IAQ 2016

KUNST HISTORISCHES MUSEUM WIEN

Preventive conservation strategies in the re-opened collection of the Kunstkammer of the Kunsthistorisches Museum Vienna. Theory versus Practice

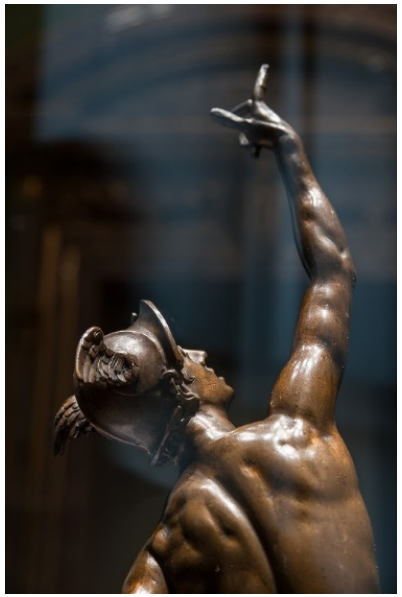
S. Stanek[2], J. Diehl[1], V. Pitthard[2], H. Hanzer[1], M. Griesser[2] and B. Goldmann[1]

[1] Kunstkammer, Conservation Department, Kunsthistorisches Museum Vienna, 1010 Vienna, Austria

[2] Conservation Science Department, Kunsthistorisches Museum Vienna , 1010 Vienna, Austria

KUNST HISTORISCHES MUSEUM WIEN

Preventive conservation strategies

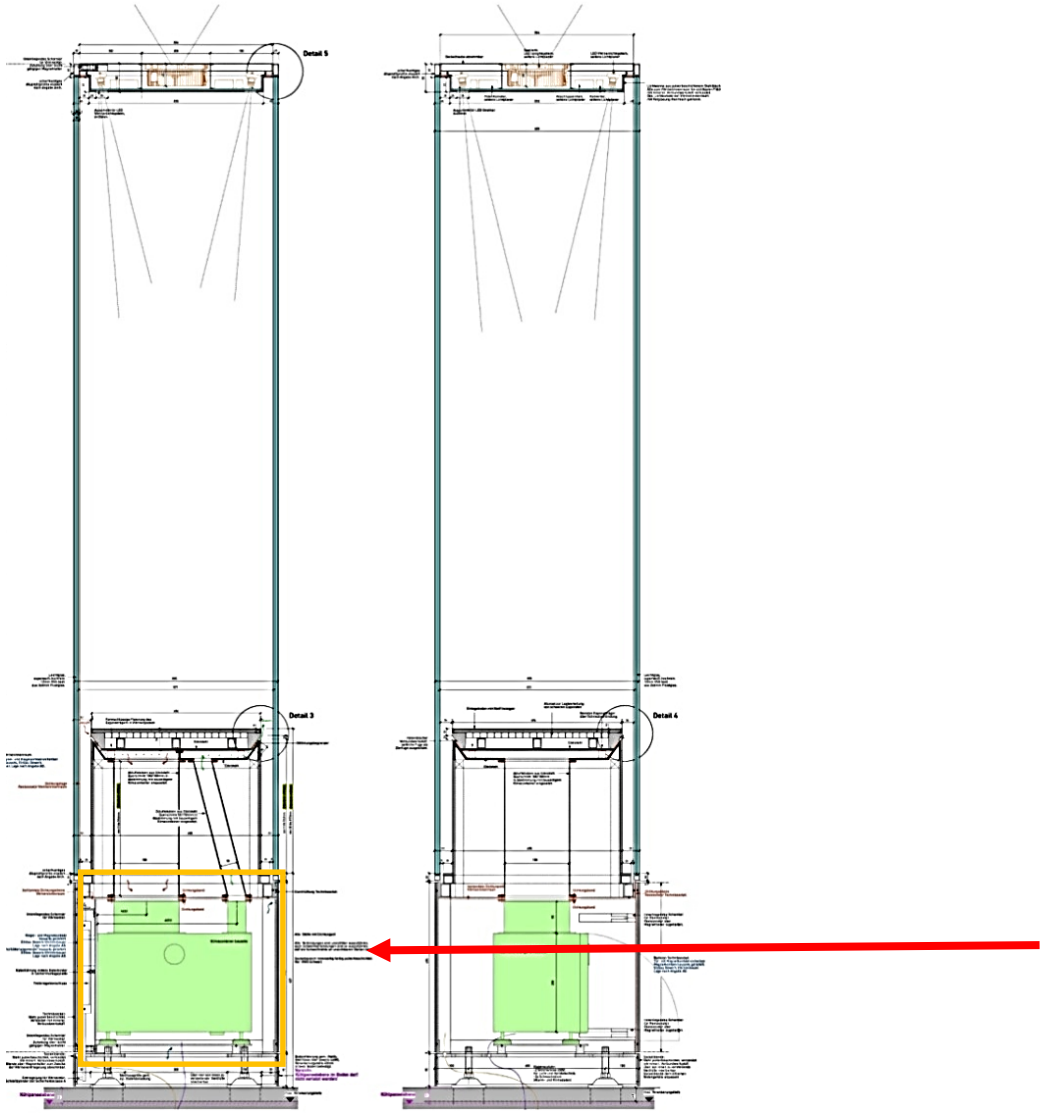


KK 5898, mercury, Giambologna

- HVAC concept of Kunstkammer
- Air circulation system of rooms (activated carbon filters for fresh air and recirculating air)
- Low-emission building materials
- Air circulation system in showcases with passive air conditioning and pollutant filtering
- Showcases: integration of pollutant prevention into tendering process and contract documents
- Testing of showcase materials and emission measurements in test showcases

