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⑥ **HIGH-RATE CHROMIUM ALLOY PLATING.**

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**EP 0073221 B1**

**Description**

## Background of the invention

This invention relates to the high-speed plating of chromium alloys.

5 Extensive use of relatively scarce materials, such as nickel and chromium, in corrosive environments may be reduced by an acceptable plating process which may form a corrosion-resistant coating of, say, 25  $\mu\text{m}$  of a chromium alloy, on an inexpensive substrate, such as steel or brass. A bright, decorative coating of chromium alloy is also valued in some uses.

10 In the past, most commercial plating of bright chromium has been carried out from solutions of hexavalent chromium, such as chromic acid. Unfortunately, these baths, where chromium is complexed as an anion, are historically ineffective for plating alloys. Efforts at plating from divalent and/or trivalent chromium solutions have allowed the production of some alloy plate, but at low deposition rates and typically at current densities below about 1 A/in<sup>2</sup> (15 A/dm<sup>2</sup>), and often much lower.

15 Moreover, in electrodepositing an alloy from a solution containing metal ions, it is well known that a less active metal will deposit in preference to a more active metal. Considering chromium alloys containing iron and/or nickel, the relative nickel, iron and chromium reduction potentials would be expected to result in deposits which are rich in nickel and iron. The chromium is clearly more active with a potential of about -0.74 volts for the Cr<sup>+3</sup> to Cr<sup>0</sup> reduction.

20 US—A—3,917,517 discloses hypophosphite containing chromium alloys electroplating baths providing chromium platings at current densities of up to 100 A/dm<sup>2</sup>. US—A—4,142,948 discloses chromium electroplating baths containing trivalent chromium and operating at pH below 5 and at current densities up to 100 A/dm<sup>2</sup> due to the presence, as additives, of amino- or hydroxy-substituted carboxylic acids.

## 25 Summary of the invention

It is an object of the present invention to provide a method of plating chromium alloy with iron and, optionally nickel and/or cobalt.

30 It is also an object to plate such alloy composition which may substantially approximate the metal ratio in the electrolyte, in spite of the difference in activity of the metals.

It is also an object to provide a high-rate plating process for chromium alloy.

It is further an object to provide such electrodeposition process for producing chromium alloy from solutions comprising divalent and trivalent chromium.

It is finally an object that such process be controllable to yield a thick, dense chromium alloy deposit.

35 In accordance with the objectives, the invention disclosed in claim 1 is a method for high-rate plating of chromium alloy from an electrolyte solution containing divalent and trivalent chromium ions, ions of iron and, optionally, ions of nickel and/or cobalt as additional alloying constituents. The high-rate plating is carried out at a current density of at least about 75 A/dm<sup>2</sup> (preferably at least about 150 A/dm<sup>2</sup>), a pH of between about 0.5 and 2.0 and with relative motion between the cathode and the plating solution of at least  
40 about 1 m/sec (preferably 1—8 m/sec).

Deposits of composition 5—80% (by weight) chromium, 20—95% iron and 0—50% nickel are preferably formed by electrolyzing an electrolyte solution having metal ion concentrations of 20 g/l to saturation divalent/trivalent chromium, 1—50 g/l iron and 0—50 g/l nickel. Complexing anions of sulfuric, sulfamic, hydrochloric, phosphoric and boric acids are preferred in the electrolyte. When using insoluble  
45 anodes, a porous barrier is typically positioned around the cathode to prevent migration of anode oxidation reaction products to the cathode where they would otherwise oxidize the divalent/trivalent chromium to the hexavalent state.

50 Within the general conditions stated above, the inventor has also discovered that the best deposits of chromium alloy may be obtained by strictly maintaining the free acid of the electrolyte within a narrow range corresponding to a pH of about 1.7 to 1.8. Very accurate metering must be used to monitor pH or a titration may be necessary to establish the amount of free-acid in the bath.

