Freie Universität Berlin

BfR
Bundesinstitut für Risikobewertung

FEDERAL INSTITUTE FOR RISK ASSESSMENT

The Chemistry of Tattoos

Section I: Analytics & Exposure

Jutta Tentschert

Traditional Tattoos: Examples

Pigments used

- **Charcoal** (e.g. Iceman “Ötzi”)
- **Ochre** ($Fe_2O_3 \bullet H_2O$, Fe_2O_3)
- Mixtures of **charcoal, soot, honey, milk** (e.g. Chatolic Croatian Women in Bosnia)

Skythian Chieftain; Source: http://en.wikipedia.org/wiki/History_of_tattooing

Application techniques

- Cutting and rubbing
- Pricking
- Punching / Poking

} different angle of tattooing instrument

Christian tattooing in Bosnia and Herzegovina; Source: http://en.wikipedia.org/wiki/Christian_tattooing_in_Bosnia_and_Herzegovina

Consequences of the application method

- Placement of pigment into dermis (depth)
- Duration / fading
- Successful removal

Modern Tattoos or PMU:

Tattoo inks:

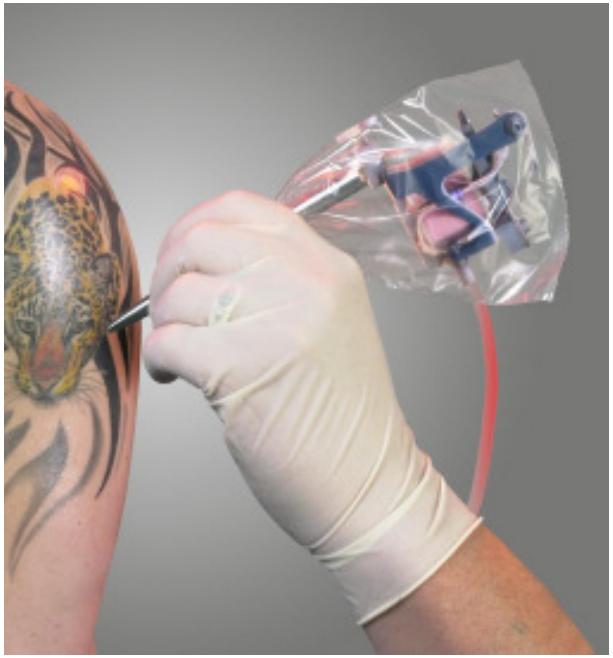
- Single substance or mixtures
- Inorganic Pigments
- Organic Pigments
- **Not always specially designed for this purpose**

What is expected from modern tattoo inks:

- Even distribution of the colour
- New colour variations, wide colour range
- High brightness and intensity
- High duration / no fading

Health and safety:

- Tattoo procedure should be safe
- Hygienic aspects considered
- **Tattoo inks should be safe**



Modern Tattoo-Machine; Source: BfR

Permanent Make Up; Source: http://en.wikipedia.org/wiki/Permanent_makeup

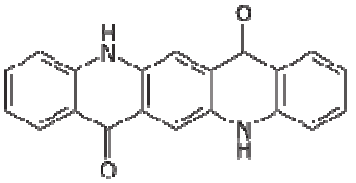
Tattoo-Ink-Chemistry

Pigments:

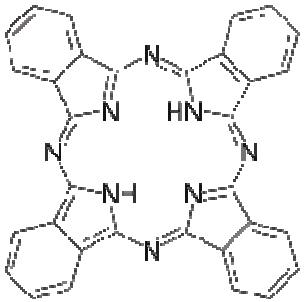
Tattoo-Ink = **Pigment** + Carrier

- Inorganic Pigments:
  - Oxides (TiO_2, Cr_2O_3)
  - Sulphides (CdS, HgS)
  - Chromates, Cyanides (Lead chromates, Ferrocyanides)
  - Aluminum salts

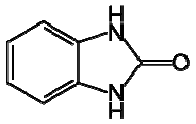
- Organic Pigments (Synthetic Compounds):
  - Insoluble organic compounds
  - Dyes converted to insoluble pigments
    1. Quinacridones
    2. Phthalocyanines
    3. Benzimidazolones
    4. **Azo-Compounds**
    5. Anthraquinones
    6. Indigoide Structures



