Pigments, Preservatives and Impurities in Tattoo Inks

U. Hauri – State Laboratory of Basel-City

Regulation and Control of Tattoo Inks in Switzerland

State Laboratory of Basel-City – Official food authority of Basel-City

•Main laboratory for analysis of tattoo inks in Switzerland

•First study on tattoo inks 2004 (> 200 samples) – Status before regulation

•Analysis of 416 Tattoo inks of 73 brands since 2008

- Organic Pigments
- Carcinogenic Aromatic Amines / Forbidden Azo Dyes
- Preservatives, Ingredients and Impurities
- Nitrosamines
- Polyaromatic Hydro Carbons (PAH)
- (Microbiological contamination)

Swiss Studies on Tattoo Inks and PMU 2009 and 2011

- Regulation for Tattooing and PMU Inks in Switzerland since 2006 / 2008
- The regulation is based upon the European Council resolution ResAP(2003)2

	Investigated Samples		Objected Samples		Banned Samples	
	2011	2009	2011	2009	2011	2009
Tattoo Inks	167	105	53%	87%	33%	54%
PMU	23	47	35%	60%	9%	11%

Results of 2009 study (german and french only)

D: www.bag.admin.ch/pdf_link.php?download=bulletin_Tattoofarben_d

F: http://www.vsnews.bag.admin.ch/api/redirect.php?redirect=bGlua3w4NHwxNzR8NXxmcg==.

Results of 2011 study

http://www.kantonslabor-bs.ch/files/berichte/6729_111012_JB_Tattoo_PMU_2011_EN.pdf

List with banned products 2011 and 2012

http://www.bag.admin.ch/themen/lebensmittel/04861/04987/index.html?lang=de

Organic Pigments in 416 Samples (2008 – 2012)

74160	16%
12475/12477	9%
74260	7%
11741	6%
73915	6%
51319	5%
561170	5%
11767	4%
12490	4%
21110	3%
56110	3%
21095	3%
11680	2%
56300	2%
74265	2%
13980	2%
11740	1%
73360	1%
11710	1%
12370	1%
12085	1%
21090	1%
73900	1%
12385	1%
12485	1%
12510	1%
15585	1%
15850	1%
21108	1%
21160	1%
51345	1%
73907	1%
21115	0.5%
12075	0.2%
12315	0.2%
15580	0.2%
45160	0.2%
45170	0.2%
47005	0.2%

Allowed in Cosmetics for all Purposes – «allowed» in tattoo inks

Restricted admission in Cosmetics – not allowed in tattoo inks

Not allowed in Cosmetics and Tattoo inks

Not allowed for Cosmetics – «allowed» in tattoo inks

Organic Pigments – Main source of Non-Conformity

Reasons for Banning	2011 (190 Samples)	2009 (152 Samples)
Unallowed Pigments	29%	23%

Some producers still use unallowed pigments but do conceal them (10 samples/2 producers!)

Pigments are usually not controlled!

Examples

Samples	Colour	Declaration	Analytics
3	Green	74265 (green)	74260 (green)
2	Violet/Purple	74160 (blue), 12475 (red)	51319 (violet)
1	Magenta!	77891 (white), 74160 (blue)	73915 (red/magenta)

Hardly bad quality control…

Organic Pigments – The problem of the lacking positive list

Lack of toxicological data ⇒ no positive list for pigments only negative lists

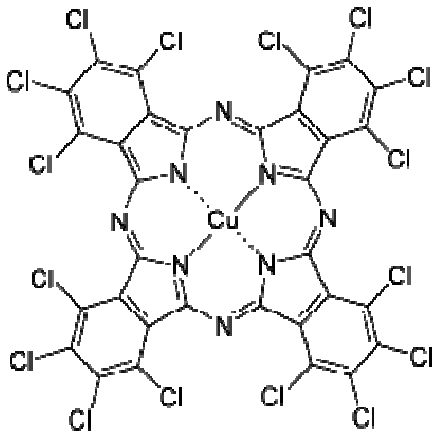
⇒ Replacement of banned «cosmetic» pigments by «technical» pigments

Pigments that were meant or tested for usage in contact with the human body

Legal Status in Cosmetics	Legal Status in Tattoo inks	2011	2009
Allowed for all Purposes	«allowed» in tattoo inks	24%	32%
Restricted admission	not allowed in tattoo inks	32%	28%
Forbidden (Annex II)	not allowed in tattoo inks	1%	1%
Not allowed (not listed!)	«allowed» in tattoo inks	56%	39%

Missing Positive List for Pigments – Do we do the right thing?