KUNST HISTORISCHES MUSEUM WIEN

Showcases

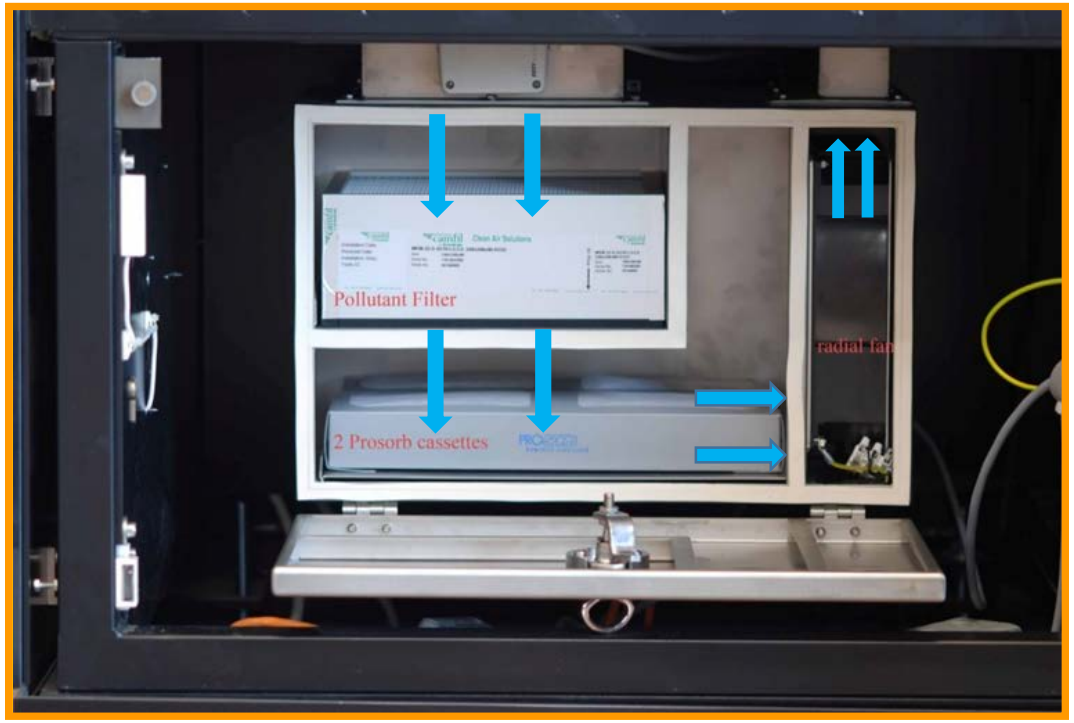


195 Showcases

- internal air circulating system with passive air conditioning (different micro-climates)
- Pollutant filter
- air-thight enclosures with an air exchange rate of <0,1 per day

99 showcases

- air tight enclosures with **no** technical equipment



Climate module for RH control and pollutant filtering

KUNST HISTORISCHES MUSEUM WIEN

Results of emission measurements* in showcases with and without pollutant filtering

KK 3727, fury, Furienmeister

showcase number *Room*	pollutant filter yes/no	VOCs total amount µg/m³	form-aldehyde µg/m³	acet-aldehyde µg/m³	acetic acid µg/m³	formic acid µg/m³
room 1		*788*	*11,7*	*16,1*	*552,6*	*216,3*
showcase 1	yes	719	16,7	18,0	363,9	153,6
room 2		*293*	*11,7*	*16,1*	*552,6*	*216,3*
showcase 2	yes	635	10,4	8,8	262,5	108,6
room 3		*270*	*14,4*	*16,8*	*705,9*	*326,2*
showcase 3.1	yes	1509	16,1	58,2	381,3	187,5
showcase 3.2	yes	2186	20,4	54,1	500,7	161,8
room 4		*1001*	*12,1*	*19,3*	*739,7*	*291,3*
showcase 4	yes	4325	35,3	32,0	419,9	174,8
room 5		*823*	*13,1*	*22,1*	*845,5*	*527,9*
showcase 5.1	yes	2900	16,8	40,8	375,9	156,8
showcase 5.2	yes	2409	18,9	55,3	562,4	217,6
room 6		*227*	*9,7*	*10,1*	*329,0*	*154,9*
showcase 6.1	no	12642	51,2	174,3	539,0	229,6
showcase 6.2	no	13992	51,9	273,4	614,0	113,0

* Measurements performed by BAM

KUNST HISTORISCHES MUSEUM WIEN

Film on object surfaces in showcases without air circulation and pollutant filtering

Milky, glittering crystalline layer

KK 5846, Hercules and the Erymanthian Boar, Giambologna

KK 5501, bassin with snakes, unknown

KUNST HISTORISCHES MUSEUM WIEN

Crystal deposits on objects: open questions

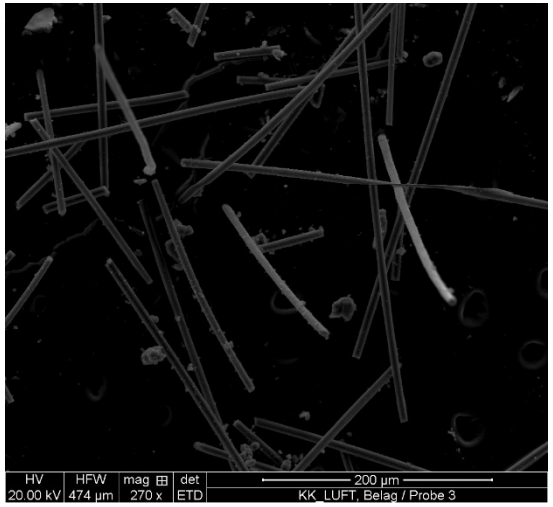
- **Chemical identification/characterisation**
  - What kind of material do we find on the surface?
- **Source of emission**:
  - Where do the crystals come from?
  - Can we locate which part of the showcase is responsible for the formation?
  - What can we learn about the transport mechanism?
- **Assessment of the impact of the contaminants** to **human health** as well as to **metal surfaces**
  - How harmful are they for human health?
  - What is the damaging risk for the objects?
- **Removement of the contaminant** from the objects
  - How to handle/clean the objects?
- **Reduction of concentration**
  - Can we prevent further damage?

KUNST HISTORISCHES MUSEUM WIEN

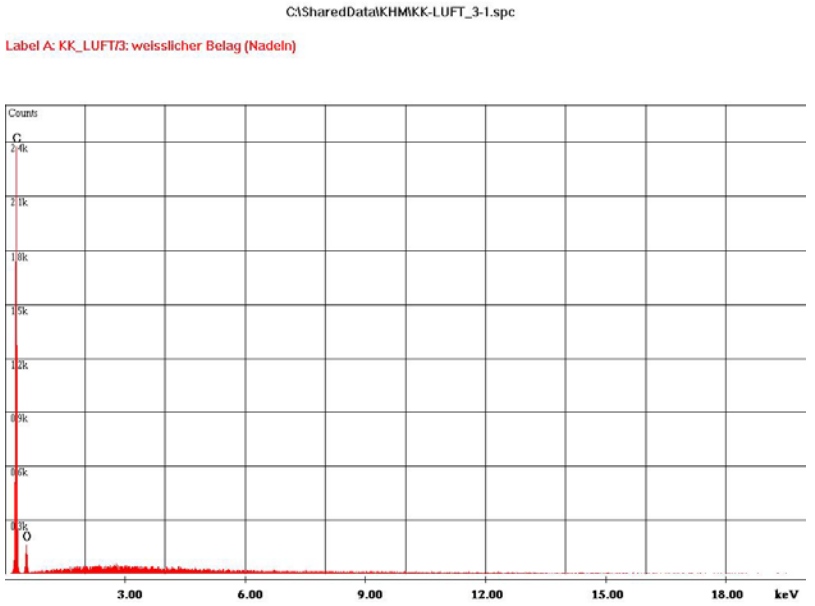
Chemical identification/characterisation- first investigations

What is this crystalline-like deposit?

