PLATING: Live Long & Prosper

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Prognostications about the demise of plating have been rampant since the seventies. Beginning with a replay of a scene that likely was duplicated throughout many job and captive shops in subsequent years, this article illustrates why the accounts of the death of plating have been greatly exaggerated. Bolstered by outstanding cleanup efforts within the industry as a result of governmental regulations, new technologies in processes and equipment, and its absolutely unbeatable properties for many applications, plating is now expected to live long and prosper.

1976—When the newly hired manager of plating operations of a large electrical connector manufacturing firm met his company's Director of Engineering and the Manager of the Material Research and Development Laboratory for the first time, the two cordially welcomed the new employee aboard, then nonchalantly advised him that, in less than two or three years, materials and manufacturing techniques currently under development would all but obviate the need for electroplating. Imagine his shock.

Ten years later, however, the size of the plating department had doubled and was processing four times as many plated parts. This leads to the question, "How could two such eminent and knowledgeable company officials have been so wrong?" The logical explanation is that they, as did many of their peers, considered plating processes too costly, too unreliable, too unhealthy and too polluting.

Confident that there had to be a better way or ways, companies and government funding agencies instituted numerous R&D programs to discover new materials that did not require an electroplated coating. Alternative coating techniques which were, in their opinion, less obnoxious than electroplating, were also investigated. Because very few of these programs bore fruit, the researchers ultimately concluded that when it comes to providing a plated component with three, two or even just one important capability or function, electroplated deposits are irreplaceable.

While those attempts to eliminate plating were under way, efforts were being made by the plating industry to reduce plating costs, improve solutions and procedures, and increase product quality. At the same time, problems relating to safety, employee health and environmental pollution were being resolved, motivated to some degree by the mandates of local and national governments.

These efforts by the plating industry* were eminently successful, and the result was that electroplating (or electrochemical deposition—ECD) came to be recognized as a critically important industrial science. Furthermore, electroplating in most of the leading countries of the world is no longer considered a dangerous, unhealthy and polluting enterprise, and the plating industry is acknowledged as a respectable sector of commerce. We believe there is a promising future for the plating industry during the 21st century.

A Look Forward

In an article, "Future Trends in Electroplating for the Electronics Industry," J.R. Christie[4] perfectly stated the feelings of an author who's trying to predict the future: "It is thus with considerable trepidation that this attempt is made to predict where the industry is going."

We, on the other hand, as the authors of this thesis, are going to prognosticate without trepidation, even though we recognize that considerably more scientific understanding of electroplating processes is required. This is especially so in relation to the predictable need for increased productivity and the expanded functional requirements of various ECDs. Nor are we unaware that many plating operations in some captive and jobshops have yet to graduate from craft to science and that many plating installations throughout the world are without waste treatment and fume abatement capabilities. Nevertheless, the incredible inventions, improvements and developments we have witnessed during our plating careers enable us to confidently predict that the plating industry faces an incredibly bright new century.

There has never been a time in history when the inventions, developments and capabilities of electroplaters actually led the way in the industrial scheme of things. Nevertheless, it is electroplaters who make that way possible. When designers and product engineers need a deposit of a certain thickness and

Authors' definition of the plating industry—The plating industry encompasses plating companies or jobshops; manufacturing companies with plating facilities; plating chemical and equipment manufacturers; suppliers and distributors; and all persons directly or indirectly associated with plating activities.

Famous Last Words—1976

"Hello, Bob. The president and I wanted to welcome you as our new manager of plating operations. Oh, by the way, we expect the plating department to be phased out within the next two to three years. Keep up the good work. See you around."

quality on a part or at some precise area of that part, someone in the plating industry develops the way to do it, even if it means inventing new equipment, procedures and solutions.

The destiny of the electroplating industry during the 21st century will be decided by the same factors that promoted its dynamic growth in the 1900s, particularly during the last 50 years. The need for plated deposits because of their corrosion resistance, wear resistance, physical properties, solderability, lubricity, ability to replicate substrates, etc., is certainly going to be at least as pronounced during the 21st century, and probably more so. In addition, many products can only be manufactured by electrochemical deposition processes. Furthermore, electrodeposited coatings are what make many products affordable. The impact on ECD: We should never forget that one liter of vacuum (with all accessories) is always more expensive than one liter of electrolyte.