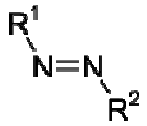
1



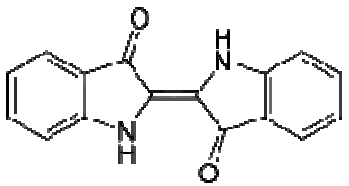
2



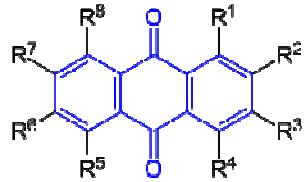
3



4



6



5

Tattoo-Ink-Chemistry

Tattoo-Ink	=	**Carrier**	+	Pigment

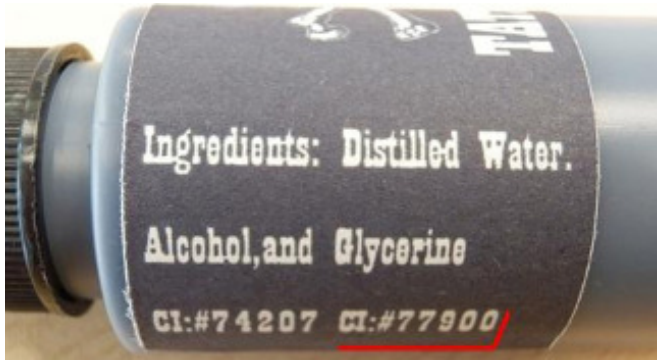
Carrier:

Single substance or mixture

Purpose:

- Even distribution of pigments in liquid formulation
- Prevention of pigment clumping
- Inhibition of pathogen growth
- Examples
  - Water, Ethanol
  - Propylene glycol
  - Glycerine (glycerol), sorbitol
  - Witch hazel
  - Mouth wash (Listerine™)

RAPEX 2013
Source:http://ec.europa.eu/consumers/safety/rapex/alerts/main/



RAPEX 2013
Source:http://ec.europa.eu/consumers/safety/rapex/alerts/main/

Regulatory status of tattoo inks and pigments

National		Provisions
No specific legislation	Denmark	**Product Safety** Act & REACH
	Finnland	Act of **Consumer Product** & Services (Directive 2001/95/EY)
	Great Britain	General **Product Safety** Regulations *1994*
	Luxembourg	EU ResAP(2008)1 is not counter-singed
EU-regulation only	Belgium	**Requirements and Criteria for the safety of tattoos and Permanent make-up (EU ResAP(2008)1); *since 2008***
additional national provisions	Austria	• Documentation has to be kept for **10 years**. BGbl., Part II; 2008 • Used colorants not be known to be harmful. BGbl., Part II; 2003
	Germany	• LFGB (German Food and Feed Code) • **TätoV (German provision on tattoos);** *2008* • Database for Tattoo- & Permanent Make-Up Products by CTL, *2009*
	Netherlands	Stb. 2003, 342; **Regulations for Tattoo Colorants & Permanent Make-Up**; *since 2003*
	Sweden	Regulation LVFS 2012:25 by the Medical Product Agencey *2013*
	Switzerland	SR 817.023.41; **Regulation about objects for the human skin contact;** *since 2006, (update 2012)*

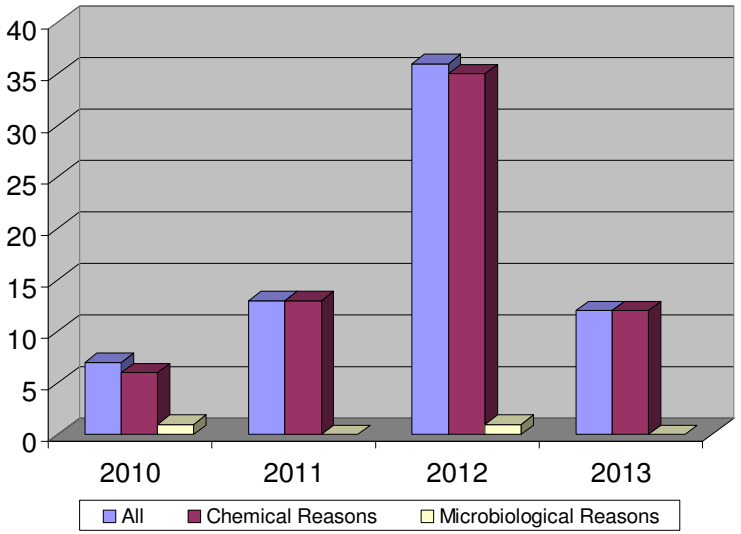
See also Session V Risk Assessment & Regulation on Friday

