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(54) **Title:** ELECTROLYTE AND ITS USE FOR THE DEPOSITION OF BLACK RUTHENIUM COATINGS AND COATINGS OBTAINED IN THIS WAY

(57) **Abstract:** The invention relates to a ruthenium electrolyte which is suitable for the deposition of decorative and industrial layers having a particular blackness. The invention further relates to the use of the electrolyte of the invention in a process for the deposition of decorative and industrial layers of ruthenium having a particular blackness ("black ruthenium") on jewelry, decorative goods, consumer goods and industrial articles. The invention therefore likewise relates to corresponding layers and the articles coated in this way. The electrolyte is characterized in that it operates in the weakly acidic to alkaline pH range.



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**Electrolyte and its use for the deposition of black ruthenium coatings and coatings obtained in this way**

The invention relates to a ruthenium electrolyte which is suitable for the deposition of decorative and technical layers having a particular blackness. The invention further relates to the use of the electrolyte of the invention in a process for the deposition of decorative and industrial layers of ruthenium having a particular blackness ("black ruthenium") on jewelry, decorative goods, consumer goods and industrial articles. The invention therefore likewise relates to corresponding layers and the articles coated in this way.

Consumer goods and industrial articles, jewelry and decorative goods are coated with thin oxidation-stable metal layers for protection against corrosion and/or for optical upgrading. These layers have to be mechanically stable and should not display tarnishing or wear phenomena even on prolonged use. A proven way of producing such layers are electroplating processes by means of which many metal and alloy layers can be obtained in high-quality form. Examples which are well known from everyday life are electrolytically deposited bronze and brass layers on door handles or knobs, chrome coatings on vehicle parts, zinc-plated tools or gold plating on watch straps.

A particular challenge in the field of electroplating is to produce oxidation-stable and mechanically strong metal layers which have a black color and can be of interest not only in the decorative and jewelry sector but also for industrial applications, for example in the field of solar technology. Only a few metals are available for the production of oxidation-stable, black layers. Apart from ruthenium, rhodium and nickel are suitable. The use of the noble metal rhodium is restricted to the jewelry sector because of the high raw material costs. The use of inexpensive nickel and nickel-containing alloys is possible only in exceptional cases and with observance of strict regulations, especially in the jewelry and consumer goods sector, since nickel and nickel-containing metal layers are contact allergens. The use of ruthenium is an attractive alternative for all the fields of application described.

Electrolytes for producing black ruthenium layers in electrolytic plating processes are known in the prior art. The most widely used baths contain ruthenium in the form of a complex with amidosulfonic acid or ruthenium as nitridochloro or nitridobromo complex

(US6117301, US3576724, JP63259095, WO2001/011113, DE19741990, US4375392, JP2054792, EP1975282). The pH of the baths is frequently in the acid range.

DE1959907 describes the use of binuclear ruthenium complexes  $[\text{Ru}_2\text{NCl}_x\text{Br}_{8-x}(\text{H}_2\text{O})_2]^{3-}$  in an electroplating bath. In one embodiment, the nitridochloro complex

5  $[\text{Ru}_2\text{NCl}_8(\text{H}_2\text{O})_2]^{3-}$  is used. JP56119791 relates to a ruthenium electrolyte which contains from 1 to 20 g/l of ruthenium together with one or more compounds selected from the group consisting of dicarboxylic and tricarboxylic acids, benzenesulfonic acid, N-containing aromatics and amino acids or derivatives of the compounds mentioned and in which from 0.01 to 10 g/l of a thio compound as blackening additive are  
10 additionally used.

For upgrading jewelry and decorative goods, black layers have to have not only an excellent mechanical adhesive strength but also a defect-free optical quality. They have to be able to be produced as required in bright or matte form and with a very deep blackness. The same applies for applications in the industrial sector, in particular in  
15 solar technology. Black layers for upgrading consumer goods also have to satisfy demanding requirements in terms of the mechanical stability. In particular, they must not have any black abrasion even on frequent use over a long period of time.

