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(71) Applicant: **MACDERMID ACUMEN, INC.** [US/US]; 245 Freight Street, Waterbury, CT 06702 (US).

(72) Inventors: **HARA, Masahiro**; 6-40-1 Kamikodanaka, Nakahara-ku, Kawasaki-shi, Kanagawa 2110053 (JP). **NISHIYAMA, Tatsuya**; 1-15-19 Hishinuma, Chigasaki-shi, Kanagawa 2530011 (JP).

(74) Agent: **MCKIRRYHER, Colleen, S.**; Carmody Torrance Sandak & Hennessey, 195 Church Street, P.O. Box 1950, New Haven, CT 06509-1950 (US).

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(54) Title: DARK COLORED CHROMIUM BASED ELECTRODEPOSITS

(57) Abstract: An aqueous trivalent chromium electrolyte comprising trivalent chromium ions and amino acids that allow for producing a dark colored hue in the trivalent chromium coating which is plated on a substrate. The amino acids described herein comprise a cationic side chain and are at least essentially free of sulfur. The cationic side chain of the amino acid further comprises nitrogen. When used in the trivalent chromium electrolyte, these amino acids allow for producing significantly darker trivalent chromium deposits. The trivalent chromium electrolyte is used in a method for producing the desired dark colored hue in the trivalent chromium coating that is produced on a substrate using electrodeposition.

DARK COLORED CHROMIUM BASED ELECTRODEPOSITS

FIELD OF THE INVENTION

The present invention generally relates to a composition and method for producing dark coloured chromium coatings by electrodeposition.

BACKGROUND OF THE INVENTION

Chromium has been used for many years as a decorative coating and has many applications. For decorative purposes, the chromium is generally applied as a thin coating, which is typically less than 1 micrometre in thickness, over a coating of nickel. The chromium provides a hard, wear resistant layer and excellent corrosion performance is also obtained due to the chromium layer being cathodic with respect to the underlying nickel deposit. Thus the underlying nickel becomes the anode in the corrosion cell and corrodes preferentially leaving the chromium layer uncorroded.

Typically, these thin decorative chromium layers have been applied by electrodeposition from electrolytes based on hexavalent chromium, which typically comprise chromic acid. The chromium deposits obtained from these electrolytes are essentially pure chromium and have a uniform and invariant colour. A thin oxide layer forms on the top of the coatings giving a blue/white appearance which is very well known. In addition to the incentive to use alternative electrolytes due to serious health and environmental hazards associated with chromic acid, there is also a market demand for coatings having a darker hue.

An initial solution to providing a darker hued deposit from chromium electrolytes can be obtained by electrodepositing the chromium coatings from electrolytes based on trivalent chromium. Due to the nature of the deposition mechanism from these electrolytes, the chromium coating produced is less pure than that produced from hexavalent electrolytes. This is due to co-deposition of other elements within the coating. Most commonly, these co-deposited elements are iron, sulphur and carbon or combinations thereof. By adjusting the electrolyte formulation of trivalent chromium based processes to maximize the darkness of the deposit produced by the incorporation of these co-deposited elements, coatings of a fairly

dark hue can be obtained.

While coatings provided by trivalent chromium electrolytes typically produce darker hued deposits than that of hexavalent chromium electrolytes, the resulting coatings from the prior art are still not dark enough to fulfill the needs of the market and a demand exists to produce darker chromium based coatings. It is the object of this invention to provide a means of producing these coatings.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a trivalent chromium plating electrolyte that is capable of providing dark colored chromium deposits on a substrate.

It is an object of the invention to provide amino acids in the trivalent chromium electrolyte that are capable of creating a dark hue in the resulting trivalent chromium deposit.

It is another object of the invention to provide amino acids in the trivalent chromium electrolyte that have nitrogen containing side chains.

It is another object of the invention to provide amino acids that do not contain sulfur in the trivalent chromium electrolyte to provide darker hues of chromium deposits on substrates.

It is yet another object of the invention to provide a darker hued deposit on a substrate using a trivalent chromium electrolyte with select amino acids than the prior art trivalent chromium plating electrolytes can achieve.

It is still another object of the invention to provide a method of plating a trivalent chromium deposit with a dark hue over a nickel deposit.