SEM/EDS



BSE image, 270x



→ **organic compound**

→ needle-shaped appearance

KUNST HISTORISCHES MUSEUM WIEN

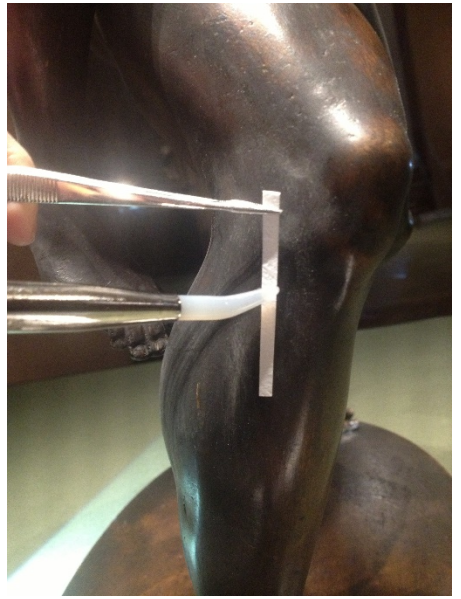
Chemical identification - external investigations

- BAM/Berlin
  analysis of 5 swipe samples by thermodesorption-GC/MS

  → **1,2,2,6,6-pentamethyl-4-piperidinol**
  → benzophenone

- TNO/Utrecht*
  verification of the first analyses:

  → **1,2,2,6,6-pentamethyl-4-piperidinol**



KK6029 Raptusgruppe, showcase 32.11

* special thanks to John Havermans

KUNST HISTORISCHES MUSEUM WIEN

Chemical identification/characterisation-external investigations

- Fraunhofer/WKI

  Swipe samples from object-surfaces, but also from inner glass surface of showcases (hazing)

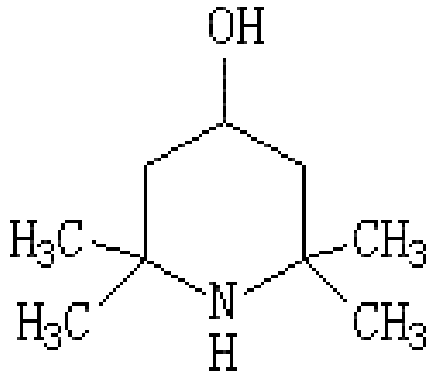
  Extraction in acetone/cold trap-GC/MS

Glass:	→ mainly long-chained **fatty acids**
Object surface:	→ **1,2,2,6,6-pentamethyl-4-piperidinol**
	→ **2,2,6,6-tetramethyl-4-piperidinol**

KUNST HISTORISCHES MUSEUM WIEN

What is this compound like?
2,2,6,6-tetramethyl-4-piperidinol (CAS-Nr. 2403-88-5)*

- Molecular formula: $C_9H_{19}ON$
- Appearance: white powder, microcrystalline
- Soluble in: acetone, ether, chloroforme
- Absorbs moisture easily
- Boiling point: 212-215°C
- Melting point: 131 °C
- Highly alkaline 1% solution pH: 11,47
- Fugacity: 0,4% into air (theoretical distribution, calculation)
- Production volume: ≈ 2.500t/year (main producers: Germany, Switzerland)

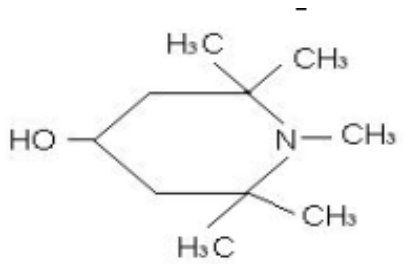


* Source: *UNEP (United Nations Environment Programme) publications/ OECD SIDS*

KUNST HISTORISCHES MUSEUM WIEN

What is this compound like?
1,2,2,6,6-pentamethyl-4-piperidinol (CAS-Nr. 2403-89-6)

- Molecular formula: $C_{10}H_{21}ON$
- Appearance: white solid, cloggy
- Soluble in: acetone, ether, chloroform
- Absorb moisture easily
- Melting point : 70-76°C (literature)



solidified compound after melting at 60 °C

** Source: UNEP (United Nations Environment Programme) publications/ OECD SIDS*

KUNST HISTORISCHES MUSEUM WIEN

What is this chemical applied for?

Used in polymers industry

Production of **plastic antioxidants and/or stabilizers**

- **H**indered **A**mine **L**ight **S**tabilzer (abbreviated as **HALS**):
  - Extremely efficient stabilizers **against light-induced degradation** of most polymers
  - Act as catalysts to minimize the activation of the peroxy radicals to prevent discoloring in varnishes, rubbers and polymers

Source: U.S. Patent 4,405,579 ***Sterically hindered amino acids and tertiary amino acids as promoters in acid gas scrubbing processes***. *S. Guido and W. A. Thaler*

KUNST HISTORISCHES MUSEUM WIEN

Assessment of the impact of piperidinol to human health (2,2,6,6-tetramethyl-4-piperidinol)

How harmful are the contaminants for the museum workers? What are the best precautions to be taken?

Oral toxity: * LOAEL(rats) ≈ 60mg/kg
LD50 (rats) ≈1500mg/kg
no data about human exposure

** LC_{50} inh. (rats): 278 mg/l/48 h
LD_{50} oral (rats): 2413 mg/kg
LD_{50} dermal (rats): >2000 mg/kg

Dermal exposure: chemical is highly irritating to skin,
strong grade of skin-sensitizing potential (pH)

Inhalation exposure: estimated emission amount is low

No available information on **toxicokinetics and metabolism** of these substances

Source: * *UNEP (United Nations Environment Programme) publications/ OECD SIDS*
** *Roth, Daunderer Giftliste Ausgabe 4/2015*

KUNST HISTORISCHES MUSEUM WIEN

Assessment of the impact of piperidinol derivates to metal surfaces

What is the effect on objects?

- **Altered aesthetic:** disfiguring of objects in display
- **Alterable/unsteady structure:**
  - Non-adhesive under exhibition conditions:
    crystalline appearance
  - Modification under lab conditions:

    Crystals liquefy: quite invisible film
    Adhering effect to surface of object?

    Caused by slightly increased T and RH?

- **Long-term damage to object?**

KK 5846, detail
Hercules and the Erymanthian Boar/Giambologna

KUNST HISTORISCHES MUSEUM WIEN

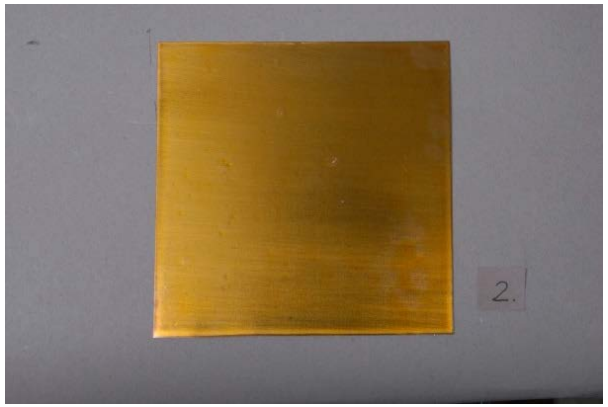
Fabrication of bronze model coupons with organic Renaissance patina

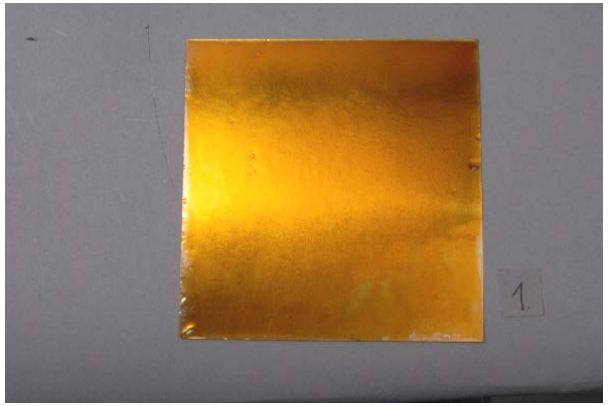
Research project/KHM[1]

