

Black Ruthenium 479

Operating Instructions

Edition: 3 July 2007

- Acidic black ruthenium electrolyte
- Decorative dark to black layers
- Good colour constancy
- Simple bath maintenance
- Long bath life

Bath Characteristics

Black Ruthenium 479 is a strongly acidic electrolyte from which decorative, particularly dark to black coatings can be deposited. The bath is easy to operate, the deposits have a high colour constancy and retain their brightness.

Black Ruthenium 479 is used as a final coating for decorative applications, e.g. in the industries producing jewellery, spectacle frames and writing utensils.

Depending of the degree of blackening, the wear resistance of the coatings is good to excellent.

Pregilding as an undercoat under the black ruthenium layer is strongly recommended. If palladium-nickel or palladium are used as undercoats, pregilding is not necessary.

Bath type:	Acidic	
Ruthenium content:	5 g/l	(2 - 10 g/l)
pH-value:	1.4	(65 °C)
Temperature:	65 °C	(60 - 70 °C)
Current density:	1.5 A/dm ² (0.5 - 3.0 A/dm ²)	
Deposition speed:	Approx. 0.02 µm/min at 5 g/l Ru, 15 ml/l Blackening Agent and 1.5 A/dm ²	

Coating Characteristics

Coating:	Black ruthenium
Colour:	Grey to anthracite (black)
Density:	Approx. 12 g/cm ³
Max. coating thickness:	0.2 - 0.3 µm, depending on degree of blackening

Form of Supply

- | | |
|---------------------|--|
| Bath makeup: | for 1 litre of bath: |
| | a) Black Ruthenium 479 Initial Concentrate, 50 g/l Ru
100 ml containing 5 g Ru
Storage stability: min. 2 years |
| | b) Black Ruthenium 479 Blackening Agent, free from precious metals
10 - 15 ml
Storage stability: min. 2 years |
| | c) Wetting Agent 16
free from precious metals
2 ml
Storage stability: min. 2 years |
| Bath replenishment: | for 1 g of ruthenium: |
| | d) Black Ruthenium 479 Replenisher Solution, 50 g/l Ru
20 ml
Storage stability: min. 2 years |
| | e) Black Ruthenium 479 Blackening Agent, free from precious metals
For amount see "Bath Replenishment"
Storage stability: min. 2 years |
| Bath corrections: | f) Wetting Agent 16
For corrections of the content of wetting agent. See paragraph "Bath Monitoring and Corrections" |
| | g) Black Ruthenium 479 Blackening Agent, free from precious metals
For amount see "Bath Monitoring and Corrections" |
| | h) For pH corrections dilute sulphuric acid (AR) and ammonia solution (AR) should be available. |

Black Ruthenium 479

Bath Makeup

Makeup sequence: To make up 1 litre of bath, stir 100 ml of Black Ruthenium 479 Initial Concentrate into 800 ml of deionized water.
Then add the amount of Black Ruthenium 479 Blackening Agent required for the desired degree of blackness and 2 ml of Wetting Agent 16 and fill up to 1 litre with deionized water.
Heat up the bath to 65 °C and measure the pH-value with a glass electrode. If required, adjust the pH to 1.4.

Operating Conditions

Ruthenium content: 5 g/l (2 - 10 g/l)

Concentration of Blackening Agent: 10 - 15 ml/l (0.0 - 30 ml/l)
Depending on the desired degree of blackening.

Operating temperature: 65 °C (60 - 70 °C)

pH-value: 1.4 (1.0 - 1.5) at 65 °C
1.0 (0.6 - 1.1) at 25 °C
Correct the pH with sulphuric acid AR or ammonia solution AR (both diluted 1:10).

Bath density: 1.02 g/cm³ - rising
3 °Bé - rising
The bath density normally increases during the lifetime of the bath. If the bath density should fall below 1.02 g/cm³ (3 °Bé) due to heavy drag-out, it must be re-adjusted to specified value by adding Ruthenium Density Correction Salt 1. Approx. 20 g/l of Ruthenium Density Correction Salt 1 are needed to increase the density by 0.01 g/cm³.

Product agitation: Strong agitation required!
At least 5 - 10 cm/s!

Bath agitation: Bath circulation required,
at least 2 bath volumes per hour

Filtration: Continuous filtration through polypropylene filters recommended.

Current density: 1.5 A/dm² (0.5 - 3.0 A/dm²)

Maximum coating thickness: Depending on the degree of blackening, the maximum coating thickness is between 0.2 and 0.3 µm (at L* = 55 - 60 (CIE Lab System)). With very dark layers (L* < 45), the maximum coating thickness will decrease considerably.

Throwing power: The throwing power of the electrolyte depends on the amount of Blackening Agent used. With increasing concentration of Blackening Agent, the throwing power of the electrolyte will drop.

Deposition speed: The deposition speed strongly depends on the amount of Blackening Agent used. The more Blackening Agent used, the lower the deposition speed.

Density of the coating: Approx. 12 g/cm³

Dependence of Degree of Blackening, Deposition Speed and Deposition Rate on Amount of Blackening Agent Used

Deposition rate and deposit colour depend on the amount of Blackening Agent used. The data^{*)} given in the table below are meant as a rough guide how to achieve the desired degree of blackening.

