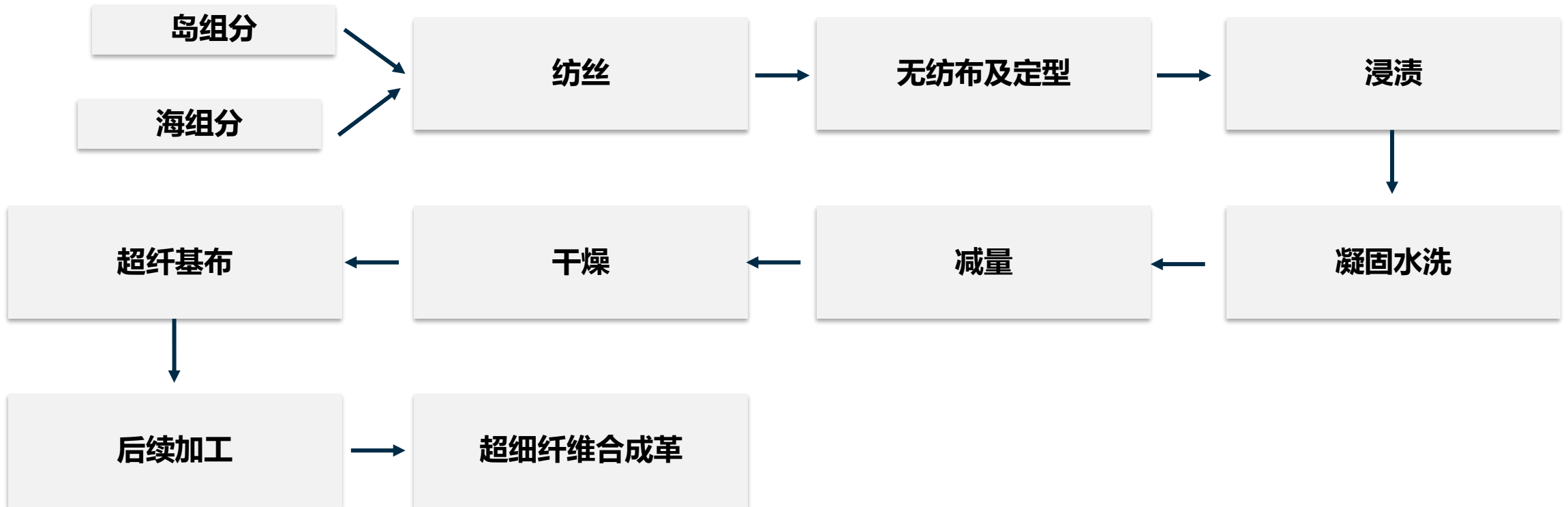
定岛海岛纤维截面

不定岛纤维截面



Manufacturing method of Ultrafine fiber synthetic leather 超细纤维合成革生产方法

Marine-Island method: Ultrafine fiber synthetic leather manufacturing process flow chart
海岛法：超细纤维合成革制造工艺流程图



Negative effects of Man-made Leather on Environment 人工革对环境的影响

Solvent-based resins are used in traditional manufacturing processes of man-made leather, synthetic leather and super-fibre leather wastes for dry-wet surface-making, wet filling, bonding and finishing. The volatilization of organic solvents in slurries is the main source of environmental pollution.

在传统的人造革、合成革和超纤革废制造工艺中均使用溶剂型树脂，用于干湿法造面、湿法填充、黏结、后整理涂饰等，浆料中的有机溶剂的挥发是环境污染的主要源头。

- Synthetic leather industry: Because of the single solvent component (mainly DMF), most organic solvents can be recovered by distillation column with a recovery rate of about 90%, which has little impact on the environment. However, the solvent component is complex (including DMF, toluene, acetone, formaldehyde, acetate) in the process of dry-process bass manufacturing and finishing, which has strong volatility and solvent is very difficult to recover.

合成革行业：湿法贝斯制备过程中，由于溶剂组分单一（主要为DMF），大部分有机溶剂可通过精馏塔回收利用，回收率在90%左右，对环境影响较小；但在干法贝斯制造和后整理过程中溶剂组分复杂（含DMF、甲苯、丙酮、甲缩醛、乙酸酯类），挥发性强，溶剂回收相当困难；

- The main pollution in the production line of superfine fibre synthetic leather is the high concentration alkali or toluene wastewater produced in the reduction process. Especially alkali reduction wastewater, which contains a large number of ethylene glycol organic compounds produced by hydrolysis of polyester fibers and sodium terephthalate in the form of sodium salt under alkaline conditions. The COD value of this wastewater is over 20 000 mg/L.

超细纤维合成革生产线上的污染主要是减量工序产生的高浓度碱或甲苯废水。尤其是碱减量废水，其中含有大量涤纶水解生成的乙二醇有机物及在碱性条件下以钠盐形态存在的对苯二甲酸钠。这种废水的COD值高达20000mg/L以上。

Activity 活动

Which chemical residual could be present in finished PU Synthetic Leather?
在成品PU合成革中可能有哪些化学品残留?

Chemical's Application in Leather Industry

化学品在皮革工业中的应用



Leather 皮革

Leather manufacturing process 皮革加工过程

- From a raw leather with fur to a leather that meets the requirements of use, it must undergo three major sections, namely, preparation section, tanning section and finishing section (from raw leather to leather, this qualitative change is achieved in tanning section). 从一张带毛生皮，制造成符合使用要求的革，须经过三个大工段，即准备工段、鞣制工段和整理工段(由皮变到革，这一质的变化是在鞣制工段实现的)。
- The task of the preparation section is to remove all the fur on the skin, the contaminants attached to the skin and the subcutaneous tissues that are not needed in leather making, so that the raw leather can meet the requirements of suitable tanning. 准备工段的任务是把皮上的毛，所附的污物及制革所不需要的那些皮下组织，统统去掉，使生皮达到适宜鞣制的要求。
- Preparatory section is the basis of leather making, which has a great relationship with the quality of finished leather. If the preparation section is not handled properly, it is difficult to find a remedy in the later process. Therefore, we must attach great importance to the strict control of each process operation in the preparation section. 准备工段是制革的基础，对成品革的质量关系极大，如果在准备工段处理不当，以后工序很难找到补救的办法。因此，必须高度重视，严格控制准备工段的每一道工序操作。

Leather 皮革

Leather manufacturing process - Preparatory section 皮革加工过程-准备工段

- Peeling: Peeling the skin off an animal. 剥皮：把皮从动物体上剥下来
- Antisepsis: Prevent decay during transportation or preservation. Such as salting and so on.
防腐：在运输或保存期间防止腐烂。如用盐腌等
- Immersion: Remove sediment, feces, blood and preservatives from the skin; dissolve soluble proteins such as albumin and globulin in the skin; restore the microstructures and sufficiency of the raw skin to the state of fresh skin, making it suitable for the subsequent processing procedures.
浸水：除去皮上的泥沙、粪便、血液和防腐剂等污物；溶解皮中可溶性蛋白质、如白蛋白、球蛋白；使原料皮在显微结构和充分度方面回复到接近鲜皮状态，使之适宜于以后各工序加工
- Degreasing: The process of removing grease from skin by mechanical and degreasing agents is called degreasing. Most of the grease can be removed by alkaline leaching and enzymatic softening, and the quality of the finished leather will not be affected by degreasing. However, skins containing more fat, such as pigskin and sheep skin, must be degreased.
脱脂：使用机械和脱脂剂把皮中油脂除去的过程叫做脱脂。脂肪含量不多的原料皮通过浸碱、酶软化工序可除去大部分油脂，一般不经脱脂工序也不会影响成革质量。但对含脂肪多的原料皮如猪皮、绵羊皮等必须进行脱脂操作。
- Meat removal: Remove unwanted fat and appendages. Meat removal is done manually or mechanically.
去肉：去掉不需要的脂肪和附肉，有手工或机械去肉

Leather 皮革

Leather manufacturing process - Preparatory section 皮革加工过程-准备工段

- Lime soaking: Lime and other additives are used to loosen and loosen the hair, remove fat and appendages, and "expand" the raw skin to prepare for tanning
浸灰：使用石灰等助剂，使毛松动、松散，除去脂肪及附肉等，以及使生皮“膨胀”，为鞣制做准备
- Hair removal: removal of hair from the skin, such as lime, sodium sulfide, or enzyme + salt activator or inhibitor (soaking is one of the methods of hair removal)
脱毛：从皮上除去毛，如：石灰、硫化钠等或者酶+盐类激活剂或抑制剂（浸灰是脱毛的方法之一）
- Deashing: neutralizing alkali in lime-soaking skin. After alkali expansion treatment, raw skin has a high PH value and contains Ca, Na and other cations in the skin. Fiber gap is filled with various ions and water molecules, and the skin is stiff and expandable, which is not suitable for later processing. Therefore, it is necessary to dealkali.
脱灰：中和浸灰皮中的碱，经碱膨胀处理后，生皮的PH值高，皮内含有Ca、Na等多种阳离子，纤维间隙被多种离子和水分子充塞，皮身挺硬膨胀、不适于后工序加工，因此必须进行脱碱
- Softening: Softening and whitening the skin, such as trypsin, protease, etc.
软化：使皮柔软、洁白，如用胰酶、蛋白酶等
- Soaking: Fermentation softening or acidification to give raw skin a suitable tanning acidity
浸酸：发酵软化或酸化，使生皮具有合适鞣制的酸度

Leather 皮革

Leather manufacturing process - Tanning section 皮革加工过程-鞣制工段

- Prepared raw skins are suitable for any tanning method, such as vegetable tanning or **chrome tanning** or alum tanning or oil tanning or aldehyde tanning.

准备好的生皮，无论用哪种方法，如植物鞣法或**铬鞣法**或明矾鞣法或油鞣法或醛鞣法等鞣制都是适宜的

- Principle of leather tanning 皮革鞣制的原理：

Through a series of processes and some chemicals, a series of changes of proteins in animal skin were made and collagen was denatured. Tanned leather is soft, firm, wear-resistant and not easy to spoil.

通过一系列工艺，并采用一些化学药剂，使动物生皮内的蛋白质发生一系列变化，使胶原蛋白发生变性做哟个。鞣制后的皮革即柔软、牢固，又耐磨、不容易腐败变质。



Leather 皮革

Leather manufacturing process – Finishing section 皮革加工过程-整理工段

The task of finishing section is to make leather possess the required physical-mechanical and external properties. 整理工段的任务是使革具有所需要的物理-机械性质和外观性质。

The finishing process varies greatly for different kinds of leather. The general process is as follows: 整理工序对不同品种的皮革变化很大, 大致的工序如下:

- Cut or peel evenly: to make the thickness uniform 削匀或片皮: 使厚度均匀
- Washing: Removing excess chromium salts or neutralized salts 水洗: 除去多余的铬盐或中和的盐类
- Neutralization: adjusting pH value 中和: 调节PH值
- Dyeing: Give leather the color it needs 染色: 赋予革所需颜色
- Emulsion oil: use a way of oil to make leather soft or feel good. 乳液加油: 采用一种加油的方法使皮革柔软或手感好
- Flattening: Eliminate wrinkles and excess moisture 平展: 消除皱纹和除去多余水分
- Dry 干燥
- Painting or polishing: improving the appearance of leather 涂饰或上光: 改善革的外观
- Smoothing or ironing or embossing: polishing is done by pressure; ironing is done on a hydraulic press to smooth the leather; embossing is done on a press to produce various patterns. 打光或熨平或压花: 打光是用压力磨光; 熨平是在液压熨平机上熨平, 使革光滑; 压花是在压花机上压花, 压出各种式样的花纹

Activity 活动

Which chemical Residual could be present in finished Leather?
在成品皮革中可能有哪些化学品残留?

Chemical Application in Apparel and Textile Industry

化学品在纺织服装工业中的应用



Question: How the cotton becomes an apparel products

问题：棉花是怎样变成服装产品的？

- | | | | |
|---------------|--------------------|----------------------|------------------|
| 1) Sewing 车缝 | 6) Weave 梭织 | 11) Sliver 棉条 | 16) Scutching 清棉 |
| 2) Washing 水洗 | 7) Seeds Cotton 籽棉 | 12) Gray Fabric 坯布 | 17) Spinning 纺纱 |
| 3) Cutting 裁剪 | 8) Fabric 织物 | 13) Final product 成品 | 18) Finishing 整理 |
| 4) Yarn 纱 | 9) Dyeing 染色 | 14) Printing 印花 | 19) Knitting 针织 |
| 5) Lint 皮棉 | 10) Carding 梳理 | 15) Twist 捻线 | 20) Ginning 轧花 |

Chemical's Application in Apparel and Textile Industry

化学品在服装纺织工业中的应用

How to understand the apparel and textile industry?

怎样理解服装纺织工业？

3 main factors: textile material, textile chemicals, textile manufacturing process;

三大要素：纺织材料，纺织化料，纺织加工过程；

Textile Material: providing manufacturing base; 纺织材料：提供本底；

Textile Chemical: achieve color and other functions; 纺织化料：实现颜色和实现各种功能的原料；

Textile Manufacturing Process: The technology that apply textile chemical on the textile material.

