United States Patent Office 2,766,138 Patented Oct. 9, 1956

2,766,138

PROCESSES OF CHEMICAL NICKEL PLATING

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No Drawing. Application September 18, 1953, Serial No. 381,125

13 Claims. (Cl. 117—102)

The present invention relates to improved processes of chemical nickel plating of catalytic materials employing baths of the nickel cation-hypophosphite anion type, and more particularly to continuous processes of chemical nickel plating of the general character disclosed in the copending application of Paul Talmey and William J. Crehan, Serial No. 222,222, filed April 21, 1951, now Patent No. 2,658,839, granted November 10, 1953.

The chemical nickel plating of a catalytic material employing an aqueous bath of the nickel cation-hypophosphite anion type is based upon the catalytic reduction of nickel cations to metallic nickel and the corresponding oxidation of hypophosphite anions to phosphite anions with the evolution of hydrogen gas at the catalytic surface. The reactions take place when the body of catalytic material is immersed in the plating bath, and the exterior surface of the body of catalytic material is coated with nickel. The following elements are catalytic for the oxidation of hypophosphite anions and thus may be directly nickel plated: iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum. The following elements are examples of materials which may be nickel plated by virtue of the initial displacement deposition of nickel thereon, either directly or through a galvanic effect: copper, silver, gold, beryllium, germanium, aluminum, carbon, vanadium, molybdenum, tungsten, chromium, selenium, titanium and uranium. The following elements are examples of non-catalytic materials which ordinarily may not be nickel plated: bismuth, cadmium, tin, lead and zinc. The activity of the catalytic materials varies considerably; and the following elements are particularly good catalysts in the chemical nickel plating bath: iron, cobalt, nickel and palladium. The chemical nickel plating process is autocatalytic since both the original surface of the body being plated and the nickel metal that is deposited on the surface thereof are catalytic.

In the continuous nickel plating system disclosed in the Talmey and Crehan application, previously mentioned, periodic or continuous regeneration of the plating bath is effected by the corresponding additions thereto of appropriate ingredients for the purpose of maintaining substantially constant the composition of the plating bath. More specifically, in this system, there are provided a plating chamber and a reservoir; one portion of the plating solution is stored at a relatively low temperature well below the boiling point thereof (about 150° F.) in the reservoir; and another portion of the plating solution is held as a bath at a relatively high temperature slightly below the boiling point thereof (about 210° F.) in the plating chamber. The plating solution is continuously circulated at a low rate from the reservoir to the plating chamber and then back to the reservoir, the solution being heated substantially to the relatively high temperature after withdrawal thereof from the reservoir and before introduction thereof into the plating chamber, and the solution being cooled substantially to the relatively low temperature after withdrawal thereof from the plating chamber and before return thereof to the reservoir. The

body that is to be nickel plated is immersed in the bath in the plating chamber, and is subsequently withdrawn from the bath in the plating chamber after a time interval corresponding to the thickness of the nickel plating on the surface thereof that is desired; and during the time interval mentioned soluble reagents are added to the plating solution in the reservoir to maintain in the bath in the plating chamber during the time interval substantially the predetermined composition of the bath previously-mentioned, so as to compensate for the ingredients of the bath that are exhausted during the time interval mentioned in the plating chamber. This regeneration of the plating solution in the reservoir consists essentially of adding thereto appropriate amounts of soluble nickel-containing and hypophosphite-containing reagents, as well as an alkali for pH control.

In the continuous plating system, plating baths of the character disclosed in the copending application of Gregoire Gutzeit, Paul Talmey and Warren G. Lee, Serial No. 376,968, filed August 27, 1953, are expressly recommended, since they exhibit an exceedingly fast plating rate, and have an exceedingly long life because they accommodate the build-up of phosphite anions therein to a concentration in excess of one molar, without the precipitation of nickel phosphite and mixed basic salts. These baths consist essentially of an aqueous solution of a nickel salt and a hypophosphite and a nickel complexing agent and a separate and different plating-rate exalting additive. The nickel complexing agent is selected from the group consisting of ammonia, amines, acid amines, aminocarbonyls, amine-oxides and polyalcohols, as well as saturated aliphatic hydroxycarboxylic acids, aliphatic aminocarboxylic acids and aliphatic keto acids, and the salts of these compounds. The plating-rate exalting additive is selected from the group consisting of simple short chain saturated aliphatic dicarboxylic acids and aliphatic aminocarboxylic acids, and the salts of these compounds. In passing, it is noted that certain of the nickel complexing agents (ammonia and amines) form molecular complexes with the nickel cations, while the remainder of the nickel complexing agents (hydroxycarboxylic acids, aminocarboxylic acids, etc.) form inner complexes or chelates with the nickel cations.