## Description of the invention

55 The invention is a method for electroplating a chromium alloy containing iron and, optionally, nickel and/or cobalt. The alloy compositions preferably fall in the range (by weight) of 5—80% chromium, 20—95% iron and 0—50% total nickel and/or cobalt. We have found that alloys outside of this range may be plated according to the invention, but for the desired corrosion-resistance of the coatings, at least about 5—10% chromium is necessary. Chromium and nickel contents above the preferred range unduly raise the cost of the alloys and are, therefore not preferred. Chromium-nickel-iron alloys are the preferred coating compositions and, in particular, the 300 and 400 classes of stainless steels are preferred. Type 304 stainless  
60 (18% Cr—8% Ni—2% Mn—balance Fe) is one desirable composition. However, examples and discussion regarding chromium-iron-nickel alloys are intended to include alloys wherein cobalt may be substituted, as known in the art, for all or a portion of the nickel. Other impurities which may enter the deposit from the anode, for example, may also be deposited without harm. Manganese, silicon and copper are examples.

65 The alloy coating is formed on a conventional cathode surface of, for example, steel, iron, aluminum,

brass or copper. Insoluble anodes, such as made from lead, may be used, although soluble alloy anodes of iron and chromium have been most useful in the inventive process.

#### Plating solution

5 The electrolyte is a divalent/trivalent chromium salt solution preferably containing 20 g/l to saturation of chromium ions, 1—50 g/l iron ions and a total of 0—50 g/l of nickel and/or cobalt ions. The trivalent chromium may be converted to the divalent form and vice versa so that the exact ratio thereof was not clearly identified. Therefore, the two species are believed to both be present and necessary, and the reference to trivalent chromium is also intended to include the lower specie which coexists in the bath.  
10 Excess divalent form can adversely affect nickel deposition because it tends to reduce the nickel ions to the metal, resulting in precipitation or plating on the walls, etc. of the cell.

Some electrolyte solutions require a period of stabilization before yielding superior product. This may be due to a need to produce some particular minimum quantity of divalent chromium in the bath.

15 Conventional complexing anions for chromium plating are also necessary in the inventive method. In particular, these include the anions from the mineral acids: sulfuric, sulfamic, hydrochloric, phosphoric and boric acids.

The pH of the electrolyte has been found to be a critical factor in depositing thick, bright and semi-bright coatings. Within the pH range of 0.5—2.0, good chromium alloy coatings can be deposited which are matte textured, but which are still useful in some applications of corrosion and wear resistance. These coatings are generally limited in thickness to about 12 to 25  $\mu\text{m}$ . Thicker coatings tend to crack or peel as a result of increasing internal stresses.  
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It has been found, however, that when the acidity of the electrolyte corresponds to a pH of between about 1.7 and 1.8, bright and semi-bright coatings can be obtained which are adherent, dense and crack-free, even at thicknesses above 125  $\mu\text{m}$ . The reason for this phenomenon is not understood at this point, but the result is dramatic over this range.  
25

The acidity range is so narrow that difficulty may be encountered in accurately measuring and maintaining it throughout the solution. Certainly, sensitive instruments exist for measuring the pH, and in practice a pH meter might be used for convenience. However, for accuracy, we prefer to determine the acidity by measuring the amount of "free acid" by titration against a standard basic solution. We define the "free acid" content as the quantity of 0.1 N NaOH solution needed to bring a 1.0 ml aliquot of electrolyte to pH 3.5. The preferred range of free acid using this titration method is about 0.5 ml—1.5 ml NaOH, corresponding to the pH of about 1.8—1.7, respectively.  
30

The temperature of the plating solution is preferably in the range of 25—75°C.

#### Operating conditions

35 Along with acidity, the most critical operating parameters to obtaining crack-free, adherent coatings are the current density and the agitation or solution flow. The acidity and solution flow particularly affect the deposition rate and the density of the coating, but acidity does not significantly affect composition of the deposit except at very low pH where nickel and iron plating reactions decrease in efficiency. Composition is more particularly affected by the current density and the electrolyte composition.  
40

It is well understood that the least active metal will deposit in preference to a more active metal. But in the inventive method, using high current density and solution flow, the composition of the deposit can be made to more closely approximate the electrolyte composition than in prior plating methods, especially for the iron-chromium binary alloy from sulfamate solutions, even for high-chromium deposits.

45 Current densities for the inventive method are at least 75 amps/dm<sup>2</sup>, but preferably within the range of about 150—400 amps/dm<sup>2</sup>. The higher current densities favor deposition of chromium over the iron or other metals and are necessary for obtaining the high-chromium alloys from the trivalent chromium solutions.