To provide evidence that the plating industry will remain very much alive and well during the next century, there follows a discussion of some specific products and processes that could or should promote an even stronger dependence on electroplating in the coming years.

Alternative Coating Methods

Considering our opening scenario, the threat implied to the recently hired plating manager by the two company officials in 1976 was that new materials and alternative processes would in a few years do away with his department and his job. Physical vapor deposition (PVD) processes, vacuum evaporation, ion plating and sputter deposition were undoubtedly some of the processes they had in mind because of the claims and inferences being made in numerous published papers and advertisements at that time. As recently as 1995, it was suggested that certain hazardous electrochemical deposition processes (hexavalent chromium and cadmium come immediately to mind) could be replaced by PVD.

PVD processes have most certainly established an important niche in the metal finishing world, because PVD is a good method for producing decorative—and even functional—coatings on a wide variety of parts. Because it is a purely physical process, however, there are too many shortcomings to the technique (such as line of sight trajectories, little or no film property control, low deposition rates, excessive substrate heating, nonuniform distribution, and, relative to plating, high process costs and low production rates).[6] For these reasons, PVD will continue to have an insignificant impact on ECD.

Mechanical Plating

Another "potentially pollution reducing" coating technique—mechanical plating—was introduced about 1950. It is a viable alternative to ECD, and an especially good one when hydrogen embrittlement is of particular concern. The drawbacks to this process include the limits on size, weight, process specifications and shape of the pieces to be coated and the inability to coat recesses, IDs, sharp corners and projections. As with PVD, mechanical plating has had relatively little impact on ECD during

Great Strides in the Electronics Industry—Less is More

Over the years, the plating industry has met many challenges—particularly in electronics applications. Electroplated coatings on electronic components perform critically important tasks. Because very large numbers of many of these components are plated with precious metals (gold, palladium, rhodium and platinum), it is important that the amount of precious metal be minimized, per part and per plated lot. To accomplish this, highly specialized selective plating equipment and plating techniques were developed, along with "tailored" plating solutions (conventional plating solutions with the metal content and/or other variables altered to improve throw, deposition rate and uniformity). Platers also began utilizing statistical process controls to ensure optimum quality and productivity while consuming the least amount of precious metal possible.

These conservation efforts produced remarkable results. In 1960 *250,000* troy oz of gold were used to plate electronic parts. By 1969, the number had soared to almost eight times as much (*1,961,000 troy oz*). By 1979, only *1,276,000* troy oz were used (*a reduction of 685,000 oz*) although the total number of parts gold plated had doubled. The savings in 1979, when the average price for gold was $300/ troy oz, was $205 million.[3]

the past few decades, and that will certainly not change after the year 2000.

Alloys

Electrodepositing brass and copper-tin bronze has been done for nearly 150 years, but it was not until the mid-1900s that the alloys began to be valued for what they could do—not because of their appearance. Brass-plated wire, for example, is used to produce metal-organic adhesion in tires and in metal-resin laminates. Non-allergenic, copper-tin rich "speculum" alloys provide corrosion and wear resistance on a wide range of items.

In the latter half of the 20th century, a number of electrodeposited alloys (some new, some old) began to be used extensively because of their improved chemical and physical capabilities. Examples are gold-iron, gold-nickel and gold-cobalt for better wear and corrosion resistance on electrical contacts; zinc-nickel alloys on steel for better corrosion than provided by electrogalvanizing, cadmium or zinc; tin-bismuth for its electromagnetic compatibility on computer frames; palladium-nickel (with gold flash), which performs like gold at much less cost; and nickel-tungsten as chromium replacement.

Many specifications require certain properties of deposits that are often obtained only by the incorporation of metallic or, on occasion, nonmetallic elements. By electroplating, true solid solutions between metals, and metals and nonmetals, can be produced as well as stable or metastable, crystalline or X-ray amorphous intermetallic compounds. Examples of a solid solution and a compound are the Cr-H and the Pd-H systems. In both cases, with properly arranged deposition conditions, X-ray amorphous and truly crystalline h.c.p. CrH and beta Pd-H can be produced. Every hard chromium deposit contains h.c.p. CrH, which is partly responsible for its hardness. On the other hand, it is not only hardness that determines the practical properties, but also internal stress and tensile strength. Compressive deposits reduce the tendency of stress cracking, not only for chromium but also for low-karat gold alloys. The tendency for the stress corrosion of brass and highly alloyed gold-plated jewelry can be greatly reduced by layers of gold with compressive stresses.