In the formation of aqueous plating baths of this type, the soluble nickel salt may take a variety of forms, such, for example, as nickel chloride, nickel sulfate, nickel acetate, etc., or mixtures thereof; and the soluble hypophosphite may take a variety of forms, such, for example, as hypophosphorous acid, sodium hypophosphite, potassium hypophosphite, calcium hypophosphite, etc., or mixtures thereof. In the plating bath the absolute concentration of hypophosphite anions is is in the approximate range 0.15 to 1.20 mole/liter, and the ratio between nickel cations and hypophosphite anions is in the approximate range 0.25 to 1.60.

A typical malic acid-succinate plating bath of this type further comprises an absolute concentration of malic acid anions sufficient to complex at least 100% of the nickel cations, an absolute concentration of succinic acid anions of at least 0.04 mole/liter; and a pH within the approximate range 4.5 to 7.0.

A typical malic acid-glycine plating bath of this type further comprises an absolute concentration of malic acid anions sufficient to complex at least 100% of the nickel cations; an absolute concentration of glycine anions of at least 0.04 mole/liter; and a pH within the approximate range 4.5 to 9.5.

Also for the purpose of increasing the stability of a plating bath of the character of that of Gutzeit, Talmey and Lee, it is highly advantageous to add thereto a stabilizing ion, as disclosed in the copending application of

Paul Talmey and Gregoire Gutzeit, Serial No. 358,428, filed June 3, 1953. For example, Pb^{++}, Te^{++}, etc. stabilizing cations are added to the plating bath in small amounts of about 2 p. p. m. (parts per million) by weight. The addition of the stabilizing ions to the plating bath inhibits random decomposition thereof and the consequent formation of "black precipitate" therein. The formation of the black precipitate results from a decomposition of the plating bath, and is otherwise particularly objectionable in that it causes the nickel deposit on the body that is being plated to be coarse, rough and frequently porous.

In the carrying out of the continuous nickel plating process of the character of that of Talmey and Crehan, employing a plating bath of the character of that of Gutzeit, Talmey and Lee, the regeneration of the relatively cool portion of the aqueous plating solution in the reservoir may be effected either periodically or continuously during the time interval that the body of catalytic material is being plated in the hot portion of the plating solution in the plating chamber, as previously noted; whereby the additions of the nickel salt (such as nickel chloride, nickel sulfate, nickel acetate, etc.) bring about the introduction of the corresponding foreign anions into the aqueous solution, with the consequent build-up thereof through the successive cycles of regeneration to a point where the concentration of the foreign anions in the aqueous solution is excessive. More particularly, the concentration of the foreign anions in the aqueous plating solution is excessive in the sense that the plating rate of the bath in the plating chamber is slowed-down considerably; and moreover, these foreign anions, in excessive concentration, serve as crystal nuclei for the precipitation of nickel salts, resulting in plating bath instability.

Specifically, by way of illustration, it has been discovered that the plating rate of a plating bath of the character of that of Gutzeit, Talmey and Lee decreases linearly with the concentration of NaCl therein resulting from the employment of nickel chloride in the regeneration thereof. More particularly, the rate of decrease of the plating rate of the plating bath with the increase in the concentration of NaCl is:

(0.000053 gms./min./cm.^{2})/(moles NaCl/liter)

In other words, if the sodium chloride concentration is raised from zero to 6.0 moles/liter in the plating bath, the plating rate becomes less than half of its original value.

Moreover, another phenomenon has been discovered in this connection that is sometimes undesirable; i. e., the hardness of the nickel deposit upon the body of catalytic material increases with the chloride concentration in the plating bath.

Accordingly, it is a general object of the present invention to provide an improved process of chemical nickel plating of bodies formed of catalytic material, employing a continuous chemical nickel plating operation involving plating bath regeneration, wherein the build-up of foreign anions as a consequence of the introduction of the soluble nickel salt into the plating bath is not excessive as the regeneration of the plating bath proceeds.

