Institut
für Galvano- und
Oberflächentechnik
Solingen GmbH & Co. KG

Report on Findings

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-english edition-

dated
14th July 2012

Commissioning Party:

Merck KGaA
Dr Gerhard Jonschker
Frankfurter Strasse 250
64293 Darmstadt

Testing location:

Institut für Galvano- und Oberflächentechnik
Solingen GmbH & Co. KG
Grünewalder Str. 29-31
42657 Solingen

The task

Dr Jonschker of Merck KGaA commissioned IGOS to analyse the way a particular wetting agent produced by his company worked in comparison with two other wetting agents (competitors' products) in a Cr(VI) electrolyte under real plating conditions.

Cr(VI) electrolytes are used to create high-gloss and hard chromium coatings. When chromium is deposited from solutions containing Cr(VI), large quantities of hydrogen gas are released which causes corresponding amounts of aerosols containing Cr(VI) to collect on the surface of the electrolyte. The efficiency rating of Cr(VI) electrolyte is approx. 20%, i.e. 20% of the electricity applied is used for metallic deposition while the remaining 80% is used to generate hydrogen gas.

The wetting agents are used in conjunction with Cr(VI) electrolyte mainly to reduce the amount of chromium aerosols generated during electrolysis or prevent them completely.

It was agreed that IGOS would analyse the effectiveness of the three wetting agents by comparing the volumes of Cr(VI) in the extracted air in a controlled experimental set-up.

Wetting agents

Designations of wetting agents:

1. Merck KGaA	MAFS-010 (batch OF1TM0146)
2. Atotech Deutschland GmbH	Fumetrol FL 21
3. HSO Herbert Schmidt GmbH & Co. KG	HSO chrome wetting agent FL

The solution concentration was in accordance with supplier's instructions:

1. MAFS-010 (batch OF1TM0146)	0.4 ml/l
2. Fumetrol FL 21	2.0 – 2.5 ml/l
3. HSO chrome wetting agent FL	0.1 ml/l

Implementation

Test period: 01/2012 – 05/2012

Tester: Kuhn

It was agreed that, initially, the wetting agents would be analysed in connection with deposition using a hard chromium electrolyte and, in a second phase, deposition in connection with a high-gloss chromium electrolyte.

1st test phase

In the first test phase, a series of tests was carried out for deposition of hard-chromium coatings.

For all these tests, the following basic electrolyte was used:

Atotech Heef 25 hard-chromium electrolyte

a) Process parameters of the chromium electrolytes used:

	260 g/l Atotech Heef 25 make-up salt	
	approx. 3 g/l Cr(III)	
	approx. 3 g/l sulphate	
Electrolyte volume:	4.5 l (5 l glass beaker)	
Electrolyte surface:	2 dm²	
Electrolyte temperature:	55-60 °C	
Electricity supply:	40 A	
Specimen surface area	0.8 dm²	
Current density:	50 A/dm²	
Cathode:	1 round Cu rod	dimensions ∅ 1.5 x 20 cm
	Immersion depth:	1.7 dm, equivalent to 0.8 dm²
Anodes:	2 x PbSn6	dimensions: 17 x 5 cm

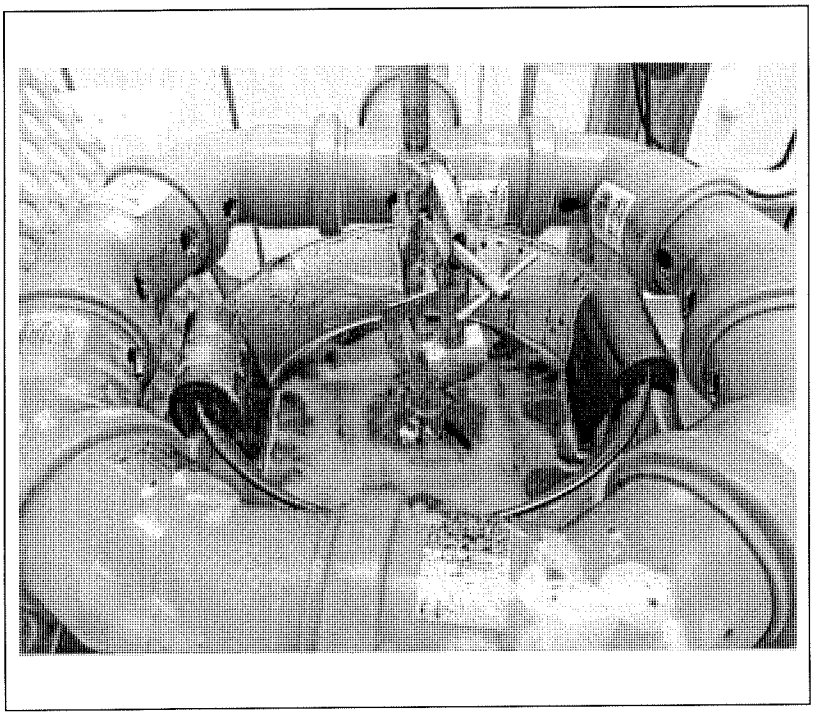


Fig. 01

Experimental set-up
Electrolytic cell

b) Process parameters for extracted air by analogy to DIN EN 13284

Exhaust system:	Piping: ∅ 50 mm with 13 drilled holes,
	Each hole: ∅11 mm, arranged around the rim of the glass beaker
Air exhaust speed:	approx. 5 m/s
Quantity of air exhausted:	3 l/min