With regard to the properties of alloys, water, which is often the main constituent of electroplating, is considered a disadvantage. Few people comprehend that water is a very active constituent in nearly every deposit. Incorporated hydrogen, for example, is essential for the hardness and wearing capability of hard chromium, nickel and gold deposits. Very little is known about the effects of hydrogen and other nonmetallic impurities on deposits, even though the electroplating process seems to be a type of "poor man's ion implantation." This is an area ripe for investigation during the coming years.

The magnetic storage properties of electrodeposited alloys give them a characteristic of special interest. About 10 years ago, coauthor Raub began working with Professor Pietro Cavallotti at Politecnico de Milano. They focused on the magnetic storage properties of electrodeposits and found a most promising system—platinum-cobalt. At the same time, Cavallotti electrolytically synthesized a permanent magnetic layer, a Co-rich platinum-cobalt alloy, which still has the highest known BH of any deposit. The values of the electrodeposited alloy are higher than those produced metallurgically. With the exception of nickel-iron deposits, the magnetic properties of electrodeposits are a much neglected field. This should be researched in the coming years, because it is rather easy to vary the magnetic properties by changing deposition parameters.

Patent number 5,389,226, "Electrodeposition of Nickel-Tungsten Amorphous and Microcrystalline Coatings," D. Scruggs et al, was issued February 14, 1995. This alloy, deposited from a specially formulated alkaline solution, is about 65 percent nickel and 35 percent tungsten, plus a small amount of boron. What makes the deposit unique is that it is about 85 percent amorphous and 15 percent nanocrystalline. As a result of its chemistry and amorphous or "glass-like" nature, the coating has remarkable wear and corrosion-resistant properties. Numerous studies conducted at various companies in the United States, Japan and Germany have shown that its chemical and physical attributes exceed those of chromium in almost every respect.[6] Because of the demonstrated superiority of this (primarily) amorphous electrodeposit, it is hypothesized that further efforts to produce (primarily) amorphous deposits of other metals and alloys will be made in the future.

For the past 20 or 25 years, few plating journals have been published without at least one article describing the properties of some newly developed electrodeposited binary, tertiary and even quaternary alloy. Almost without exception, the alloys are reported to have performance characteristics better than single-metal deposits, and a number of the alloys are plated from solutions that are nontoxic, noncorrosive and, in a relative sense, nonpolluting. The thing that will help move these solutions and additional alloy plating processes yet to be discovered from laboratories into plating tanks during the next quarter-century will be the introduc-

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tion of relatively inexpensive, foolproof and fully automated on-line analytical and control equipment. The chemistry of most alloy plating solutions must be maintained within very close limits if the alloy deposited is to be of the desired composition and have the required properties.

With or without this equipment, however, platers can anticipate filling more and more of their tanks with alloy plating solutions during the 21st century.

Multilayers

Another area where further studies should result in economic and technical advances is multiple or sandwiched layers of electrodeposits. Contemporary examples are 24K gold over 23K to improve solderability and reduce contact resistance; a gold flash over palladium to provide good electrical properties at greatly reduced costs; microcracked chromium in combination with a normal chromium deposit to improve corrosion resistance; and bright nickel combinations to improve properties such as catalytic action, wear or corrosion resistance.

Another species of unique multilayer electroplated materials that show considerable promise for numerous applications, and which will no doubt become more commonly used in the coming years are those with dispersion layers. Various kinds of materials (including plastics, capsules filled with organic liquids, refractory compounds, metallic and ceramic superconductors and magnetic particles) are embedded in an electrochemically deposited matrix. The type, size and distribution of these materials determine the properties of the multilayer sandwich. Modern aluminum-based combustion engines mostly run on dispersions of silicon-carbide in nickel and/or on pistons partically plated with hard iron deposits.