纺织加工过程：将纺织化料应用于纺织材料的方法。

Cotton and Cotton Field 棉花和棉田



关于棉花的部分环保相关认证：Certificate for cotton



- Chemicals component : Fertilizer and biocide
- 化学品应用：化肥和农药

Ginning 轧花



- ❑ Remove the cotton shell, and seeds, break up the cotton boll, and compress.
- ❑ 去皮，去籽，打散，压缩，纯粹的物理过程。

Opening and scutching 开清棉



- ❑ **Opening cotton:** release the compressed cotton to cotton flocks;
开棉：将紧压的原棉松解成较小的棉块或棉束，以利混合、除杂作用的顺利进行；
- ❑ **Scutching:** Furtherly remove the impurities, and useless short fibers;
清棉：清除原棉中的大部分杂质、疵点及不宜纺纱的短纤维。
- ❑ **Fixing:** Fix the cotton fibers in different length together to make sure the steady quality of the cotton sliver.
混棉：将不同成分的原棉进行充分而均匀地混和，以利棉纱质量的稳定。

Carding 梳理



- ❑ Carding, removing the impurity, fixing, and slivering are totally physical process.
梳理，除杂，混合，成条，基本上完全物理过程。

Spinning and Twisting 纺纱



- ❑ Spanning means from sliver to thinner yarn; 捻纱主要指的是从棉花到纱线;
- ❑ Twisting means from yarn to thicker thread; 而捻线的目的是将多跟纱线合并用以增加线的强度;
- ❑ Twist and Spinning is almost a pure physical process; 捻纱，并线是纯物理过程。

Knitting and Weaving 织布：针织与梭织



- ❑ Question: What's the difference between Knitting and Weaving? 问题：针织和梭织有什么区别？
- ❑ Chemicals component Knitting oil and sizing agent. 化学品应用:针织油和织布浆料。

Dyeing-Pretreatment 染色-前处理



- ❑ The purpose of pretreatment is removing the impurities, and prepare for the dyeing;前处理的主要目的是去除杂质（仅保留纤维素），以及为上染做好其他方面的准备；
- ❑ singeing, desizing, scouring, Bleaching, mercerizing, fluorescent whitening 烧毛，退浆，煮练，漂白，丝光，荧光增白；
- ❑ acid, alkali, salt, desizing agent, bleaching agent, and fluorescent whitening agent.大化料的应用，退浆剂，漂白剂，荧光增白剂。

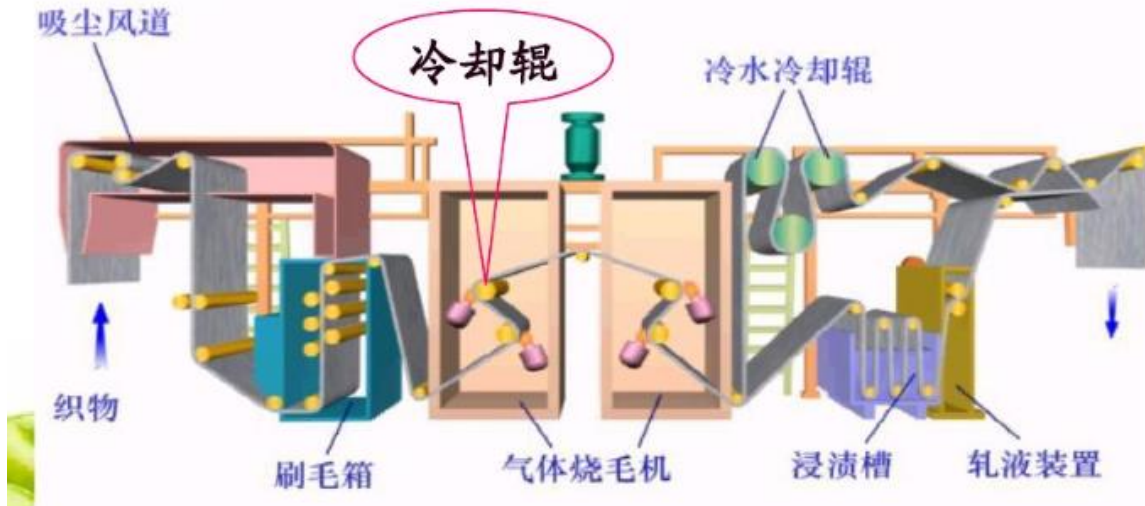
Singeing 烧毛

The purpose of singeing is to remove the small villus on the surface of the fabric. The existing of the villus can cause problems like uneven dyeing, hazy outline, and fuzz ball.

烧毛是为了去除在织布过程中由于摩擦而产生的细小绒毛，绒毛的存在会导致，染色不均，印花轮廓模糊，以及起毛球等品种问题；

Usually, gaseous flame singing method was used, and should use a high temperature and fast speed. In this way it can allow only the villus was burned rather than the fabric.

一般采用气体火焰，高温快烧的方法，仅将绒毛点燃，而不影响织物。



Desizing 退浆

The purpose of desizing process is to remove the sizing agent from the fiber. The sizing agents are often starch (modified starch), polyvinyl alcohol (PVA), polyacrylic acid (PA), and hydroxymethyl cellulose (CMC). Sometimes the sizing agent may include some organic auxiliary, which might be a source of the hazardous substance. The desizing agent's selection should be based on the sizing agents used on the gray fabric.

退浆的目的是去除织布过程为了加强经纱强度而在纱线上涂得一层浆料，最常见的浆料为，淀粉（改性淀粉），聚乙烯醇（PVA），聚丙烯酸（PA），以及羟甲基纤维素（CMC）；有些浆料也含有部分有机助剂，有机助剂的存在时有害物质的可能来源，另外退浆配方的选择应根据浆料的成分来决定。

The sizing agents are mainly: caustic soda, starch amylase; and oxidizing agent. Some time organic auxiliary also used in the desizing process.

退浆剂主要包括，烧碱，淀粉酶，氧化剂，以及一些有机助剂。

The desizing process can be continuous or non continuous, but the trend is continuous.

退浆可以是连续式退浆或非连续式退浆，但是连续式退浆是行业的发展趋势。

Sourcing agent 煮练

The purpose of the sourcing process is to remove the natural impurity in the cotton fiber. Apart from cellulose, semi-sellulose, pectin, waxiness, cotton seed shell, and natural colorant need to be removed.

煮练的目的是去除纤维内部的非有效成分的杂质，对于棉织物，就是去除所有除纤维素之外的杂质，包括半纤维素，果胶，蜡质，棉籽壳，以及天然色素；

The sourcing agents are mainly alkali and enzyme, while other assistant sourcing agents are surfactant, sodium silicate, sodium sulfite.

主要的煮练剂包括，烧碱和生物酶，同时还需要应用多种助练剂，例如，表面活性剂，硅酸钠，亚硫酸钠，等

Question:

What's the difference between desizing and sourcing process?

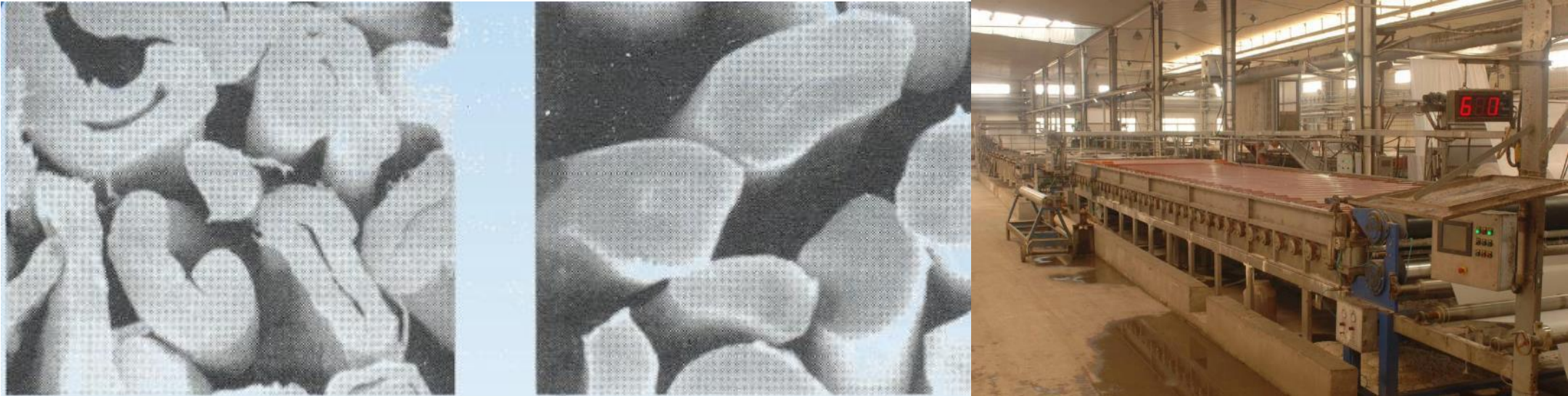
退浆和助练过程有哪些异同之处？

Mercerization 丝光

An special manufacturing process for cotton, ramie, and viscose fiber:

一种针对棉，麻，黏胶纤维的特殊的加工工序；

By using the tension inside of the fabric, caustic can make the fiber molecule swelling, which will bring the fabric glossiness on the surface: 丝光是在张力的作用下，利用烧碱溶液在一定温度下，使得纤维溶胀，从而增加棉，麻，黏胶纤维表面光泽度的一类工序。



Fluorescent brightening 荧光增白

After bleaching, Fluorescent brightening is a process in order to achieve better white and bright degree.
漂白后，为了在织物上获得更高的白度，和鲜艳度的一种工序。

Fluorescent brightening agent can absorb UV-light (ultraviolet light) and emit blue-violet light, so it is regarded as a fluorescent brightening dye or a white dye.

荧光增白剂能吸收近紫外光而发射蓝紫光，可以被看做一种荧光染料，或白色染料。

The difference between fluorescent brightening agent and bleaching agent is that the bleaching agent's function is breaking the conjugated double bond structure on the fabric to achieve no color effect, but fluorescent agent is by its own characteristics, and will not break the fabric structure.

荧光增白与漂白的区别在于，漂白的原理是通过破坏共轭双键来达到无色效果，而荧光增白是通过自身的特点显色，不会破坏原有纤维结构。

Alkali peeling 碱减量

Alkali peeling is a special pre-treatment process for polyester fabric. In the high temperature and high concentration caustic soda solution, the molecular structure of the polyester will be broken down, the weight will be reduced, the fibre diameter will be getting thinner, and the surface of the fiber will be poned. All these changes, can give the fabric a silk like glooming and softer touch feeling, and it also improves the hygroscopicity and breathability

碱减量是针对涤纶纤维的一种特殊前处理工艺，在高温和较浓的烧碱液中处理涤纶织物，涤纶表面蚀刻后质量变轻，纤维直径变细，表面形成坑洼，使织物具有如真丝一般的光泽，和手感，并且也会改善涤纶的吸湿性和透气性；

The alkali peeling agent are mainly caustic soda, potassium hydroxide, sodium carbonate, and the caustic soda is the most frequently used chemical.

碱减量的化料主要为氢氧化钠，氢氧化钾，碳酸钠等，但以氢氧化钠居多；

The auxiliary can help to promote the alkali peeling section, main auxiliary are quaternary ammonium salt cationic surfactants, cationic polymers.

另外，加入碱减量促进剂能促进碱减量的发生，主要助剂有季铵盐阳离子表面活性剂，阳离子聚合物等

碱减量之后的织物应尽快进行酸中和水洗，以去除碱的存在，避免残留的碱和染料的水解反应。

Dyeing-Dyeing and printing 染色-上染与印花



□Dyeing: allow the fabric and the dye stuff bond together; 上染的目的是使织物和染料结合在一起;

□Chemicals application: dye stuffs, leveling agent, dye-fixing agent, dispersing agent 化学品应用: 各类染料, 匀染剂, 固色剂, 分散剂等助剂;

Dyeing-Finishing 染色-后整理



- Finishing: to achieve some specific functions; 整理的目的是预缩定型，以及实现织物的某些功能；
- Chemical application: Antistatic agent, anti-bacteria agent, water proof agent, flame retardant, softening agent, soaping agent, coating treatment. 化学品应用：防静电剂，抗菌剂，防水剂，阻燃剂，柔软剂，皂洗剂，覆膜等

Cutting, sewing and washing 剪裁,车缝,水洗



□ 剪裁，车缝基本上是纯物理过程，水洗工艺需要清洗剂的参与。

Cutting and sewing are almost pure physical process; washing process needs cleaning agent participation.

Apparel and textile industry supply chain mapping

纺织服装工业供应链一览



A physical Process
物理过程

A physical and chemical Process
物理与化学过程

Quiz 小测试

Which chemical residual could be present in finished textile?

在成品布料上可能有哪些化学品残留？

(solved by trainers and trainees together)

Module 8: Chemicals in Adhesives

模块八：胶黏剂中的化学物质

TÜV Rheinland
March 2019



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01. Footwear Manufacturing Process 制鞋工艺

- Gluing Process 胶粘工艺
- Vulcanization process 硫化鞋工艺
- Injection Process 注塑鞋工艺
- Molding Process 模压鞋工艺
- Sewing Process 缝制鞋工艺

02. Adhesive 胶黏剂

- Composition of Adhesive 胶黏剂的构成
- Classification of Adhesive 胶黏剂分类
- How does Adhesive work? 胶黏剂怎么作用?

03. Commonly used Adhesive in footwear industry 制鞋常用胶黏剂

- Rubber adhesive 橡胶胶黏剂
- PU Adhesive 聚氨酯胶黏剂
- Selection of Adhesive 胶黏剂的选择
- Domestic Requirements on Adhesive 国内胶黏剂要求

Learning objectives 学习目标:

1. To review typic shoe manufacturing processes 审查典型的制鞋工艺
2. To learn different types of adhesive and its chemical components 学习不同类型的粘合剂及其化学成分
3. To learn different solvents used in different adhesive system 学习不同的溶剂在不同的粘合剂体系中的应用
4. To learn how to speed up the VOC's evaporation in factory side 了解如何加速VOC在工厂的蒸发
5. To learn about the advancement of water based adhesives 了解水基胶粘剂的发展

Target Group 目标群:

5% of participating factory workers may include: 工厂5%的员工应包括:

- 1.High management: factory Board Chairman, Managing Director, General Manager 高层: 董事长、常务董事、总经理;
2. Department Manager in Quality, EHS, R&D, Manufacturing, Purchasing, IT, HR, Sales, and Admin 部门经理 (质量、EHS、研发、生产、采购、IT、人力资源、销售、行政)
3. All staff in quality department, lab, and EHS department 质量部门、实验室和EHS部门的所有员工
- 4.Shift leaders in each manufacturing line, in chemical warehouse 每条生产线、每个化学品仓库领班
- 5.All interested workers are welcomed 所有感兴趣的员工
6. Minimum 10 people for each factory 每家工厂至少10人

Length: 时长

3 Hours 3小时

Training outcomes 培训成果

By the end of this training, you should be able to ...