The ruthenium baths and processes described in the prior art which satisfy these requirements either require the use of toxicologically problematical compounds such as  
20 thio compounds as blackening additive or contain a further transition metal to provide the required mechanical adhesive strength, which makes maintenance of the bath during the deposition process difficult. In addition, acid baths allow deposition only on metals which have a relatively noble character.

According to US4082625, light-colored ruthenium deposits can also be obtained in the  
25 alkaline range. US350049 describes a process for the deposition of ruthenium in a pH range of 9-10. The ruthenium is kept in solution in this pH range by means of complexing anions (EDTA, NTA, CDTA). Stable but light-colored deposits of ruthenium are obtained.

The nitridochloro complex of ruthenium is also used in the aqueous, nonacidic bath for  
30 the electrodeposition of ruthenium which is described in US4297178. It additionally contains oxalic acid or an oxalate anion. It is questionable whether the deposits produced in this way have an appropriate blackness.

In view of the prior art cited here, it was an object of the present invention to provide a stable electrolyte and the use thereof by means of which as durable and as black deposits of ruthenium as possible on metallic articles can be produced. In addition, deposits on articles which are not stable in a strongly acidic environment should also  
5 be possible.

These objects and further objects which can be derived in an obvious manner from the prior art are achieved by an electrolyte having the characterizing features of claim 1. Advantageous embodiments of the electrolyte of the invention are indicated in claims 2-9. The use of the electrolyte of the invention in the process of the invention is  
10 described in claims 10-19. The deposited layers follow in claims 20-24. Claim 25 is directed at articles which have been coated in this way.

Provision of an electrolyte having a pH of from  $\geq 5$  to 12 for the deposition of decorative and industrial layers of ruthenium having a particular blackness, which electrolyte has the following constituents:

- 15 a) dissolved ruthenium in a concentration of from 0.2 to 20 gram per liter (g/l) of electrolyte, calculated as ruthenium metal;
- b) one or more anions of a dicarboxylic, tricarboxylic or tetracarboxylic acid in a concentration of 0.05-2 mol per liter;
- c) one or more sulfur heterocycles;
- 20 d) one or more cationic surfactants, in particular surfactants based on quaternary ammonium salts,

leads extremely effectively and simply but nonetheless advantageously to achievement of the stated objects. The electrolyte provides very resistant and extremely black deposits of ruthenium on conductive, in particular metallic, articles. The deposition of  
25 black ruthenium coatings on conductive, in particular metallic, articles was hitherto possible only when using strongly acidic electrolytes. To avoid attack on the substrate in the case of base metals to be coated, these therefore had to be provided with corrosion-resistant intermediate layers (gold, palladium or palladium/nickel, etc.) before coating. However, the electrolyte of the invention makes it possible also to work in a  
30 medium in which substrates composed of die-cast zinc, brass or bronze can be plated without intermediate coating.

Ruthenium can be used in the form of a water-soluble compound known to those skilled in the art, preferably as a binuclear, anionic nitrido halo complex of the formula

[Ru<sub>2</sub>N(H<sub>2</sub>O)<sub>2</sub>X<sub>8</sub>]<sup>3-</sup>, where X is a halide ion. Particular preference is given to the chloro complex [Ru<sub>2</sub>N(H<sub>2</sub>O)<sub>2</sub>Cl<sub>8</sub>]<sup>3-</sup>. The amount of the complex in the electrolyte of the invention can preferably be selected so that the concentration of ruthenium after complete dissolution of the compound is in the range from 0.5 to 10 gram per liter of electrolyte, calculated as ruthenium metal. The finished electrolyte particularly preferably contains from 1 to 8 gram of ruthenium per liter of electrolyte, very particularly preferably from 3 to 6 gram of ruthenium per liter of electrolyte. Preference is given to exclusively ruthenium being deposited from the electrolyte of the invention. In this case, the electrolyte contains no further transition metal ions in addition to ruthenium.