- Test on about 70 sculptures
- Good knowledge about surface composition of our Renaissance bronzes

Fabrication of model coupons[2]

- Cooking together equal weights of linsed oil and mastic resin
- Applied on polished metall surface
- Drying at room T
- Heated to 130°C for 48h





[1] *V. Pitthard, R. Stone, S. Stanek, M. Griesser, C. Kryza-Gersch, H. Hanzer: Organic patinas on Renaissance and Baroque bronzes. Interpretation of compositions of the original patination by using a set of simulated varnished bronze coupons, Journal of Cultural Heritage 12(2011), 44-53*

[2] *R. Stone; Organic Patinas on small Bronzes of the Italien Renaissance,Metropolitan Museum Journal 45, 2010*

KUNST HISTORISCHES MUSEUM WIEN

Direct/indirect influence of piperidinol on metal surfaces

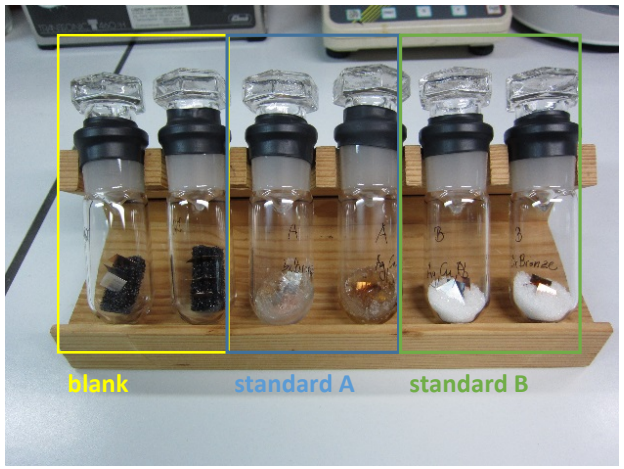
Test conditions:

1,2,2,6,6-pentamethyl-4-piperidinol (CAS-Nr. 2403-89-6): **standard A**

2,2,6,6-tetramethyl-4-piperidinol (CAS-Nr. 2403-88-5): **standard B**

5 different metal surfaces: **Ag, Cu, Pb, bronze , patinated bronze**
Heated to 60 °C, t= 4 weeks,
Visually compared to blanks

Direct contact:



metal coupons immersed in piperidinol-standards

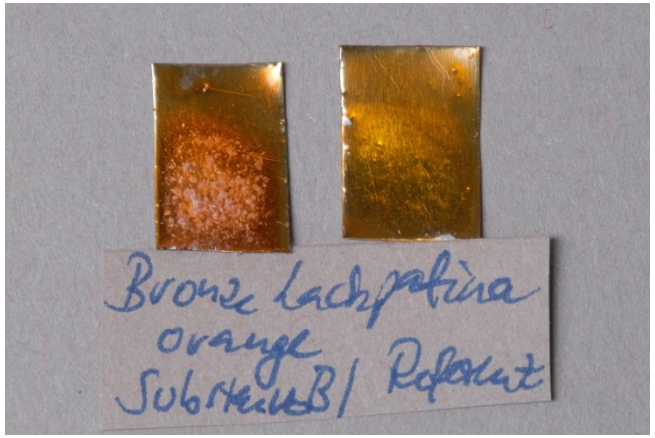
Indirect contact:

metal coupons on nylon filament hanging freely above standard A and B

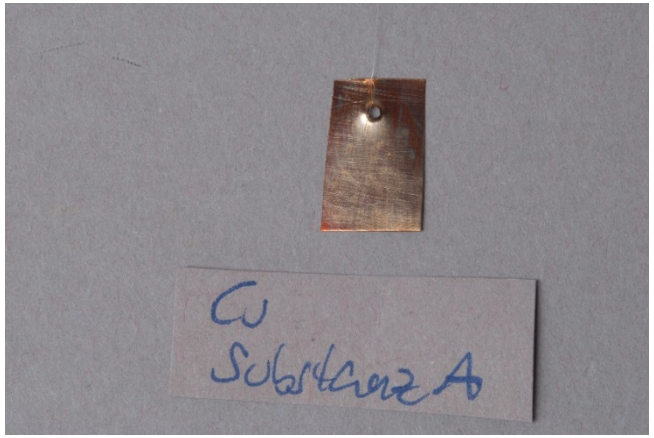
KUNST
HISTORISCHES
MUSEUM
WIEN

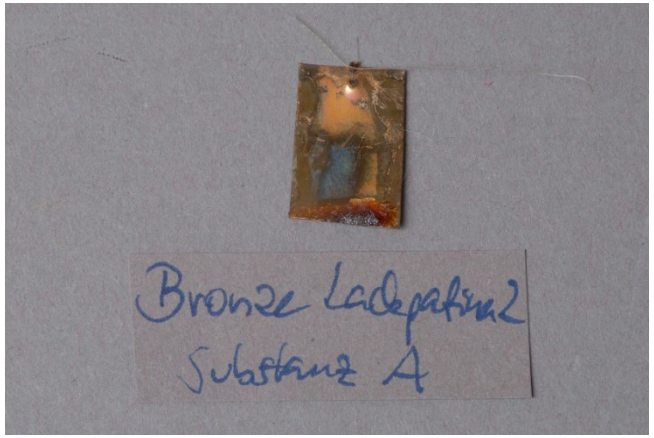
Effects of piperidinol on metal surfaces