培训结束后，您应该能够

- Know adhesives work and how to choose appropriate adhesives
了解粘合剂的工作以及如何选择合适的粘合剂
- Know what potential hazardous substances exist in adhesives
了解粘合剂中存在的潜在危险物质
- Purchase glues according to Chinese regulation
按中国规定购买胶水
- Understand the advantages and disadvantages in water based adhesive
了解水性胶粘剂的优缺点

Footwear Manufacturing Process

制鞋工艺



Footwear Manufacturing Process 制鞋工艺

5 types of shoes Manufacturing Process 五种制鞋工艺

- Glueing Process 胶粘工艺
- Vulcanization process 热硫化工艺
- Injection Process 注塑工艺
- Molding Process 模压工艺
- Sewing Process 缝制工艺



Footwear Manufacturing Process 制鞋工艺

Glueing Process 胶粘工艺

Glueing technology, also known as cold bonding technology, is the use of adhesives to connect the upper, inner sole and outer sole together. Due to the differences among materials of upper and sole adhesives, the types and properties of adhesives used are different, such as chloroprene adhesives, polyurethane adhesives, SBS adhesives, etc. Because of its simple technology, short production cycle, high production efficiency, low manufacturing cost, fast variety change and easy to expand reproduction, Gluing technology is the most widely used assembly technology in shoemaking industry, accounting for more than 80% of the total shoemaking products. This technology is most widely used in leather shoes and sports shoes.

胶粘鞋工艺也称冷粘工艺，是利用粘合剂将鞋帮、内底、外底连接在一起的工艺方法。由于鞋帮和鞋底粘合面材料的不同，所使用粘合剂的类型和性质也不同，如氯丁胶粘剂、聚氨脂胶粘剂、SBS胶粘剂等。由于胶粘工艺的工艺简单、生产周期短、生产效率高、制造成本低、花色品种变化快、易于扩大再生产，所以在制鞋工业中是应用最多的装配工艺，占制鞋产品总量的80%以上。该工艺在皮鞋、运动鞋产品中应用最多。



Footwear Manufacturing Process 制鞋工艺

Vulcanization process 硫化鞋工艺:

It is a process of vulcanizing the raw rubber film such as outsole, strip and outsourcing head in a vulcanization tank by heating and pressing after bonding with the upper. The outsole of the process is partially mouldless (calendering) and moulded. Because the process is relatively rough and the quality is not easy to control, it can only produce low-grade products. In recent years, due to the introduction of advanced production technology from abroad, the product grade has been greatly improved. Because vulcanized shoes are comfortable and economical in wear, efficient in production and cost-effective, this technology is still applied in the production of rubber cloth shoes, rubber shoes and leather shoes, and the production is large.

硫化工艺是将外底、沿条和外包头等生胶片与鞋帮粘合后，在硫化罐中加热加压而硫化成型的工艺方法。该工艺的外底分无模（压延）成型和有模成型。因工艺相对粗糙、不易控制品质，通常只能生产低档产品。近年来，由于国外先进生产技术的引进，产品档次有了较大提升。由于硫化鞋在穿着上具有舒适和经济、在生产上具有效率高和成本低的特点，所以在布胶鞋和胶鞋以及皮鞋生产中仍应用此工艺，且生产量大。



Footwear Manufacturing Process 制鞋工艺

Injection Process 注塑鞋工艺:

Injection moulding process is a process that melted plastic is injected into the external mould and bonded with the upper. The materials of outsole are polyvinyl chloride, thermoplastic polyurethane, thermoplastic rubber, etc. Its technology is to complete the bonding assembly of the bottom under the conditions of automatic feeding, automatic plasticizing, automatic metering, automatic injection, automatic closed die and open die, automatic moulding, so it has the advantages of high production efficiency and automatic production. It is used in the production of leather shoes, cloth shoes, sports shoes and plastic shoes.

注塑工艺是将熔融的塑料注射入外模具并与鞋帮粘合为一体的工艺方法。外底的材料多为聚氯乙烯、热塑性聚氨脂、热塑性橡胶等。其工艺是在自动送料、自动塑化、自动计量、自动注射、自动闭模和开模、自动成型的条件下完成帮底粘合装配的，所以具有生产效率高和自动化生产的优势。它在皮鞋、布鞋、运动鞋、塑料鞋生产中都有应用。



Footwear Manufacturing Process 制鞋工艺

Molding Process 模压鞋工艺:

Molding process is a process of bonding the outsole and the upper of the shoe by using the rubber material flow and clamping pressure produced during the vulcanization process of the rubber outsole. Its outsole and upper are bonded under high temperature and high pressure, so the moulding technology has the characteristics of firm bottom bonding, not easy to be tackless, wear resistance and flexibility resistance. Because of the long production cycle and the slow variety of patterns, the moulding process is suitable for the production of large batches of products. Safety shoes, mountaineering shoes, military and Police shoes and other products are mostly produced by moulding process. Molding process is a kind of molded vulcanization process derived from moldless vulcanization process, which is mostly used in leather shoes.

模压工艺是利用橡胶外底在模具硫化过程中所产生的胶料流动和合模压力，将外底和鞋帮粘接在一起的工艺方法。其外底和鞋帮是橡胶的高温 and 高压下粘合连接的，所以模压鞋工艺具有帮底粘合牢固且不易开胶和耐磨、耐曲挠的特点。由于模压鞋的模具生产周期长和花色品种变化慢，因此它适合批量大的产品的生产。劳动保护鞋、登山鞋、军警鞋等产品多采用模压工艺生产。模压工艺是由无模硫化工艺而衍生的有模硫化工艺，多用于皮鞋产品。



Footwear Manufacturing Process 制鞋工艺

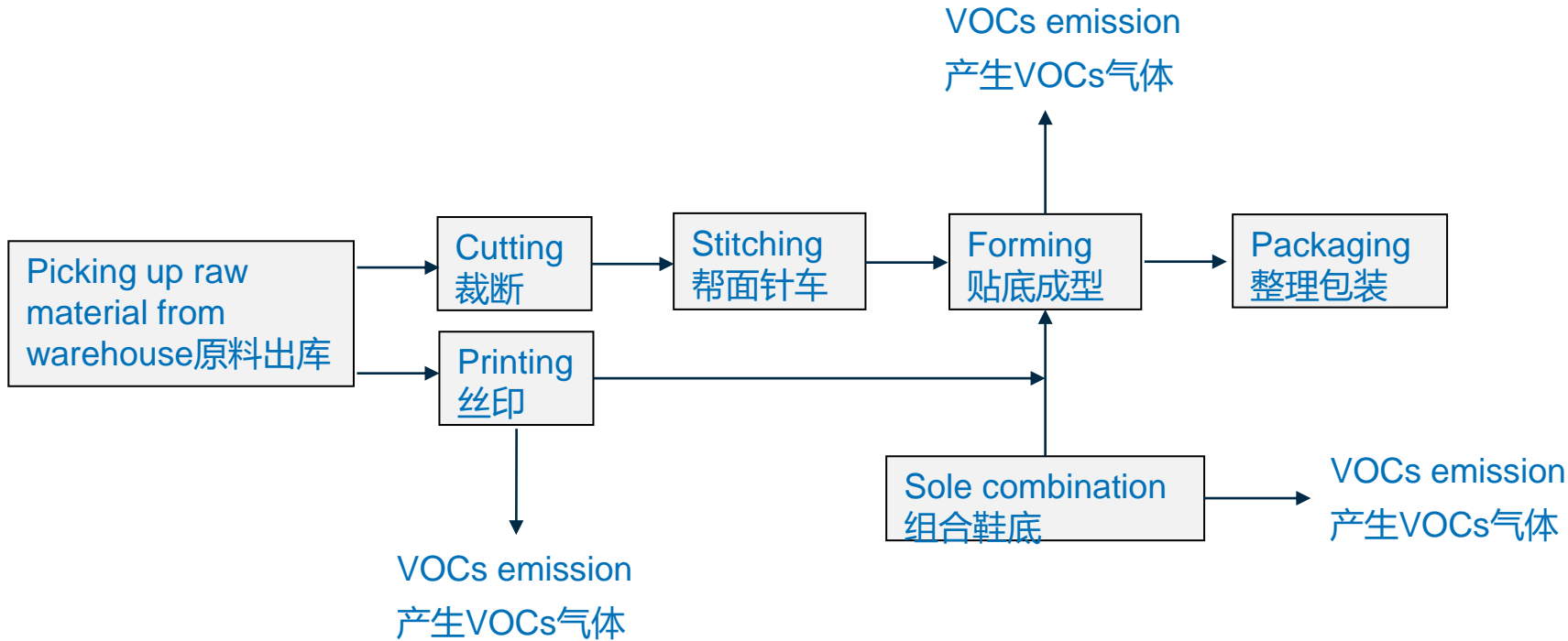
Sewing Process 缝制鞋工艺:

Sewing technology is the process of sewing the upper, sole and other connecting parts together by sewing thread. The sewing thread used is ramie yarn, which has the characteristics of high strength, low elongation, fast moisture absorption and moisture removal, and high wear resistance. Sewing shoe technology is most widely used in leather shoes products, mainly sewing welt leather shoes, sewing flanging leather shoes and so on. Although the process has a long history, complex operation and low production efficiency, the product structure, style and durable characteristics are irreplaceable by other processes. With the development and improvement of machine sewing technology, it is more in line with the needs of modern production and consumption, thus occupying an important position in footwear products, and has auxiliary functions in the gluing technology.

缝制鞋工艺是利用缝纫线将鞋帮和鞋底及其他连接部件缝合在一起的工艺方法。所使用的缝纫线是苧麻线，具有强力大、伸长率小、吸湿排湿快、耐磨性能高的特点。缝制鞋工艺在皮鞋产品中应用最多，主要有缝制沿条皮鞋、缝制翻边皮鞋等。其工艺历史虽然悠久、作业复杂、生产效率低，但是产品结构、风格和结实耐用的特点是其他工艺无法取代的。加上机器缝制工艺的发展和改进，是其更加符合现代生产和消费的需求，从而在鞋类产品中占有重要地位，而且在胶粘鞋工艺中具有辅助功能。



Process of shoes - making 制鞋工艺流程



Adhesive 胶黏剂

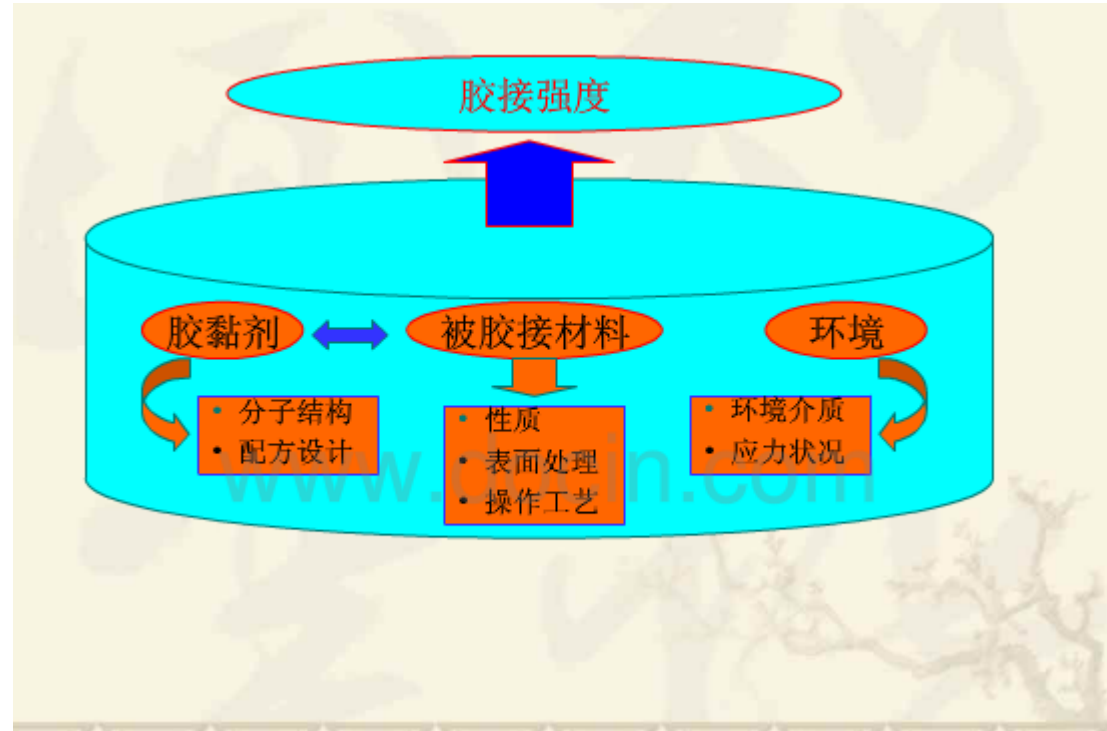


Adhesive 胶黏剂

Definition of Adhesive 胶黏剂的定义

Adhesive is a kind of non-metallic material which can connect two kinds of similar or heterogeneous bonded materials closely through surface adhesion under certain conditions, and can meet certain physical and chemical performance requirements.