Another object of the invention is to provide an improved process of chemical nickel plating of the characted noted; wherein the plating bath regeneration is at least partially effected by the utilization of nickel hypophosphite, whereby there is no foreign anion of this soluble nickel salt introduced into the plating bath.

A further object of the invention is to provide an improved nickel plating process of the character described, wherein the plating bath regeneration proceeds without the build-up therein of foreign anions, such as the chloride, the sulfate, the acetate, etc.

These and other objects and advantages of the invention pertain to the particular arrangement of the steps of the process, as will be understood from the foregoing and following description.

In accordance with the process of the present invention, the article or body to be nickel plated, and normally having a catalytic surface, is properly prepared by mechanically cleaning, degreasing and light pickling substantially in accordance with standard practices in electroplating processes. For example, in the nickel plating of a steel object, it is customary mechanically to clean the rust and mill scale from the object, to degrease the object, and then lightly to pickle the object in a suitable acid, such as hydrochloric acid. The article is then immersed in the plating bath provided in the plating chamber of the continuous system, previously described; whereupon almost immediately hydrogen bubbles are formed on the catalytic surface of the steel object and escape in a steady stream from the plating bath, while the surface of the steel object is slowly coated with metallic nickel (containing some phosphorus). The reactions are continued until the required thickness of the nickel coating has been deposited upon the surface of the steel object; whereupon the steel object is removed from the plating bath in the plating chamber of the continuous system, and is rinsed off with water so that it is ready for use.

In the formation of the plating solution of the character of that of Gutzeit, Talmey and Lee that is employed in the continuous plating system of the character of that of Talmey and Crehan, and in accordance with the present invention, the soluble nickel salt that is employed is selected from the group consisting of nickel chloride, nickel sulfate, nickel acetate and nickel hypophosphite; and the other hypophosphite that is employed is selected from the group consisting of hypophosphorous acid, sodium hypophosphite, potassium hypophosphite and calcium hypophosphite; the organic additives and appropriate stabilizing cations are then introduced into the aqueous plating bath; and the pH thereof is appropriately adjusted employing NaOH and HCl. Thereafter and during the time interval that the body is being nickel plated the plating bath is regenerated, as previously described, employing nickel hypophosphite, another hypophosphite (ordinarily an alkaline hypophosphite, such as sodium hypophosphite) and a weak alkali, such as, sodium bicarbonate or a dilute aqueous solution of caustic soda for pH control. In the regeneration of the plating solution, the depletion of the nickel cations is compensated for by the addition of the nickel hypophosphite, and the depletion of the hypophosphite is compensated for by the additions of the nickel hypophosphite and the other hypophosphite; it being necessary to add both the nickel hypophosphite and the other hypophosphite to the plating solution to maintain the desired ratio between the nickel cations and the hypophosphite anions in the approximate range 0.25 to 1.60, as previously noted. The addition of the alkali to the plating solution in the regeneration thereof is necessary since the pH of the plating solution is automatically reduced as the reactions therein proceed, whereby the addition of the alkali mentioned maintains the pH of the plating solution in the approximate range 4.5 to 9.5, as previously mentioned.

In accordance with the present process, the initial concentration of sodium chloride present in the aqueous plating solution, when nickel chloride is employed in the initial formation thereof, is not excessive; and the concentration of sodium chloride therein is not built-up as a consequence of the regeneration thereof by virtue of the utilization of nickel hypophosphite, thereby avoiding the build-up of the foreign chloride anion, as previously explained.