The dispersion of a third metal or material in ECD layers provides the coating with three-dimensional characteristics. Through the appropriate distribution of lead particles in copper, it has been shown that the superconducting transition temperature of the composite can vary between less than 1 K and that of lead, about 7 K. By electrolytically depositing a supersaturated, and, in the as-deposited state, a paramagnetic solid solution of cobalt in gold, then heat-treating it, the cobalt separates from the gold. Depending on the heat treatment and the cobalt concentration, a three-dimensional distribution of cobalt particles in gold, varying from very small to large, can be prepared, showing a wide range of magnetic properties.

The disintegration of electrolytically prepared supersaturated copper-lead solid solutions by heat treatment is currently being studied in the Technische Hochschule Freiberg, Saxonia, by modern X-ray methods. This is something not previously investigated, despite the fact that such layers are widely used for sliding bearings. Only in recent years have scientists began to investigate the influence of the base material's crystallography and roughness on the beginning, or nucleation, of the metal being deposited.

Because the trend toward thinner coatings will no doubt continue into the coming decades, the continuation of the studies of incorporated substances is important. It will also be especially necessary to examine the growth of ECD and PVD layers. P. Klimanek and his collaborators at Freiberg used X-ray methods to study thin copper layers deposited on various base materials at different deposition conditions, discovering the great similarities between ECD and PVD layers. Such work will be not only important for the future monolayers, but even more so for layers up to a few microns thick.

Furthermore, considerably more information must be acquired about the influence of the base material's surface structure and morphology—whether it is metal, plastics or ceramics—on the behavior of the coated item. The concept that the lowest or cheapest class of material can be used as the base material because its defects will be covered will unquestionably be invalidated once this information is made public. Generalizing, we believe the existing knowledge about incorporated substances is limited, however, ongoing basic investigations of layered electroplated deposits will result in many new and extended applications.

Electroplated Deposits

The trend has been to avoid solutions that threaten employee health and safety and poison the environment.

A Look Back—Milestones in Plating As Noted by Donaldson & Raub

- 1906—Phosphate conversion coatings were revealed in J.W. Coslett's British patent.
- 1909—The AES got its start as the National Electro-Platers Association (NEPA).
- 1920—Horizontal barrels of hardwood, hard rubber or bakelite began to be used.
- 1923—First AES Research Committee was appointed.
- 1920s—Dr. William Blum wrote papers describing the different structures and properties of electrodeposited metals that could be achieved by electrodepositing a given metal in a variety of ways. [1]
- 1930s—The mechanical properties of plated coatings became important when they began to be used industrially (for example, on sliding bearings for combustion engines).
- 1924—C.G. Fink and C.H. Eldridge were awarded a patent for the first successful chromium plating solution.
- 1930—P.A. Jacquet formulated the first theory of the electro-polishing phenomenon.
- 1930s—The first oblique barrel automatic line went into production during the same year practical processes for bright nickel plating emerged.
- 1940s—High-speed electroplating was introduced on a commercial scale in the steel industry.
- 1946—Dr. Abner Brenner and Grace Riddell discovered electroless plating.
- 1950—The first chromate treatment for aluminum was instituted.
- 1958—Chrome trim was in its heyday on automobiles.[2]
- 1950s–1970s—The plating industry began to increase almost exponentially as it tried to keep up with an expanding worldwide population's purchases of appliances, tools, radios, televisions, telephones, recreational equipment and automobiles. This corresponded with the beginning of the "Age of Electronics," when a number of electronic inventions were introduced. Follow-on innovations include the transistor, integrated circuit, printed circuit, microchip, light emitting diode, the industrial computer and the personal computer. With each invention and the products that would exploit its capabilities, the number of new and sometimes seemingly impossible parts to electroplate grew at an awesome rate.
- 1970—Birth of the U.S. Environmental Protection Agency; introduction of focused regulation of the plating industry.

About 1985, it was taken somewhat for granted by many in the United States and elsewhere that chromium and cadmium would be forced out of existence before the year 2000. This might actually have happened, at least in the U.S., had it not been for meetings between the U.S. Environmental Protection Agency (EPA) and the American Electroplaters and Surface Finishers Society (AESF), the National Association of Metal Finishers (NAMF) and the Metal Finishing Suppliers Association (MFSA), and also if the plating industry had not done its part by developing and installing effective air and water treatment systems that ensured compliance with the agreed-upon limits. It is now quite apparent that chromium and cadmium will be around for another 25 years, maybe 50. Unless, of course, new alloys or multilayered plating combinations are not developed which, for about the same cost, match or better the special and unique combination of attributes of those two electrodeposited metals.