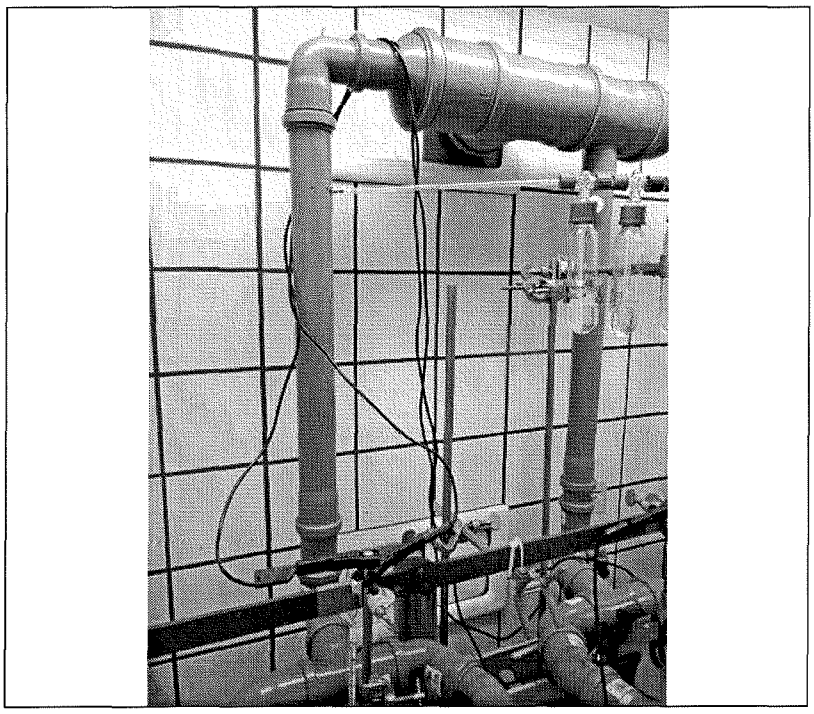


Fig. 02

Experimental set-up for air exhaust

Overview

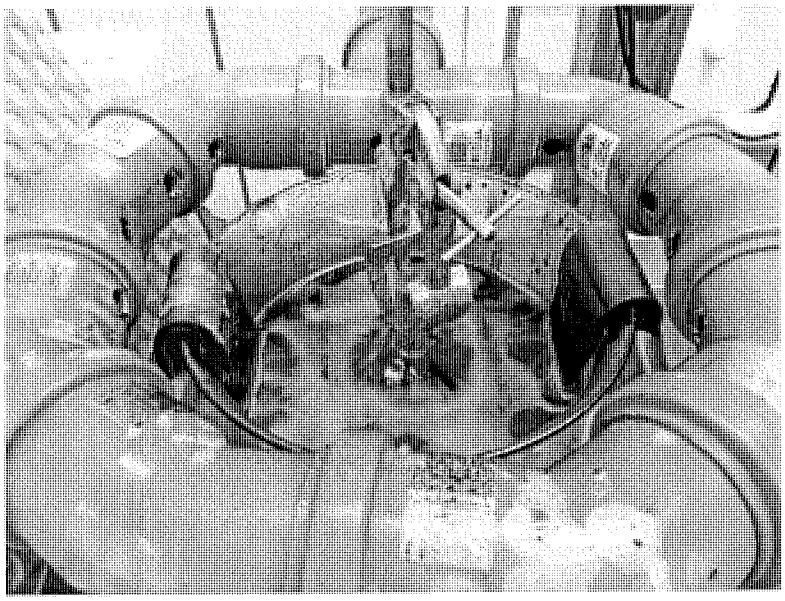


Fig. 03

Experimental set-up for air exhaust

Detail view of electrolyte air exhaust on the electrolyte

c) Process parameters Cr(VI) for taking specimens from exhaust air

Specimen hole:	55 cm above level of electrolyte
Measuring probe diameter:	4 mm
Taking sample of air:	Muenke wash bottles with filter cartridges
Exhaust quantity:	between 100 and 150 l; the exact volume was recorded using a calibrated gas meter

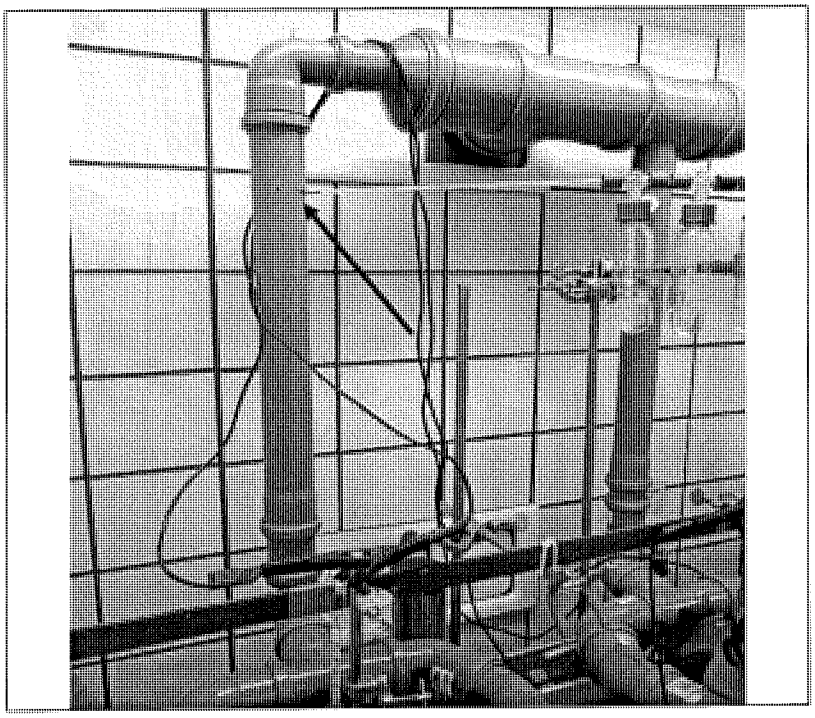


Fig. 04

Overview
Sampling the exhaust air (arrow)

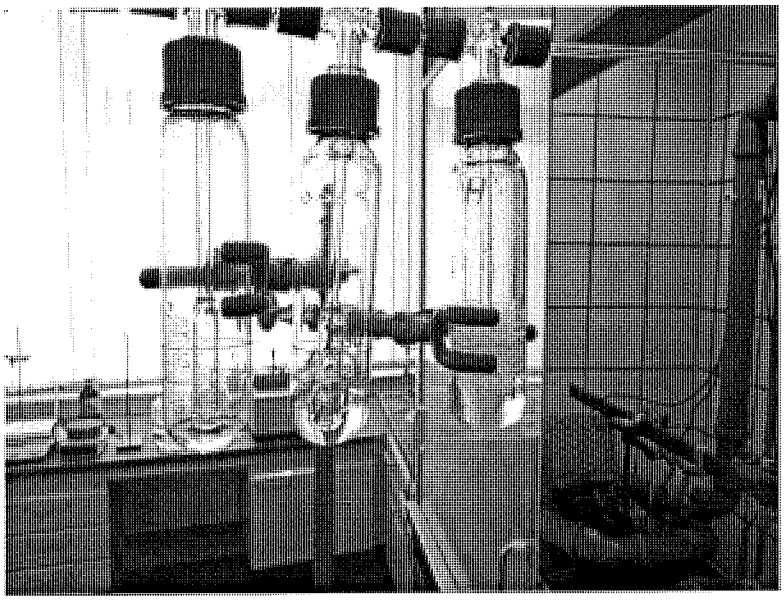


Fig. 05

Sampling using wash bottles

d) Process parameters for Cr(VI) analysis in accordance with DIN EN 15205
   - Transfer eluate to a 100 ml volumetric flask
   - Add 2 ml of phosphoric acid (700 g/l)
   - Add 1 ml diphenylcarbazide (0.1 g/10 ml acetone)
   - Wait to allow 10 min reaction time
   - Measurement of absorption in a UV spectrometer at 540 nm using a 50 mm cuvette