In one embodiment, a composition is provided for a trivalent chromium electrolyte comprising:

i. trivalent chromium ions,

ii. one or more complexants capable of maintaining the trivalent

chromium ions in solution; and

iii. one or more amino acids; wherein the amino acids comprise a cationic side chain comprising nitrogen and wherein the cationic side chain is at least essentially free of sulfur; and

wherein the electrolyte is substantially free of hexavalent chromium salts.

In another embodiment, a method is provided for producing a dark colored chromium deposit on a substrate, comprising the steps of:

i. providing a trivalent chromium based electrolyte comprising:

a) trivalent chromium ions,

b) one or more complexants capable of maintaining the trivalent chromium ions in solution, and

c) one or more amino acids,

wherein the amino acids comprise a cationic side chain comprising nitrogen and wherein the cationic side chain is at least essentially free of sulfur; and

wherein the electrolyte is substantially free of hexavalent chromium salts; and

ii. electrodepositing a dark colored chromium deposit on the substrate using the trivalent chromium based electrolyte.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts various classes of amino acids.

DETAILED DESCRIPTION OF THE PREFERED EMBODIMENTS

The inventors have surprisingly found that the incorporation of select amino acids which comprise nitrogen containing side chains into the trivalent chromium electrolyte results in coatings which are substantially darker than those obtained from the same electrolyte in the absence of these compounds. The amino acids useful in the current

invention are additionally at least essentially free of sulfur. By essentially free of sulfur, it is meant that sulfur is not present in any concentration, aside from trace amounts that may occur as contaminants in such compounds. The darkest coatings are obtained when select amino acids are added to electrolytes which have already been optimised to produce dark coatings by the incorporation of other elements such as sulfur, iron, carbon or combinations thereof.

The use of amino acids as complexants in trivalent chromium plating baths has been described in U.S. Patent No. 4,107,004 to Ward et al. and U.S. Patent No. 4,157,945 to Barnes et al., which describe the use of glycine as a complexant. U.S. Patent No. 4,161,432 to Barclay et al. describes the use of glycine, aspartic acid, arginine and histidine as complexants. U.S. Patent No. 4,448,648 and U.S. Patent No. 4,448,649 both to Barclay et al., describe the use of aspartic acid as a complexant. The subject matter of each of these patents of which is herein incorporated by reference in its entirety. These patents are all focused on producing coatings which are light in color and do not provide for changing the color of the deposit produced or variation of deposit color associated with different amino acids.

Amino acids fall into several groups as shown in Figure 1. The amino acids methionine and cysteine (and cystine) contain bivalent sulphur in their side chains. The use of these sulphur-containing compounds as darkening agents in trivalent chromium baths has been previously disclosed, as for example in WO 2012/150198A1 to Schulz et al., which is hereby incorporated herein by reference in its entirety. This is understood to be a function of the presence of sulfur in the compound, as sulfur is known to cause darker hues in trivalent chromium deposits as compared to the more pure deposits produced from hexavalent chromium electrolytes.

The inventors of the present invention have surprisingly found that sulfur-free amino acids, including those selected from the group having nitrogen containing cationic side chains, have the desired effect of darkening the deposit in a uniform manner. The side chains are cationic under the normal pH conditions of most commercially available trivalent chromium electroplating baths (pH 2.5 – 4.0) due to the presence of a nitrogen-containing (amine) functional group in the side chain.

The amino acids that are useful in the current invention include, for example, arginine, histidine, lysine and combinations thereof. It was found that these amino acids will

produce significant darkening of the trivalent chromium deposits. Additionally tryptophan, although not listed under the amino acids containing a positively charged group in Figure 1, has a nitrogen-containing side chain and is also found to have enhanced darkening effects. From this result, while not wishing to be bound by theory, it is also believed that the side chain of tryptophan is cationic under the normal pH conditions in the trivalent chromium electroplating bath.

The effective concentration range of the preferred amino acids in the trivalent chromium electrolyte is preferably between about 1 g/L and about 50 g/l and more preferably between about 2 g/L and about 20 g/l. The concentration of amino acids in the trivalent chromium electrolyte is most preferably between about 5 g/L and about 10 g/L.

When electroplating from electrolyte solutions described herein, inert anodes, such as carbon anodes, are typically used. Other inert anodes such as platinized titanium, platinum, iridium oxide coated titanium, or tantalum oxide coated titanium may also be used.