The electrolyte contains particular organic compounds which have one or more carboxylic acid groups. These are in particular dicarboxylic, tricarboxylic or tetracarboxylic acids. These are adequately known to those skilled in the art and can be found, for example, in the literature (Beyer-Walter, Lehrbuch der Organischen Chemie, 22nd edition, S. Hirzel-Verlag, p. 324 ff). In this context, particular preference is given to acids selected from the group consisting of oxalic acid, citric acid, tartaric acid, succinic acid, maleic acid, glutaric acid, adipic acid, malonic acid, malic acid. The acids are naturally present in their anionic form in the electrolyte at the pH to be set. The carboxylic acids mentioned here are added to the electrolyte in a concentration of 0.05-2 mol per liter, preferably 0.1-1 mol per liter and very particularly preferably 0.2-0.5 mol per liter. This applies particularly to the use of oxalic acid which is assumed also to serve as conducting salt in the electrolyte.

Particular sulfur compounds are likewise present in the electrolytes in question here. These are in particular one or more sulfur compounds which contain at least one sulfur atom in a heterocyclic ring system (sulfur heterocycle) (Beyer-Walter, Lehrbuch der Organischen Chemie, 22nd edition, S. Hirzel-Verlag, p. 703 ff). These can be optionally aromatic or fully or partially saturated five- or six-membered rings based on carbon or corresponding fused ring systems which contain at least one sulfur atom and/or at least one further heteroatom such as nitrogen. The sulfur heterocycles to be used are preferably sufficiently water-soluble to be able to be used effectively in the appropriate concentration range in the electrolyte. Preferred compounds are those selected from the group consisting of 3-(2-benzothiazolyl-2-mercapto)propanesulfonic acid sodium salt, saccharin sodium salt, saccharin-N-propylsulfonate sodium salt, 6-methyl-3,4-dihydro-1,2,3-oxathiazin-4-one 2,2-dioxide, benzothiazole, 2-mercaptobenzothiazole,

thiazole, isothiazole and derivatives thereof. Without being tied to the theory proposed here, it is assumed that the sulfur heterocycle contributes to the deep blackening in the deposition of the ruthenium. The sulfur heterocycle is used in a concentration of from 0.001 to 4 mol per liter, preferably from 0.002 to 1 mol per liter and very particularly preferably in a concentration of from 0.004 to 0.01 mol per liter, in the electrolyte.

One or more surface-active substances of the cationic surfactant type are likewise present in the electrolyte. Possible surfactants of this type are, in particular, quaternary ammonium salts. These are adequately known to those skilled in the art (Beyer-Walter, Lehrbuch der Organischen Chemie, 22nd edition, S. Hirzel-Verlag, p. 251 ff).

Preference is given to ammonium salts selected from the group consisting of octyltrimethylammonium bromide, octyltrimethylammonium chloride, decyltrimethylammonium bromide, decyltrimethylammonium chloride, dodecyltrimethylammonium bromide, dodecyltrimethylammonium chloride, tetradecyltrimethylammonium bromide, tetradecyltrimethylammonium chloride, hexadecyltrimethylammonium bromide, hexadecyltrimethylammonium chloride, ethyldimethylhexadecylammonium bromide, ethyldimethylhexadecylammonium chloride, benzyldimethyldodecylammonium chloride, benzyldimethyltetradecylammonium chloride and benzyldimethylhexadecylammonium chloride.

The cationic surfactants under consideration here are used in a concentration of 0.1-20 mmol per liter, preferably 0.5-10 mmol per liter and very particularly preferably from 1 to 5 mmol per liter, in the electrolyte and are likewise decisive for a deeper black of the deposited layer.

The pH of the electrolyte is preferably in the only weakly acidic to alkaline range. The pH is preferably set to a value in the range from 5 to 12. The pH of the electrolyte during use is more preferably in the range from 6 to 9, particularly preferably from 7 to 8. A pH of about 7.5 is especially preferably set. The pH is kept constant by addition of buffer substances. These are adequately known to those skilled in the art (Handbook of Chemistry and Physics, CRC Press, 66th Edition, D-144 ff). Preferred buffer systems are borate, phosphate and carbonate buffers. Compounds for producing these buffer systems can be selected from the group consisting of boric acid, potassium dihydrogenphosphate, dipotassium hydrogenphosphate, potassium hydrogencarbonate and dipotassium carbonate. The buffer system is used in a concentration of 0.08-1.15 mol per liter, preferably 0.15-0.65 mol per liter and very particularly preferably 0.2-0.4 mol per liter (based on the anion).