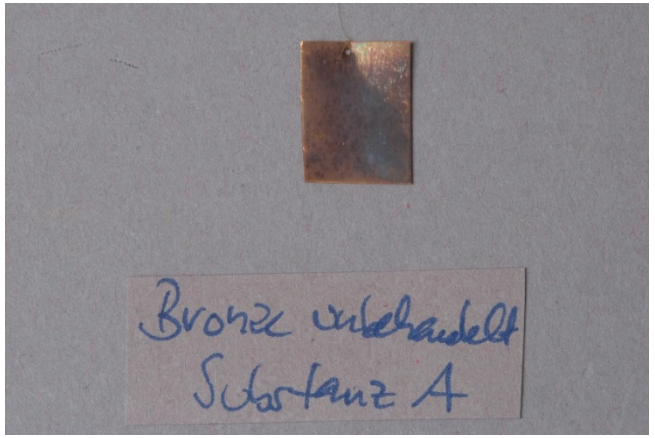
Direct contact



Indirect contact



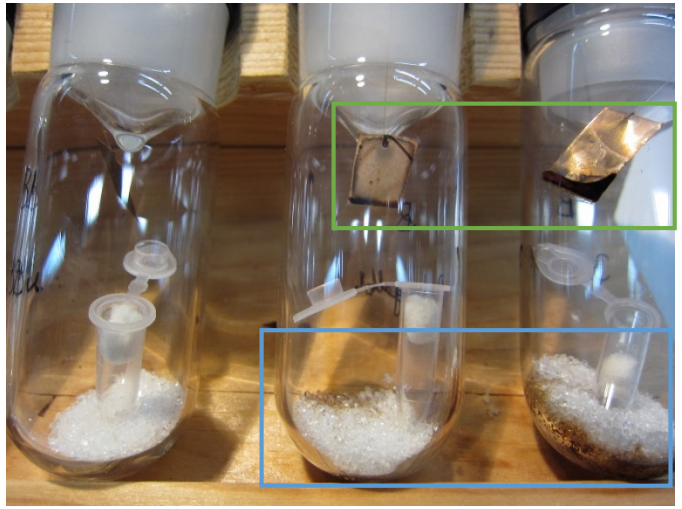




KUNST HISTORISCHES MUSEUM WIEN

Effects of piperidinol on metal surfaces: first results

- Similar influence of standard A and B on metal surfaces
- Direct contact less severe damages than via gaseous reactions
  although piperidinol has a low theoretical fugacity, already small concentration in air seems to affect metals
  - **Silver and lead:** nearly not affected
  - **Copper and bronze:** severe visual changes
    - corrosion dots/ tarnishing surface
    - irregular and/or dull surface
  - **Patinas**: worst damage observable
    - **„etching“** of the patina: gets liquid
    - **brownish residues** on bottom of glass tube



KUNST HISTORISCHES MUSEUM WIEN

Effects of piperidinol on metals: influence of RH?

Repetition of experiments **under increased relative humidity and raised temperature**

SET1: patinated bronze coupons, 0,25g of standard A (powdered) directly on surface, water

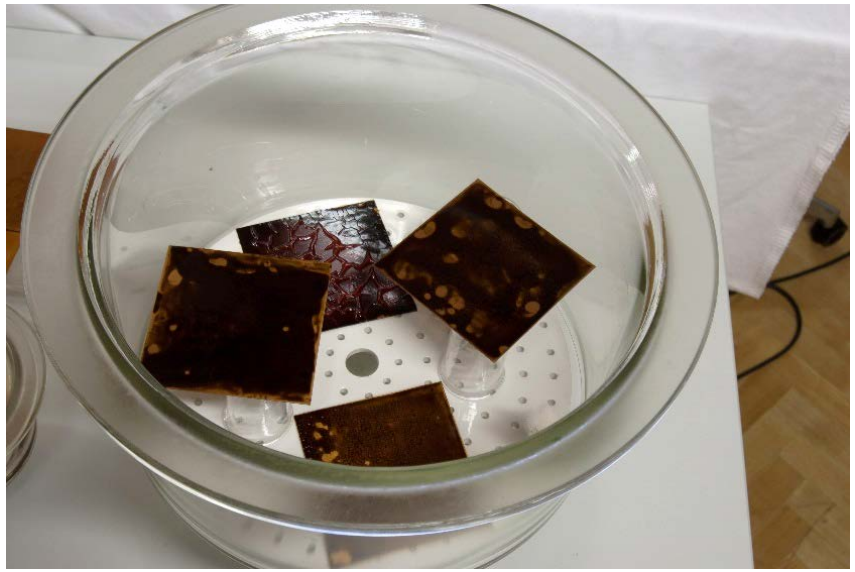
SET2: patinated bronze coupons on perforated base, standard A above: no direct contact, water

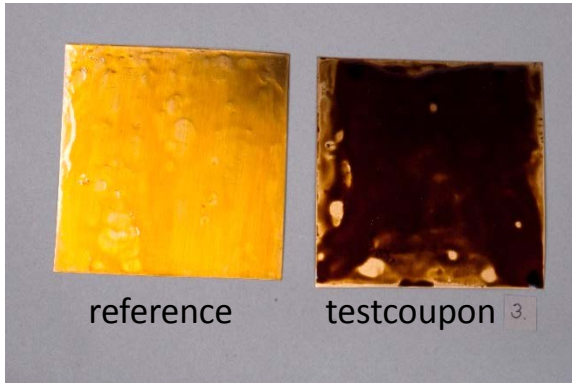
BLANKS: patinated bronze coupons

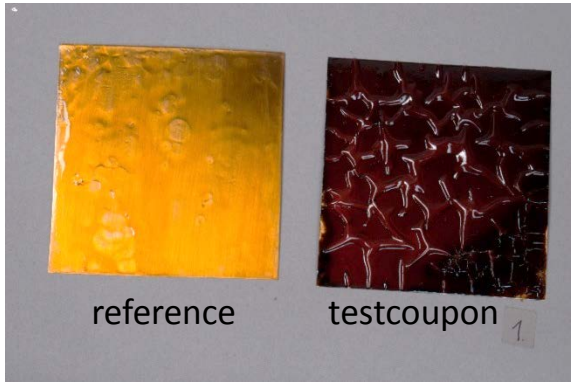
heated to 60 °C

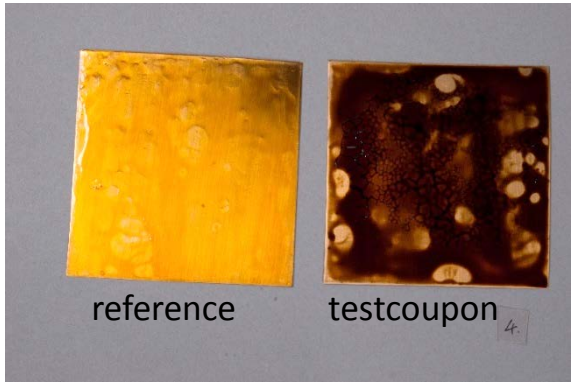
KUNST HISTORISCHES MUSEUM WIEN

Observations: direct contact piperidinol and patinated bronze coupons/ increased RH









Notable changes:

in **colour**: darkening

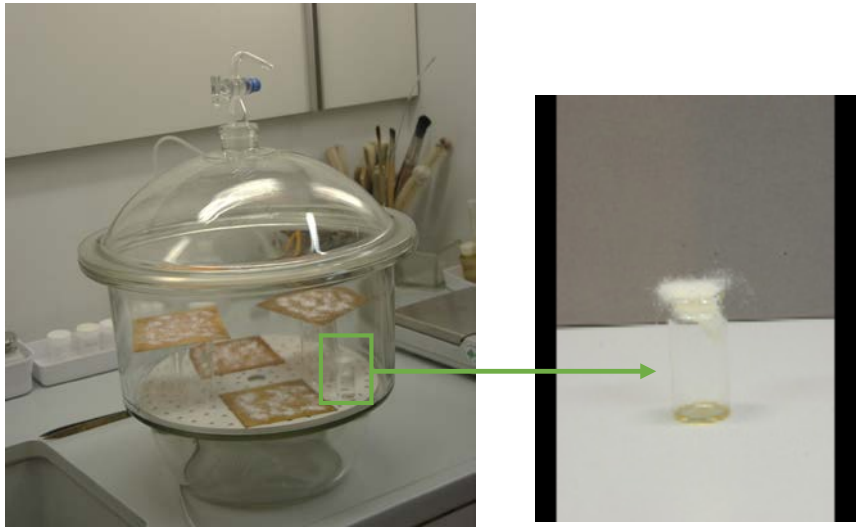
in **surface texture**: wrinkling (in various degrees)