Example:



~~C.I. 74260~~

Former main green pigment

Chlorinated

Allowed for cosmetics safe for eye decoration

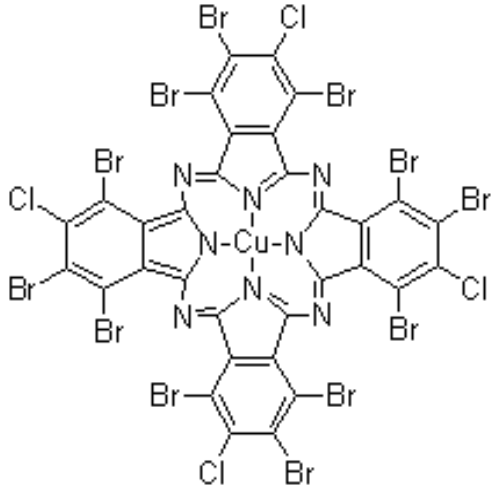
Not allowed in tattoo inks!

Main replacement pigment

Chlorinated & Brominated

Not allowed in cosmetics

Allowed in tattoo inks!



C.I. 74265

Azo-Pigments / Carcinogenic Primary Aromatic Amines

Regulation in Switzerland –

No Azo Pigments allowed that split off into carcinogenic aromatic amines when analysed **according to EN 14362** (Limit 30 mg/kg)

Reasons for Banning	2011 (190 Samples)	2009 (152 Samples)
Aromatic Amines / Azo (Textile Norm: 30 mg/kg)	0.5%	6%

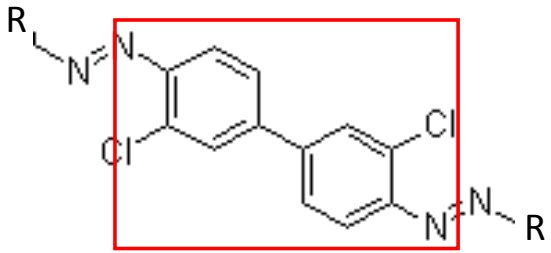
A lot of testing by producers and enforcement labs -> Situation is much improved since 2004

Carcinogenic aromatic amines found:

- o-anisidine
- o-toluidine
- 3'3'-dichlorobenzidine
- 2,4-diainotoluene
- 2,4-diaminoanisole

Diarylide Pigments – Azo-Testing

Diarylides *(C.I. 21090, 21095, 21100, 21105, 21108, 21110, 21115)*
belong to the most often used yellow and orange pigments



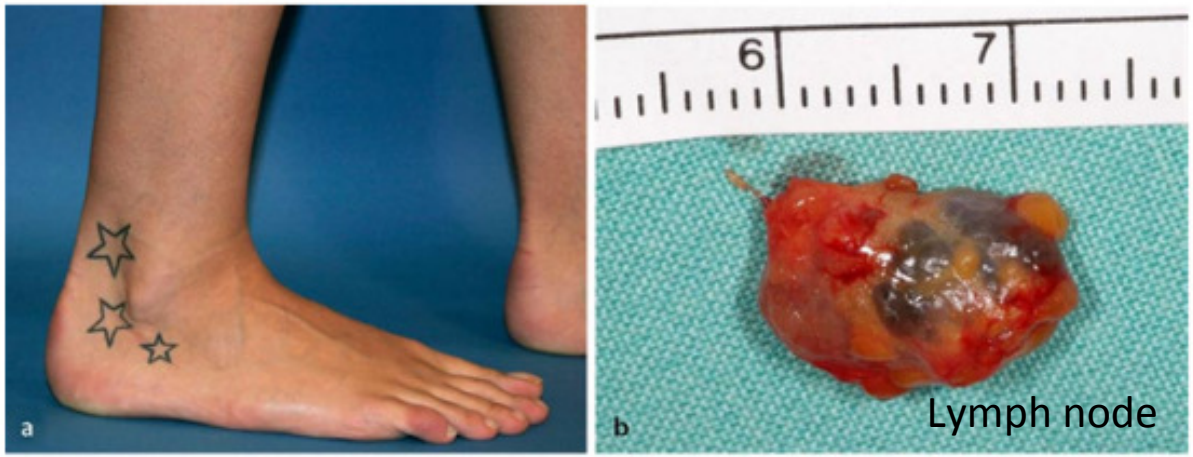
3,3‘-Dichlorbenzidine (3,3-DCB), Carc. Cat. 1B