At such high current, the chromium, iron and particularly the nickel or cobalt, would be hard to plate in dense, adherent deposits were it not for high agitation or solution flow rates in conjunction therewith. Turbulent action near the cathode, resulting from cathode motion or solution flow, creates a transport mechanism for replacing depleted electrolyte with cation-rich solution. Relative motion of at least 1 m/sec between the cathode surface and the plating solution is generally sufficient to create the turbulent conditions necessary for good deposits. Typically, velocities of 1—80 m/sec could be used, but 1—8 m/sec is preferred.  
50

55 With the agitation and other means for migration of anode products to the region of the cathode, it may be necessary to erect a barrier between an insoluble anode and the cathode to prevent the anode products from oxidizing the divalent and trivalent chromium near the cathode. Conventional porous membranes (ceramic cups) may be used around the cathode for this purpose.

#### 60 Examples of the preferred embodiments

##### Example 1—Iron-chromium alloy

##### Composition comparable to bath composition

65 According to the invention, an alloy may be deposited having a composition ratio virtually the same as the metal ratio in the electrolyte, despite the difference in reduction potentials of the chromium and iron plating reactions.

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In samples identified as 43F and 52A, an iron and chromium sulfamate electrolyte was made by dissolving the metals in an acid solution of sulfamic acid. The concentrations were 0.25 molar chromium (13 g/l Cr) and 0.75 molar iron (42 g/l Fe). The current density was 160 amps/dm<sup>2</sup> and the rod-shaped steel cathode was rotated with a 2.5 m/sec surface velocity. A lead anode was utilized and was isolated from the cathode by a porous alumina diaphragm. Temperatures were between about 37° and 49°C.

Sample 43F used a 10 minute deposition at pH 1.6 while sample 52 plated for 5 minutes at pH 1.7. In both cases the alloy composition weight ratio was substantially the same as the electrolyte, 72 Fe—28 Cr and 75 Fe—25 Cr ( $\pm 3\%$ ) respectively. Cathode efficiencies were about 26—27%.

At the end of the deposition, the lead anode showed signs of dissolving in the sulfamate bath. To avoid this in longer depositions, a platinum or graphite anode or, preferably, a soluble anode could be used.

### Example 2—pH effects

Recognition of the importance of pH occurred when plating several 47 mm-diameter rings (as cathodes) in succession in a bath containing chromium sulfate (0.9 moles), iron sulfate (0.4 moles) and sulfuric "free acid" (1.3 ml). pH was measured at 1.75. A lustrous deposit having a few matte spots was plated at 160 amps/dm<sup>2</sup> and 3 m/sec cathode surface velocity. Deposits on successive carbon-steel rings improved to almost full bright plate and then began getting more matte textured as the pH increased to about 1.8 (free acid of 0.5 ml). Sulfuric acid was added to bring the free acid to about 1.1 ml and adherent, bright plates were again deposited.

The bright plates were tested and found to be extremely adherent, corrosion resistant to nitric acid and resistant to high-temperature oxidation. Hardness was on the order of 410 (Knoop) with a 100 gram load, equivalent to Vickers DPH=360 or Rockwell C=39.

### Example 3—Preferred alloy compositions in chloride and sulfate baths

A number of coatings were applied to 12.5 mm-diameter steel rods, 25 mm long, from sulfate and mixed sulfate/chloride solutions having the following compositions:

Chemical	Added as:	Concentration (g/l)			
		1	2	3	4
Chromium	Chromium chloride	39	49	0	0
Chromium	Chromium sulfate	0	0	26	39
Iron	Ferrous sulfate	3	1	6.6	1
Nickel	Nickelous sulfate	45	11	11	5.6
Boric acid	Boric acid	35	35	23	35
Ammonia	Ammonium sulfate	14	14	8.5	13
Manganese	Manganous sulfate	0	0	2.2	3.3

A Type 304 stainless steel alloy anode was used. Operating parameters are given in Table 1. Manganese content in the alloy samples was less than 1% and is, therefore, not reported.