Blackening Agent [ml/l]	L* (CIE Lab System)	Deposition speed [µm/min]	Deposition rate [mg/Amin]
0	75	0.08	8 - 10
10	60 - 65	0.035 - 0.045	3 - 7
15	55 - 59	0.02 - 0.03	2 - 5
20	51 - 54	0.015 - 0.02	1 - 4
25	47 - 50	0.01 - 0.015	1 - 3
30	43 - 46	0.005 - 0.01	1 - 2
35	40 - 42	0.002 - 0.005	0.5 - 1

^{*)} at 1.5 A/dm², 5 g/l Ru and 65 °C

Calculation of Coating Thickness and Plating Time

The maximum coating thickness should not exceed 0.3 µm (cracking).

Coating weight in mg = surface in cm² x 1.2 x coating thickness in µm

Plating time in minutes =
$$\frac{\text{required coating weight in mg}}{10 \times \text{current in amperes}}$$

Black Ruthenium 479

Bath Replenishment

The bath should be replenished at the latest after depositing 10 - 20 % of ruthenium, otherwise the deposition speed will drop.

To replenish 1 g of Ru, add to the bath:
20 ml Black Ruthenium 479 Replenisher Solution

The consumption of Blackening Agent depends on the desired degree of blackening and is different according to the initial concentration.

We recommend monitoring the ruthenium content by regular analyses.

Bath Monitoring and Correction

Degree of blackening

The degree of blackening is controlled by replenishing Black Ruthenium 479 Blackening Agent.

If deviations (too light layers) should occur, the concentration can be carefully increased by adding Blackening Agent in small steps of 1 - 2 ml/l. An excess of Blackening Agent is indicated by too dark layers, very low deposition rates and defects on the parts. The Blackening Agent cannot be removed by active carbon treatment.

pH-value:

The pH-value should be checked every day with a glass electrode and adjusted with sulphuric acid or ammonia solution (both AR quality and diluted 1 : 10), if required.

Caution: If the pH-value is too high, the bath will become unstable!

Content of wetting agent:

The wetting agent is mainly reduced by drag-out and should be replenished occasionally. The standard value in the bath is 2 ml/l. If hydrogen pores should occur despite sufficient movement or after drag-out of half the bath volume, 25 % (0.5 ml/l) of Wetting Agent 16 should be added.

Metallic impurities:

The bath attacks the usual basic materials and is sensitive to metallic contaminants like copper, zinc, lead and other metals. See "Special Process Hints", paragraph "Pretreatment". Common metallic impurities such as copper or zinc can be removed by dummy plating at 0.1 A/dm² with corrugated metal sheets or by means of special precipitation methods.

Special Process Hints

Pretreatment: The acidic bath attacks the usual basic materials and is sensitive to metallic contaminants. The parts, particularly materials containing copper and nickel, must be protected by pregilding (layer thickness at least 0.1 µm). If sufficiently thick undercoats of PdNi or Pd are used, pregilding is not necessary.

Post-treatment: After plating, the parts should be rinsed under running water. Then post-treatment for approx. 15 – 30 seconds in a 50 °C warm dilute sodium hydroxide solution (50 g/l NaOH). This post-dip solution neutralizes any electrolyte rests on the surface of the parts and in pores. The solution can be removed by longer rinsing under running water. The last rinse before drying should be deionized water.

Loading of bath when current is on: If possible, the parts should be immersed when the current is on.

Barrel: Due to the reasons stated above under "Pretreatment", the bath is only limitedly suitable for barrel applications.

If the parts have a complicated geometry, a 100 % protection of the parts by pregilding possibly cannot be reached which during subsequent ruthenium plating will lead to faulty deposits and contamination of the bath. Using the bath for barrel applications should therefore be previously tested.

Equipment

Materials: All parts coming into contact with the bath must be resistant to strong acids. We recommend using polypropylene natural and titanium. All plastic equipment such as tanks, rack insulations, pumps, hoses, filter cartridges etc. prior to use must be rinsed in dilute acid (e.g. 5 % sulphuric acid) for several hours and afterwards cleaned of the contaminated acid by intensive rinsing with water which should be changed several times.

Bath tanks: Acid-resistant plastic (polypropylene)

Black Ruthenium 479

Heating:	Adjustable immersion heater with porcelain or quartz sheath, or Teflon-coating
Anodes:	Platinized titanium, e. g. PLATINODE® coated with 2.5 µm of platinum. For fixing, we recommend titanium screws. Anode surface : parts surface at least 2 : 1
Racks:	With acid-resistant coating, contact points of stainless steel or sufficiently gold-plated
Exhaust system:	An efficient exhaust system is required

Note

Our information relating to the storage stability refers to storage in closed original storage containers under the conditions stated on the label.

Precautionary Measures/Safety Hints

For information on safety, please see the corresponding Material Safety Data Sheets!

The valid accident prevention regulations and safety instructions must be observed.

Reference to

Trouble-shooting table: Available on request

Analytical methods: Available on request

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