Naturally, further additives advantageous for the deposition can be added to the electrolyte under consideration here. These are adequately known to those skilled in the art. Preference is given to those selected from the group consisting of conducting salts, further blackening additives, brighteners (Praktische Galvanotechnik, 5th edition, Eugen G. Leuze Verlag, Bad Saulgau, p. 39 ff).

The present invention likewise provides for the use of the electrolyte of the invention. In the use, a person skilled in the art will immerse the conductive, in particular metallic, article to be coated as cathode in the electrolyte and bring about a flow of electric current between the anode and the cathode. The use of the electrolyte of the invention is preferably carried out in the same advantageous embodiments which have been described above for the electrolyte. The flow of electric current should be sufficient to bring about the deposition of the black ruthenium coatings on the conductive, in particular metallic, article within an acceptable period of time. A person skilled in the art will know the strength of the electric field which has to be set for this. A current density of 0.1-10 A/dm<sup>2</sup> is preferably set. The current density is particularly preferably from 0.2 to 5 A/dm<sup>2</sup> and very particularly preferably from 0.5 to 2 A/dm<sup>2</sup>.

The temperature of the electrolyte during deposition can be set appropriately by a person skilled in the art. The temperature range to be set is advantageously 10-80°C. Preference is given to setting a temperature of from 50° to 75°C and particularly preferably 60° and 70°C. It can be advantageous for the electrolyte in question to be stirred during deposition.

As anode, it is likewise possible to select embodiments which a person skilled in the art would consider for this purpose. Preference is given to using anodes made of a material selected from the group consisting of platinized titanium, graphite, iridium-transition metal mixed oxide and special carbon material ("Diamond-Like Carbon", DLC) or combinations thereof. Insoluble anodes made of a platinized titanium or iridium-transition metal mixed oxide have been found to be advantageous. Particular preference is given to using an anode made of platinized titanium.

The present invention likewise provides black ruthenium layers which can be obtained by the process of the invention. The layers have a thickness of from 0.1 to 3 µm, preferably from 0.2 to 1.5 µm and very particularly preferably from 0.3 to 1.3 µm. The layer of the invention has a sulfur content of from 3% by weight to 6% by weight, preferably from 3.1% by weight to 5% by weight and particularly preferably from 3.2%

by weight to 4.5% by weight, in its outer region (viewed from the visible surface inward) of about  $1.1 (\pm 0.2) \mu\text{m}$ . The sulfur content is especially preferably about 4% by weight. The ruthenium layer also has a carbon content of from 1% by weight to 2% by weight, preferably from 1.1% by weight to 1.8% by weight and very particularly preferably from 1.15% by weight to 1.5% by weight, in the same outer region. The value is especially preferably about 1.2% by weight. The ruthenium layer has an oxygen content of from 15% by weight to 20% by weight, preferably from 16% by weight to 19% by weight and particularly preferably from 17% by weight to 18.5% by weight, in the same outer region. The oxygen content here is especially preferably about 18% by weight. It appears to be particularly advantageous for the concentration of sulfur in this layer under consideration to have a gradient with the concentration increasing from the outside inward. Thus, a concentration of sulfur directly at the surface of about 2% by weight which can increase in an inward direction to 5% by weight is often measured. The values determined here have been determined by the GDOES method (Glow Discharge Optical Emission Spectrometry; R. Kenneth Marcus, Jose Broekaert: Glow Discharge Plasma in Analytical Spectroscopy, Wiley ISBN 0-471-60699-5 and Thomas Nelis, Richard Payling: Glow Discharge Optical Emission Spectroscopy - A Practical Guide, Royal Society of Chemistry, ISBN 0-85404-521-X).

The invention further provides particular articles such as decorative goods, consumer goods and industrial articles which have a layer according to the invention. Particular preference is given to articles in the case of which corresponding deposition in the acid range is not possible because of their base metal character.