The temperature of the trivalent chromium based electrolyte is in the range of 40°C to 60°C, most preferably around 50°C. The pH of the electrolyte is in the range from about 2 to about 5, most preferably about 3.5. The current used during plating is in the range of about 1 amp to about 10 amps, most preferably about 4 amps. Agitation is not required during the plating of substrates in the trivalent chromium electrolyte.

As used herein, the term "about" refers to a measurable value such as a parameter, or a concentration or the like and is meant to include variations of +/- 15% or less, preferably variations of +/- 10% or less, more preferably variations of +/- 5% or less, and most preferably variations of +/- 0.1% or less from the particularly recited value in so far as such variations are appropriate to carry out the invention as described herein. Furthermore, it is also to be understood that the value to which the modifier "about" refers is itself specifically disclosed herein.

In a preferred embodiment, the substrate comprises nickel deposited on the underlying substrate and the chromium is electroplated on the nickel deposit.

In order to demonstrate the scope of the invention, a Konica Minolta CM2600d

spectrophotometer was used to determine the "lightness" values of the various deposits by measuring the L* value according to the L*a*b* colorspace system. The colorspace system gives a quantitative value (L*), which can be used to compare the degree of darkening obtained by the various combinations of amino acid additives. The higher the L* value, the lighter the deposit and the lower the L* value the darker the deposit. An L* value of 0 is black and an L* of 100 is white. Lower L* values are the desire of the current invention.

Dark hued coatings produced by the electrodeposition of trivalent chromium using the electrolytes described herein preferably have an L* value, measured according to an L*a*b* colorspace system, of less than that of typical trivalent chromium deposits that produce light colored coatings and those that have already been maximized for darkness in the resulting deposits.

The trivalent chromium based electrolytes may contain thiocyanate ions. The thiocyanate ions may be present in a concentration anywhere from about 0.2 g/L up to about 5.0 g/L.

The trivalent chromium based electrolytes presented herein are at least substantially free of hexavalent chromium salts, wherein no Cr(VI) ions can be detected in the electrolyte by ordinary measurement techniques.

The trivalent chromium electrolyte comprises a source of trivalent chromium ions, one or more complexants (complexing agents) capable of maintaining the trivalent chromium ions in solution, and the select amino acids as described herein. The amino acids have provided darker hues in the plated deposit compared to the use of the same electrolyte without such amino acids.

The trivalent chromium electrolyte used as a standard is an electrolyte designed to produce light colored chromium deposits. The electrolyte and plating process is based on U.S. Patent No. 4,473,448 to Deeman. This patent is hereby incorporated by reference in its entirety.

Additionally, inventive examples are also provided based on a trivalent chromium electrolyte solution that has already been formulated to produce dark deposits, based on U.S.

Patent No. 4,161,432 to Barclay et al. The amino acid used in the electrolyte composition is aspartic acid. This reference is hereby incorporated by reference in its entirety.

The following non-limiting examples illustrate the effectiveness of the invention. All of the examples were prepared by electroplating a trivalent chromium deposit onto Hull cell panels. The Hull Cell panels had previously been electroplated with 10 microns of a bright nickel deposit and are then placed in a Hull Cell with the trivalent chromium electrolyte being tested. For the trivalent chromium plating step, the conditions are as shown in Table 1. Conditions for the trivalent chromium plating remained consistent regardless of the composition being tested.

The lightness or L* value of the trivalent chromium deposit was measured at a point on the Hull Cell panel corresponding to a current density of 8 amps per square decimeter in all cases, which is representative of a normal working range for chromium plating.

Table 1. Trivalent Chromium Plating Hull Cell Conditions

Parameter	Value
Temperature	50°C
pH	3.5
Plating time	5 minutes
Plating current	4 Amps
Agitation	none
Anode	titanium coated with a conductive mixed metal oxide film

Comparative Example 1

Table 2 provides the L* values measured using the electrolyte based on U.S. Patent No. 4,473,448 to Deeman as a Standard (1), with various amino acids added that were not effective darkening agents.

Table 2.