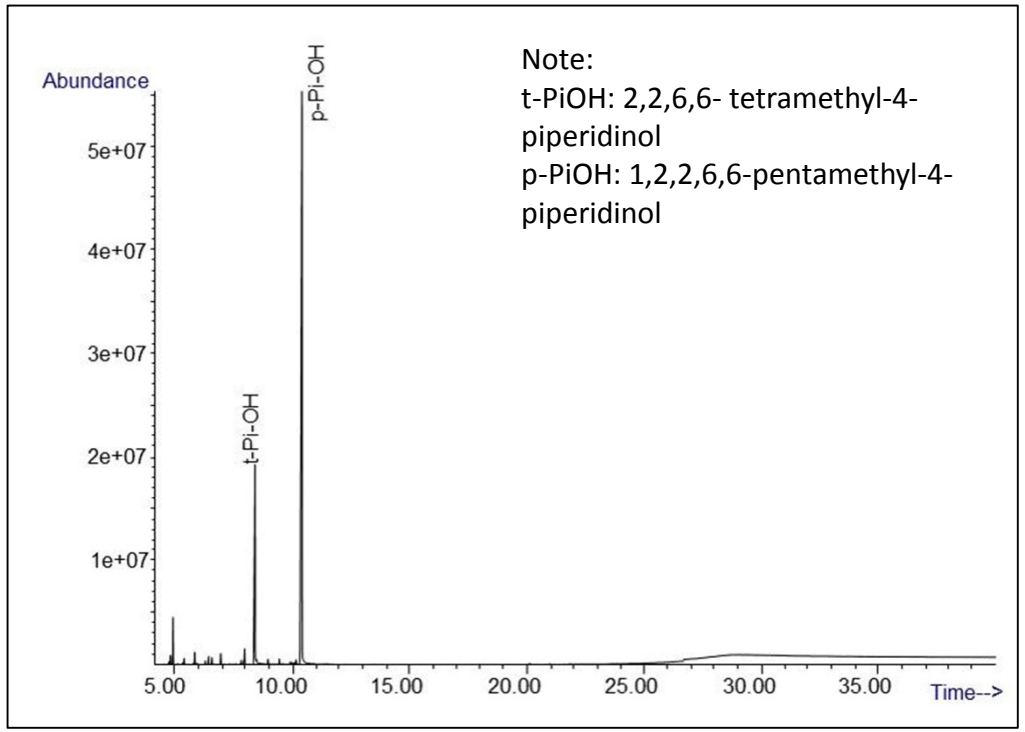
KUNST HISTORISCHES MUSEUM WIEN

What is the residue in the glasstube for water supply composed of?

GC-MS

Extraction/methylation
in methanol: toluene 1:2, Meth-Prep II





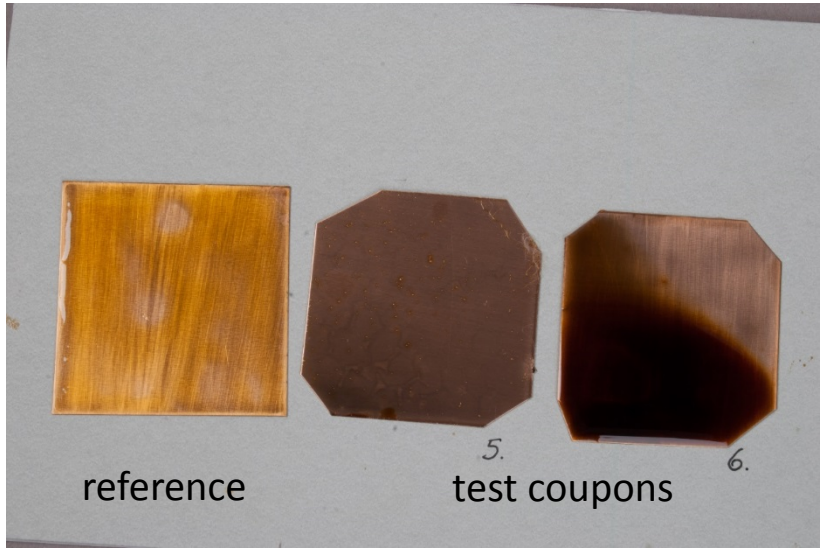
Note:
t-PiOH: 2,2,6,6- tetramethyl-4-piperidinol
p-PiOH: 1,2,2,6,6-pentamethyl-4-piperidinol

chromatogram: brownish residue in water-tube

Is the emission of piperidinol correlated somehow to humidity??

KUNST HISTORISCHES MUSEUM WIEN

Observations: indirect contact piperidinol and patinated bronze coupons/ increased RH



Notable changes:

in **colour**: darkening

in **surface consistency**: from solid to a sticky liquid

in **surface coverage**: patination gets lost

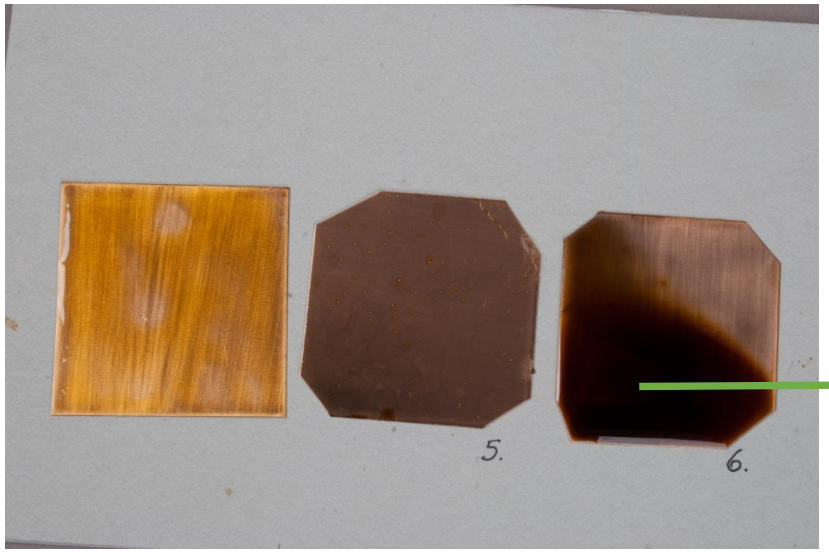
KUNST HISTORISCHES MUSEUM WIEN

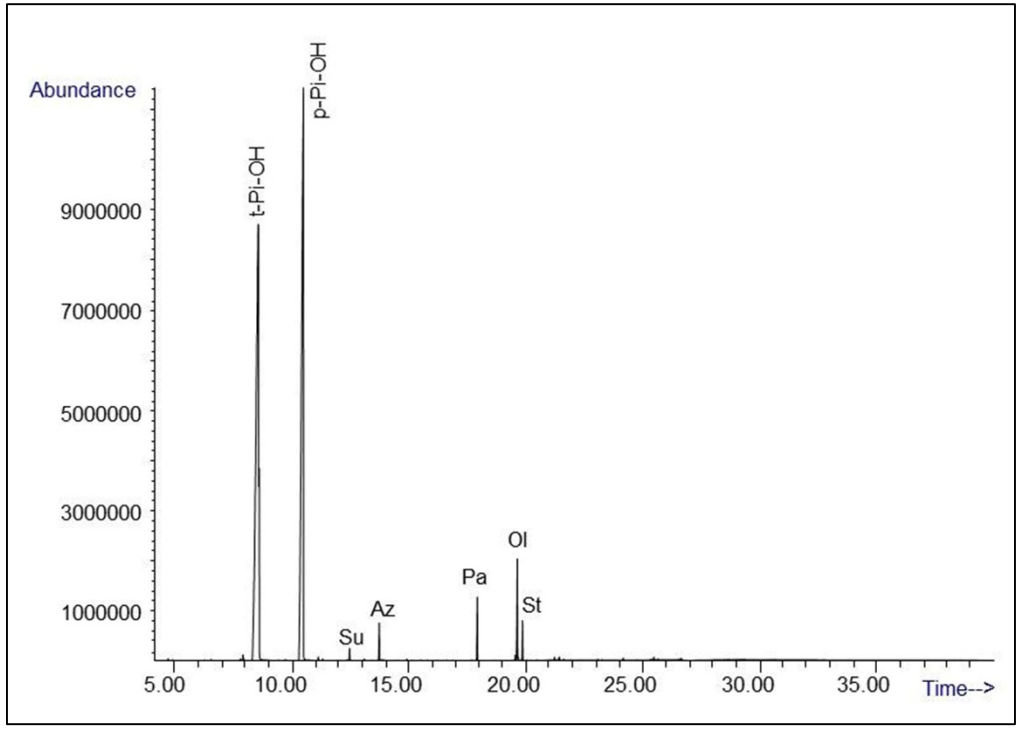
What is the liquidised patina composed of?

GC-MS

Extraction/methylation

TMSH in methanol





Note:
t-PiOH: 2,2,6,6- tetramethyl-4-piperidinol
p-PiOH: 1,2,2,6,6-pentamethyl-4-piperidinol

fatty acids methyl esters from drying oil
(Su=suberic acid, Az=azelaic acid, Pa=palmitic acid, Ol=oleic acid, St=stearic acid)

KUNST HISTORISCHES MUSEUM WIEN

Source of emission- what is the possible cause of the deposit?

- Deposit only **observed after the reinstallation** of the collection

  → correlation between occurrence of deposits and emission from new displaycases

- Focus on **main emission sources** (all construction materials pretested for suitability)

  - Wood (no wood/woodbased materials used)
  - Lacquers (only powder coatings used)
  - **Sealants**

→ **Check of material safety data sheets**

→ **Emission retests**

KUNST HISTORISCHES MUSEUM WIEN

Is it really the sealant?

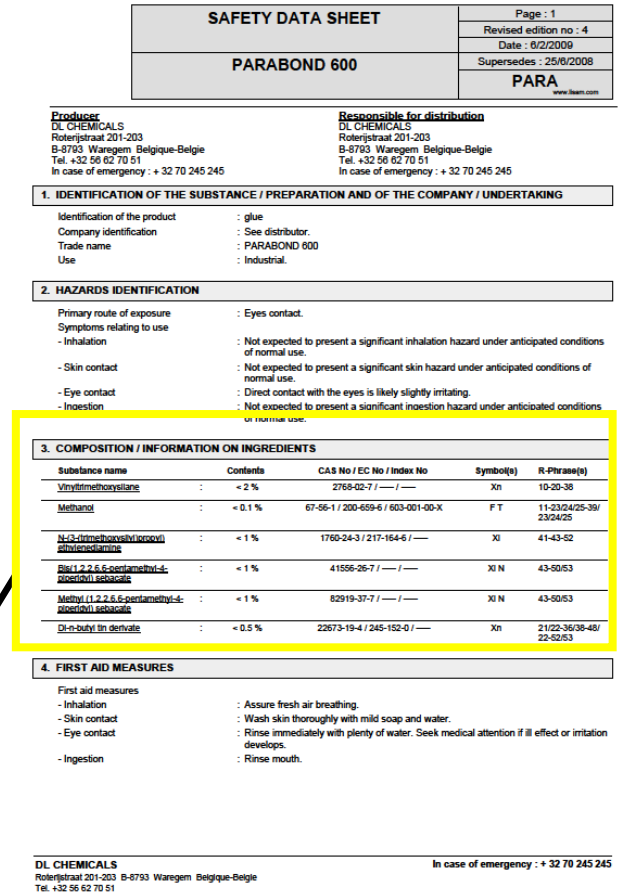
- **Sampling and testing of different construction materials** from the newly installed showcases/BAM-Berlin:

  presence of 1,2,2,6,6-pentamethyl-4-piperidinol

  in two sealants confirmed

- Check of **material safety data sheets of used sealant**

COMPOSITION / INFORMATION ON INGREDIENTS
Substance name Contents CAS No / EC No / Index No Symbol(s) R-Phrase(s)
Vinyltrimethoxysilane : < 2 % 2768-02-7 / ----- / ----- Xn 10-20-38
Methanol : < 0.1 % 67-56-1 / 200-659-6 / 603-001-00-X F T 11-23/24/25-39/23/24/25
N-(3-(trimethoxysilyl)propyl) ethylenediamine : < 1 % 1760-24-3 / 217-164-6 / ----- Xi 41-43-52
Bis(1,2,2,6,6-pentamethyl-4- piperidyl) sebacate : < 1 % 41556-26-7 / ----- / ----- Xi N 43-50/53
Methyl (1,2,2,6,6-pentamethyl-4- piperidyl) sebacate: < 1 % 82919-37-7 / ----- / ----- Xi N 43-50/53
Di-n-butyl tin derivate : < 0.5 % 22673-19-4 / 245-152-0 / ----- Xn 21/22-36/38-48/22-52/53



SAFETY DATA SHEET | Page : 1
Revised edition no : 4
Date : 6/2/2009
PARABOND 600 | Supersedes : 25/6/2008
PARA

Producer
DL CHEMICALS
Roterijstraat 201-203
B-8793 Waregem Belgique-Belgie
Tel. +32 56 62 70 51
In case of emergency : + 32 70 245 245

Responsible for distribution
DL CHEMICALS
Roterijstraat 201-203
B-8793 Waregem Belgique-Belgie
Tel. +32 56 62 70 51
In case of emergency : + 32 70 245 245

1. IDENTIFICATION OF THE SUBSTANCE / PREPARATION AND OF THE COMPANY / UNDERTAKING

Identification of the product : glue
Company identification : See distributor.
Trade name : PARABOND 600
Use : Industrial.

2. HAZARDS IDENTIFICATION

Primary route of exposure : Eyes contact.
Symptoms relating to use
- Inhalation : Not expected to present a significant inhalation hazard under anticipated conditions of normal use.
- Skin contact : Not expected to present a significant skin hazard under anticipated conditions of normal use.
- Eye contact : Direct contact with the eyes is likely slightly irritating.
- Ingestion : Not expected to present a significant ingestion hazard under anticipated conditions of normal use.