The deposition of black ruthenium coatings on conductive, in particular metallic, articles according to the present invention can be carried out by way of example as follows, taking account of what has been said above:

for the electrolytic application of black ruthenium layers, the pieces of jewelry, decorative goods, consumer goods or industrial articles (referred to collectively as substrates) dip into the electrolyte of the invention and form the cathode. An anode made of, for example, platinized titanium (product information for PLATINODE® from Umicore Galvanotechnik GmbH) is likewise dipped into the electrolyte. An appropriate flow of electric current between the anode and the cathode is subsequently applied. In order to obtain firmly adhering, uniform layers, a maximum current density of 10 ampere per square decimeter  $[\text{A}/\text{dm}^2]$  should not be exceeded. Above this value,



proportions of amorphous ruthenium can be deposited. As a result, the layers can be nonuniform and have dark abrasion under mechanical stress. The current density selected is also determined by the type of coating process. In a barrel plating process, the preferred current density is in the range from 0.1 to 1 A/dm<sup>2</sup>. In rack plating processes, a current density of from 0.5 to 5 A/dm<sup>2</sup> leads to optically defect-free black ruthenium layers.

The ruthenium electrolyte described, which is provided by the present invention, is particularly well-suited in a process for the deposition of decorative deep black and optionally bright layers, for example on jewelry and decorative goods. The latter are likewise provided by the present invention. The electrolyte can preferably be used in barrel and rack plating processes. The electrolyte described here makes it possible to produce particularly compact and deep black deposits (L up to 50) of ruthenium on the appropriate material (see drawing 1, which shows the results of the comparative example and of example 1 according to the invention). Furthermore, it is possible, when using the electrolyte, to work in the weakly acidic to alkaline region which for the first time allows the deposition of black ruthenium coatings on base metals without the latter having to be provided beforehand with a precious metal intermediate layer. This was not at all obvious in the light of the known prior art.

Five samples were examined. The production of the samples can be taken from the examples.

Table 1:

Electrolyte type	Ruthenium	Sulfur	Carbon	Oxygen	L*
Acidic black ruthenium electrolyte Type I*	73.87%	0.03%	0.09%	12.68%	66.0
Acidic black ruthenium electrolyte Type II**	75.43%	0.12%	0.17%	16.97%	64.6
Electrolyte Type I according to the invention	76.52%	3.90%	0.20%	17.83%	55.5
Electrolyte Type II according to the invention	75.04%	4.00%	1.20%	17.97%	52.3
Electrolyte Type III without sulfur heterocycle	84.76%	0.33%	0.10%	12.90%	69.2

\* according to JP2001049485, \*\* according to EP 1975282

It can clearly be seen that the processes in the alkaline range (electrolytes according to the invention) give comparatively good  $L^*$  values. Further blackening is promoted by the addition of a cationic surfactant as wetting agent.

5 Color values were measured on the resulting layers using a standard color measuring instrument according to the CIE- $L^*$   $a^*$   $b^*$  system.

The layers were also examined by means of GDOES (**G**low **D**ischarge **O**ptical **E**mission **S**pectroscopy). The specimens are "sputtered-off" over an approximately flat plane in an argon plasma and excited to emit specific radiation. The radiation is detected in an optical spectrometer. The calculation of concentrations and depths is  
10 carried out by multimatrix calibration.

Examples:

General method:

A brass sheet is dipped in an electrolyte which has the compositions described below.

Comparative example - formulation according to US4297178:

- |    |  |
|----|--|
| 5  | 6.2 g/l of Ru as $[\text{Ru}_2\text{N}(\text{H}_2\text{O})\text{Cl}_8]^{3-}$ |
|    | 80 g/l of oxalic acid  |
|    | pH set to 7.5 by means of potassium hydroxide                                |
|    | pH 7.5 (70°C)  |
|    | Working temperature 70°C   |
| 10 | Current density 1 A/dm <sup>2</sup>  |
|    | L* = 68.6  |

Example 1 according to the invention (type I):

- |    |  |
|----|--|
| 15 | 6.2 g/l of Ru as $[\text{Ru}_2\text{N}(\text{H}_2\text{O})\text{Cl}_8]^{3-}$ |
|    | 80 g/l of oxalic acid  |
|    | 20 g/l of potassium dihydrogenphosphate                                      |
|    | 2 g/l of saccharin-N-propylsulfonate sodium salt                             |
|    | 600 mg/l of a quaternary ammonium salt                                       |
|    | pH 7.5 (70°C)  |
| 20 | Working temperature 70°C   |
|    | Current density 1 A/dm <sup>2</sup>  |
|    | L* = 55.5  |