RAPEX-Alerts: 2010 - 2013

Alerts: 68

Due to chemical reasons: **66**

Graphical Overview of the RAPEX Alerts from 2010 – 2013



RAPEX 2013
Source:http://ec.europa.eu/consumers/safety/rapex/alerts/main

Substances mentioned in 2013:

- Heavy Metal
  - Nickel: **4900 mg/kg** (ALARA)
  - Chromium: **61 mg/kg** (0.2 mg/kg)
- primary aromatic amines (PAA) from azo dyes
  - o-Anisidine: **1753 mg/kg** (should not be present, **carcinogenic**)
  - Toluidine: **120 mg/kg** (**carcinogenic**)
- Polycyclic aromatic hydrocarbons (PAH): **96 mg/kg** (0.5 mg/kg)
  - Benzo[a]pyrene (BaP): **0.2 mg/kg** (0.005 mg/kg)

Analytics:

Technologies used for trace analysis

General techniques (pigments in general)

- Scanning electron microscopy (SEM)
- X-Ray micro-analysis
- (micro-) Raman spectroscopy

Sample Preparation; Source: BfR

Techniques for inorganic pigments

- Tools for element analytics
  - sector field inductively coupled plasma mass spectrometry (HR-ICP-MS)
  - graphite furnace atomic absorption spectrometry (GF-AAS)
  - flame atomic absorption spectrometry (F-AAS)

Techniques for organic pigments

- Mass spectrometry tools
  - Tandem mass spectrometry (LC-MS/MS)
  - Time of flight mass spectrometry (ToF-MS)
  - Gas chromatography mass spectrometry (GC-MS)

Analysis of organic pigments, LC-MS/MS; Source: BfR

Analytics – available data:

Data present:

- For many inorganic pigments
- For some organic pigments / dyes and their impurities (e. g. Azo pigments, PAA)

Sample Preparation; Source: BfR

Data gap:

Carriers

- Less harmful ones:
  - Ethanol, propylene glycol, glycerol, witch hazel, Listerine™
- Presumably toxic ones:
  - Methanol, isopropyl alcohol, ethylene glycol
  - Formaldehyde, glutaraldehyde

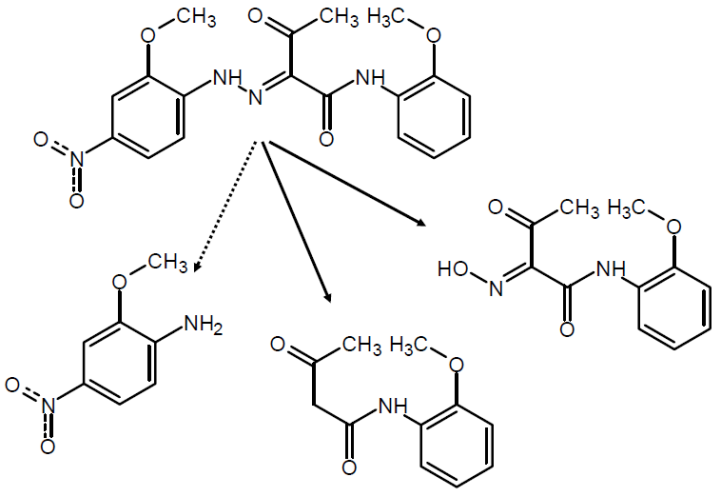
Azo dyes; Source: BfR

Other Chemicals

- Various surfactants or detergents
- Biocidal substances
- Plasticiser like phthalates
- Impurities

Photodecomposition of Pigment Yellow 74:

Tattoo inks:	Yellow, Dark Yellow, Sun Yellow, Mohawk Yellow, Canary Yellow, Tulip Yellow and Poppy
Substance class:	Azo Compound
Amount present:	0.7 -12.7 % wt/wt
Characterisation:	NMR, MS
Photostability:	simulated solar light: 6.5 kW xenon arc lamp, filtered via WG320 glass filters, duration: 5 h
Decomposition products:	HPLC, MS, NMR



Yanyan Cui et al. (2004) Photochemistry and Photobiology, 80: 175–184.