In order to demonstrate the present process, a first continuous plating test was performed in the continuous plating system described, employing properly cleaned cold rolled steel samples and a plating bath of the character described, and having the particular composition indicated below:

Plating bath No. 1

Nickel chloride	m. p. l.	0.0675
Sodium hypophosphite	m. p. l.	0.225
Sodium succinate	m. p. l.	0.06
Malic acid	m. p. l.	0.135
Pb^{++} as stabilizing ion	p. p. m.	3.0
Ratio: Ni^{++}/hypo$^-$		3.0
Initial pH adjusted with NaOH		5.57

In this first continuous plating test, it was assumed that the hypophosphite utilization was 0.3 for purposes of plating bath regeneration; and in this connection hypophosphite utilization may be defined as the ratio between the number of moles of nickel deposited in the plating operation and the number of moles of hypophosphite consumed in the plating operation. In other words, in this continuous system in order to plate 3 moles of nickel upon the steel bodies approximately 10 moles of hypophosphite are oxidized to phosphite; which, of course, indicates that in the regeneration of the plating bath, it is necessary to add thereto somewhat in excess of three times as many moles of hypophosphite as moles of nickel. This first continuous plating test was conducted through 11 cycles, the temperature of the plating bath in the plating chamber being approximately 100° C., with plating bath regeneration at the conclusion of each cycle (employing nickel hypophosphite and sodium hypophosphite to supply the required nickel cations and hypophosphite anions and to maintain the desired ratio therebetween, and employing caustic soda to maintain the pH within the desired range).

The results of this first continuous plating test were as follows:

Cycle No.	1	2	3	4	5	6	7	8	9	10	11
Initial pH	5.57	5.52	5.60	5.60	5.55	5.52	5.52	5.50	5.52	5.51	5.51
Final pH	4.92	5.20	5.22	5.28	5.24	5.33	5.32	5.35	5.41	5.40	5.37
Time of plating (min.)	112	116	106	100	122	106	104	101	111	108	111
Sample area, cm.^{2}	97	97	97	97	97	81.5	81.5	81.5	81.5	81.5	98.5
Wt. gain, gms.	5.01	5.38	4.91	4.92	5.74	4.57	4.43	4.24	4.63	4.55	5.77
Rate, RX10^4	4.62	4.78	4.86	5.08	4.85	5.29	5.20	5.15	5.12	5.16	5.27
Soln. flow rate, cc./min.	51	49	50	57	47	54	55	50	51	53	51

A second continuous plating test was performed in the continuous plating system described, employing properly cleaned cold rolled steel samples and a plating bath of the character described and having the particular composition indicated below:

Plating bath No. 2

Nickel chloride	m. p. l.	0.0675
Sodium hypophosphite	m. p. l.	0.225
Aminoacetic acid	m. p. l.	0.0675
Malic acid	m. p. l.	0.2025
Pb^{++} as stabilizing ion	p. m. m.	3.0
Ratio: Ni^{++}/hypo$^-$		0.3
Initial pH adjusted with NaOH		6.52

In this second continuous plating test, it was assumed that the hypophosphite utilization was 0.3 for purposes of plating bath regeneration, as previously explained. This second continuous plating test was conducted through 11 cycles, the temperature of the plating bath in the plating chamber being approximately 100° C., with plating bath regeneration at the conclusion of each cycle (employing nickel hypophosphite and sodium hypophosphite to supply the required nickel cations and hypophosphite anions and to maintain the desired ratio therebetween, and employing caustic soda to maintain the pH within the desired range).

The results of this second continuous plating test were as follows:

Cycle No.	1	2	3	4	5	6	7	8	9	10	11
Initial pH	6.52	6.51	6.53	6.51	6.49	6.50	6.51	6.50	6.48	6.48	6.48
Final pH	5.51	5.87	5.82	5.95	5.95	6.09	6.28	6.28	6.29	6.20	6.30
Time of plating (min.)	120	106	120	118	97	127	119	125	135	136	111
Sample area, cm.^{2}	97	97	97	97	97	81.5	81.5	81.5	81.5	81.5	98.5
Wt. gain, gms.	5.71	6.00	6.96	6.65	5.34	6.01	5.72	6.02	6.18	6.37	6.60
Rate, RX10^4	4.92	5.33	5.98	5.82	5.68	5.81	5.90	5.91	5.62	5.80	6.04
Soln. flow rate, cc./min.	48	54	48	48	59	45	48	49	42	42	51

A third continuous plating test was performed in the continuous plating system described, employing properly cleaned cold rolled steel samples and a plating bath of the character described and having the particular composition indicated below:

Plating bath No. 3

Nickel hypophosphite	m. p. l.	0.0675
Sodium hypophosphite	m. p. l.	0.09
Aminoacetic acid	m. p. l.	0.0675
Malic acid	m. p. l.	0.135
Pb^{++} as stabilizing ion	p. p. m.	3.0
Ratio: Ni^{++}/hypo$^-$		0.3
Initial pH adjusted with NaOH		6.5

In this third continuous plating test, it was assumed that the hypophosphite utilization was 0.33 for purposes of plating bath regeneration, as previously explained. This third continuous plating test was conducted through 8 cycles, the temperature of the plating bath in the plating chamber being approximately 100° C., with plating bath regeneration at the conclusion of each cycle (employing nickel hypophosphite and sodium hypophosphite to supply the required nickel cations and hypophosphite anions and to maintain the desired ratio therebetween, and employing caustic soda to maintain the pH within the desired range).