Example 2 according to the invention (type II):

- |    |  |
|----|--|
| 25 | 3 g/l of Ru as $[\text{Ru}_2\text{N}(\text{H}_2\text{O})\text{X}_8]^{3-}$ X = halide ion |
|    | 40 g/l of oxalic acid  |
|    | 20 g/l of potassium dihydrogenphosphate  |
|    | 1 g/l of 3-(2-benzothiazolyl-2-mercapto)propanesulfonic acid sodium salt                 |
|    | 400 mg/l of a quaternary ammonium salt   |
| 30 | pH 8 (75°C)  |

Working temperature 75°C

Current density 1 A/dm<sup>2</sup>

L\* = 52.3

5 Example 3 without sulfur heterocycle (type III):

3 g/l of Ru as [Ru<sub>2</sub>N(H<sub>2</sub>O)X<sub>8</sub>]<sup>3-</sup> X = halide ion

60 g/l of oxalic acid

40 g/l of potassium dihydrogenphosphate

300 mg/l of a quaternary ammonium salt

10

pH 6 (75°C)

Working temperature 75°C

Current density 1 A/dm<sup>2</sup>

L\* = 69.2

**Claims**

1. An electrolyte having a pH of from  $\geq 5$  to 12 for the deposition of decorative and industrial layers of ruthenium having a particular blackness, characterized in that,  
5 the electrolyte has the following constituents:
  - a) dissolved ruthenium in a concentration of from 0.2 to 20 gram per liter (g/l) of electrolyte, calculated as ruthenium metal;
  - b) one or more anions of a dicarboxylic, tricarboxylic or tetracarboxylic acid in a concentration of 0.05-2 mol per liter;
  - 10 c) one or more sulfur heterocycles;
  - d) one or more cationic surfactants.
2. The electrolyte as claimed in claim 1, characterized in that  
ruthenium is present as a binuclear, anionic ruthenium nitrido halo complex of the  
15 formula  $[\text{Ru}_2\text{N}(\text{H}_2\text{O})_2\text{X}_8]^{3-}$ , where X is a halide ion.
3. The electrolyte as claimed in claim 1 and/or 2, characterized in that  
the concentration of ruthenium after complete dissolution of the compound is in the range from 2 to 8 gram per liter of electrolyte.
- 20 4. The electrolyte as claimed in one or more of the preceding claims, characterized in that  
the electrolyte is free of further transition metal ions.
5. The electrolyte as claimed in one or more of the preceding claims, characterized in that  
25 the carboxylic acid is selected from the group consisting of oxalic acid, citric acid, tartaric acid, succinic acid, maleic acid, glutaric acid, adipic acid, malonic acid, malic acid.
6. The electrolyte as claimed in one or more of the preceding claims, characterized in that  
30 the sulfur heterocycle is selected from the group consisting of 3-(2-benzothiazolyl-2-mercapto)propanesulfonic acid sodium salt, saccharin sodium salt,

saccharin N-propylsulfonate sodium salt, 6-methyl-3,4-dihydro-1,2,3-oxathiazin-4-one 2,2-dioxide, benzothiazole, 2-mercaptobenzothiazole, thiazole, isothiazole and derivatives thereof.