e) Measuring surface tension

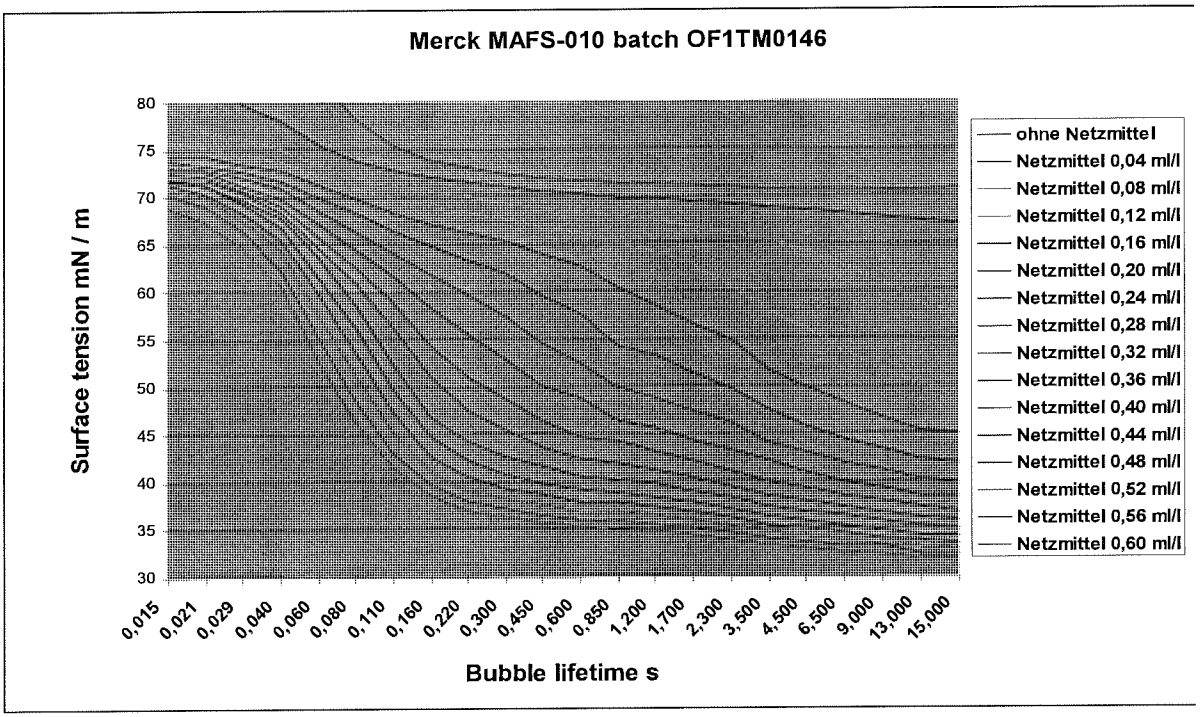
Measuring equipment:	Sita pro line t15
Measuring temperature:	23-25 °C
Sample taken:	approx. 40 ml electrolyte

Bubble lifetime:	Merck wetting agent:	0.16 s
	Atotech wetting agent:	6.5 s
	HSO wetting agent:	13 s

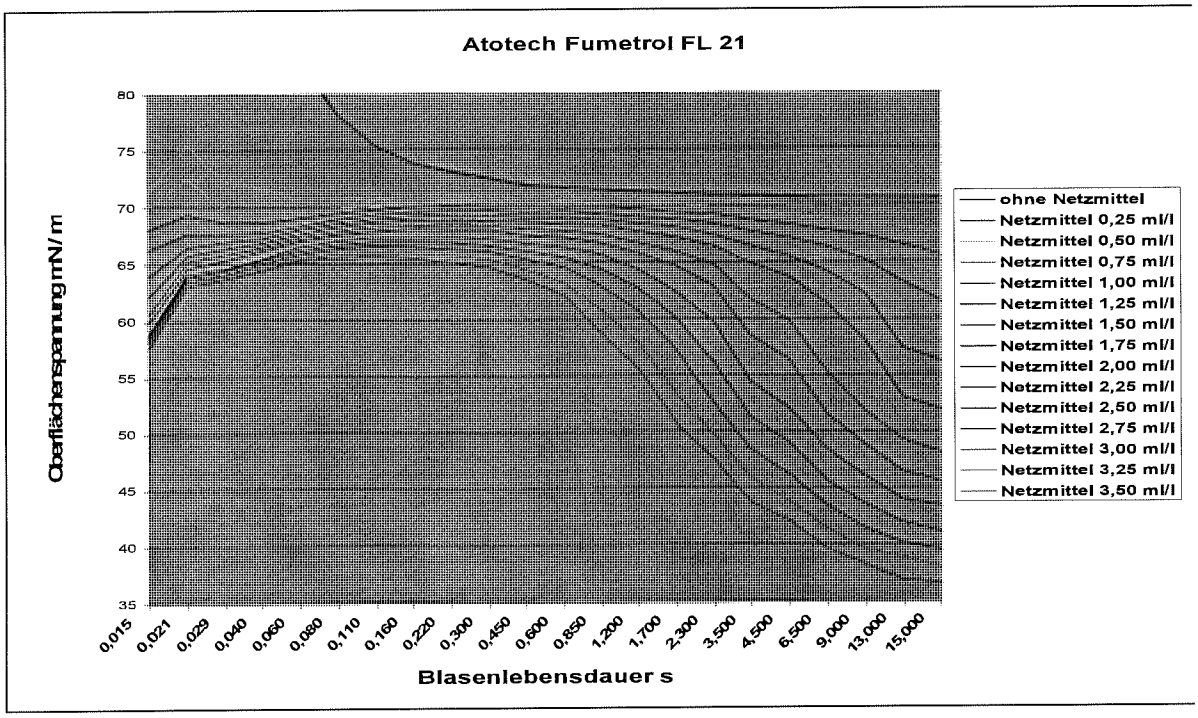
A change in the surface tension can allow the concentration of wetting agent in the electrolyte to be deduced for a given bubble lifetime.

To generate the calibration curve, we selected the bubble lifetime of each additive that produced the maximum change in surface tension for different concentrations.