Electrolyte Composition	L* Value
Standard (1) with no additional amino acids	82.84
Standard (1) plus 5g/l Glycine	81.15

Standard (1) plus 5g/l Alanine	81.9
Standard (1) plus 5g/l Valine	82.83
Standard (1) plus 5g/l Isoleucine	82.47
Standard (1) plus 5g/l Proline	82.23
Standard (1) plus 5g/l Phenylalanine	82.25
Standard (1) plus 5g/l Serine	80.7
Standard (1) plus 5g/l Threonine	82.78
Standard (1) plus 5g/l Tyrosine	83.72
Standard (1) plus 5g/l Glutamine	80.51
Standard (1) plus 5g/l Aspartic acid	80.05

As can be seen from the results set forth in Table 2, none of the amino acids tested produced any significant reduction in the L* values when compared to the trivalent chromium electrolyte without amino acids added. The average reduction in L* value was 1.17%.

Example 1

Table 3 provides the L* values obtained when the amino acids described herein are added to the electrolyte based on U.S. Patent No. 4,473,448 to Deeman. The same Standard (1) electrolyte is used as in the comparative example above. As previously noted, this electrolyte typically produces light colored trivalent chromium deposits.

Table 3.

Electrolyte Composition	**L* Value**
Standard (1) with no additional amino acids	82.84
Standard (1) with 5g/l Arginine	75.26
Standard (1) with 5g/l Histidine	69.33
Standard (1) with 5 g/l Lysine	78.47
Standard (1) with 5g/l Tryptophan	46.31 (but deposit cosmetically unacceptable)

In this case, the average reduction in L* value was 12.7% using the examples of the invention of arginine and histidine. This is a significant difference which can easily be seen by eye. The addition of arginine, histidine or lysine gave uniform color across the entire

deposit. The addition of tryptophan gave a dramatic effect but produced very uneven and streaky deposits, which although significantly darker, were commercially unacceptable.

Example 2

Table 4 gives the L* values obtained when amino acids of the invention are added to the electrolyte based on U.S. Patent No. 4,161,432 to Barclay et al. This electrolyte was used as the Standard (2) to compare the L* values after the amino acids are added. As previously noted, deposits produced using this electrolyte process were previously formulated to provide dark colored trivalent chromium deposits.

Table 4

Electrolyte Composition	L* Value
Standard (2) with no additional amino acids	69.33
Standard (2) with 5 g/l Arginine	60.32
Standard (2) with 5 g/l Histidine	58.71
Standard (2) with 2.5g/l Histidine and 2.5g/l Arginine	59.41
Standard (2) with 5g/l Histidine and 5g/l Arginine	57.21

In this case, the average reduction in the L* value was 15.02%. This is a very noticeable difference in color. While the electrolyte based on U.S. Patent No. 4,161,432 to Barclay et al. naturally produces a dark deposit, it was possible to increase the deposit darkness by the addition of the amino acids as described herein.

As it has been shown by way of the examples presented herein, the inventors have surprisingly found that darker hued deposits can be obtained from trivalent chromium electrolytes that contain the amino acids as described within. The result was unexpected as the effective amino acids did not contain sulfur, but the presence of cationic nitrogen containing side chains allowed for darker hues in the deposits obtained using the trivalent chromium electrolyte of the current invention.

It should also be understood that the following claims are intended to cover all of the generic and specific features of the invention as described herein and all statements of the scope of the invention that as a matter of language might fall there between.

WHAT IS CLAIMED IS:

1. A trivalent chromium electrolyte comprising:
   i. trivalent chromium ions,
   ii. one or more complexants capable of maintaining the trivalent chromium ions in solution; and
   iii. one or more amino acids; wherein the amino acids comprise a cationic side chain comprising nitrogen and wherein the cationic side chain is at least essentially free of sulfur; and
   wherein the electrolyte is substantially free of hexavalent chromium salts.

2. A trivalent chromium electrolyte according to claim 1, wherein the one or more amino acids are selected from the group consisting of arginine, histidine, lysine, tryptophan, and combinations thereof.

3. A trivalent chromium electrolyte according to claim 1, wherein the total concentration of amino acids is between about 1 g/L and about 50 g/l.

4. A trivalent chromium electrolyte according to claim 3, wherein the total concentration of amino acids is between about 2 g/L and about 20 g/l.

5. A trivalent chromium electrolyte according to claim 4, wherein the total concentration of amino acids is between about 5 g/L and about 10 g/l.

6. A trivalent chromium electrolyte according to claim 1, wherein the trivalent chromium plating electrolyte contains thiocyanate ions.