胶黏剂是一种在一定条件下能够把两种同类或异类被胶接材料通过表面粘附作用紧密地连接起来起着传递作用，并且能够满足一定物理化学性能要求的非金属物质。



Adhesive 胶黏剂

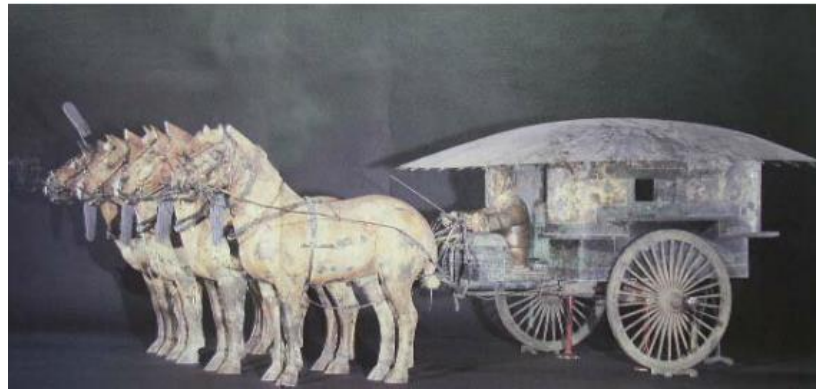
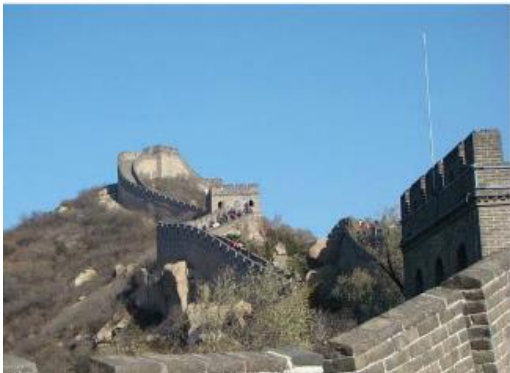
Development of Adhesive 胶粘剂的发展简史

- Adhesive is an old and young material. As early as thousands of years ago, human ancestors began to use adhesives. Many unearthed cultural relics show that:
胶粘剂是一种古老而又年轻的材料。早在数千年前，人类的祖先就已经开始使用胶黏剂。许多出土文物表明:
- Our ancestors used clay, starch and other natural products as adhesives 5000 years ago;
5000年前我们祖先就会用粘土、淀粉等天然产物做胶黏剂;
- More than 4,000 years ago, raw lacquer was used as adhesives and coatings to make appliances;
4000千多年前就会用生漆做胶黏剂和涂料制造器具;
- Animal glue was used as sealant for wooden boats in the Zhou Dynasty 3000 years ago;
3000年前的周朝已用动物胶作木船的填缝密封胶;

Adhesive 胶黏剂

Development of Adhesive 胶粘剂的发展简史

- 2000 years ago, the Qin Dynasty used glutinous rice mortar and lime as mortar to bond the cornerstone of the Great Wall.
2000年前的秦朝用糯米浆与石灰作砂浆粘合长城的基石;
- Phosphate inorganic adhesives were used in the manufacture of large painted copper carriages unearthed from the Museum of Qin Terracotta Warriors
秦俑博物馆出土的大型彩绘铜马车的制造中，用了磷酸盐无机胶黏剂。
- By the beginning of the last century, the invention of synthetic phenolic resin initiated the modern development history of adhesives.
- 到上世纪初，合成酚醛树脂的发明，开创了胶黏剂的现代发展史。



Adhesive 胶黏剂

Development of Adhesive 胶粘剂的发展简史

At present, the application of adhesives has penetrated into all sectors of the national economy, becoming an indispensable technology in industrial production, and also widely used in high-tech fields. 目前，胶黏剂的应用已渗入到国民经济中的各个部门，成为工业生产中不可缺少的技术，在高科技领域中的应用也十分广泛。

For Example 如：

内饰装配粘接：

顶棚，车门内护板，地毯，挡风玻璃等。

汽车结构件粘接：

发动机中罩与前后加强梁，通常用改性环氧树脂胶黏剂。



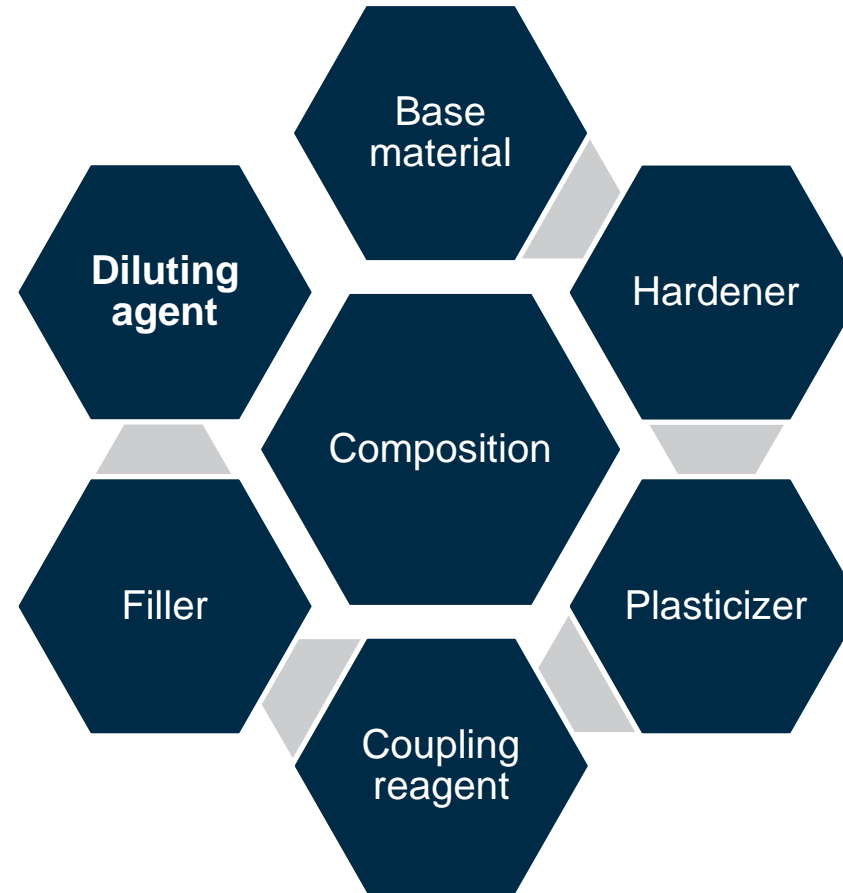
Adhesive 胶黏剂

Development of Adhesive 胶粘剂的发展简史

- With the development of science and technology, the requirements for adhesives and bonding technology in different industries are getting higher and higher. The total demand for adhesives in the world was 17 million tons in 1999 and 25 million tons in 2010.
随着科学技术的发展，目前不同行业对胶黏剂及粘接技术的要求越来越高。1999年世界胶黏剂总需求量为1700万吨，2010年为2500万吨。
- From the perspective of market application, construction industry accounts for 51.8% of the total rubber volume, followed by paper packaging industry, accounting for 12.6% of the total rubber volume, and footwear industry, accounting for 9.0%.
从市场应用看，建筑业用量最大，约占总胶量的51.8%，其次是纸包装业，约占总胶量的12.6%；第三是制鞋业，约占9.0%

Adhesive 胶黏剂

Composition of Adhesive 胶黏剂的组成



Adhesive 胶黏剂

Composition of Adhesive 胶黏剂的组成

- Adhesive: Also known as base material, is the main component of the adhesive. Generally, they are natural polymers and synthetic polymers.

粘料： 又称基料，是胶黏剂的主要成分。一般是天然聚合物和合成聚合物。

Natural Polyester 天然聚合物： Natural rubber, Starch 天然橡胶、淀粉

Synthetic Polyester 合成聚合物： PU, PVA, Neoprene 聚氨酯、聚乙烯醇、氯丁橡胶

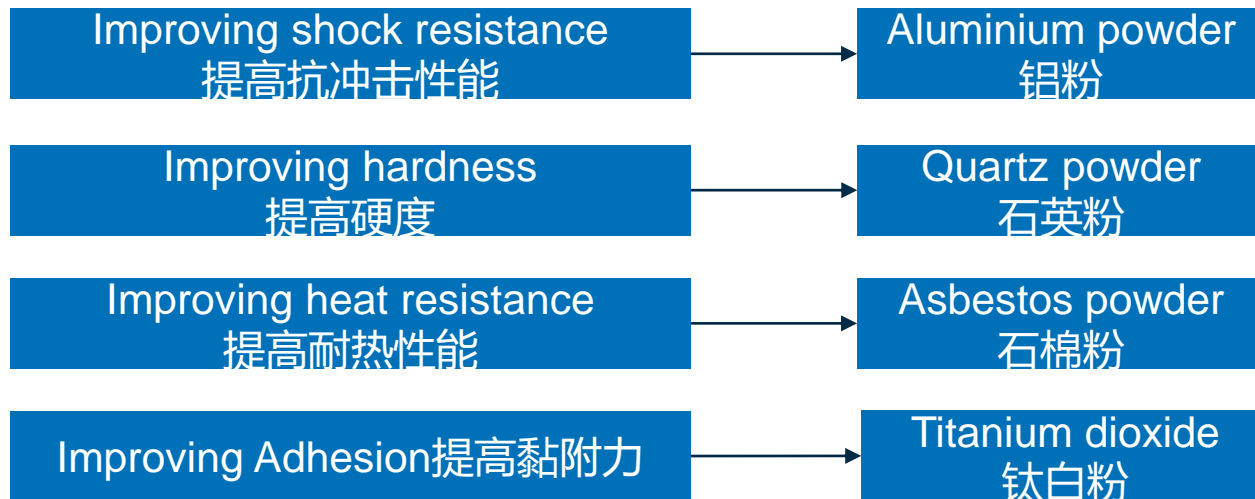
- Hardener: It is a kind of material that makes liquid base material change into high molecular weight solid through chemical reaction, such as polymerization, condensation or cross-linking reaction, so that the bonded joint has mechanical strength and stability.

固化剂： 是使液态基料通过化学反应，发生聚合、缩聚或者交联反应，转变成高分子量固体，使胶接接头具有力学强度和稳定性的物质。

Adhesive 胶黏剂

Composition of Adhesive 胶黏剂的组成

- Filler: It is an inert material that does not participate in the reaction. It can improve the bonding strength, heat resistance, dimensional stability and reduce the cost. It has many varieties, such as asbestos powder, aluminium powder, mica, quartz powder, calcium carbonate, titanium dioxide, talc powder and so on.
填料：是不参与反应的惰性物质，可提高胶接强度、耐热性、尺寸稳定性并可降低成本。其品种很多，如石棉粉、铝粉、云母、石英粉、碳酸钙、钛白粉、滑石粉等。



Adhesive 胶黏剂

Composition of Adhesive 胶黏剂的组成

- Toughener: It can improve the flexibility, reduce brittleness and improve impact resistance of adhesives.
增韧剂：能提高胶黏剂的柔韧性，降低脆性，改善抗冲击性等。
- Diluting agent: Reduce the viscosity of adhesives, easy to operate. There are two kinds of active diluents and inert diluents which can participate in curing reaction.
稀释剂：降低胶黏剂的粘度，便于施工操作，有能参与固化反应的活性稀释剂和惰性稀释剂两种。
- Coupling agent: It has two groups which can be bonded separately by the reaction of adhesives and adhesives. Increase the handover strength.
偶联剂：具有能分别和被粘物及粘合剂反应成键的两种基团。提高交接强度。
- Stabilizers: Components that prevent the change of properties of adhesives during long-term thermal decomposition or storage.
稳定剂：为防止胶黏剂长期受热分解或贮存时性能变化的成分。
- Thixotropic agent: A kind of compounding agent which can prevent the colloidal fluid from hanging by thixotropic reaction and make the 2 colloidal fluid have larger viscosity at static state.
触变剂：利用触变反应，使2胶液静态时有较大的粘度，从而防止胶液流挂的一类配合剂。

Quiz 小测试



Do you know how to classify Adhesives? Which Adhesives are you using now?
你知道怎么给胶黏剂分类吗?
你的工厂正在使用哪种胶黏剂?

Adhesive 胶黏剂

Classification of Adhesive 胶黏剂的分类

- According to chemical constituents 按照化学成分分类:

Chloroprene, modified chloroprene, polyurethane, polyvinyl acetal, polyester, polyamide, EVA, solvent-based natural rubber, SBS

氯丁胶、改性氯丁胶、聚氨酯胶、聚乙烯醇缩醛胶、聚酯胶、聚酰胺胶、EVA胶、溶剂型天然橡胶、SBS胶

- According to morphology 按照形态分类:

Solvent-based Adhesive, water-based Adhesive, solid hot melt Adhesive 溶剂胶、水基胶、固体热熔胶

- According to use 按照用途分类:

合布胶、绷植胶、抿边胶、包头胶、外底胶、围条胶

Glue Types 胶黏剂类型

Solvent based Adhesive 溶剂型胶黏剂

- Solvent based adhesives have dominated the shoemaking industry for decades, but this is mainly attributed to their excellent adhesion to various shoemaking materials, including leather, polymers and fabrics, and they have low requirements for the use of the environment. 溶剂胶胶粘剂在制鞋工业中占主导地位已有数十年，但这主要归因与其对各种制鞋材料都具有很好的粘接效果，这些材料包括皮革、聚合物和织物，而且他们对使用环境的要求比较宽松。
- Because it contains a large number of harmful volatile organic compounds, the common CR adhesive contains about 30% toxic toluene, while the GCR adhesive is almost of all aromatic hydrocarbons. Although PU adhesive uses ethyl acetate with lower toxicity as solvent, its stimulation to human respiratory system and nervous system can not be ignored. Considering environmental protection and safety, the emission of VOC is strictly limited. Therefore, in shoemaking industry, solvent-based adhesives will gradually be replaced by water-based adhesives, and the bonding performance of the latter is gradually steadily improving.因为它含有大量的有害挥发性有机物，CR胶系中，普通CR胶含有30%左右的毒性较大的甲苯，而GCR胶则差不多全是芳烃。PU胶虽多用毒性较低的醋酸乙酯为溶剂，但其对人体呼吸系统和神经系统的刺激也不容忽视。处于环境保护和安全等方面的考虑，对VOC的排放进行了严格的限量。因此，在制鞋工业中，溶剂基胶黏剂将逐渐被水基胶黏剂取代，而后者的粘结性能正在逐渐稳步的提高。

Adhesive Types 胶黏剂类型

Water based Adhesive 水基型胶黏剂

- Water based adhesives include natural latex, synthetic latex and water dispersions of various polymers, such as natural latex, starch glue, acrylic emulsion, polyvinyl alcohol and its derivatives latex, neoprene latex and waterborne polyurethane emulsion. 水基胶包括天然乳胶、合成乳胶以及各种聚合物的水分散体，如天然乳胶、淀粉胶、丙烯酸酯乳胶、聚乙烯醇及其衍生物乳胶、氯丁乳胶和水基聚氨酯乳液等。
- Water-based adhesives is the least polluted adhesives. 水基胶是污染最少的胶种
- The polymer emulsion used for shoemaking mainly consists of chloroprene latex, natural latex, polyurethane emulsion and vinyl acetate and copolymer emulsion. The biggest feature of these emulsion adhesives is that they do not use organic solvents, which can avoid environmental pollution. 可用于制鞋的聚合物乳液主要有氯丁胶乳、天然乳胶、聚氨酯乳液与醋酸乙烯以及共聚物乳液。这些乳液胶最大的特点是不用有机溶剂，避免了环境污染。