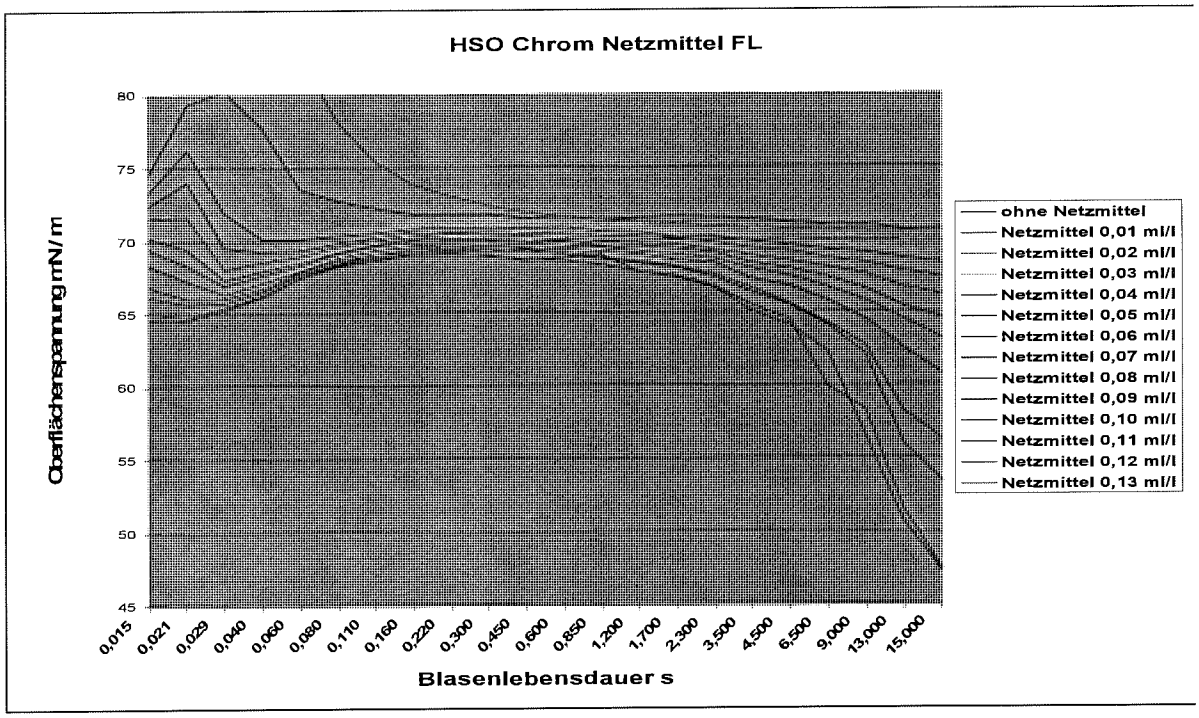
Measuring surface tension



Graph 01: Measurement of surface tension for Merck wetting agent
Calibration curves



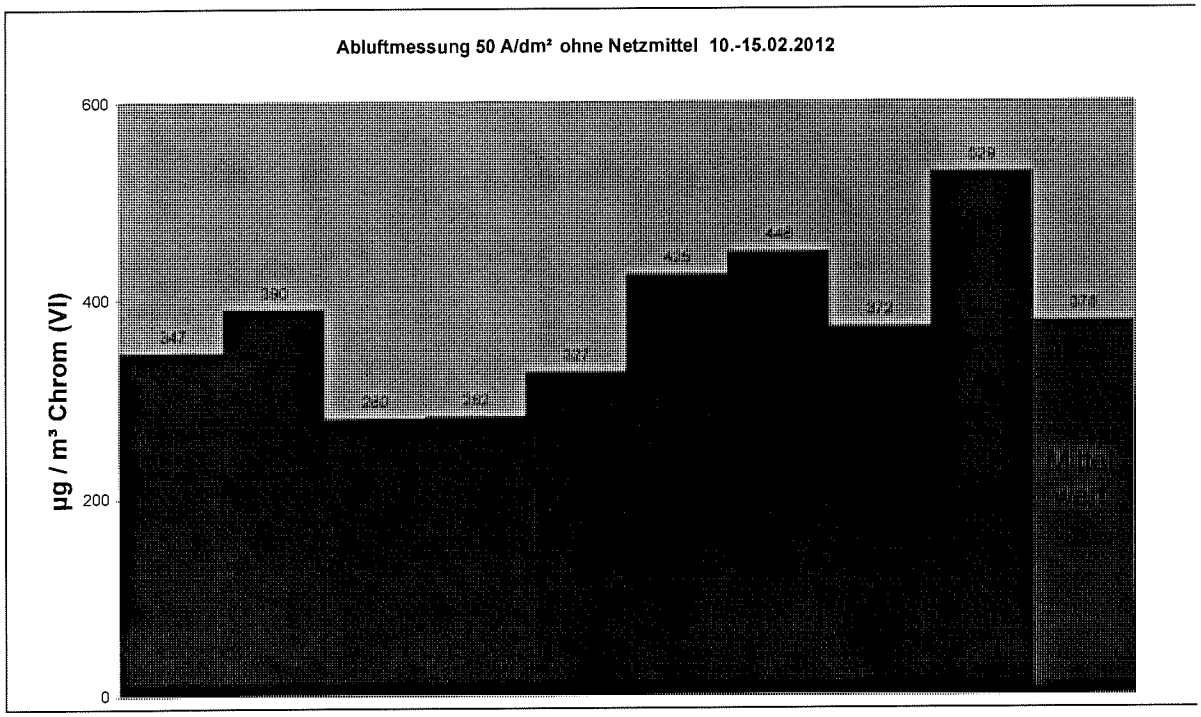
Graph 02: Measurement of surface tension for Atotech wetting agent
Calibration curves



Graph 03: Measurement of surface tension for HSO wetting agent
Calibration curves