Very low solubility ->
Negative Results (< 30 mg/kg) in Azo Testing

EXAMPLES		Dichlorobenzidine	
Sample	Pigments	Azo Cleavage	Impurity
137	21095, 21110	36	1
134	21095, 21110	< BG	
116	21095	< BG	
81	21095	< NWG	
133	21095	< BG	
73	21095	< NWG	2
49	21095	< NWG	
25	21095	< NWG	
110	21108	< BG	
136	21110	11	1
77	21110	< BG	
52	21110	34	
111	21115	52	1

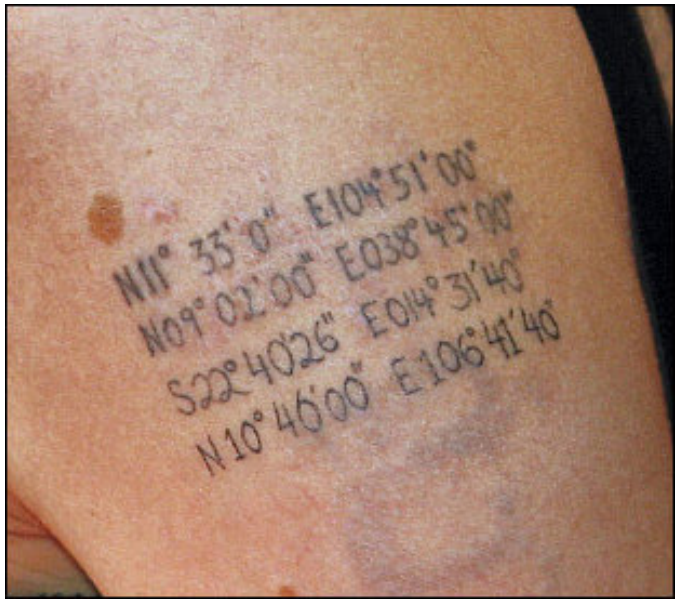
Tattoo Fading / Laser Removal of Tattoos

Physiological distribution of the pigment in the body



S. Kürle et al. :Hautarzt: 2009 Oct;60(10):781-3

Laser Removal



Old Dragon tattoo

Photodegradation:
Tattoo Ink with yellow and orange pigment

20h (!) of Irradiation with Suntester

Diarylide Pigments – Laser Removal of Tattoos

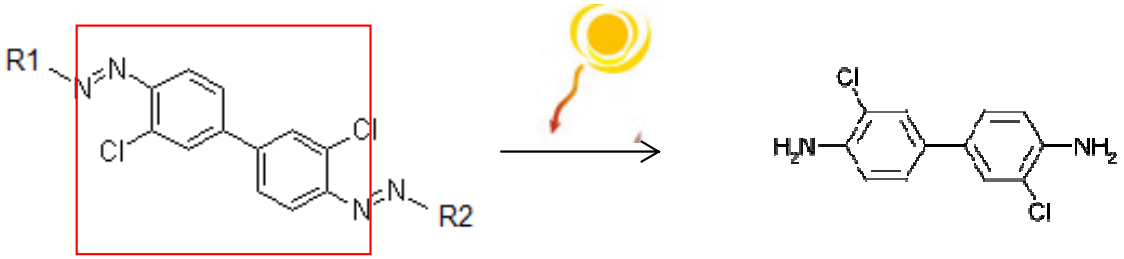
Typical Analysis Results of tattoo ink containing C.I. 21110