7. The trivalent chromium electrolyte according to claim 6, wherein the thiocyanate ions are present in a concentration between about 0.2 g/L and about 5 g/L.

8. The trivalent chromium electrolyte according to claim 2, wherein the amino acid comprises histidine.

9. The trivalent chromium electrolyte according to claim 2, wherein the amino acid comprises arginine.

10. The trivalent chromium electrolyte according to claim 2, wherein the amino acid comprises a mixture of histidine and arginine.

11. A method of producing a dark colored chromium deposit on a substrate comprising the steps of:

i. providing a trivalent chromium based electrolyte comprising:
   a) trivalent chromium ions,
   b) one or more complexants capable of maintaining the trivalent chromium ions in solution, and
   c) one or more amino acids,
      wherein the amino acids comprise a cationic side chain comprising nitrogen and wherein the cationic side chain is at least essentially free of sulfur; and
   wherein the electrolyte is substantially free of hexavalent chromium salts; and

ii. electrodepositing a dark colored chromium deposit on the substrate using the trivalent chromium based electrolyte.

12. The method according to claim 11, wherein the one or more amino acids are selected from the group consisting of arginine, histidine, lysine, tryptophan, and combinations thereof.

13. The method according to claim 11, wherein the total concentration of amino acids is between about 1 g/L and about 50 g/l.

14. The method according to claim 13, wherein the total concentration of amino acids is between about 2 g/L and about 20 g/l.

15. The method according to claim 14, wherein the total concentration of amino acids is between about 5 g/L and about 10 g/l.

16. The method according to claim 11, wherein the trivalent chromium based electrolyte further comprises thiocyanate ions.

17. The method according to claim 16, wherein the thiocyanate ions are present in a concentration between about 0.2 g/L and about 5 g/L.

18. The method according to claim 12, wherein the one or more amino acids comprises histidine.

19. The method according to claim 12, wherein the one or more amino acid comprises arginine.

20. The method according to claim 12, wherein the one or more amino acids comprises a mixture of histidine and arginine.

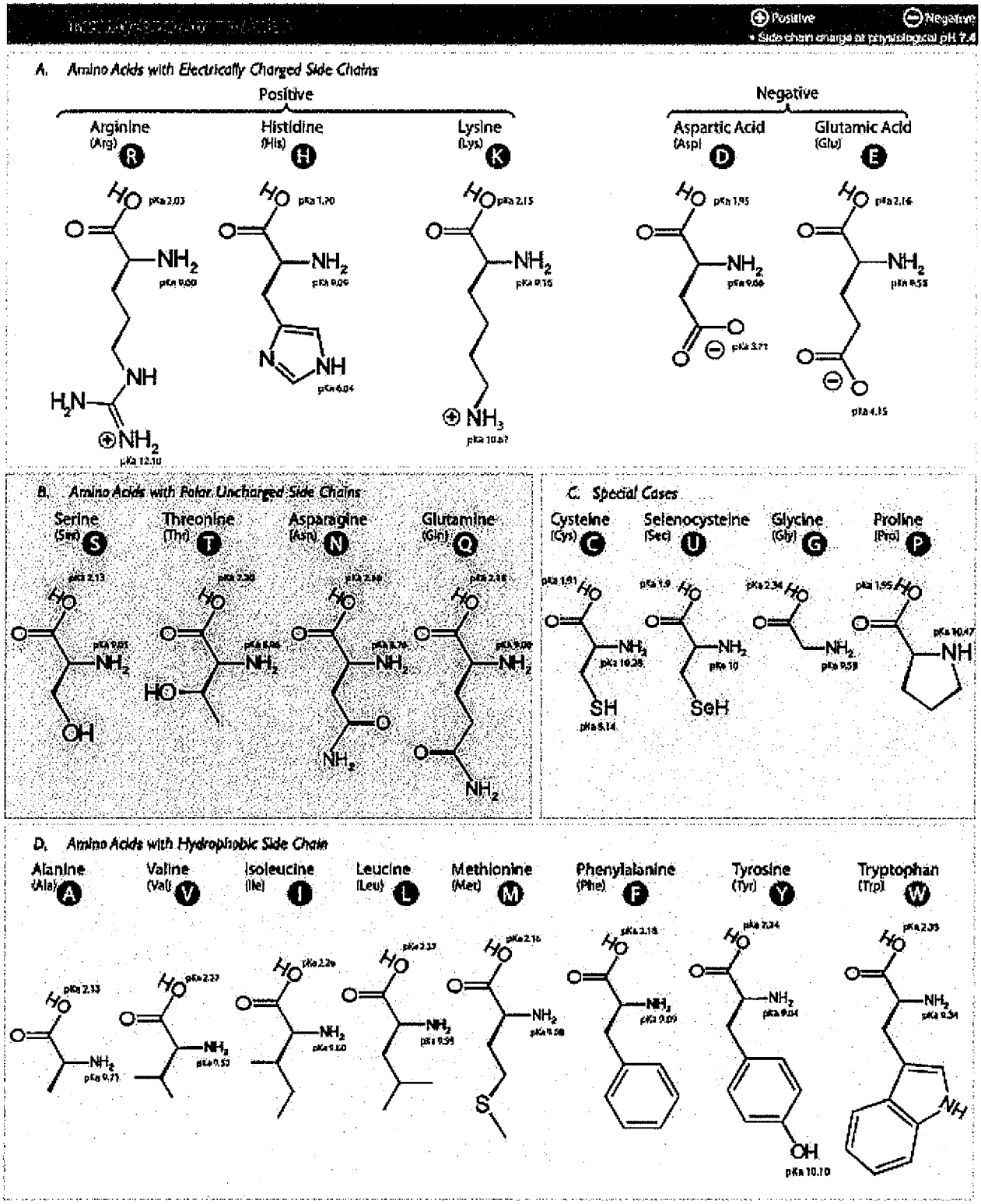
21. The method according to claim 11, wherein the chromium coating produced on the substrate has an L* value, measured according to an L*a*b* colorspace system, lower than the trivalent chromium deposit produced by the same trivalent chromium electrolyte that does not comprise the one or more amino acids.