Results under hard chrome-plating conditions

1. Cr(VI) measurement with chromium electrolyte without wetting agent



Graph 04 Results of extracted air measurements at 50 A/dm² without wetting agent

All measurements are in µg/m³

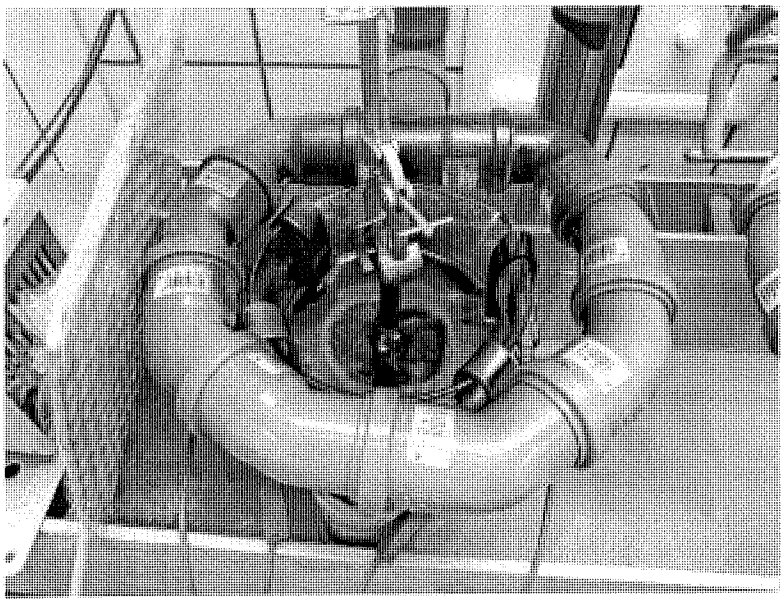


Fig. 06

Electrolytic cell for
Graph 04

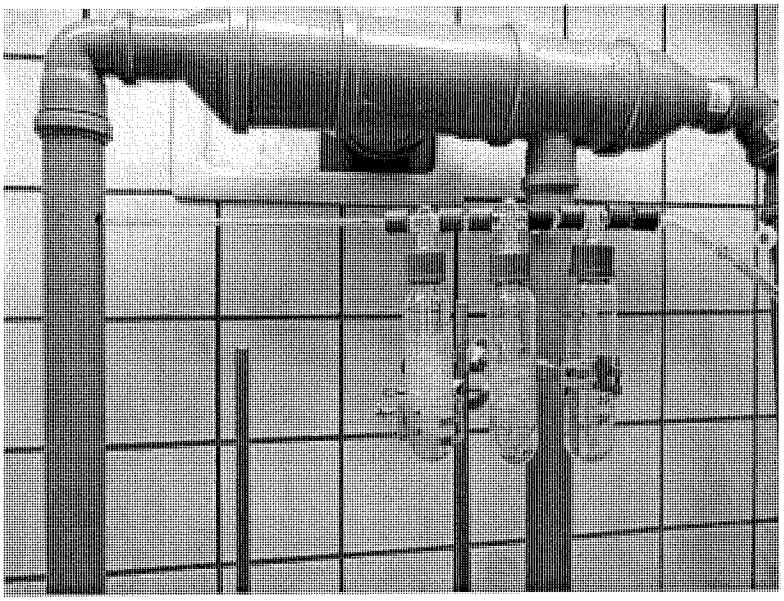
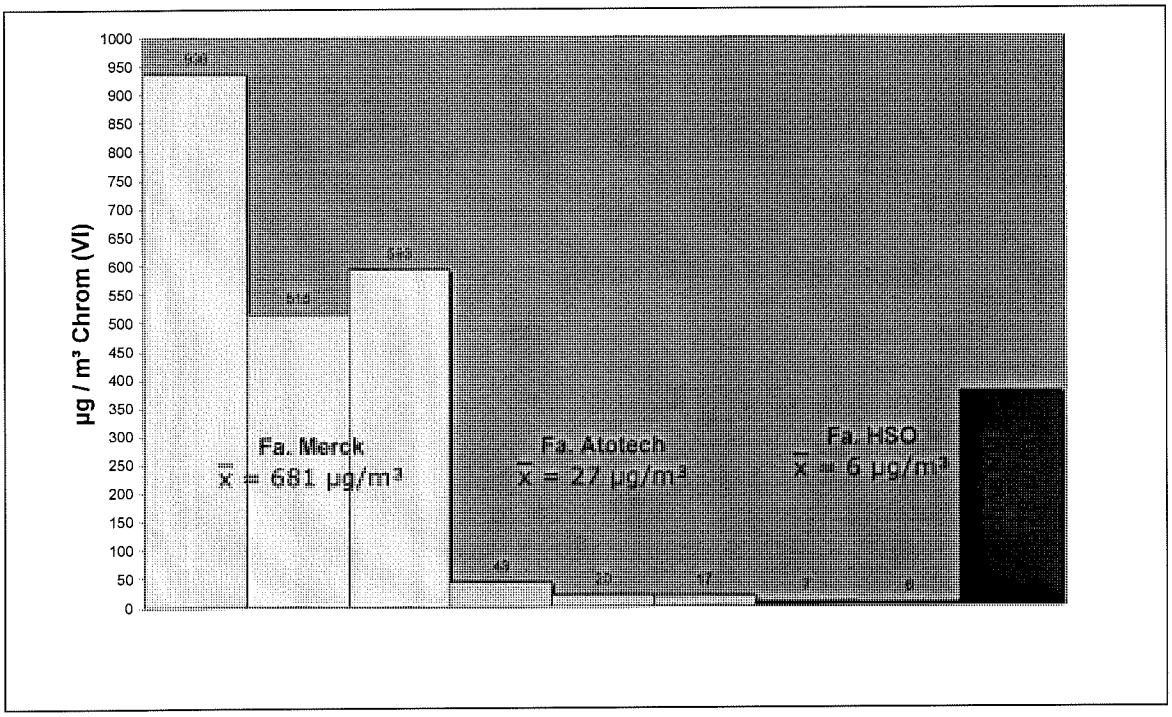


Fig. 07

Exhaust air sampling for
Graph 04

2. Cr(VI) measurements with chromium electrolytes with wetting agent



Graph 05 Results of extracted air measurements at 50 A/dm² with wetting agent

All measurements are in µg/m³

Type of wetting agent	Concentration of Cr(VI) in extracted air
Without wetting agent	approx. 378 µg / m³
Merck wetting agent	approx.600 µg / m³
Atotech wetting agent	approx.20 µg / m³
HSO wetting agent	approx.10 µg / m³

Table 01: Summary of measuring results – 50 A/dm²

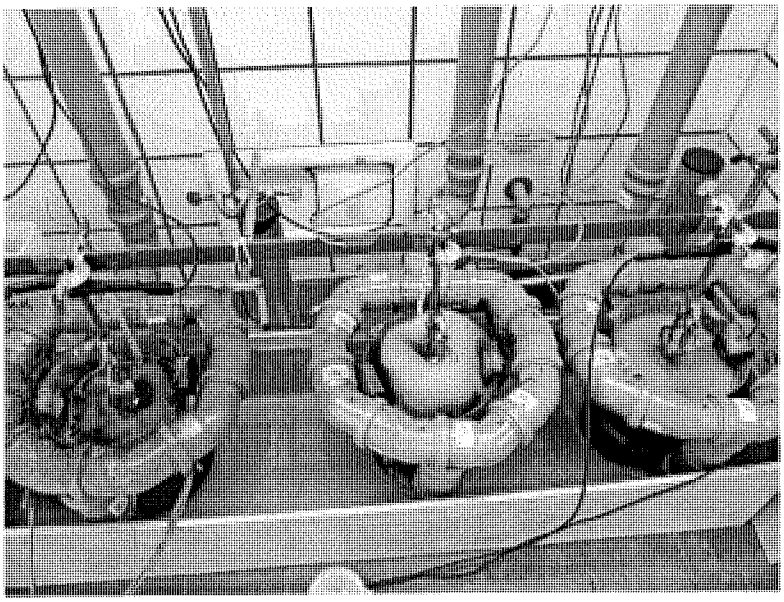


Fig. 08

Electrolytic cells for
Graph 5

Overview:

Electrolytes from left to right:
with Merck wetting agent
with Atotech wetting agent
with HSO wetting agent