3,3-DCB Impurity	3,3-DCB Reductive cleavage	3,3-DCB Laser Irradiation
10 mg/kg	8 mg/kg	110 mg/kg

Thermolabile pigments decay under laser irradiation

Diarylide-Pigments in Tattoo inks release 3,3‘-dichorobenzidine by Irradiation with Laser Light

Sun light splits Azo-Pigments in tattoo inks in vitro



C.I. 21095, 21108, 21110, 21115

3,3‘-Dichlorobenzidine

Sonja Gaugler (University of Hohenheim / State laboratory of Basel-City**):**
“Analysis of bioactive Compounds in Tattoo Inks before and after Irradiation with Sunlight using HPTLC and in situ Detection with Vibrio fischeri”

Experimental design:
39 days in the «sun» between glass plates

All Diarylide Pigments tested released 3,3-Dichlorobenzidine under sunlight

Preservatives

- Positive list – Cosmetics Regulation, Leave-on- Cosmetics
- For unallowed preservatives – 50 mg/kg are tolerated at the moment

Reasons for Banning	2011 (190 Samples)	2009 (152 Samples)
Unallowed Preservatives (Limit 50 mg/kg)	8%	14%
Preservatives (Limits of Cosmetics Regulation)	3%	0.7%

- Tattoo inks usually not preserved with classical microbiocides
- Main preservative formaldehyde?
- Main group of preservatives: isothiazolinones (MI/MCI, BIT, OIT)
- «Cosmetic» Preservatives hardly used, often low concentrations
- In 2004 «Cosmetic» Presevatives were far more often used

Preservatives: 2008 - 2012

Preservative	Samples		Min	Max	Limit
Formaldehyde	55	13%	0.004%	**0.23%**	0.2%
Benzisothiazolone (BIT)	48	12%	0.4 mg/kg	245 mg/kg	
Methylisothiazolinone (MI)/ Methylchlorisothiazolinone (MCI)	18	4%	0.5 mg/kg	**82 mg/kg**	15 mg/kg
Benzoic Acid	17	4%	0.004%	0.07%	0.5%
Octylisothiazolinone (OIT)	15	4%	40 mg/kg	450 mg/kg	
Phenol	11	3%	0.004%	0.43%	
Phenoxyethanol	5	1.2%	0.06%	**1.49%**	1.0%
Glyoxal	5	1.2%	**0.01%**	**0.02%**	0.01%
Methyl Paraben	2	0.5%	0.04%	0.06%	0.4%
Salicylic Acid	2	0.5%	0.02%	0.02%	0.5%
Sorbic Acid	1	0.2%	0.01%		0.6%
Ethyl Paraben	1	0.2%	0.02%		0.4%
Propyl Paraben	1	0.2%	0.01%		0.4%
Bronopol	1	0.2%	0.02%		0.1%
Chlorhexidine	1	0.2%	0.02%		0.3%
o-Phenylphenol	1	0.2%	0.06%		0.2%
4-Chloro-3,5-Dimethylphenol	1	0.2%	0.25%		0.5%