Nickel-bearing chemicals are also deemed carcinogenic. Currently, the pressure is slowly mounting to restrict their use, but the plain fact is that electroplated and electroless nickel coatings are probably the most important of all ECD coatings for technical and economic reasons. It seems very unlikely that nickel plating will be curtailed except at those companies where effective handling techniques and pollution abatement systems are not being used.

Chromium remains *the* wear-resistant layer and most likely it will continue as such for the next 50 years, especially for larger pieces such as hydraulic cylinders, where it will certainly not be replaced by PVD-TiC, because PVD chromium is relatively soft. Because of the expanding use of noncarcinogenic trivalent chromium for decorative applications and the effective measures taken by plating companies to reduce the health, safety and environmental hazards of chromium plating processes, chromium has been reprieved from the death penalty once avowed by health officials and environmentalists. It is surmised that during the next century the deposition of chromium will occur in equipment that is different from most of that now being used—equipment designed to absolutely protect employees and the environment from the unhealthy effects of the process.

Electrodeposition From Non-aqueous Electrolytes

All of the world's aluminum and magnesium is electrolytically produced from non-aqueous salt melts. Electroplated aluminum-layers from organic electrolytes are not widely used in industry, however. The processes are expensive and do pose environmental problems, therefore they cannot compete with aluminizing or mechanical cladding. Non-aqueous processes in general will be used for a restricted number of applications.

Electrochemical Conversion Layers

A very interesting field, which up until now has only been scratched on its surface by scientific methods, is that of chemically and electrochemically prepared conversion layers. Typically, the layers are of oxidic nature, the most well-known ones being those on aluminum and zinc. Not only can electrolytically produced aluminum oxide be colored by organic and inorganic pigments, its unique structure seems to offer nearly unlimited possibilities that are not being exploited. The small honeycomb channeled structure can be filled with organic matter, offering improved capacitors, or they can assist adhesion by gluing aluminum. They can also be filled with metals, offering electroluminescence or unparalleled magnetic storage properties, as studied in Japan and Germany. Tiny cobalt crystals directionally built into those channels of aluminum oxide layers seem to offer the highest storage capacity of any magnetic storage device.

The absorption, adsorption and chemical or biochemical filtering properties of the layers have only been touched upon. Most of the properties exploited were found empirically, as are the techniques of production in industry. This state of the art is the result of practical observations; later scientific investigations for the most part only explained the facts but did not predict them. This must be changed in the future; science should lead the way, showing industry promising directions. There would be a tremendous market if a true sapphire or ruby layer could be deposited on aluminum. The same is true regarding passivating or electrodeposited corrosion protection conversion layers on zinc and other metals. Magnesium, lithium and, to a certain extent, titanium, cannot be used without protective layers. They are considered the metals of the future.

Electrochemically Formed Dispersion Layers

Dispersion layers and their importance were mentioned earlier. Nearly every substance—metallic, nonmetallic and organic—can be incorporated into a matrix. A post-plating heat treatment may cause dispersoids to decompose and react in a matrix, and in this way oxidation-resistant, rare-earth-containing layers are produced for turbines. Included gases and nonmetallics (hydrogen) are in principle special kinds of dispersion alloys.

A well-researched example of dispersion hardening by way of electrochemical deposition is the inclusion of cobalt, nickel and iron compounds in hard gold deposits, particularly for use on electronic components. The wearability of these deposits is superior to those of gold-iron, gold-cobalt and gold-nickel alloys prepared metallurgically.

The incorporation of nonmetals is very dependent on the deposition parameters, especially electrolyte speed and/or current conditions, such as the use of pulse or laser plating.

Electroless Plating

A great moment in plating history occurred in 1946, the day Dr. Abner Brenner of the National Bureau of Standards calculated that the nickel solution he was experimenting with had a plating efficiency of 130 percent! The reason, he decided, was attributed to something he called *autocatalytic plating*. Afterward, Dr. William Blum, himself a pioneer plating scientist, called Brenner's discovery *electroless plating*.