TABLE 1

Sample No.	Deposition conditions					Alloy composition		
	pH	C.D. (A/dm <sup>2</sup> )	Temp. (°C)	Agitation (m/sec)	Solution No.	Cr (w/o)	Ni (w/o)	Fe (w/o)
203/4—13A	0.45	160	62	2	1	53.7	1.6	44.7
—14C	1.4	310	62	2	2	26.5	1.9	71.6
—19E	1.8	160	62	2	3	21	22	57
—18D	1.5	160	62	2	3	4	41	55
—18F	1.65	220	62	2	3	16	36	48
—19L	1.8	160	65	2	3	8	48	44
—20G	1.8	160	50	2	4	31	7	62

The chromium content in the alloy deposit is dependent on several operating conditions, including current density, agitation, pH, ratio of metal ions in solution and type of anion used to complex the metal ions. Comparing samples 13A and 14C, the difference in pH is the major variable and the chromium content is higher when the pH was lower (higher acid content). This is reasonable because the coulombic (cathode) efficiency for plating both iron and nickel is known to be poor at the lower pH values.

Samples 18D and 18F were plated under similar conditions with the exception of current density. The results show that the higher current density used for sample 18F resulted in a higher chromium content.

Temperature also affects the percentage of chromium in a deposit. Comparing samples 19E and 19L, the temperature was increased from 62 to 65°C and the chromium content in the deposit was reduced from 21 to 8 percent. In general, the temperature does not appear to be quite this critical, but higher temperatures do not favor the chromium deposition.

It is evident that by making several changes in the plating parameters, for example, lower temperatures, higher pH, higher concentration of chromium and lower concentrations of both nickel and iron, the alloy deposit may be pushed to a higher chromium and a lower nickel content.

Generally, good bright and semi-bright coatings were obtained in the deposits plated between about pH 1.7 and pH 1.8 while the others were matte textured and subject to cracking in thicker deposits.

#### Example 4—Cr-Fe-Ni alloy in mixed chloride/sulfate bath

Sample 202/98—14e was plated in a conventional cell using a soluble Type 304 stainless steel anode and a solution of:

Chromium (chloride salt)	48.8 g/l
Iron (sulfate salt)	1.0 g/l
Nickel (sulfate salt)	11.2 g/l
Boric acid	35.0 g/l
Ammonium sulfate	55.0 g/l

The temperature was 62°C and the pH was 1.4.

With a cathode surface velocity of 2 m/sec and a current density of 155 amps/dm<sup>2</sup>, a 125 μm coating was applied in 30 minutes. The relatively dense coating was matte textured on the surface but otherwise generally crack free and had a composition of 16 Cr-21 Ni-63 Fe.

#### Example 5—Fe-Cr alloy coatings from chloride bath

Iron-chromium alloy coatings were deposited from an electrolyte solution of the chromium (56 g/l) and iron (52 g/l) chloride salts at about 30°C. The apparatus of Example 1 was used (with the exception of a soluble 30/70 chromium-iron anode) to plate the alloy coatings shown in Table 2. Cathode efficiency is conventionally defined as the percentage of the applied current used to deposit the chromium alloy.

TABLE 2

Sample No.	Deposition conditions				Alloy composition	
	Efficiency	pH	C.D. (A/dm <sup>2</sup> )	Agitation m/sec	Cr	Fe
97A	5	0.8	3	0	2	98
96C	22	0.6	40	2.4	6	94
96B	36	0.6	80	2.4	8	92
96D	40	0.7	160	2.4	18	82

These samples were made prior to our recognition of the importance of pH and they are within our broad range, but outside of our preferred pH range. Nevertheless, the effect of current density and agitation upon efficiency and the final alloy composition was clearly shown, wherein the chromium content and efficiency of the deposit were proportional to the current density. The importance of using high current densities and agitations can be seen by observing sample 97A wherein the efficiency and percent chromium in the deposit were both low because of low current density and low agitation. The deposit was also limited to a very thin section because of poor adherence and cracking in thicker deposits. Because the coating was thin and low in chromium it had poor corrosion resistance.

Samples 96B, 96C and 96D were marginally cracked but were otherwise suitable coatings similar to conventional hard chromium plates deposited in catalyzed chromic acid solutions. These cracks in the deposits may not be detrimental where wear resistance in the main property desired in a coating.