Adhesive Types 胶黏剂类型

Water based Adhesive 水基型胶黏剂

Advantages and Disadvantages of water-based adhesives 水基胶的优缺点

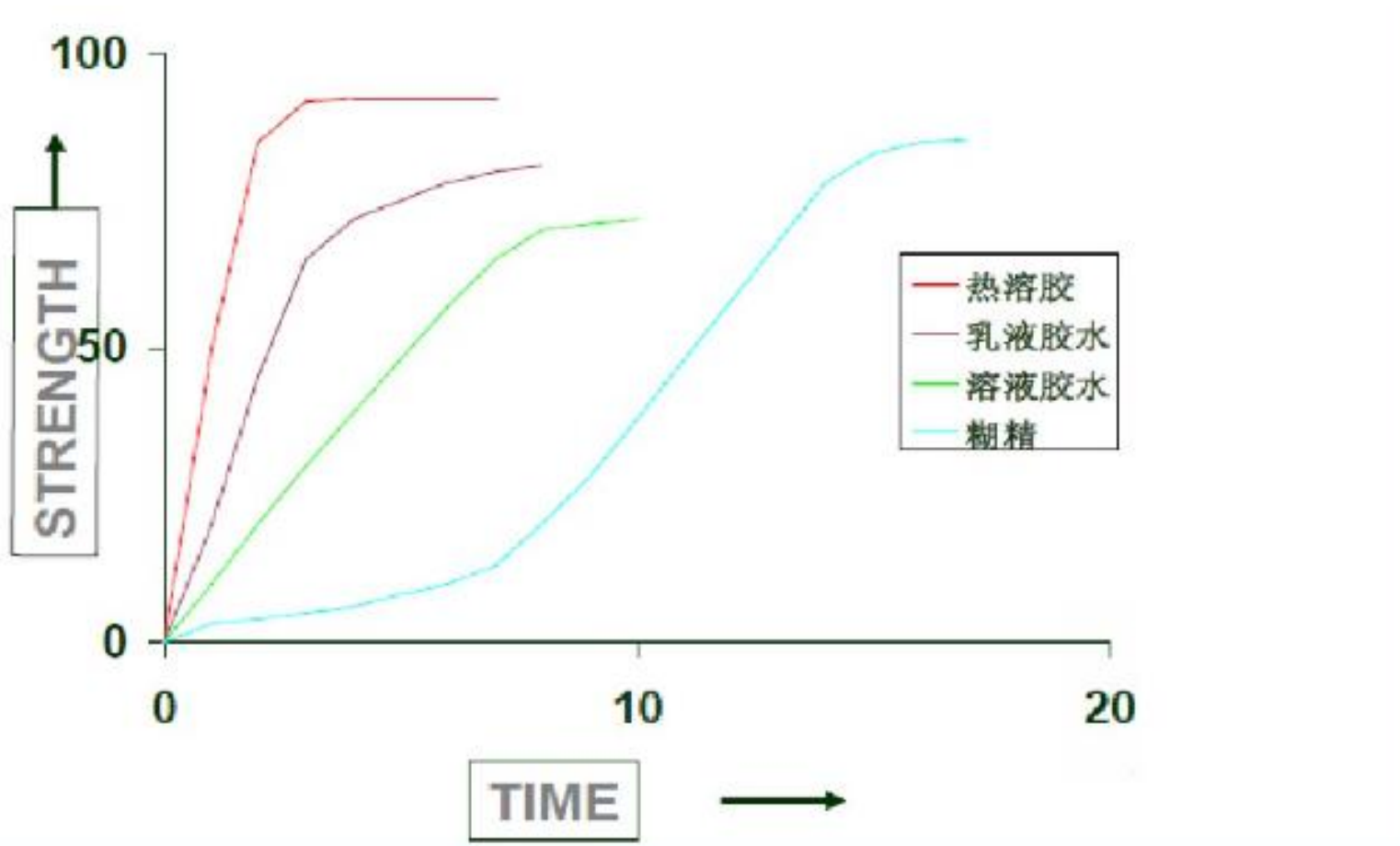
Advantages: 优点

- No VOCs, environment friendly
无VOCs, 环保
- Not easy to burn 不易燃烧
- Reduce the generation of harmful waste
减少了有害废弃物的产生
- Protect workers' health 保护工人健康

Disadvantages: 缺点

- Long curing time 固化时间长
- High energy consumption 耗能高
- High Purchase Cost 购买成本高
- Viscosity is not as good as solvent-based glue
黏性没有溶剂型胶水好

Set speed of different types of water-based glue 不同水基胶的固化速度



Adhesive Types 胶黏剂类型

Hot melt Adhesive 热熔胶

- Hot melt adhesives are another kind of environmentally friendly adhesives for shoemaking. 热熔胶是另一种环境友好的制鞋用胶黏剂，它们具有100%的含固量
- The first use of hot melt adhesives is as bandage adhesives. So far, polyamide and polyester adhesives are still the main adhesives in the bandaging process. 热熔胶的第一个用途是用作捆绑胶。到目前为止，聚酰胺胶和聚酯胶仍是捆绑工序的主要胶种。
- Coating head is the second most important use of hot melt adhesives in shoes. Coated head glue is mainly used for making the head of some middle and low-grade fashion shoes. At present, there are two main types of the adhesive, one is polyamide type and the other is EVA type. 涂包头是热熔胶在鞋上的第二大用途。涂包头胶主要用于某些中低档时装鞋的包头制作。目前，该胶主要有两种类型，一种是聚酰胺型，一种是EVA型。
- The third use of hot melt adhesive on shoes is the folding (Sipping) of the upper part of the shoe. 热熔胶在鞋上的第三个用途是鞋帮部件的折边(抿边)。
- The use of hot melt adhesives to bond the sole has attracted the attention of many scientists. Its speed and pollution-free are unparalleled in solvent based adhesives. But practices have proved that its bonding strength can not meet the wearing requirements of shoes. 用热熔胶粘大底，曾引起很多科学家的关注。它的快速无污染是溶剂胶无可比拟的，然后实践证明，它的粘接强度还满足不了鞋的穿着要求。

Adhesive Types 胶黏剂类型

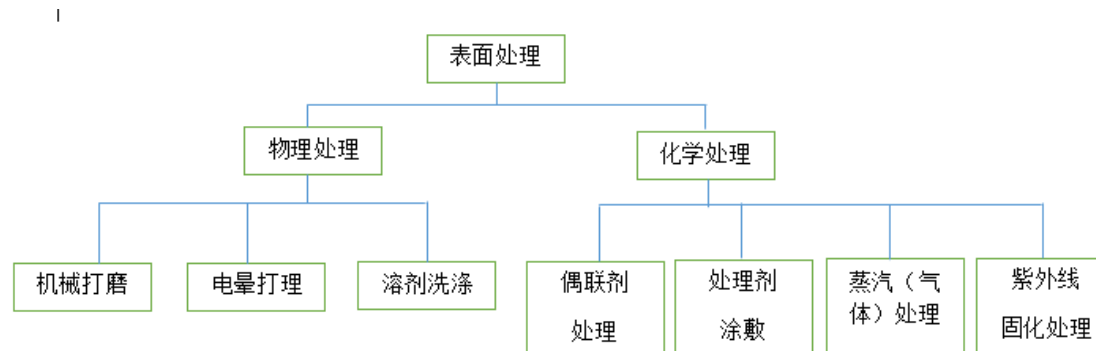
Reactive Adhesive 反应型胶

- Reactive adhesives, also known as solvent-based adhesives, are two components that can chemically react, be applied on the surface of the material to be bonded, and then, under thermal activation or other conditions, the components are closely contacted for chemical reaction to achieve the purpose of cross-linking and bonding. 反应型胶又称溶剂型胶，是将可进行化学反应的两组分分别涂刷在需粘接的物料表面，而后在热活化或其他条件下，组分紧密接触进行化学反应，达到交联粘接的目的。
- For example, the upper foot coated with polyester polyols and the sole with isocyanate layer are closely contacted under the condition of thermal activation to form polyurethane, thus forming a firm bond. This requires that the two reaction components must have strong adhesiveness to their respective adhesives, and the reaction time, pressure, temperature and other technological factors are appropriate. 例如，涂有聚酯多元醇的鞋帮脚和粘附有异氰酸酯图层的鞋底，在热活化的条件下，使之紧密接触，生成聚氨酯甲酸酯，从而形成牢固的粘接。这要求两个反应组分必须对各自的粘接物具有较强的粘附性，并且反应的时间、压力、温度等工艺因素适当。

How does Adhesive work? 胶黏剂如何作用?

Step 1: Surface treatment of objects to be bonded 被粘物的表面处理

- According to the bonding theory, the primary condition for a firm bond is the complete infiltration of the adhesives and objects to be bonded. 由粘接理论可知，粘接牢固的首要条件是粘胶剂和被粘物的完全浸润。
- Due to various oils, resins and dust on the surface of the objects, a weak interfacial layer is formed on the interface, which seriously affects the bonding effect. 由于被粘物表面有各种油污、树脂、灰尘等，在界面上形成弱界面层，严重影响粘接效果。
- The method suitable for surface treatment of shoe materials is shown as follows:
适用于鞋用材料表面处理的方法如图示:



How does Adhesive work? 胶黏剂如何作用?

Surface treatment method 表面处理方法

(1) Mechanical Grinding 机械打磨

- The purpose is to increase the bonding area, clean the surface and remove the resin, oil and dust on the surface of the objects to be bonded. 目的在于增加粘接面积, 清洁表面, 除去被粘物表面树脂、油污灰尘等
- When grinding, it should be even and master the depth well. Leather surface strength is weak, so bee-like surface must be touched when grinding.. 打磨时要均匀, 掌握好深度。皮革表面强度较弱, 打磨时一定要摸到蜂状表面为止。
- Placing for long time after grinding will make the surface inactive, so it should be used in time 打磨后放置时间过长会使表面失去活性, 故应及时使用

How does Adhesive work? 胶黏剂如何作用?

Surface treatment method 表面处理方法

(2) Solvent scrubbing 溶剂涂刷

- To clean surface dirt, plasticizer, etc., to keep the surface clean. The choice of solvents depends on the type of substrates. 为了清洗表面污物、增塑剂等，使表面保持清洁。
- It is conducive to the diffusion and penetration of adhesives. When washing, in order to ensure the washing effect, clean cloth should be applied instead of brushing. 有利于胶黏剂的扩散、渗透作用。
- When scrubbing, in order to ensure the washing effect, clean cloth should be applied instead of brushing. 洗涤时，为保证洗涤效果，应用清洁布擦，而不是涂刷。
- Usually, butanone and acetone are mostly used to treat synthetic leather, artificial leather, plastics and so on. Rubber, EVA and other materials are often cleaned with toluene. 溶剂的选择要根据基材种类而异。通常，丁酮、丙酮多用来处理合成革、人造革、塑料等。而橡胶、EVA等材料常用甲苯清洗。

How does Adhesive work? 胶黏剂如何作用?

Surface treatment method 表面处理方法

(3)处理胶涂敷 Coating of treatment adhesive

- The treatment glue contains high polarity mixed solvents, low content of solid components and some active substances, which can enhance the penetration of the adhesives, and can also produce oxidation, cyclization or addition reaction on the surface of the adhesives to increase the adhesiveness of the adhesives..

处理胶含有极性较高的混合溶剂，低含量的固体成分和某些活性物质，能加强对被粘材料的渗透作用，还能在其表面发生氧化、环化或者加成反应，增加被粘材料的粘接性。

- The treatment adhesives have good compatibility with the treated adhesives and adhesives, and can act as a bridge between them, thus improving the bonding strength.

处理胶与被粘物和胶黏剂都有良好的相容性，能在两者之间起桥梁作用，从而提高粘接强度

How does Adhesive work? 胶黏剂如何作用?

Step 2: Brushing of Adhesive 胶黏剂的涂刷

- In order to ensure the penetration of adhesives into materials, repeated gluing should be applied, especially after leather grinding. If only one-way brushing, the fibers will turn in one direction, the glue is not easy to penetrate into all the fibers' sides, so that the contact area will be reduced and the fibers' pore will be covered up, resulting in gluing defects and affecting the bonding strength. 为了保证粘胶剂对材料的渗透，应反复涂胶，特别是皮革打磨以后，若只单向涂刷，纤维就会倒向一个方向，胶不易渗透到所有纤维侧面
- It is required to be uniform and maintain a certain amount of glue. The excessive amount of glue causes the film to be too thick, and the residual solvent is easy to occur, and the phenomenon of pseudo-drying occurs. For porous materials, such as leather, canvas, foam bottom, etc.. Because of the good permeability of adhesives, it is easy to cause the lack of glue. We should choose adhesives with high viscosity and high solid content. Conversely, for non-porous materials, such as PVC, PU leather, the adhesive with low viscosity and low solid content should be selected. 涂胶要求均匀，保持一定的涂胶量。涂胶量过大，造成胶膜过厚，易发生溶剂残留，出现假干现象。对多孔材料如皮革、帆布、泡沫底等，由于胶黏剂渗透性好，容易造成涂胶量不足，应选择黏度较高、固含量大的胶黏剂。反之，对于非多孔材料，如PVC、PU革等，则应选择粘度较低、固含量小的胶黏剂。
- Generally, the primer needs to be brushed twice, once dried, then brushed twice. 一般底涂胶需涂两次，一遍干燥后再涂第二遍。

How does Adhesive work? 胶黏剂如何作用?

Step 3: Drying 干燥

- To volatilize the solvent sufficiently, promote the better diffusion of adhesives, and recrystallize the molecules, so as to improve the cohesion of the film. Drying involves natural drying and heating.
使溶剂充分挥发，促使胶黏剂更好地扩散，使分子重新结晶，从而提高胶膜的内聚力。
- Heating can obviously enhance the activity of adhesives and objects to be bonded. It is more effective to bond the interface and deepen the degree of crosslinking. In addition, heating can soften the tackifier resin in the glue and increase the initial viscous force. 加热可明显增强胶黏剂和被粘物的活性，是粘接界面更有效地粘接，交联程度加深。此外，加热可使胶液内的增黏树脂软化，增加初粘力。
- Excessive drying will lose the best bonding time. Insufficient drying may result in that solvent in the film can not be fully volatilized, which affects the bonding effect.
干燥过度会失去最佳粘接时间；干燥不足，胶膜内溶剂不能充分挥发，影响粘接效果。

How does Adhesive work? 胶黏剂如何作用?