Conclusion:

Decomposition of tattoo inks may occur during:

- Sunlight exposure
- Tanning
- Laser removal

➔ May generate toxic products

Azo Dyes:
Source: BfR

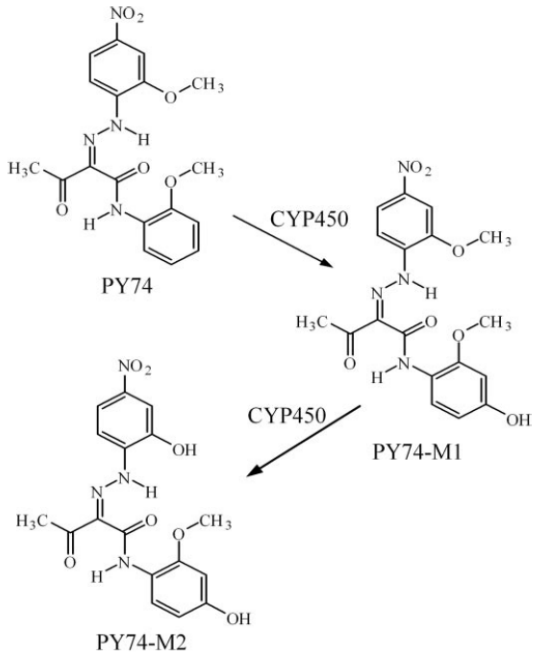
Bio-kinetic studies of tattoo ink pigments:

Hardly any data available!

Tattooing of skin results in transportation and light-induced decomposition of tattoo pigments – a first quantification in vivo using a mouse model, Engel et al., 2009 Experimental Dermatology, 19, 54–60.

Metabolism studies: on rat liver and human liver microsomes

- Some pigments can be metabolized by phase I enzymes (P450s)
- P450s exist in the skin of rodents and humans



Yanyan Cui et al. (2005) Drug Metabolism and Disposition 33 (10) 1459-1465.

No reports exist regarding

mutagenic, carcinogenic, or photocarcinogenic potential of azo compounds like PY74

But:

o-Anisidine: (*in vitro)* DNA adducts
urinary bladder carcinogen in mice and rats (Stiborova et al., 2001, 2002)

Oxidation of PY74-M1:

may form active intermediates for *o*-anisidine & *N*-acetyl *p*-benzoquinone imine (Stiborova et al., 2002 Rogers et al., 1997)

Fading of tattoos and tattoo removal:

Source BfR

Fading of tattoos (esp. yellow and orange):

- Dispersion through the skin
- Phagocytosis and removal
- Metabolism of the pigments in the skin
- Photochemical decomposition of the pigments

Tattoo Removal

- **IPL technology:** (intense pulsed light technology)
  - polychromatic, high-intensity light penetrates skin just below the surface
- **Laser removal**
  - Q-switched **ruby Lasers**, Q-switched **Nd-YAG Lasers**, Q-switched **alexandrite Lasers**
  - 1960: "hot vapour bursts"; left behind "cosmetically acceptable scars"
  - present: not always successful, duration up to 20 h
- "**Dissolving" ink:**
  - beta-carotene in polymer shells
  - ~ one laser session;
  - available in the US only; medical trials are ongoing

Trends: tattoo inks and pigments

New challenges for analytical chemists?

- Fluorescent tattoo inks
- Tattoo inks glowing in the dark
- White Ink Tattoos
  - Considered to be feminine
  - Look like scars
- Bio-tattoo inks
  - Self degradable after specific time
- Tattoo inks using nanotechnology
  - Encapsulated pigments in polymer shells in nano size

Source: BfR

RAPEX 2013 Source:http://ec.europa.eu/consumers/safety/rapex/alerts/main/

FEDERAL INSTITUTE
FOR RISK ASSESSMENT

Freie Universität Berlin

BfR
Bundesinstitut für Risikobewertung

Thank you for your attention

Jutta Tentschert

Federal Institute for Risk Assessment
Max-Dohrn-Str. 8-10 • 10589 Berlin, GERMANY
Tel. +49 30 - 184 12 - 0 • Fax +49 30 - 184 12 - 47 41
bfr@bfr.bund.de • www.bfr.bund.de