The ability to deposit metals, particularly copper and nickel, without having to use an electric current or anodes proved to be such a boon that in only 50 years electroless plating grew to be one of the most important areas of plating. Now, whole industries depend on electroless plating to manufacture various products, most notably printed circuits, memory disks and plated plastics. In addition, such large industries as aerospace, automobile, electronic components, food processing, heavy equipment manufacturing, and gas and oil all depend on electroless deposits to provide many of their products with certain attributes, or a combination of attributes, not obtained in electroplated coatings.

Suppliers and users of electroless processes have considerably improved the performance, turnover rate and dependability of their solutions, as well as the quality of the deposits. The cost to deposit a mil-square foot has been steadily reduced by extending the life of the solutions through various techniques. There remains a significant gap, however, between the cost of electroless plating and electrodeposition.

What seems peculiar to us is that the same electroless electrolytes are employed regardless of the kind of parts being plated or their end use. For instance, whether plating electronic components, tubular products for the gas and oil industry, turbine blades for aircraft engines, crankshafts or lithographic cylinders, the chemistry of the electroless nickel solution is essentially the same. Only the percent of phosphorus or boron in the deposit is altered to change its performance capabilities. It would seem that more basic research of the electroless deposition phenomenon might be rewarded with solutions that plate crankshafts, blades and rolls faster with a harder deposit, tubular products with a more corrosive resistance plating, and electronic components with coatings having more corrosion resistance that could be soldered, bonded and/or formed. Doubtless such basic research activity will be undertaken during the next decade.

While there does not seem to be much basic research of electroless deposits occurring at this time (such as for electronics on the size limitations on ceramic substrates), the same is not so with regard to electroless plated alloys and composites. In the previous discussion about alloys, it was noted that one or more papers about electrochemically deposited alloys are appearing in most issues of most finishing industry magazines published around the world each month. The observation was meant to include alloys produced from electroless solutions also, inasmuch as the term "electroless plating" describes the methods of depositing metals and alloys by *electrochemical* reactions. During the last quarter-century, a great deal of time and money was spent developing alloys and composites that can only be produced by electroless plating solutions. The objective was to produce alloys and composites with exceptional corrosion resistance, lubricity and wearing properties. Industries such as aerospace, heavy equipment, oil and gas, mining, and tool and die, are constantly searching for improved product performance. Because that interest is not going to abate during the foreseeable future, one can predict that many new electroless coatings with outstanding properties will be discovered.

All Systems Go for Y2K & Beyond

It should be emphasized that most of the information in this report and the premises offered about the future of the plating industry are based on what has occurred in the first-world countries, particularly England, Germany and the rest of Europe, the United States, Australia, Canada and Japan. Little was mentioned about plating equipment in the body of this paper, but equipment stands as testimony to the ingenuity of platers.

In the 20th century, when equipment was needed to increase productivity or meet particular plating specifications on a new product and said equipment did not exist, the plating industry invariably responded by inventing it. Cases in point are: oblique and horizontal barrels to handle the steadily increasing demands for plated hardware items in the early 1900s; automatic plating lines introduced during the 1930s to produce increasing volumes of automobile bumpers, grills and accessories; high-speed plating processes for plating steel strip in 1940 to generate enough steel per day to keep up with tin can production (in Germany today, tin plating of steel runs at about 700 meters/min and zinc coating is not far behind!); reel-to-reel spot plating lines in the 1960s to save many millions of dollars in gold plating great numbers of lead frames; and vibratory platers around 1970 to process fragile, easily damaged electronic parts.

We believe that the inventive genius of platers will not vanish with the turn of the century, so the product designers of the 21st century will be able to depend on the plating industry to continue to find ways to do the impossible. Knowing that electrochemical deposits will be very much in demand during the foreseeable future, believing that the proliferation of new products will continue well into the next century, and being certain that the total number of parts requiring plating will increase steadily, the authors predict with a high degree of confidence that plating will remain the most absorbing, challenging and rewarding of all industries for the rest of the 21st century. It will live long and prosper, coping as always with the materials of the future. P&SF

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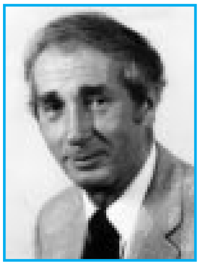

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