Moisture Getters & Barrier Sealants for Electronic Packages

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BACKGROUND

A Brief History of Devices and Packages

You might be surprised to learn that the first electronic packages were hermetic and they were invented in the late 1800's. That's right! The device package is well over a century old. The 1897 Braun Tube, or Cathode Ray Tube (CRT), is only now being replaced by solid-state flat panel display (FPD) technology. The electronic vacuum tube, developed in the early 1900's, while no longer dominant, is still in use today. Both of these packages are hermetic types. Pre-solid-state electronics required a vacuum to function and hermeticity was a basic requirement. These pioneering devices used hot filaments to produce streams of electrons; some may remember seeing the golden glow of tubes inside a radio or TV. The 1907 De Forest Audion vacuum tube amplifier marked the true beginning of electronics since it was the practical first active device. The glass packages evolved to metal and ceramic and this technology is now the modern hermetic package.

These devices required very low interior pressure. What's more, *oxygen was lethal* since it caused electrodes to oxidize and filaments to burn. The discovery of gettering and the introduction of getters was an important breakthrough that made vacuum-state electronics practical for over 50 years. As we'll learn later, high-reliability demands and new types of devices have propelled getters into an important role in today's advanced packaging. But first, a profound breakthrough -- the greatest technological event in modern times -- would forever change electronics.

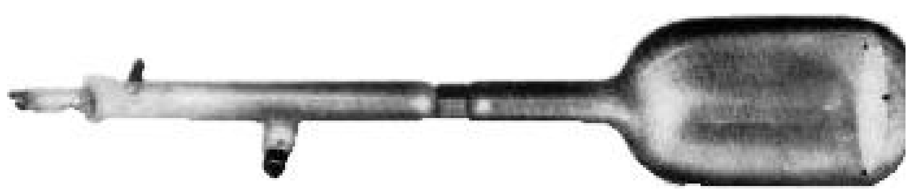
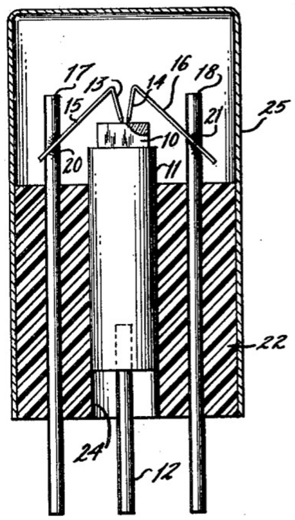


Figure 1 – 1897 Braun Tube – Early Hermetic Package

Halfway through the *century of electronics*, the discovery of solid-state electro-physical phenomenon would revolutionize devices and packaging to bring orders-of-magnitude improvements in performance. The advent of the transistor, soon followed by on-chip integration leading to the IC, would enable "non-hermetic" packaging that would come to rely on organic materials, especially plastics. The greatest revolution in packaging, plastic encapsulation, occurred around 1949. The *age of plastic packaging* enabled considerable innovation that continues, and even accelerates, today. The plastic transistor package was first (see Figure 2), but was followed by the DIP to accommodate more I/Os for the rapidly developing IC industry (see Figure 3).



1950 - RCA TA165
Araldite Epoxy Body

Figure 2 – Right is patent drawing from reference 1 and left is the product

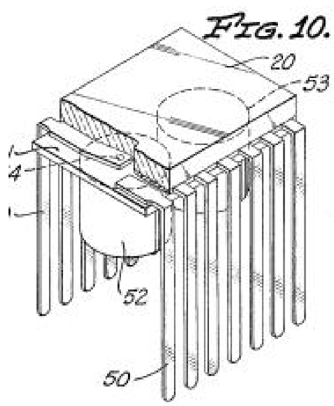


Figure 3 – Dual-in-Line (DIP) package from reference 2.

NEWER DEVICES

OLEDs

Organic Light Emitting Diodes (OLED) are the new frontier for the production of very thin, low power, vivid and cost-effective displays as well as energy-efficient lighting. More recently, OLED technology has been adopted for plastic solar cells. This newer technology couples layers of active organic materials that may be small molecules, or polymers, that are deposited by a variety of methods. A cathode is formed that can be made from a reactive metal such as Ba or Ca. Most of the materials, especially the cathode, are very sensitive to moisture and some are degraded by oxygen. The double challenge is excluding moisture and oxygen while maintaining a light path. Thus, cost-effective, mass-produced packaging is one of the most significant challenges for the emerging OLED display industry. The industry continues to struggle with extending the operating lifetime of products. While work is underway to develop air-stable materials, most products need substantial environmental protection. Some set the moisture transmission limit at no more than 10-5 to 10-6g/m2/day. But current commercially available films have a water vapor transmission rate of about 10-3g/m2 per day. The OLED dilemma is how to achieve these requirements without resorting to expensive 1800's hermetic glass technology. Earlier strategies involved the use of metal back plates and glass frit sealing.