The results of this third continuous plating test were as follows:

Cycle No.	1	2	3	4	5	6	7	8
Initial pH	6.51	6.61	6.58	6.60	6.48	6.51	6.50	6.55
Final pH	5.68	5.82	6.09	6.00	6.01	6.06	6.12	6.22
Time of plating (min.)	99	102	100	103	101	106	120	107
Sample area, cm.^{2}	97	97	97	97	97	97	97	98.7
Wt. gain, gms.	4.67	5.26	5.17	5.29	5.27	5.34	6.24	5.73
Rate, RX10^4	4.88	5.33	5.33	5.29	5.39	5.20	5.36	5.42
Soln. flow rate, cc./min.	58	56	57	55	57	54	47	53
Turnover, m. p. l. Ni^{++}	0.0151	0.0292	0.0444	0.0585	0.0726	0.0868	0.1035	0.1187

In the foregoing continuous plating tests, the nickel deposits upon the cold rolled steel samples were homogeneous, smooth and bright; the plating rates indicated correspond to rates in excess of 1.5 mils (0.0015") per hour; and the plating baths were totally devoid of turbidity or black precipitate. Accordingly, these plating

tests clearly demonstrate the highly satisfactory commercial character of the present process.

In the foregoing continuous plating tests, it will be observed that in the formation of plating baths Nos. 1 and 2, the nickel salt employed was nickel chloride; whereas in the formation of plating bath No. 3, the nickel salt employed was nickel hypophosphite. On the other hand, in the regeneration of the plating baths between cycles in each of the continuous plating tests, the nickel salt employed was nickel hypophosphite. Accordingly, it becomes substantially immaterial whether the plating bath is initially formed utilizing as the nickel salt, nickel chloride, nickel sulfate, nickel acetate or nickel hypophosphite, since the introduction of the foreign anions thereinto are not excessive, as long as the regeneration of the plating bath between cycles is carried out employing nickel hypophosphite.

In the foregoing discussion and tests the plating rate may be defined: R=weight gain in the nickel plating in gram/cm.^{2}/minute of the plated surface of the test sample, or expressed simply: R=gm./cm.^{2}/min.

In view of the foregoing, it is apparent that there has been provided an improved process of chemical nickel plating of catalytic bodies that is particularly well-suited to the production of commercial coatings, since the process is continuous, and the plating bath exhibits an exceedingly fast plating rate and has an exceedingly long life.

While there has been described what is at present considered to be the preferred embodiment of the invention, it will be understood that various modifications may be made therein, and it is intended to cover in the appended claims all such modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. The process of chemically plating with nickel a catalytic article essentially comprising an element selected from the group consisting of copper, silver, gold, aluminum, iron, cobalt, nickel, palladium and platinum; which process comprises contacting said article throughout a time interval with an aqueous bath comprising nickel ions and hypophosphite ions, and regenerating said bath only with nickel hypophosphite and another soluble hypophosphite and a soluble alkali, said other hypophosphite being selected from the group consisting of hypophosphorous acid and alkaline hypophosphites, thereby to minimize the introduction of extraneous ions into said bath and the consequent build-up of undesirable salts therein incident to the regeneration thereof.

2. The process of chemically plating with nickel a catalytic article essentially comprising an element selected from the group consisting of copper, silver, gold, aluminum, iron, cobalt, nickel, palladium and platinum; which process comprises contacting said article throughout a time interval with an aqueous bath comprising a nickel ion content in a first given range and a hypophosphite ion content in a second given range and a pH in a third given range, and regenerating said bath only with nickel hypophosphite and another soluble hypophosphite and a soluble alkali in order to maintain the ion content of said bath within said first given range and to maintain the hypophosphite ion content of said bath within said second given range and to maintain the pH of said bath within said third given range, said other hypophosphite being selected from the group consisting of hypophosphorous acid and alkaline hypophosphites, thereby to minimize the introduction of extraneous ions into said bath and the consequent build-up of undesirable salts therein incident to the regeneration thereof.