Step 4: Stitching 压合

- Pressure promotes the diffusion of macromolecules and increases the bonding opportunities.
压合是影响粘接效果的重要过程。通过加压，促使大分子扩散，增加粘接机会。
- The sole bonding surface is uneven, there is a certain degree of warping, irregular surface. External pressure can make full contact with all parts.
鞋底粘接面凹凸不平，还有一定的翘度，呈不规则曲面，通过外力加压，才能使得各部位充分接触。
- Generally, the pressure is over 0.5 MPa and the pressure time is over 7 seconds. Insufficient pressure or too short compression time will cause the contact surface not to be fully pressurized, and the film will lose its activity and bonding ability. The bonding surface will be destroyed by re-pressing.
一般加压在0.5MPa以上，加压时间在7s以上。压力不足或加压时间太短，会造成接触面不能完全加压，时间过长胶膜失去活性和粘接能力，再加压反而会破坏粘接面。

Effect Factors of Gluing Strength 影响胶接强度的因素

Five aspects should be mainly considered: 应主要考虑五个方面:

- Properties of Bonded Materials 被粘接材料的性质
- Application occasion and force condition of bonded body 被粘接体应用的场合及受力情况
- Special requirements for bonding process 粘接过程有关特殊要求
- Adhesion efficiency and cost 粘接效率和粘接成本
- Adhesives should be selected for bonding with the same or different materials. 同材料或不同材料实施胶接, 应对胶黏剂进行选择

There are three main links in the bonding process: 胶接工艺中最主要的三个环节:

Selection of Adhesives 选择胶黏剂

Design of Adhesive Joints 胶接接头设计

surface treatment 表面处理





**Commonly used Adhesive in Footwear
Industry**
制鞋常用胶黏剂

Commonly used Adhesive in Footwear Industry 制鞋常用胶黏剂



**Leather shoes
皮鞋**

- 氯丁橡胶胶黏剂
- 聚氨酯胶黏剂
- 聚酯类胶黏剂
- 聚酰胺类胶黏剂 (热熔胶)



**Tourist shoes
旅游鞋**

- SBS胶黏剂.
- 聚氨酯胶黏剂.



**Rubber shoes
胶鞋**

- 天然橡胶胶黏剂.
- 丁腈橡胶胶黏剂
- 其他橡胶胶黏剂



**Plastic shoes
塑料鞋**

- EVA热熔胶.
- 聚醋酸乙烯胶黏剂
- 氯乙烯类胶黏剂
- 其他胶黏剂.



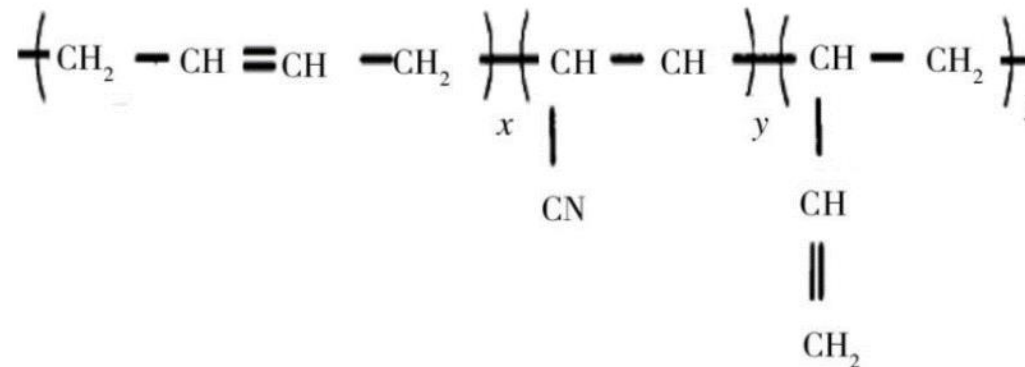
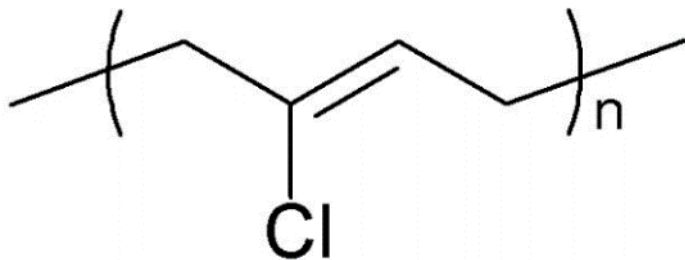
**Cloth shoes
布鞋**

- 淀粉类胶黏剂.
- 聚乙烯醇类胶黏剂
- 纤维素类胶黏剂
- 蛋白质胶黏剂.

Rubber adhesives 橡胶类胶黏剂

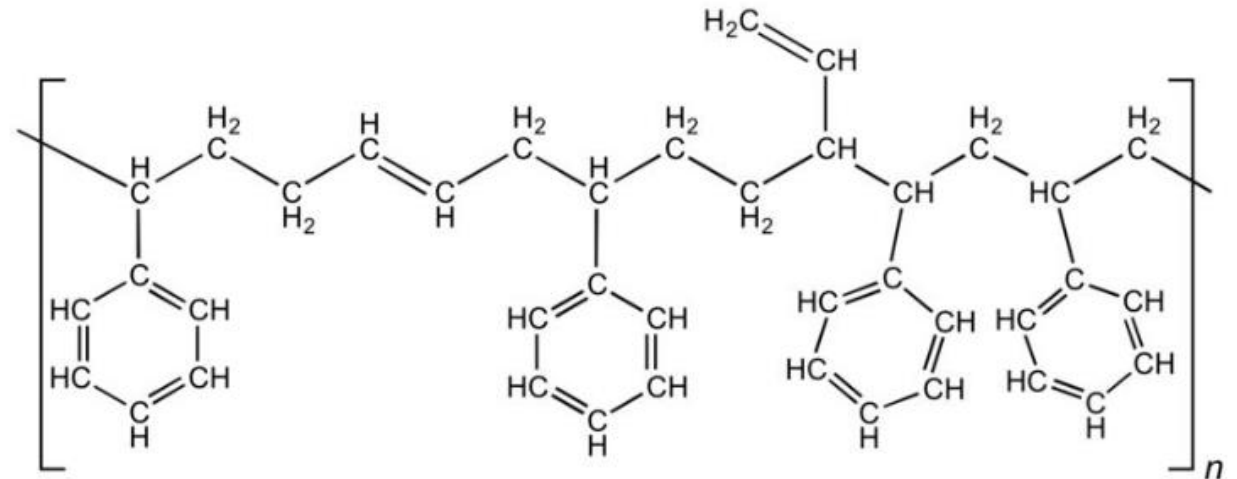
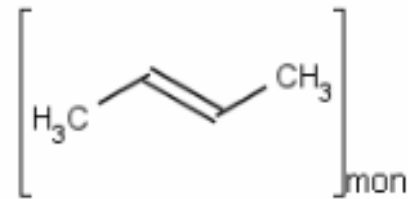
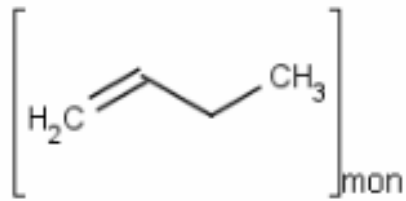
A large class of adhesives, which is made of rubber or elastomer as base material, additives and solvents. It is one of the pillars of modern solvent-based non-structural adhesives. It has the characteristics of good elasticity, impact resistance, good fatigue strength and wide application. Base materials include chloroprene, nitrile-butadiene, butyl, isobutylene, styrene-butadiene and other synthetic rubber, natural rubber, SBS and so on. 以橡胶或弹性体为基料，配以助剂、溶剂而成的一大类胶黏剂。是构成现代溶剂型非结构胶黏剂的一大支柱。具有弹性好，耐冲击，抗疲劳强度好，应用面广的特点。基料包括氯丁、丁腈、丁基、异丁烯、丁苯等合成橡胶，天然橡胶、SBS等。

- Chloroprene rubber adhesives: high bonding strength, high initial bonding force, can adhere to most materials; 氯丁橡胶胶黏剂：黏合强度高，初粘力大，可粘大多数材料；
- Nitrile butadiene rubber: oil resistance, water resistance, good heat resistance, wear resistance, aging resistance and medium resistance; 丁腈胶：耐油性、耐水性最好，有良好的耐热、耐磨；耐老化及耐介质性；



Rubber adhesives 橡胶类黏剂

- Butyl rubber: excellent sealability, excellent electrical insulation, aging resistance, acid and alkali resistance, oxygen, ozone and chemical media; 丁基胶：密封性特优，有优良的电绝缘性，耐老化性、耐酸碱、氧、臭氧及化学介质；
- Polyisobutylene gum: It has transparency, aging resistance, oxidation resistance, low temperature resistance and excellent electrical insulation. It can stick polyethylene, polypropylene and other refractory materials.
聚异丁烯胶：有透明、耐老化、抗氧化、耐低温和优良电绝缘性，能黏聚乙烯、聚丙烯等难黏材料。
- Styrene butadiene rubber: heat resistance, wear resistance, aging resistance, low price.
丁苯胶：耐热、耐磨、耐老化、价廉。



Rubber adhesives 橡胶类胶黏剂

Chloroprene rubber adhesives 氯丁橡胶胶黏剂

- Chloroprene rubber is the main raw material of chloroprene rubber adhesives. It has high bonding strength, excellent comprehensive performance and wide application...

氯丁橡胶是氯丁橡胶胶黏剂的主体原料

- The prepared adhesives can be cold cured at room temperature, with high initial adhesion and rapid strength establishment.

所配成的胶黏剂可室温冷固化、初粘力很大、强度建立迅速

- It can bond rubber, leather, fabrics, artificial leather, plastics, wood, paper, glass, ceramics, concrete, metal and other materials.

粘结强度较高，综合性能优良，用途极其广泛，能够粘接橡胶、皮革、织物、人造革、塑料、木材、纸品、玻璃、陶瓷、混凝土、金属等多种材料

Rubber adhesives 橡胶类胶黏剂

Chloroprene rubber adhesives 氯丁橡胶胶黏剂

The chloroprene adhesive has the following characteristics: 氯丁胶黏剂具有以下特点:

- There are chlorine atoms with strong electronegativity in CR molecule structure, which can provide the polarity needed for bonding. It has good cohesion without vulcanization and good initial adhesion. After being aired by adhesive material, it has strong bonding strength after contacting. CR分子结构中有电负性较强的氯原子, 可提供粘接所需的极性, 不需硫化就有很好的凝聚力, 初粘力好, 被粘材质涂胶晾干后一经接触便有很强的粘接强度
- When bonding soft materials, the stress concentration caused by expansion and contraction can be alleviated. 粘接软性材质时, 能够缓解由于膨胀、收缩所引起的应力集中
- It has good water resistance, aging resistance, flexibility resistance, good adhesion to various materials and reliable performance. 有良好的耐水、耐老化、耐曲挠性, 对多种材质有良好的粘接力, 性能可靠
- Solvent-based neoprene has the advantages of simple manufacturing process, convenient operation and low price. 溶剂型氯丁胶制造工艺简单, 操作方便, 价格低

Chloroprene rubber adhesives 氯丁橡胶胶黏剂

1) Mixed type (solvent type) chloroprene rubber adhesive 混配（溶剂型）氯丁橡胶胶黏剂

Mixed type (solvent type) chloroprene rubber adhesive consists of chloroprene rubber, resins, metal oxides, solvents, antioxidants, fillers, accelerators, crosslinking agents, etc. Solvent-based chloroprene rubber adhesives are prepared by dissolving chloroprene rubber and resin with solvent. After the solvent evaporates, the adhesive force is produced by the rapid crystallization of chloroprene rubber. 混配型（溶剂型）氯丁橡胶胶黏剂由氯丁橡胶、增黏树脂、金属氧化物、溶剂、防老剂、填充剂、促进剂、交联剂等组成。溶剂型氯丁胶黏剂是以溶剂使氯丁橡胶和树脂等组分溶解制成的，胶液涂布溶剂挥发后借助氯丁橡胶的快速结晶性而产生粘接力。

2) Graft chloroprene rubber adhesive 接枝型氯丁胶黏剂

The latex was prepared by graft copolymerization of chloroprene rubber with methyl methacrylate (MMA) and other monomers. The bonding strength of polyvinyl chloride (PVC) and other materials is much higher than that of ordinary or phenolic resin, chlorinated rubber, polyisocyanate and other modified chloroprene adhesives, among which methyl methacrylate is the most commonly used graft monomer. 利用氯丁橡胶与甲基丙烯酸甲酯(MMA)等单体进行接枝聚合生成的胶液。对聚氯乙烯(PVC)等材料的粘接强度比普通或酚醛树脂、氯化橡胶、多异氰酸酯等改性的氯丁胶黏剂高得多，其中甲基丙烯酸甲酯是最为常用的接枝单体。

3) Chloroprene latex adhesive 氯丁胶乳胶黏剂

Chloroprene rubber is water-based adhesive, which is made of latex from latex polymerization directly added to various kinds of compounding agents. It is non-toxic, non-flammable, safe to operate and widely used in industry. 氯丁橡胶为水基型胶，是由乳液聚合所得的橡胶乳胶直接加入各种配合剂制成的。它无毒、不燃、操作安全，在工业上得到广泛的应用。

Chloroprene rubber adhesives 氯丁橡胶胶黏剂

Raw material of Chloroprene rubber adhesives 氯丁橡胶胶黏剂原料

1) Chloroprene rubber 氯丁橡胶

- Chloroprene rubber is the fundamental factor determining the properties of adhesives. Chloroprene rubber, also known as polychlorobutadiene, or CR for short, is a flaky, massive or powdery solid with white or beige toughness. It is soluble in benzene, toluene, carbon tetrachloride, chlorohydrocarbons, methyl ethyl ketone, slightly soluble in acetone, ethyl acetate, cyclohexane, insoluble in n-hexane, solvent gasoline, but soluble in mixed solution composed of appropriate proportion of good solution and bad solution. 氯丁橡胶是决定胶黏剂性能的根本。氯丁橡胶又称聚氯丁二烯，简称CR，外观为白色或米黄色韧性的片状、块状或粉状固体。可溶于苯、甲苯、四氯化碳、氯代烃、甲乙酮、微溶于丙酮、醋酸乙酯、环己烷，不溶于正己烷、溶剂汽油，但可溶于由适当比例良溶液和不良溶液组成的混合溶液。
- The room temperature curing of chloroprene adhesives mainly comes from the crystallinity of CR. The faster the crystallization speed, the stronger the initial adhesion; the higher the crystallinity, the greater the bonding strength; the higher the crystallization temperature, the better the heat resistance. All chloroprene rubber can be used to prepare adhesives, but the properties of adhesives vary greatly due to the different crystallinity and crystallization speed. The crystallization ability of domestic chloroprene rubber can be divided into four grades: micro, low, medium and high. Foreign countries are divided into five levels: small, medium, medium, large and large. 氯丁胶黏剂室温固化主要来自CR的结晶性，结晶速度越快，初粘力越强；结晶度越高，粘接强度越大；结晶温度越高，耐热性越好。所有的氯丁橡胶都可用于配制胶黏剂，但因结晶度和结晶速度不同，胶黏剂的性能有很大的差异。国产氯丁橡胶结晶能力分为四个等级：微、低、中、高。国外分为五个等级：小、中小、中、大、极大。