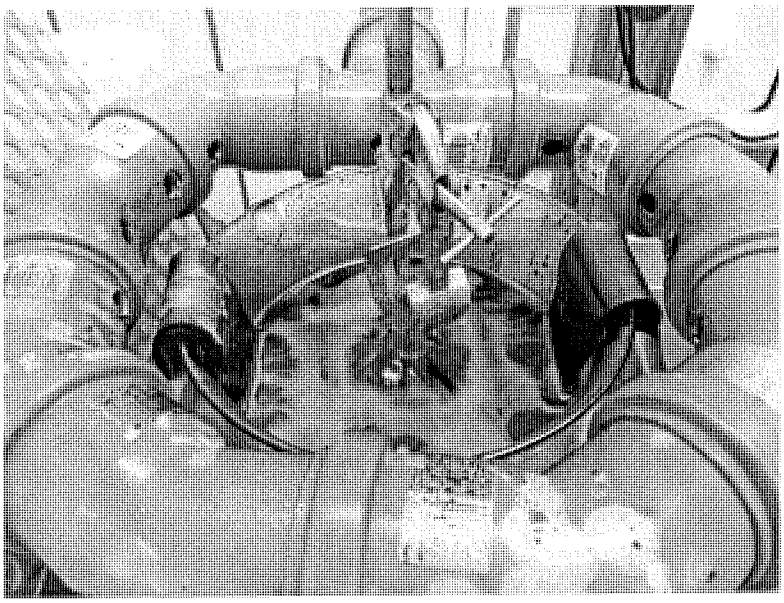


Fig. 09

Electrolytic cell with Merck wetting agent

No frothing

CrO_3 deposits in the vicinity of the intakes

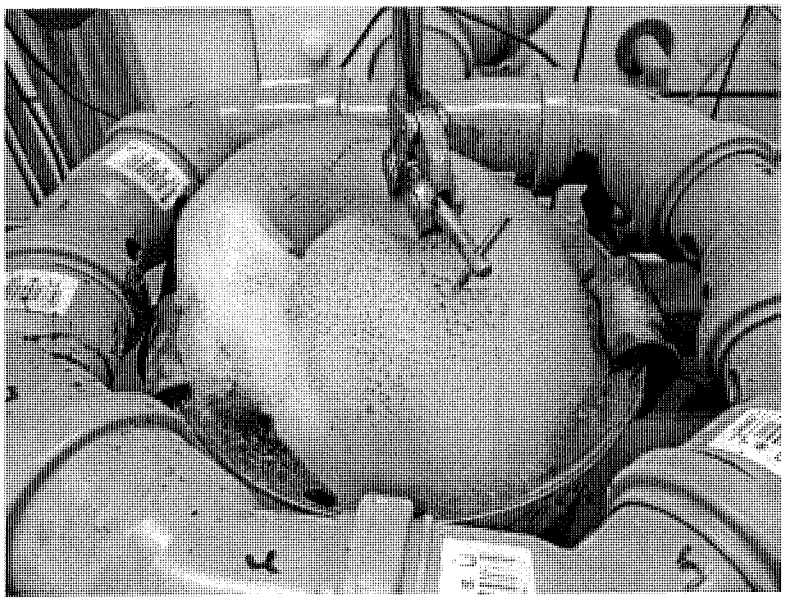


Fig. 10

Electrolytic cell
with Atotech wetting agent

Considerable frothing
(columnar)

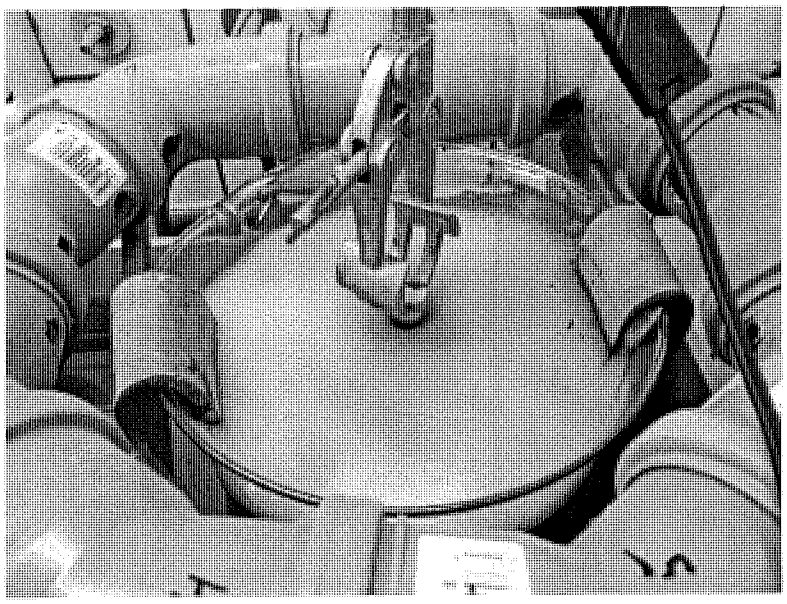


Fig. 11

Electrolytic cell with HSO
wetting agent

Considerable frothing,
pancake-type spread

2nd test phase

In the second test phase, a series of tests was carried out for deposition of decorative high-gloss chromium coatings.

For all the tests, the following basic electrolyte was used, i.e. the same electrolyte as for the hard-chromium tests:

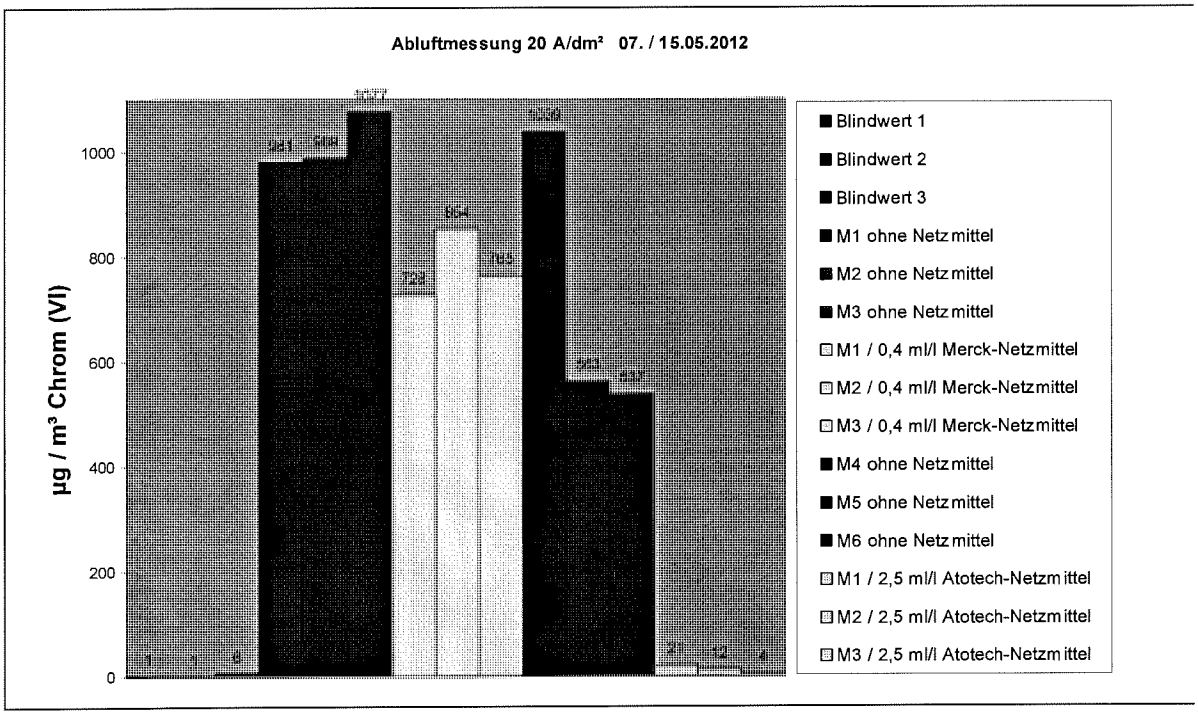
Atotech Heef 25 hard-chromium electrolyte

Process parameters for chromium electrolyte:

	260 g/l Atotech Heef 25 make-up salt	
	approx. 3 g/l Cr(III)	
	approx. 3 g/l sulphate	
Electrolyte volume:	4.5 l (5 l glass beaker)	
Electrolyte surface:	2 dm^2	
Electrolyte temperature:	55-60°C	
Electricity supply:	16 A	
Area coated:	0.8 dm^2	
Current density:	20 A/dm^2	
Cathode:	1 round Cu rod	dimensions ∅ 1.5 x 20 cm
	Immersion depth:	1.7 dm, equivalent to 0.8 dm^2
Anodes:	2 x PbSn6	dimensions: 17 x 5 cm

Wetting agent tested:

MAFS-010 (batch OF1TM0146)	0.4 ml/l
Fumetrol FL 21	2.0 – 2.5 ml/l



Graph 06 Results of extracted air measurements at 20 A/dm²

All measurements are in µg/m³

Type of wetting agent	Concentration of Cr(VI) in extracted air
Reference value*	approx. 5 µg / m³
Without wetting agent	approx. 1000 µg / m³
Merck wetting agent	approx. 800 µg / m³
Atotech wetting agent	approx.20 µg / m³

Table 02: Summary of measuring results - 20 A/dm²

* Measurement performed with no current flowing and without wetting agent to provide a lower limit value for the analysis under test conditions

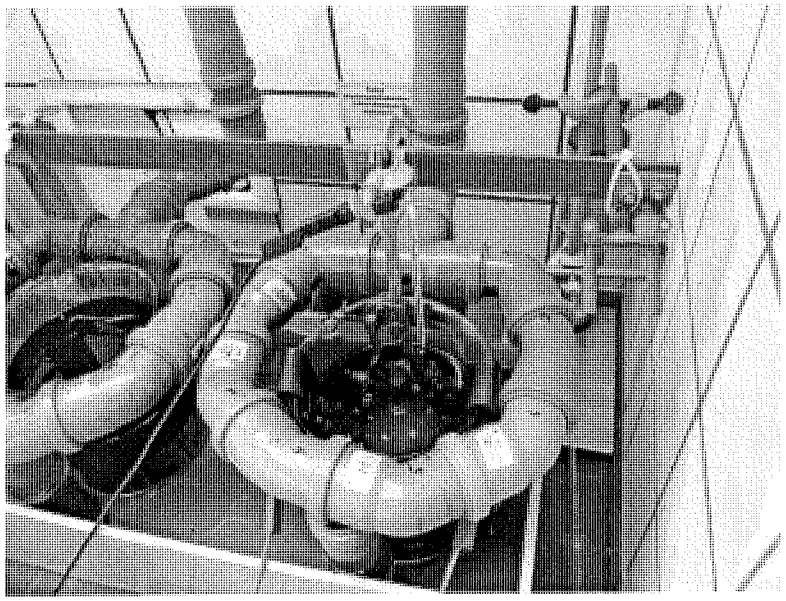


Fig. 12

Electrolytic cell with Merck wetting agent

No frothing

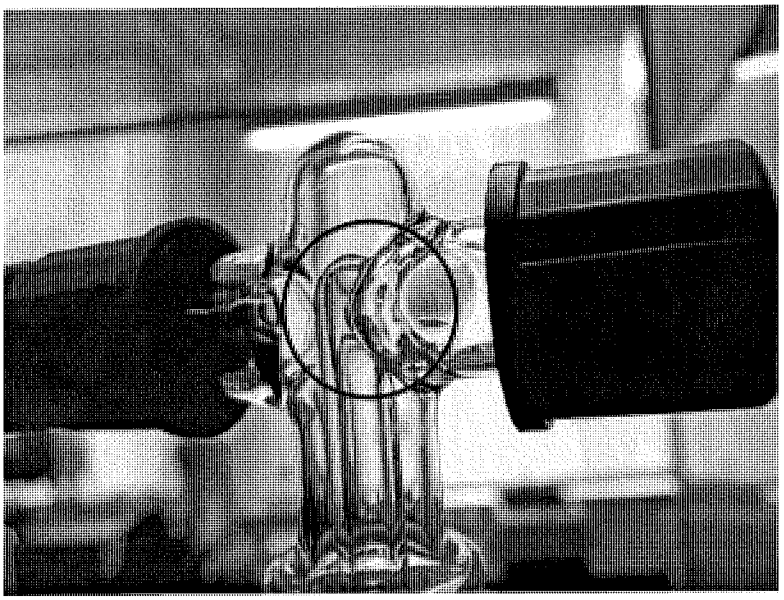


Fig. 13

Cr(VI) deposits visible in the wash bottle in the samples using Merck wetting agent

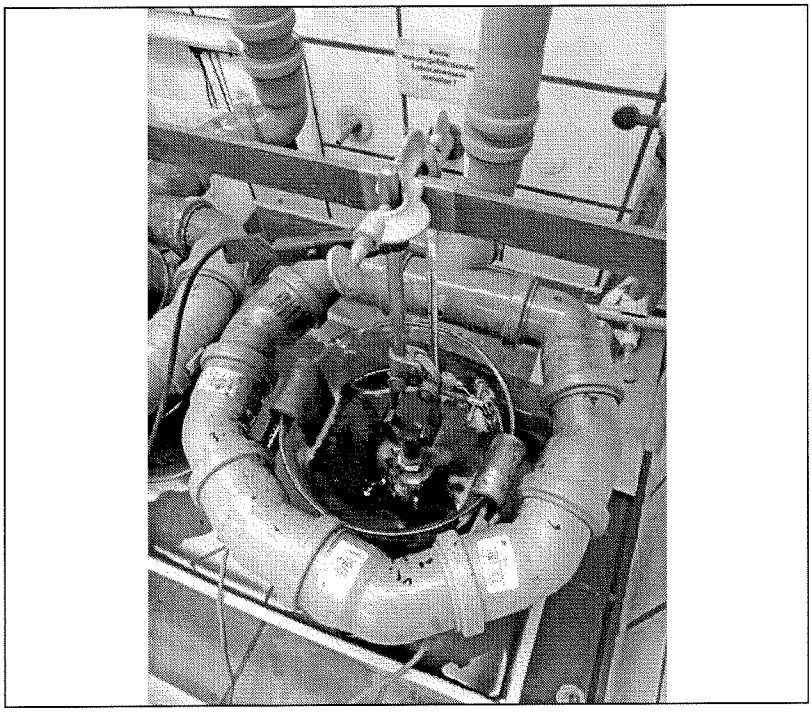


Fig. 14

Electrolytic cell with
Atotech wetting agent

Minor frothing around the
electrodes

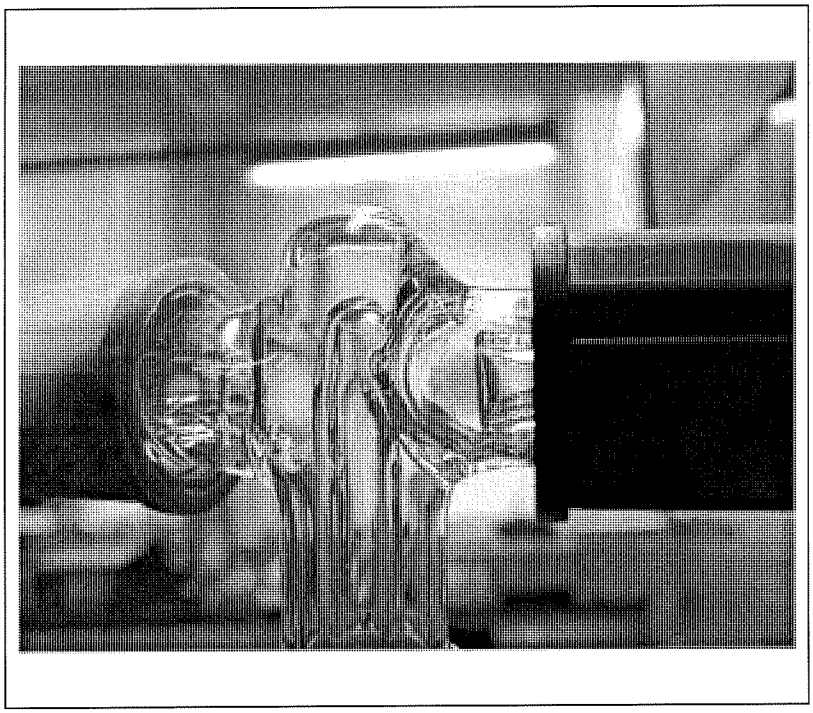


Fig. 15

No Cr(VI) deposits visible in
the wash bottle in the
samples using Atotech
wetting agent

3rd test phase

In the third test phase, a series of tests was carried out for deposition of hard-chromium coatings.