#### Example 6—Fe-Cr alloy deposits from sulfate baths

A 30/70 chromium-iron anode was again used in a sulfate solution to plate alloy coatings on a copper-coated, steel-ring cathode. The plating solution compositions were as follows:

	Concentration, (g/l)		
	1	2	3
Iron metal ions	28	14	21
Chromium metal ions	26	39	47

Alloy coatings were deposited at 50°C as shown in Table 3.

TABLE 3

Sample No.	Deposition conditions			Alloy composition		
	pH	C.D. (A/dm <sup>2</sup> )	Agitation (m/sec)	Solution No.	Cr (w/o)	Fe (w/o)
61F	1.5	160	2	1	20	80
62P	2.0	160	2	1	26	74
80D	1.9	230	3	2	24	76
80E	1.9	310	3	2	48	52
80F	1.8	390	3	2	42	58
67C	1.7	160	3	2	65	35
11B	1.8	160	3	3	29	71
11A	1.61	160	3	3	26	74
12A	1.745	160	3	3	32	68
12C	1.745	390	3	3	62	28

Some early results (Samples 61—80) were taken before the importance of pH was ascertained. Hence, a pH meter without extreme accuracy was used. Later, the meter was replaced by a more accurate instrument. Nevertheless, thin, matte coatings were obtained outside of the preferred pH range using the divalent/trivalent chromium electrolyte. These coatings may be made with high chromium contents by use of the high current densities and agitation.

Results were not always consistent when using the less accurate pH meter as can be seen in the Table 3, however, we attribute this to the lack of sufficient accuracy in measuring pH and in maintaining that pH throughout the bath. When using the more accurate meter and when within the preferred pH range it may be seen that good control of the process can be had. For example, in samples 12A and 12C, the pH was within the preferred range and the chromium content of the deposit was increased greatly with increasing current density, e.g. from 32 to 62% Cr with an increase in current density from 160 to 390 amps/dm<sup>2</sup>.

### Claims

1. A method for high rate electrodeposition of a chromium alloy coating on a cathode by means of electrolyzing an aqueous plating solution comprising iron ions and divalent and trivalent chromium ions at a current density of at least about 75 amps/dm<sup>2</sup> and a pH of between about 0.5 and 2.0 characterized in that the relative motion between the cathode and the aqueous plating solution at the cathode surface is of at least about 1 m/sec.

2. The electrodeposition method of claim 1, characterized in that the electrolyzing aqueous plating solution further comprises additional alloying metal ions selected from nickel and/or cobalt.

3. The electrodeposition method of claim 2 for producing a chromium alloy coating consisting essentially of 5—80 weight percent chromium, 20—95 weight percent iron and 0—50 weight percent nickel, characterized in electrolyzing an aqueous plating solution comprising of from about 20 g/l to saturation of divalent and trivalent chromium ions, from about 1—50 g/l iron ions and from about 0—50 g/l nickel ions.

4. The electrodeposition method of claims 1 or 2 characterized in electrolyzing the aqueous plating solution which further comprises complexing anions of mineral acids selected from sulfuric, sulfamic, hydrochloric, phosphoric and boric acids.

5. The electrodeposition method of claims 1 or 2 characterized in maintaining the pH of the aqueous plating solution at between about 1.7 and 1.8.

6. The electrodeposition method of claim 5 wherein the anode is insoluble further characterized in preventing the oxidation of divalent and trivalent chromium near the cathode by inhibiting the migration of oxidation agents to the cathode.

7. The electrodeposition method of claim 1 characterized in that the current density is between about 150 and 400 amps/dm<sup>2</sup>.