Chloroprene rubber adhesives 氯丁橡胶胶黏剂

Raw material of Chloroprene rubber adhesives 氯丁橡胶胶黏剂原料

2) 增黏树脂 Viscosifying resin

- Viscosifying resin is an important component of solvent-based chloroprene adhesives, which can improve cohesive strength, bonding properties, heat resistance, water resistance and aging resistance. The tackifying resins used are thermal reactive alkyl phenolic resin, petroleum resin, terpene phenolic resin, terpene resin, rosin modified phenolic resin, gumarone resin, rosin ester, and poly-alpha-methylstyrene, of which p-tert-butyl phenolic resin (2402 resin) is the best. 增粘树脂是溶剂型氯丁胶黏剂的重要成分，能提高内聚强度、粘接性能、耐热性、耐水性和耐老化性。所用的增黏树脂有热反应性烷基酚醛树脂、石油树脂、萜烯酚醛树脂、萜烯树脂、松香改性酚醛树脂、古马隆树脂、松香酯，聚 α -甲基苯乙烯，其中以对叔丁酚甲醛树脂(2402树脂)效果最好。
- The amount of resin has a great influence on the properties of chloroprene adhesive. With the increase of resin content, the peeling strength increases. However, when the maximum amount of resin is reached, the peeling strength decreases, and it is easy to cause the delamination of the adhesive. This is because the resin content is too large, the compatibility with chloroprene rubber is poor, and the film presents brittleness. 树脂的用量对氯丁胶黏剂的性能有很大的影响，随着树脂量的增大，剥离强度增加，但当达到最大值后，再增加树脂用量，剥离强度反而下降，且易引起胶液分层，这是因为树脂量过大，与氯丁橡胶相容性变差，胶膜呈现脆性之缘故。

Chloroprene rubber adhesives 氯丁橡胶胶黏剂

Raw material of Chloroprene rubber adhesives 氯丁橡胶胶黏剂原料

3) Metal oxides 金属氧化物

There are four functions of metal oxides in chloroprene adhesives: acid absorbent, coke inhibitor, vulcanizing agent and resin reactant. Over time, chloroprene rubber releases trace amounts of hydrogen chloride, which promotes further decomposition of polymers and corrodes metals and natural fibers. Metal oxides are added to absorb hydrogen chloride to avoid further degradation. Magnesium oxide and zinc oxide are commonly used as metal oxides. Magnesium oxide has the functions of acid absorption, pre-reaction, anti-scorching and vulcanization, and is an indispensable component of chloroprene adhesive. The reaction of magnesium oxide with resin can improve the heat resistance of the adhesive and prevent layered precipitation. Zinc oxide can absorb acid when it is added to chloroprene adhesive.

在氯丁胶黏剂中金属氧化物有4种作用：酸吸收剂、防焦剂、硫化剂、树脂反应剂。随着时间推移，氯丁橡胶会释放微量的氯化氢，能促进聚合物进一步分解，并会腐蚀金属和天然纤维，加入金属氧化物可吸收氯化氢避免降解继续进行。一般使用的金属氧化物主要是氧化镁和氧化锌，氧化镁具有吸收酸、预反应、防焦烧、硫化等功能，是氯丁胶黏剂不可缺少的成分。氧化镁与树脂反应可提高胶黏剂耐热性并防止分层沉淀。氧化锌加入到氯丁胶黏剂中能起到吸收酸的作用。

Chloroprene rubber adhesives 氯丁橡胶胶黏剂

Raw material of Chloroprene rubber adhesives 氯丁橡胶胶黏剂原料

4) Antioxidant 防老剂

Because chloroprene rubber contains unsaturated double bonds, there is aging problem. In order to maintain the bonding durability, antioxidant (antioxidant) should be added. 因氯丁橡胶含有不饱和双键，存在着老化问题，为保持粘接耐久，须加防老剂(抗氧化剂)。

The antioxidant D used in the past has good effect, but it is contaminative and carcinogenic. It should be abandoned and replaced by ODA, RD and 264. Antioxidant 2246 can also be used, but it will produce discoloration. It changes from light blue, blue to green in chlorinated solution and pink in latex. 曾用的的防老剂D效果很好，但有污染性和致癌性，应当弃用，以ODA、RD、264代替。抗氧化剂2246也可以用，但会产生变色现象，在氯化溶液中呈浅蓝、蓝至绿色变化，在胶乳中是粉红色。

Chloroprene rubber adhesives 氯丁橡胶胶黏剂

Raw material of Chloroprene rubber adhesives 氯丁橡胶胶黏剂原料

5) Solvent 溶剂

- Solvent is an indispensable component of solvent-based chloroprene rubber adhesives, which has an important impact on the properties of adhesives. 溶剂是溶剂型氯丁橡胶胶黏剂不可缺少的高量组分，对胶黏剂的性能有着重要的影响。
- At present, most of the solvents used for chloroprene adhesive and grafted chloroprene adhesive are mixed solvents. Single solvent is difficult to meet the comprehensive requirements of the glue solution. The mixed solvent system has some advantages, such as enhancing solubility, adjusting drying speed, reducing viscosity, reducing toxicity, preventing low temperature gel and reducing cost. 目前氯丁胶黏剂和接枝氯丁胶黏剂使用的溶剂大多数是混合溶剂，单一的溶剂很难满足胶液的综合要求，混合溶剂体系具有增强溶解能力、调节干燥速度、降低粘度、降低毒性、防止低温凝胶、降低成本等有点。
- The toxicity and contamination of chloroprene rubber adhesives mainly come from solvents, because the solid content of chloroprene adhesives is low, the amount of solvents is large, and most of them are toxic and harmful organic compounds. Aromatic solvents are the most toxic. They are metabolized by the liver and discharged to the bladder. They may cause bladder cancer. The incubation period is up to 20 years. Benzene is the most toxic substance and can accumulate in vivo. It has been listed as a carcinogen. 氯丁橡胶胶黏剂的毒害性和污染性主要来自于溶剂，因为氯丁胶黏剂固含量低，溶剂量大，且多数为有毒、有害的有机化合物。芳香族溶剂毒性最大，经肝脏代谢，排至膀胱，有引发膀胱癌的可能，潜伏期长达20年。苯的毒性最大，且可在体内积累，已被列为致癌物质。

Chloroprene rubber adhesives 氯丁橡胶胶黏剂

Raw material of Chloroprene rubber adhesives 氯丁橡胶胶黏剂原料

6) Crosslinker 交联剂

- Crosslinking agent, also known as curing agent, can accelerate the curing speed of chloroprene rubber adhesive, improve the bonding strength, heat resistance, water resistance, oil resistance, chemical resistance, aging resistance and so on. The common crosslinking agent is polyisocyanate. 交联剂又称固化剂，可加速氯丁橡胶胶黏剂的固化速度，提高粘接强度、耐热性、耐水性、耐油性、耐化学药品性、耐老化性等。常用的交联剂为多异氰酸酯。
- It is highly reactive to the isocyanate crosslinking agent. If 2~3h is added to the neoprene adhesive, it can be crosslinked gel, used as a two component adhesive, and ready for use before mixing. 对异氰酸酯交联剂反应活性极高，加入氯丁胶黏剂中2~3h即可交联凝胶，作为双组分胶，在临用前调配，混合后立即使用。

Chloroprene rubber adhesives 氯丁橡胶胶黏剂

Raw material of Chloroprene rubber adhesives 氯丁橡胶胶黏剂原料

7) Promoters 促进剂

- Promoters are added to improve the heat resistance of vulcanization, such as vinyl thiourea (NA-22), diethyl thiourea (DE-TU), diphenyl thiourea (accelerant C), diaminodiphenylmethane, and the dosage is generally 0.25-1 phr. It has been found that adding BRN type vulcanized black to chloroprene adhesive can accelerate vulcanization, and its adhesion is no less than that of polyisocyanate vulcanization system, while its toxicity is greatly reduced. 促进剂是为促进硫化提高耐热性而加入的物质，如乙烯基硫脲（NA-22）、二乙基硫脲（DE-TU）、二苯基硫脲（促进剂C）、二氨基二苯甲烷、用量一般为0.25~1份。有人发现在氯丁胶黏剂加入BRN型硫化黑，可加速硫化，粘接性不亚于多异氰酸酯硫化体系，而毒性大为降低。

Chloroprene rubber adhesives 氯丁橡胶胶黏剂

Recipe of Solvent-base Chloroprene rubber adhesives 氯丁橡胶胶黏剂配方

Recipe 1 配方1:

氯丁橡胶 LDJ121	100
氧化镁	4
氧化锌	5
防老剂丁	2
有机溶剂	300~400

溶剂建议选用丁酮、120#汽油、乙酸乙酯

Recipe 2 配方2:

氯丁橡胶(G40或A-90)	50
氯丁橡胶Y-30或M-130L	50
叔丁基酚醛树脂	40
萘烯酚醛树脂	10
氧化镁	10
氧化锌	2
防老剂	2
沉淀白炭黑	10
甲苯	121
正己烷	121
乙酸乙酯	121

Recipe 3 配方3:

氯丁橡胶	12
对叔丁基酚醛树脂	6.3
氯磺化聚乙烯	3
ZnO-MgO	2.04
硫磺	0.07
改性松香酯	0.15
有机溶剂	适量
稳定剂	0.3

Chloroprene rubber adhesives 氯丁橡胶胶黏剂

Recipe of chloroprene latex adhesive 氯丁乳胶胶黏剂

Recipe 1 配方1:

氯丁橡胶乳	100
氧化锌	5~10
干酪素氨水溶液 (增稠剂)	0.5~2.0
乙撑硫脲 (促进剂)	0.5~2.0
增粘树脂乳液 (二甲苯甲醛树脂)	10~20
2,6-二叔丁基-4-甲基苯酚	0.5~2.0
2,4-甲苯二异氰酸	0.1~1
胺化淀粉磷酸酯	0.5~1.5
渗透剂	0.001~0.01
消泡剂	0.001~0.01

Recipe 2 配方2:

氯丁胶乳 (LDR-403)	100
聚乙烯醇缩甲醛	20~10
稳定剂	0~2
氧化锌	5~15
高岭土	20~100

PU Adhesive 聚氨酯胶黏剂

General term for adhesives with polyisocyanate and polycarbamate as main components 以多异氰酸酯和聚氨基甲酸酯为主体的胶黏剂的统称。

Advantage 优点:

- It has excellent chemical bonding with porous materials containing active hydrogen, such as foam plastics, wood, leather, fabrics, paper, ceramics, and smooth surface materials such as metals, glass, rubber and plastics. 能与含有活泼氢的材料, 如泡沫塑料、木材、皮革、织物、纸张、陶瓷等多孔材料和金属、玻璃、橡胶、塑料等表面光洁的材料都有着优良的化学胶接力。
- The ratio and structure of soft segment to hard segment in molecular chain can be controlled by adjusting the formulation of polyurethane to make adhesives with different hardness and elongation. 调节聚氨酯的配方可控制分子链中软段与硬段比例及结构, 制成不同硬度和伸长率的胶黏剂。
- It can be cured by heating or at room temperature 可加热固化, 也可以室温固化
- Curing belongs to the addition reaction and no by-products are produced, so it is not easy to cause defects in the bonding layer. 固化属于加聚反应, 没有副产物产生, 因此不易使胶合层产生缺陷。
- It has good wear resistance, water resistance, oil resistance, solvent resistance, chemical resistance, ozone resistance and mildew resistance 具有良好的耐磨、耐水、耐油、耐溶剂、耐化学药品、耐臭氧及防霉菌等性能。

Disadvantage 缺点:

Easy hydrolysis at high temperature and humidity to reduce bonding strength 在高温、高湿下易水解而降低胶合强度。

PU Adhesive 聚氨酯胶黏剂

Polyurethane adhesives are divided into solvent-based PU adhesives, PU hot melt adhesives and water-based PU adhesives 聚氨酯胶黏剂分为溶剂型PU胶黏剂, PU热熔胶, 水基PU胶黏剂.