For all the tests, the following basic electrolyte was used, i.e. the same electrolyte as for all the chromium plating tests:

Atotech Heef 25 hard-chromium electrolyte

The objective of the tests was to analyse the de-frothing effect of MAFS-010 on the Atotech Fumetrol FL 21 wetting agent.

For the tests, the following wetting agents and wetting agent concentrations were used:

Fumetrol FL 21 / Atotech

one-off addition of 1.75 ml/l

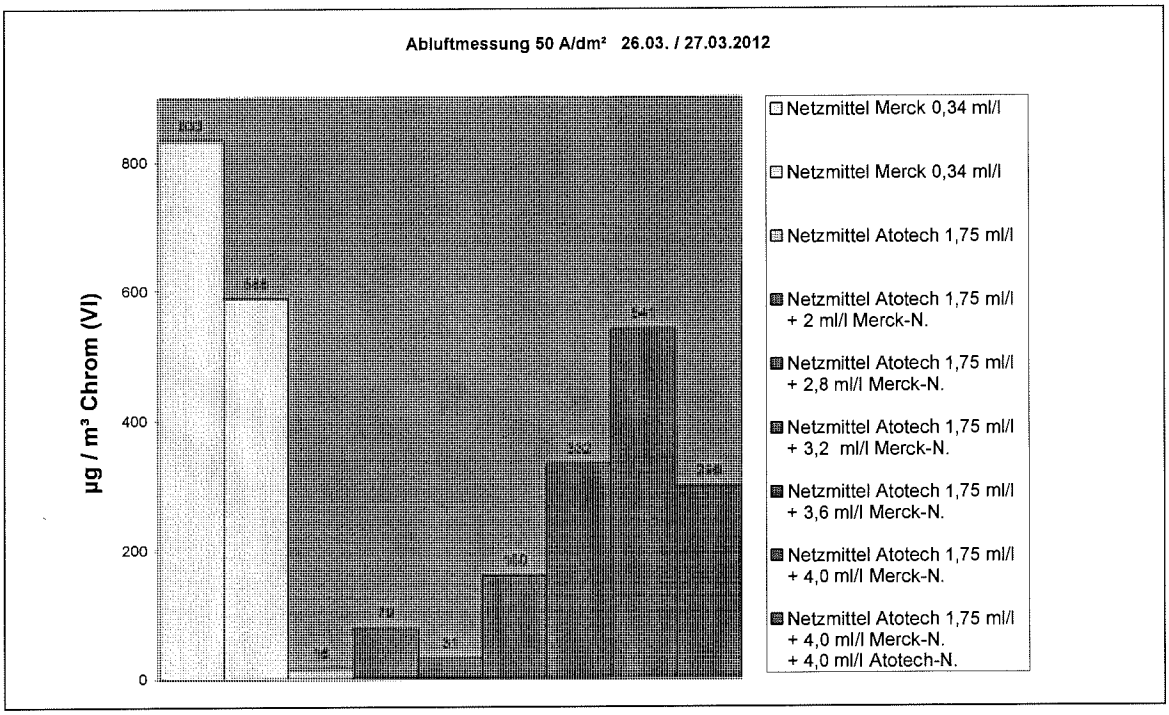
MAFS-010 (batch OF1TM0146) / Merck

additions of 2 ml/l to 4 m/l

Once the concentration of Merck wetting agent reached 4 ml/l, 4 ml/l of Atotech wetting agent was added to determine whether the tendency shown by the Merck wetting agent could be reversed by adding Atotech wetting agent.

Process parameters for chromium electrolyte:

	260 g/l Atotech Heef 25 make-up salt	
	approx. 3 g/l Cr(III)	
	approx. 3 g/l sulphate	
Electrolyte volume:	4.5 l (5 l glass beaker)	
Electrolyte surface:	2 dm^2	
Electrolyte temperature:	55-60°C	
Electricity supply:	40 A	
Area coated:	0.8 dm^2	
Current density:	50 A/dm^2	
Cathode:	1 round Cu rod	dimensions ∅ 1.5 x 20 cm
	Immersion depth:	1.7 dm, equivalent to 0.8 dm^2
Anodes:	2 x PbSn6	dimensions: 17 x 5 cm



Graph 07 Results of extracted air measurements at 50 A/dm² with wetting agent. Atotech wetting agent with added Merck wetting agent

All measurements are in µg/m³

Type of wetting agent	Concentration of Cr(VI) in exhaust air
Merck wetting agent (w.a.): 0.34 ml/l	approx. 600 µg / m³
Atotech wetting agent: 1.75 ml/l	approx. 20 µg / m³
Atotech wetting agent: 1.75 ml/l Added 2 ml/l Merck w.a.	approx. 80 µg / m³
Atotech wetting agent: 1.75 ml/l Added 2.8 ml/l Merck w.a.	approx. 40 µg / m³
Atotech wetting agent: 1.75 ml/l Added 3.2 ml/l Merck w.a.	approx. 160 µg / m³
Atotech wetting agent: 1.75 ml/l Added 3.6 ml/l Merck w.a.	approx. 330 µg / m³
Atotech wetting agent: 1.75 ml/l Added 4.0 ml/l Merck w.a.	approx. 540 µg / m³
Atotech wetting agent: 1.75 ml/l Added 4.0 ml/l Merck w.a. Added 4.0 ml/l Atotech w.a.	approx. 300 µg / m³

Table 03: Summary of measuring results – 50 A/dm²

Conclusions

1. Cr(VI) emissions during electrolytic chromium plating using MAFS-010 chrome wetting agent (batch OF1TM0146) and current density of 50 A/dm² are increased by approx. 20%.
2. Cr(VI) emissions during electrolytic chromium plating using MAFS-010 chrome wetting agent (batch OF1TM0146) and current density of 20 A/dm² are not reduced.
3. The two competitors' products tested reduced emissions by >95%.
4. Chrome wetting agent MAFS-010 showed different behaviour as regards dynamic surface tension in chromium electrolytes from that shown by the products available on the market. Even at very low bubble lifetime, MAFS-010 resulted in a considerably more pronounced reduction in surface tension by comparison.
5. In conjunction with the columnar frothing seen with Fumetrol FL 21 wetting agent, MAFS-010 had a destabilising effect on the froth. When the froth was eliminated, however, Cr(VI) emissions increased despite the presence of Fumetrol FL 21.

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