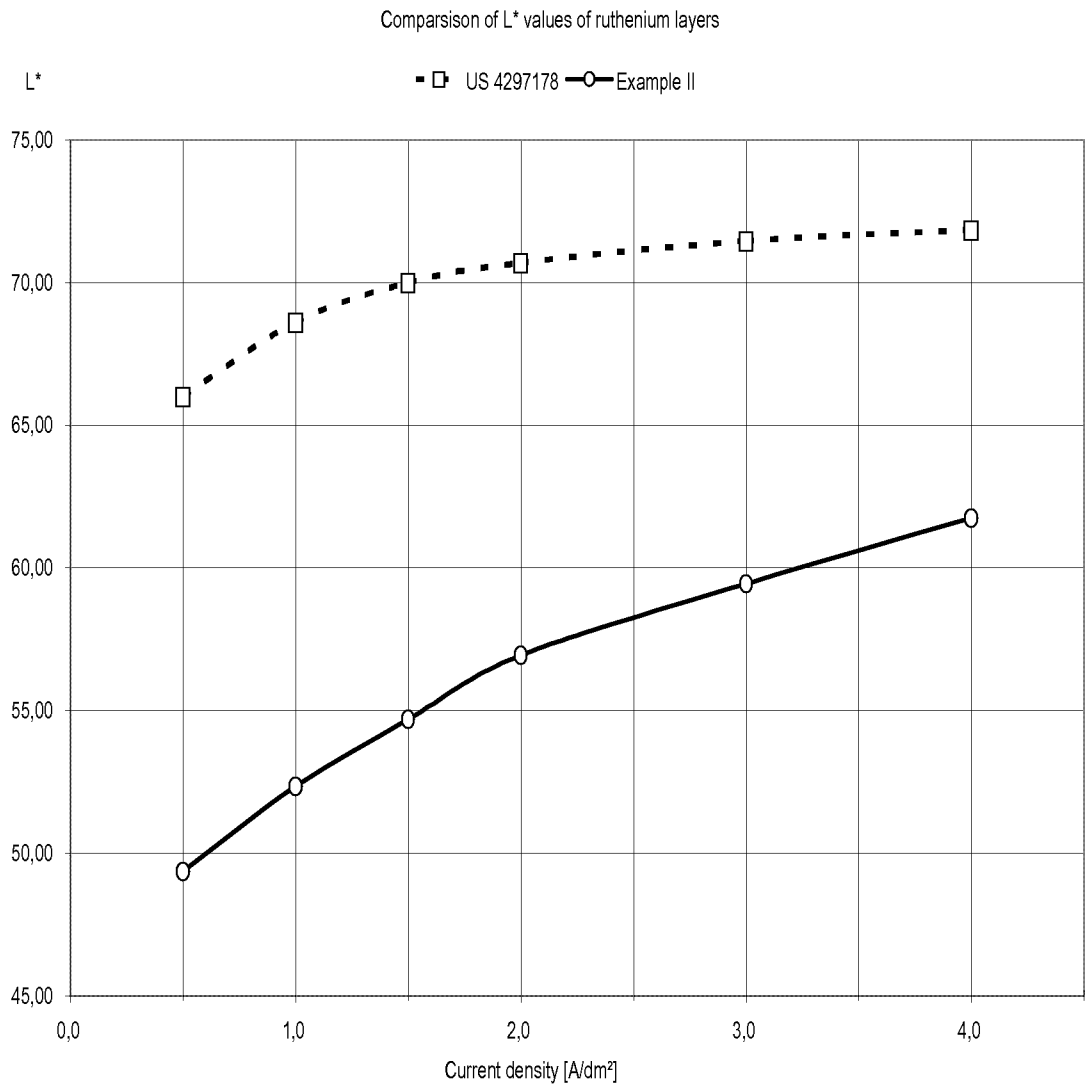
7. The electrolyte as claimed in one or more of the preceding claims,  
5 characterized in that  
the surfactant is selected from the group consisting of octyltrimethylammonium bromide, octyltrimethylammonium chloride, decyltrimethylammonium bromide, decyltrimethylammonium chloride, dodecyltrimethylammonium bromide, dodecyltrimethylammonium chloride, tetradecyltrimethylammonium bromide,  
10 tetradecyltrimethylammonium chloride, hexadecyltrimethylammonium bromide, hexadecyltrimethylammonium chloride, ethyldimethylhexadecylammonium bromide, ethyldimethylhexadecylammonium chloride, benzyldimethyldecylammonium chloride, benzyldimethyldodecylammonium chloride, benzyldimethyltetradecylammonium chloride and benzyldimethylhexadecylammonium chloride  
15 and mixtures thereof.
8. The electrolyte as claimed in one or more of the preceding claims,  
characterized in that  
the pH of the electrolyte is in the range 7-8.
9. The electrolyte as claimed in one or more of the preceding claims,  
20 characterized in that  
the electrolyte comprises a buffer system selected from the group consisting of borate, phosphate and carbonate buffers.
10. The use of an electrolyte in a process for the deposition of black ruthenium  
coatings on conductive, in particular metallic, articles by immersion of the article  
25 to be coated as cathode in the electrolyte and establishment of a flow of electric current between the anode and the cathode,  
characterized in that  
an electrolyte as claimed in one or more of the preceding claims is selected.
11. The use as claimed in claim 10,  
30 characterized in that  
ruthenium is present as a binuclear, anionic ruthenium nitrido halo complex of the formula  $[\text{Ru}_2\text{N}(\text{H}_2\text{O})_2\text{X}_8]^{3-}$ , where X is a halide ion.