3. The process set forth in claim 2, wherein said first given range of nickel ion corresponds to a ratio between nickel ion and hypophosphite ion of about 0.25 to 1.60, said second given range of hypophosphite ion is about 0.15 to 1.20 moles/liter, and said third given range of pH is about 4.5 to 9.5.

4. The process of chemically plating with nickel a catalytic article essentially comprising an element selected from the group consisting of copper, silver, gold, aluminum, iron, cobalt, nickel, palladium and platinum; which process comprises contacting said article throughout a time interval with a bath comprising an aqueous solution of nickel hypophosphite and another soluble hypophosphite, and regenerating said bath only with nickel hypophosphite and said other hypophosphite and a soluble alkali, said other hypophosphite being selected from the group consisting of hypophosphorous acid and alkaline hypophosphites, thereby to minimize the introduction of extraneous ions into said bath and the consequent build-up of undesirable salts therein incident to regeneration thereof.

5. The process of chemically plating with nickel a catalytic article essentially comprising an element selected from the group consisting of copper, silver, gold, aluminum, iron, cobalt, nickel, palladium and platinum; which process comprises contacting said article throughout a time interval with a bath comprising an aqueous solution of nickel acetate and a hypophosphite, and regenerating said bath only with nickel hypophosphite and another soluble hypophosphite and a soluble alkali, said other hypophosphite being selected from the group consisting of hypophosphorous acid and alkaline hypophosphites, thereby to minimize the introduction of extraneous ions into said bath and the consequent build-up of undesirable salts therein incident to the regeneration thereof.

6. The process set forth in claim 1, wherein said bath further comprises a soluble agent selected from the group consisting of saturated aliphatic hydroxycarboxylic acids and salts thereof, and a soluble additive selected from the group consisting of simple short chain saturated aliphatic dicarboxylic acids and salts thereof.

7. The process set forth in claim 1, wherein said bath further comprises a soluble agent selected from the group consisting of saturated aliphatic hydroxycarboxylic acids and salts thereof, and a soluble additive selected from the group consisting of aliphatic aminocarboxylic acids and salts thereof.

8. The process set forth in claim 1, wherein said bath is circulated from a plating chamber to an exterior reservoir and back to said plating chamber, said article is immersed in said bath in said plating chamber, and said bath is regenerated in said exterior reservoir.

9. The process set forth in claim 8, wherein said bath in said plating chamber is maintained at a plating temperature disposed below the boiling point thereof but well above the ambient temperature, and said bath in said exterior reservoir is maintained at a storage temperature disposed well below said plating temperature.

10. The process set forth in claim 1, wherein said regeneration of said bath in said exterior reservoir is substantially continuous during said time interval.

11. The process set forth in claim 1, wherein said regeneration of said bath in said exterior reservoir is substantially periodic during said time interval.

12. The process set forth in claim 1, wherein the ratio between the molar addition of nickel ion and the molar addition of hypophosphite ion in the regeneration of said bath is about 3 to 10.

13. The process of chemically plating with nickel a catalytic article essentially comprising an element selected from the group consisting of copper, silver, gold, aluminum, iron, cobalt, nickel, palladium and platinum; which process comprises contacting said article throughout a time interval with an aqueous bath comprising an initial nickel ion content of a concentration of less than about 10 grams per liter and an intial hypophosphite ion content of a concentration of less than about 25 grams per liter and having an initial pH within the range from about 5.8 to 7.2, and regenerating said bath only with nickel hypophosphite and another soluble hypophosphite and a soluble alkali in order to maintain substantially said

initial nickel ion content thereof and to maintain substantially said initial hypophosphite ion content thereof and to maintain substantially said initial pH thereof, said other hypophosphite being selected from the group consisting of hypophosphorous acid and alkaline hypophosphites, thereby to minimize the introduction of extraneous ions into said bath and the consequent build-up of undesirable salts therein incident to the regeneration thereof.

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