3. COMPOSITION / INFORMATION ON INGREDIENTS

Substance name		Contents	CAS No / EC No / Index No	Symbol(s)	R-Phrase(s)
Vinyltrimethoxysilane	:	< 2 %	2768-02-7 / ---- / ----	Xn	10-20-38
Methanol	:	< 0.1 %	67-56-1 / 200-659-6 / 603-001-00-X	F T	11-23/24/25-39/23/24/25
N-(3-(trimethoxysilyl)propyl) ethylenediamine	:	< 1 %	1760-24-3 / 217-164-6 / ----	Xi	41-43-52
Bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate	:	< 1 %	41556-26-7 / ---- / ----	Xi N	43-50/53
Methyl (1,2,2,6,6-pentamethyl-4-piperidyl) sebacate	:	< 1 %	82919-37-7 / ---- / ----	Xi N	43-50/53
Di-n-butyl tin derivate	:	< 0.5 %	22673-19-4 / 245-152-0 / ----	Xn	21/22-36/38-48/22-52/53

4. FIRST AID MEASURES

First aid measures
- Inhalation : Assure fresh air breathing.
- Skin contact : Wash skin thoroughly with mild soap and water.
- Eye contact : Rinse immediately with plenty of water. Seek medical attention if ill effect or irritation develops.
- Ingestion : Rinse mouth.

DL CHEMICALS
Roterijstraat 201-203 B-8793 Waregem Belgique-Belgie
Tel. +32 56 62 70 51
In case of emergency : + 32 70 245 245

KUNST HISTORISCHES MUSEUM WIEN

Removement of the contaminant: dry/wet cleaning

How can we get rid of the glittering layer?

Dry cleaning (brush, microfiber clothes)

- If film is crystalline

  not highly adhesive and could be removed dryly

- Problem of film`s modification (change of RH and T)

  non-adhesive film gets liquidised

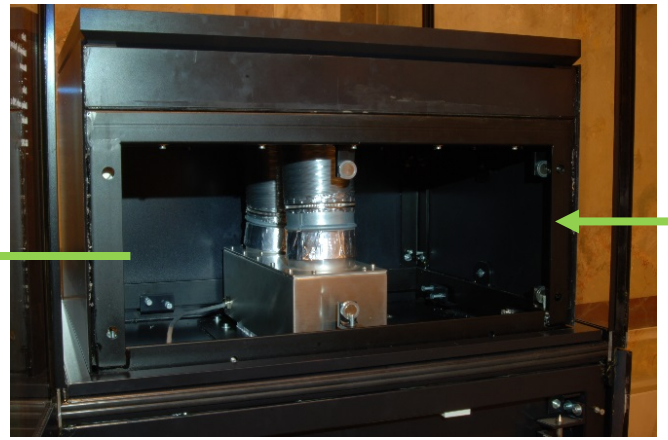
Wet cleaning (solvents)

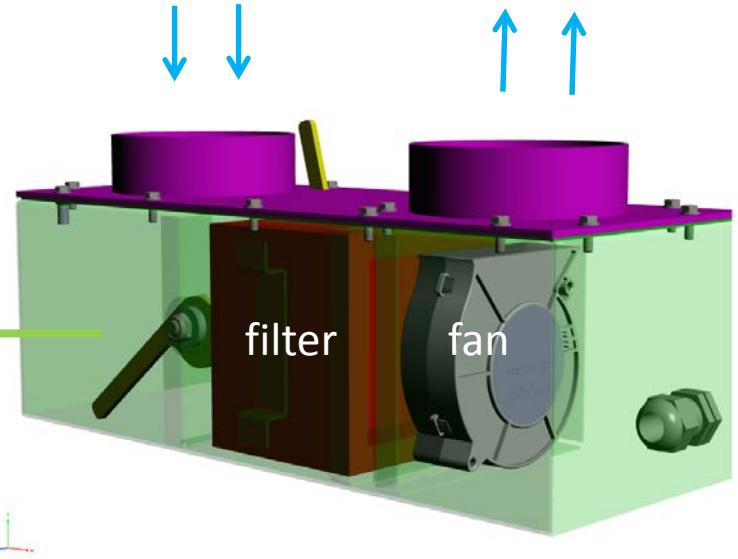
- No effect with white spirit, water less effective than alcohols
- Needs polar solvents like EtOH (but possibly a threat to patina)

KUNST
HISTORISCHES
MUSEUM
WIEN

Upgrading of show cases with a filtering system

Air *circulating* module





New filtering prototype

KUNST HISTORISCHES MUSEUM WIEN

Results of emission measurements* after 8 weeks operation time of the filtering prototype

	VOC (C6-C16)	Formaldehyde	Acetaldehyde	Formic Acid	Acetic Acid
Showcase 1	2078/2014	31/30	82/82	7/7	223/216
Room XXVII	52/54	5/5	6/7	9/8	75/68
Showcase 2	3034/3096	26/25	46/45	<5/<5	85/81
Room XIX	32/41	4/4	4/4	12/12	65/64
Showcase 3 with filter module	61/39	22/22	<3/<3	<5/<5	<5/9
Showcase 4	2740/2776	19/19	25/25	<5/<5	77/79
Room corridor	80/86	6/7	6/6	9/12	60/60

→ **Are activated carbon filters able to adsorb piperidinol????**

* Fraunhofer/WKI

KUNST
HISTORISCHES
MUSEUM
WIEN

No detection of piperidinol in the filters – what does that mean for us?

KK 1, detail
Vanitas/ M. Erhart

- Is piperidinol **also present in showcases with filtration** system and we just do not see it?
- Is it **retained somewhere else** but in the filters? (Prosorb?)
- Is there a **change in structure** through chemical reactions with other pollutants in the filter/air?

KUNST HISTORISCHES MUSEUM WIEN

Is piperidinol also present in showcases with filtration system?

GC-MS

swipe samples extracted in aceton

display-case	pollution filtering	visible deposit	piperidinol detected (not concentrated)	piperidinol detected (concentrated to 1/10 at 60°C)
36.11	**+**	**-**	**-**	**-**
33.08	**-**	**+**	**+**	**++**
33.03	**+**	**-**	**-**	**+**
27.20	**+**	**+/only traces**	-	**+**

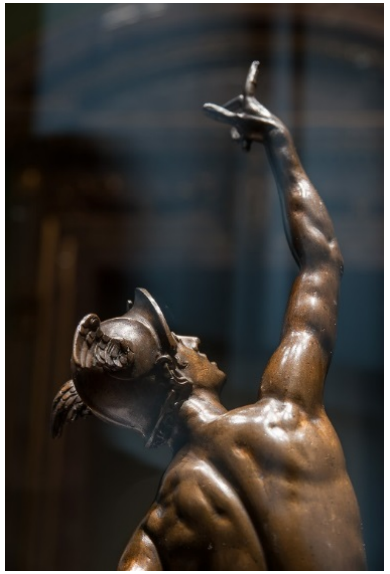
KK 5893, showcase27.20
Allegorie der Astronomie/ Giambologna

KUNST HISTORISCHES MUSEUM WIEN

Perspectives

Further investigations

- Collaboration with filter manufacturer to execute measurements about the **filtration efficiency of piperidinol**
- Better knowledge of **emission, and condensation/precipitation mechanism**
- **Monitoring of a larger variety of objects:** different surface materials, different showcase types (with/without filtering)
- Further testing for **safe cleaning** of the objects



KK 5898, mercury, Giambologna