### Patentansprüche

1. Verfahren zur galvanischen Hochgeschwindigkeitsablagerung eines Chromlegierungsüberzuges auf einer Kathode, bei der man eine wäßrige, galvanische Lösung, die Eisenionen und zwei- und dreiwertige Chromionen enthält, mit einer Stromdichte von wenigstens etwa 75 A/dm<sup>2</sup> und einem pH-Wert zwischen etwa 0,5 und 2,0 elektrolysiert, dadurch gekennzeichnet, daß die relative Bewegung zwischen der Kathode und der wäßrigen, galvanischen Lösung an der Kathodenoberfläche wenigstens etwa 1 m/sek beträgt.
2. Galvanisches Ablagerungsverfahren nach Anspruch 1, dadurch gekennzeichnet, daß die elektrolysierte wäßrige, galvanische Lösung weiters zusätzliche Metallegierungsionen enthält, die aus Nickel und/oder Kobalt ausgewählt sind.
3. Galvanisches Ablagerungsverfahren nach Anspruch 2, zur Herstellung eines Chromlegierungsüberzuges, der im wesentlichen aus 5 bis 80 Gew.-% Chrom, 20 bis 95 Gew.% Eisen und 0 bis 50 Gew.% Nickel besteht, dadurch gekennzeichnet, daß eine wäßrige, galvanische Lösung elektrolysiert wird, die von etwa 20 g/l bis zur Sättigung zwei- und dreiwertige Chromionen, von etwa 1 bis 50 g/l Eisenionen und von etwa 0 bis 50 g/l Nickelionen enthält.
4. Galvanisches Ablagerungsverfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die wäßrige galvanische Lösung elektrolysiert wird, die weiters komplexbildende Anionen von Mineralsäuren enthält, die aus den Schwefelsäuren, der Sulfaminsäure, der Salzsäure, den Phosphorsäuren und den Borsäuren ausgewählt werden.
5. Galvanisches Ablagerungsverfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der pH-Wert der wäßrigen, galvanischen Lösung zwischen etwa 1,7 und 1,8 gehalten wird.
6. Galvanisches Ablagerungsverfahren nach Anspruch 5, bei dem die Anode unlöslich ist, weiters dadurch gekennzeichnet, daß die Oxidation des zwei- und dreiwertigen Chroms nahe der Kathode verhindert wird, indem man die Bewegung der Oxidationsmittel zur Kathode unterbindet.
7. Galvanisches Ablagerungsverfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Stromdichte zwischen etwa 150 und 400 A/dm<sup>2</sup> ist.

### Revendications

1. Procédé d'électrodéposition à haute vitesse d'un revêtement d'alliage de chrome sur une cathode par électrolyse d'une solution aqueuse de plaquage comprenant des ions fer et des ions de chrome bivalents et trivalents avec une densité de courant d'au moins 75 ampère/dm<sup>2</sup> et à un pH entre environ 0,5 et 2, caractérisé en ce que la vitesse de déplacement relative entre la cathode et la solution aqueuse de plaquage à la surface de la cathode est d'au moins 1 m/sec.
2. Le procédé d'électrodéposition de la revendication 1, caractérisé en ce que la solution aqueuse électrolytique de plaquage comprend en plus des ions de métaux d'alliages choisis parmi le nickel et/ou le cobalt.
3. Le procédé d'électrodéposition de la revendication 2 pour la production d'un revêtement d'alliage de chrome, lequel comprend essentiellement 5 à 80% en poids de chrome, 20 à 95% en poids de fer et 0 à 50% en poids de nickel, caractérisé en ce qu'on électrolyse une solution aqueuse de plaquage comprenant d'environ 20 g/l à la saturation de ions chrome bivalents et trivalents, d'environ 1 à 50 g/l d'ions fer et d'environ 0 à 50 g/l d'ions nickel.
4. Le procédé d'électrodéposition des revendications 1 ou 2, caractérisé en ce qu'on électrolyse la solution aqueuse de plaquage qui comprend de plus des anions complexants dérivés d'acides minéraux choisis parmi les acides sulfuriques, sulfamiques, chlorhydriques, phosphoriques et borique.
5. Le procédé d'électrodéposition de la revendication 1 ou 2, caractérisé en ce qu'on maintient le pH de la solution aqueuse de plaquage entre 1,7 et 1,8.
6. Le procédé d'électrodéposition de la revendication 5 où l'anode est insoluble, caractérisé de plus en ce qu'on prévient l'oxydation du chrome bivalent et trivalent au voisinage de la cathode en empêchant la migration des agents d'oxydation vers la cathode.
7. Le procédé d'électrodéposition de la revendication 1, caractérisé en ce que la densité de courant est comprise entre 150 et 400 ampère par dm<sup>2</sup>.

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