Solvent-based PU adhesive 溶剂型PU胶黏剂:

- Isocyanates have high reactivity and can react with active hydrogen. Therefore, many materials containing active hydrogen or adsorbed water on their surfaces, such as metals, rubber, fibers, wood, leather, plastics, can react to form covalent bonds. 异氰酸酯具有较高的反应活性, 能与活性氢反应, 因此对许多表面含有活泼氢或吸附水的材料, 例如金属、橡胶、纤维、木材、皮革、塑料等能够反应形成共价键结合
- It can dissolve in most organic solvents, and the prepared adhesive has low viscosity, easy wetting and penetration, and is conducive to bonding formation and improving bonding performance. 能够溶于大部分有机溶剂, 配成的胶黏剂粘度低, 易于湿润渗透, 利于粘接形成, 提高粘接性能
- It can be cured at room temperature or by heating. 能室温固化, 也可以加热固化

PU Adhesive 聚氨酯胶黏剂

PU hot melt adhesive PU热熔胶:

The preparation of hot melt adhesives is mainly based on the physical crosslinking of hydrogen bonds in the composition, so that the polyurethane hot melt adhesives have excellent elasticity and strength. Hot melt polyurethane adhesive loses hydrogen bond when heated, becomes melt viscous liquid, and recovers its original physical properties after cooling 制备热熔型胶黏剂，主要是利用组成中氢键的作用发生物理交联，从而使聚氨酯热熔胶具有优秀的弹性和强度。热熔型聚氨酯胶受热后会失去氢键作用，变成熔融黏稠液，冷却后又恢复原来物性。

Water-based PU adhesives: mainly used for tourism shoes and Leather Adhesives

水基PU胶黏剂：主要用于旅游鞋与皮革胶黏剂

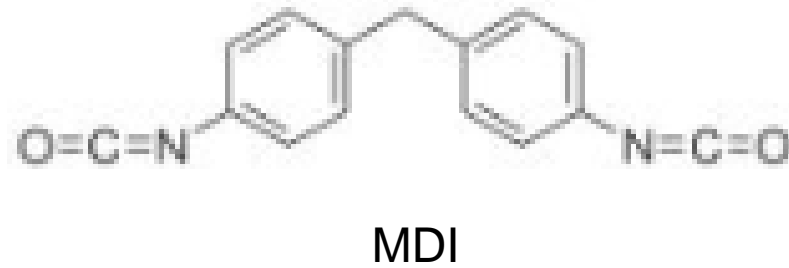
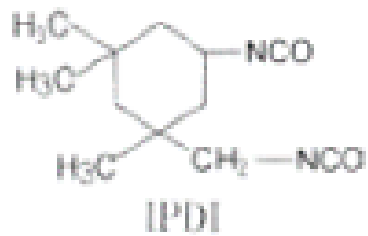
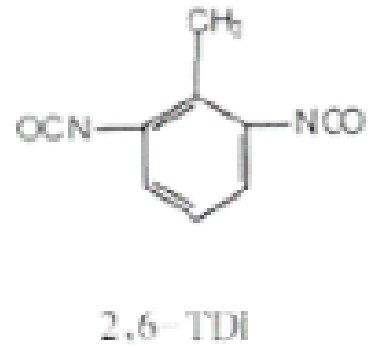
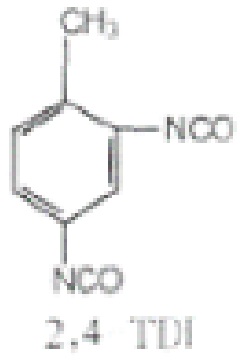
PU Adhesive 聚氨酯胶黏剂

Raw material of solvent-based PU Adhesive 溶剂型聚氨酯胶黏剂原料

1. Isocyanate 异氰酸酯

- Both isocyanate adhesives and polyurethane adhesives need isocyanate monomers. 无论是异氰酸酯胶黏剂，还是聚氨酯甲酸酯胶黏剂，都需要异氰酸酯单体。
- Isocyanates are mainly aromatic and aliphatic. Aromatic group: TDI, MDI, NDI, PAPI; aliphatic group: HDI, HMDI, IPDI. 异氰酸酯主要有芳香族类和脂肪族类两种。芳香族类：TDI、MDI、NDI、PAPI；脂肪族类：HDI、HMDI、IPDI。
- Polyurethane prepared by aromatic isocyanate has stronger strength and better antioxidant performance than polyurethane produced by aliphatic isocyanate because of its rigid aromatic ring and high cohesion of hard segment. 芳香族异氰酸酯制备的聚氨酯，由于具有刚性的芳环，硬段内聚力大，其强度比来自脂肪族的异氰酸酯生产的聚氨酯大，并且抗氧化性能也好。

Isocyanate 异氰酸酯



PU Adhesive 聚氨酯胶黏剂

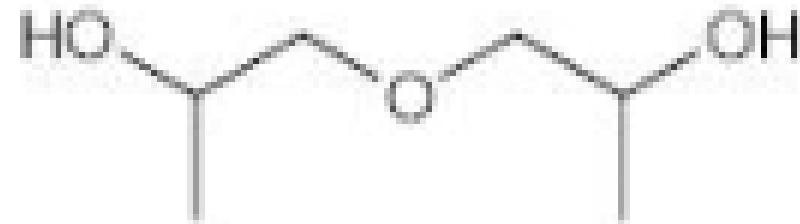
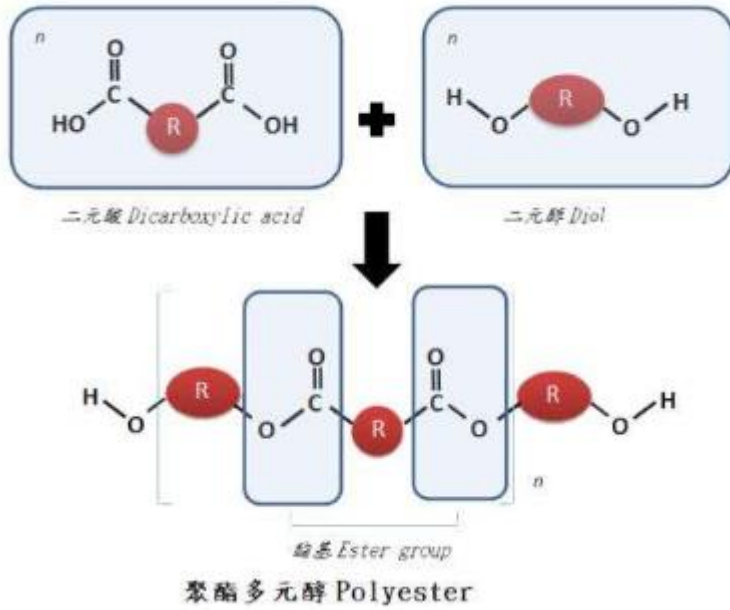
Raw material of solvent-base PU Adhesive 溶剂型聚氨酯胶黏剂原料

2. Polyols 多元醇

- 聚酯
- 大部分为二官能度。
 - 一般要求酸值为 $0.3 \sim 0.5 \text{mgKOH/g}$ 为宜。
 - 聚酯多元醇易于吸湿，贮运应避免大气中水分进入。为了减少可逆反应，温度不应超过 $120 \text{ }^\circ\text{C}$ 。

- 聚醚
- 是端羟基的齐聚物，主链上的烃基由醚键连接。
 - 是以低分子量的多元醇、多元胺或含活泼氢的化合物为起始剂，与氧化烯烃在催化剂作用下开环聚合而成。

Polyols 多元醇



PU Adhesive 聚氨酯胶黏剂

Raw material of solvent-base PU Adhesive 溶剂型聚氨酯胶黏剂原料

3. Catalyzer 催化剂

Organotin catalysts: 有机锡类催化剂:

The NCO/OH reaction catalyzed by this kind of catalyst is stronger than that catalyzed by NCO/H₂O. Most of the polyurethane adhesives are prepared with this kind of catalyst. 此类催化剂催化NCO/OH反应比催化NCO/H₂O反应强，聚氨酯胶黏剂制备时大多采用此类催化剂。

Tertiary amine catalysts: 叔胺类催化剂:

This catalyst is especially effective in promoting the reaction with water. It is generally used to prepare polyurethane foam plastics, foamed polyurethane adhesives and low temperature curable and moisture curable polyurethane adhesives. 此催化剂对促进与水的反应特别有效，一般用于制备聚氨酯泡沫塑料，发泡型聚氨酯胶黏剂以及低温固化型、潮气固化型聚氨酯胶黏剂。

PU Adhesive 聚氨酯胶黏剂

Raw material of solvent-base PU Adhesive 溶剂型聚氨酯胶黏剂原料

4.Solvent 溶剂

- The organic solvents used in polyurethane adhesives must be "urethane-grade solvents", which are basically free of water, alcohols and other active hydrogen compounds. 聚氨酯胶黏剂用的有机溶剂必须是“氨基级溶剂”，基本上不含水、醇等活泼氢的化合物。
- The solvent purity of polyurethane adhesives is higher than that of general industrial products. 聚氨酯胶黏剂用的溶剂纯度比一般工业品高。
- The solvents used in polyurethane adhesives usually include ketones (such as methyl ethyl ketone, acetone), aromatic hydrocarbons (toluene), dimethylformamide, tetrahydrofuran, etc. 聚氨酯胶黏剂采用的溶剂通常包括酮类（如甲乙酮、丙酮）、芳香烃（甲苯）、二甲基甲酰胺、四氢呋喃等。

PU Adhesive 聚氨酯胶黏剂

Raw material of solvent-base PU Adhesive 溶剂型聚氨酯胶黏剂原料

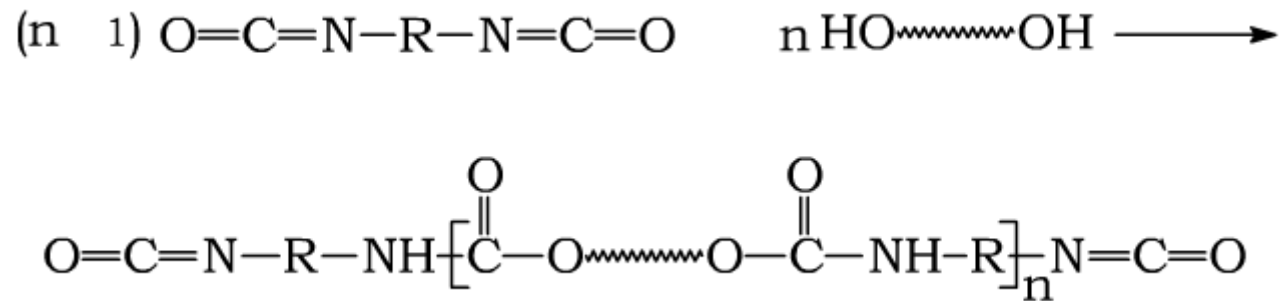
5. Other Auxiliaries 其他助剂

- 1) Chain extenders and crosslinkers 扩链剂和交联剂
- 2) Antioxidants 抗氧化剂
- 3) Light stabilizer 光稳定剂
- 4) Hydrolytic stabilizer 水解稳定剂
- 5) ...

PU Adhesive 聚氨酯胶黏剂

synthesis of PU Adhesive 聚氨酯胶黏剂的合成

There are many ways to synthesize polyurethane, but binary and polyisocyanate are widely used to react with polyester polyols or polyether polyols containing hydroxyl end groups. Linear polyurethane can be prepared by using only bifunctional reactants. 聚氨酯的合成有多种途径，但广泛应用的是二元、多元异氰酸酯与末端含羟基的聚酯多元醇或聚醚多元醇进行反应。当只用双官能团反应物时，可以制成线型聚氨酯。



Recipe of solvent-base PU Adhesive 溶剂型PU胶黏剂配方

Recipe 1 配方1:

聚氨酯树脂 (鞋用胶级)	300
甲基溶纤维素	500
四氢呋喃	500
羧基三元氯蜡树脂	20

Recipe 2 配方2:

己二酸	146
1, 4-丁二醇	45
己二异氰酸酯	30
二月桂酸二丁基锡	0.2
丁酮	适量

PU Adhesive 聚氨酯胶黏剂

Raw material of water-base PU Adhesive 水性聚氨酯胶黏剂原料

Recipe 1 配方1:

六亚甲基二异氰酸酯	807
己二酸丁二醇聚酯二醇	13992
二甲羟基丁酸	558
4,4-二苯基甲烷二异氰酸酯	2644
丁二醇	683
三乙基胺	370

Recipe 2 配方2:

聚丙二醇(PPG-400)	100
HDI	25.2
冰醋酸(HAc)	2
N-甲基二宜春胺 (N-MDEA)	5.95
硫酸二甲酯(DMS)	6.3
HCl	适量

Selection of Adhesive 胶黏剂的选择

- The main points to be considered when selecting adhesives for footwear manufacture are:
选择鞋用胶粘剂时应考虑的要点是:
 - Cost 价格
 - Strength 强度
 - Suitable for use with shoe materials and in shoe process 是否使用与鞋材和工序的使用
 - General consideration 一般考虑

Question: What is the general consideration?

问题：什么是一般考虑？

Domestic Requirements on Adhesive

Adhesive used on Footwear and Luggage 鞋和箱包用胶黏剂 GB19340-2003

项 目		指 标	
苯	≤	5.0 g/kg	
甲苯+二甲苯	≤	200 g/kg	
游离甲苯二异氰酸酯 ^a	≤	10.0 g/kg	
正己烷	≤	150 g/kg	
二氯甲烷	卤代烃	≤	50.0 g/kg
1,2-二氯乙烷			
1,1,2-三氯乙烷			
三氯乙烯			
总挥发性有机物	≤	750 g/L	
^a 聚氨酯胶粘剂测试本项目。			

- <http://www.doc88.com/p-84982463466.html>

Activity 活动

What is the composition of the Adhesive used in your factory? Which ingredients pollute the environment?
您工厂使用的胶黏剂是由哪些成分组成？哪些成分对环境有污染？



General Remarks

Origins and Purpose



These training slides, including both basic and advanced trainings, as well as Train-the-Trainer training materials, are part of factory qualification program jointly initiated by Zalando and GIZ with in the develoPPP.de program by the German Federal Ministry for Economic Cooperation and Development. The partners aim at addressing the industry-wide challenge faced by the polyurethane shoe sector in reducing the harmful impact of chemicals on workers and environment and improving chemical handling processes as well as ensuring safer working conditions.

The training slides have been developed on basis of the earlier GIZ Chemical Management Toolkit. The toolkit refers to publications of UNEP, UNIDO, ILO, HSE (UK), BAUA (Germany) and ICCA.

Furthermore, it integrates more than a decade of practical implementation experience of the “Resource Efficient Management of Chemicals” (REMC) cycle and was updated and in orientation to structure and content of the training materials developed under the develoPPP.de partnership with Tchibo and REWE “Sustainable chemicals and environmental management in the textile sector”.

While the original toolkit target group focused on chemical management especially for Small and Medium Scale Enterprises, this adapted version includes comprehensive chapters, especially on Volatile Organic Compounds (VOCs) management and hazardous chemicals substitutions in the polyurethane shoe sector to support also larger companies with the implementation of **ZDHC** and **Higg Facility Environmental Module (Higg FEM)** requirements.



These training materials, based on the GIZ [REMC](#) (Resource-efficient management of chemicals) toolkit, the [training materials](#) developed under the develoPPP.de partnership with Tchibo and REWE “Sustainable chemicals and environmental management in the textile sector”, as well as additional materials provided by TÜV Rheinland, were prepared for Zalando and GIZ by:

- TÜV Rheinland (Guangdong) Ltd. – Mr. Ray Niu and his team

Many thanks to our partners, GIZ colleagues and external consultants for comprehensive review and feedback, especially to

- Mr. Carl Chan, Sustainability Manager, Zalando SE
- Mr. Gundolf Klaehn, Head of Environment, GIZ Textile Cluster Dhaka
- Dr. Jürgen Hannak, Head of Programme Circular Economy, Adelphi



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