Cosmetic Preservatives

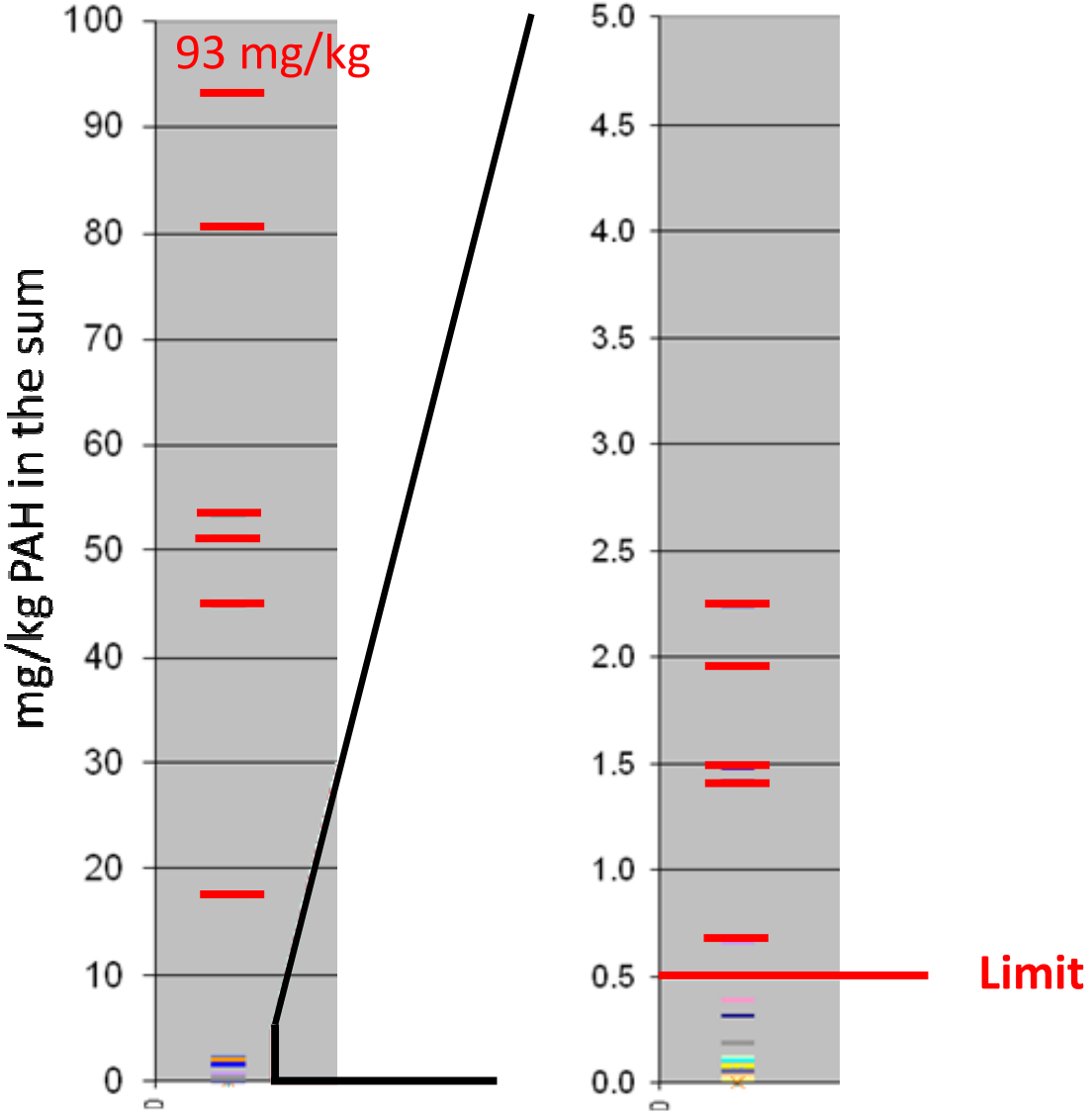
CMR- Substances: Nitrosamines

Reasons for Banning	2011 (190 Samples)	2009 (152 Samples)
N-Nitrosamines (Limit 150 µg/kg)	0%	7%

Nitrosamine	Number of Samples		Min [µg/kg]	Max [µg/kg]	Median [µg/kg]
Nitrosodiethanolamin (NDELA)	56	13%	6	24000	53
Nitrosomorpholin	9	2%	6	650	85
Nitrosodibutylamin	2	0.5%	53	93	73
Nitrosodimethylamin	1	0.2%	17	17	17

Negativ (< 20 µg/kg):
N-Nitroso -diethyl, -dipropyl, -diisopropyl, -diisobutylamin,
N-Nitrosopyrrolidin, N-Nitrosopyrimidin

CMR Substances: Poly aromatic hydrocarbons (PAH)



24 Samples containing black pigments – Microwave-assisted extraction with toluene

Carbon Black is an adsorbens: Convention Method needed!

- 6 samples > 5 mg/kg PAH in the sum
- 13 samples < 0.5 mg/kg PAH in the sum (compliant with ResAP(2008)
- 8 samples > 10 µg/kg Benzo(a)pyrene (30 - 900 µg/kg)

Thank you for your attention