12. The use as claimed in claim 10 and/or 11,  
characterized in that  
the concentration of ruthenium after complete dissolution of the compound is in  
the range from 2 to 8 gram per liter of electrolyte.
- 5 13. The use as claimed in one or more of claims 10-12,  
characterized in that  
the electrolyte is free of further transition metal ions.
14. The use as claimed in one or more of claims 10-13,  
characterized in that  
10 the carboxylic acid is selected from the group consisting of oxalic acid, citric acid,  
tartaric acid, succinic acid, maleic acid, glutaric acid, adipic acid, malonic acid,  
malic acid.
15. The use as claimed in one or more of claims 10-14,  
characterized in that  
15 the sulfur heterocycle is selected from the group consisting of 3-(2-benzothia-  
zolyl-2-mercapto)propanesulfonic acid sodium salt, saccharin sodium salt,  
saccharin N-propylsulfonate sodium salt, 6-methyl-3,4-dihydro-1,2,3-oxathiazin-4-  
one 2,2-dioxide, benzothiazole, 2-mercaptobenzothiazole, thiazole, isothiazole  
and derivatives thereof.
- 20 16. The use as claimed in one or more of claims 10-15,  
characterized in that  
the surfactant is selected from the group consisting of octyltrimethylammonium  
bromide, octyltrimethylammonium chloride, decyltrimethylammonium bromide,  
decyltrimethylammonium chloride, dodecyltrimethylammonium bromide,  
25 dodecyltrimethylammonium chloride, tetradecyltrimethylammonium bromide,  
tetradecyltrimethylammonium chloride, hexadecyltrimethylammonium bromide,  
hexadecyltrimethylammonium chloride, ethyldimethylhexadecylammonium  
bromide, ethyldimethylhexadecylammonium chloride, benzyldimethyldecyl-  
ammonium chloride, benzyldimethyldodecylammonium chloride, benzyldimethyl-  
30 tetradecylammonium chloride and benzyldimethylhexadecylammonium chloride  
and mixtures thereof.
17. The use as claimed in one or more of claims 10-16,

characterized in that  
a current density of 0.1-10 A/dm<sup>2</sup> is set.

18. The use as claimed in one or more of claims 10-17,  
characterized in that  
5 a temperature of 10-80°C is set.
19. The use as claimed in one or more of claims 10-18,  
characterized in that  
insoluble anodes made of a material selected from the group consisting of  
platinized titanium, graphite, iridium-transition metal mixed oxide and special  
10 carbon material and combinations of these anodes are used.
20. A black ruthenium layer which can be obtained as claimed in one or more of  
claims 10-19.
21. The ruthenium layer as claimed in claim 20,  
characterized in that  
15 it has a thickness of from 0.1 to 3 µm.
22. The ruthenium layer as claimed in claim 20,  
characterized in that  
the layer has a sulfur content of from 3% by weight to 6% by weight in the outer  
region of 1 µm.
- 20 23. The ruthenium layer as claimed in claim 20,  
characterized in that  
the layer has a carbon content of from 1% by weight to 2% by weight in the outer  
region of 1 µm.
24. The ruthenium layer as claimed in claim 21,  
25 characterized in that  
the layer has an oxygen content of from 15% by weight to 20% by weight in the  
outer region of 1 µm.
25. An article having a ruthenium layer as claimed in one or more of claims 20-24.





Drawing 1