22. The method according to claim 11, wherein the substrate comprises a nickel deposit on the substrate and the trivalent chromium is plated on the nickel deposit.

23. The method according to claim 11, wherein the pH of the trivalent chromium electrolyte is between about 2.0 and about 5.0.

24. The method according to claim 23, wherein the pH of the trivalent chromium electrolyte is about 3.5.

Figure 1.


Positive
Negative
• Side chain charge at physiological pH 7.4
A. Amino Acids with Electrically Charged Side Chains
Positive
Negative
Arginine (Arg) R
Histidine (His) H
Lysine (Lys) K
Aspartic Acid (Asp) D
Glutamic Acid (Glu) E
B. Amino Acids with Polar Uncharged Side Chains
Serine (Ser) S
Threonine (Thr) T
Asparagine (Asn) N
Glutamine (Gln) Q
C. Special Cases
Cysteine (Cys) C
Selenocysteine (Sec) U
Glycine (Gly) G
Proline (Pro) P
D. Amino Acids with Hydrophobic Side Chain
Alanine (Ala) A
Valine (Val) V
Isoleucine (Ile) I
Leucine (Leu) L
Methionine (Met) M
Phenylalanine (Phe) F
Tyrosine (Tyr) Y
Tryptophan (Trp) W

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US17/26951

A. CLASSIFICATION OF SUBJECT MATTER
IPC: **C25D 3/06**(2006.01),**3/10**(2006.01),**7/00**(2006.01)

CPC: C25D 3/06
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
CPC : C25D 3/06, 3/04, 3/08, 3/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 205/288, 283, 285, 287, 289, 290

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6,004,448 A (MARTYAK) 21 December 1999 (21.12.1999), entire document.	1-5 and 8-10
X --- Y	US 4,161,432 (BARCLAY et al.) 17 July 1979 (17.07.1979), entire document.	1-9, 11-19, 23 and 24 --- 10 and 20-22
Y	US 6,468,672 B1 (DONOVAN, III et al.) 22 October 2002 (22.10.2002), entire document.	22

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 April 2017 (24.04.2017)	27 APR 2017
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (571) 273-8300	Authorized officer William Krynski Telephone No. (571) 272-4300

INTERNATIONAL SEARCH REPORT	International application No. PCT/US17/26951

Continuation of B. FIELDS SEARCHED Item 3:
EAST: US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB
Search Terms: trivalent, chromium, Cr, arginine, histidine, lysine, tryptophan, thiocyanate, electropl$10, electrodeposit$10,