MEMS

MEMS, Micro-Electro-Mechanical Systems, is the ultimate enabling technology for integration of virtually every energy form and useful phenomena - motion, light, sound, radio, chemistry, and computation - **all on a single chip**. High-volume commercial products sense complex motion, measure the slightest pressures, and propel fluids. Newer products receive and send light beams, others detect specific molecules, and some deal with several “senses” simultaneously. If the logic circuit is the *brain*, MEMS adds the *eyes, nose, ears, touch, taste buds, and super-human sensing ability*. MEMS also brings control and manipulation, the *hands and fingers* that let chips operate on matter. **The *merging of motion, sensing, control and computation* represents a major leap in technology. While** MEMS technology is the grand unification of mechanical, photonic, electrical and electronic subcomponents into an integrated system it presents the greatest packaging challenge the industry has ever seen.

MOEMS

What could be more challenging than dealing with a chip that combines electronics and mechanics? Just add light to enter the ultimate tech zone of MOEMS. Developers have added optics and photonics to expand the increasingly popular subset known as MOEMS; aka optical-MEMS. We now have a potent and versatile convergence of all the world's technologies onto and into a single and remarkable chip. We can build incredibly small machines that perform the same mechanical, optical, electrical and electronic functions found in massive equipment from our macro-world. It’s like shrinking every-day machinery onto tiny chips. MEMS/MOEMS is the ultimate System on a Chip (SOP) - the new embodiment of the old cliché, ***“Shrink the world onto a chip”***. But if MEMS represented the greatest packaging challenge, MOEMS adds an extra dimension -- the need for optical transparency.

Nanoelectronics

Although nanoelectronics is only at the “transistor stage”, we can expect integrated circuitry to be developed over the next decade. Industry roadmaps place the introduction of nanoelectronics the year 2020. While it’s still too early to predict exactly what materials and designs will be succeed, the most likely bet is on carbon-based systems, such as carbon nanotubes (CNT). Metal may still be used for “wiring” the transistors, or their equivalent, together. But it’s just as likely that organic conductors, including CNTs, could be used. Packaging will almost certainly employ plastics and some designs will use a cavity type since nanoelectronics will almost certainly utilized nano-mechanics. In fact, we already have nano-electro-mechanical systems (NEMS). IBM’s Centipede is an example of Nanotechology applied to memory. But regardless of the exact materials and designs, most of the packaging requirements in place today, will be required for these emerging devices. And this includes protection from the environment, including moisture.

DEVICE PACKAGE CLASSES

Full Hermetic: The full hermetic package, now over 150 years old, has admirably served the electronics and optoelectronics industries. This package class began as the CRT, then the vacuum tube, and finally the semiconductor package. The hermetic packages evolved from glass to ceramic and metal, and are still widely used for today. Both metal and ceramic are used to make modern hermetic packages, but wafer-level packages may use silicon. Applications for these packages include photonics, high-reliability electronics and many MEMS/MOEMS products. These sealed packages often employ getters to maintain, and even improve, the in-package atmosphere.

Non-Hermetic Overmolded Plastic Package: Plastic packaging has remained the “workhorse” technology ever since the breakthrough introduction of the Dual-in-Line Package (DIP) described earlier. The metal lead frame (MLF) is still widely used, especially for lower lead-count devices. Wire bonding continues as the primary 1st level, chip-to-package, and connection method. Epoxy overmolding, using EMC (Epoxy Molding Compound) is the primary enclosure means. Molding compound, a blend of solid epoxy resins, hardeners, fillers, and additives, is melted by heating, forced into a mold that holds the lead frame assembly, and heated to polymerize the material. The molding compound makes direct contact with the die, wire bonds and lead frame. The Newer BGA (Ball Grid Array) uses similar processing but typically replaces the MLF with an organic area array substrate. The “advertised as new”, but actually old, QFN (Quad Flatpack No-lead is essentially a BGA without solder balls. The 2nd level connection uses flat conductive pads that are joined to the circuit board by applying solder. The flat pad design is similar to the decades-old ceramic leadless chip carrier (LCCC). Since all of these designs, with very few exceptions, use encapsulant applied directly over the devices, plastic overmolded packages can't be used on unprotected MEMS chips.

Cavity Style Near-Hermetic Package (NHP) - The component packaging industry has offered two extremes, the full hermetic and the non-hermetic package. Several years ago, we suggested an intermediate design that we called the Near-Hermetic Package (NHP); others, especially Professor Ampere Tseng, of Arizona State University, have used the term quasi-hermetic [3]. The NHP seeks designs that are "good enough" and "cheap enough" for MEMS and other cavity-requiring devices. The concept is still evolving and several companies are producing products. Although the plastic of choice, LCP (Liquid Crystal Polymer; a class of polyester), has excellent barrier properties, this plastic and all others (without special barriers) allow slow moisture entry that might be offset by the use of getters.

Wafer-Level Packaging - Partial - This type of package is formed while devices are still in wafer format. While a number of full WLP methods have emerged for electronic devices, MEMS is still evolving although partial WL methods have been commercial for a number of years. The dominant MEMS W-L process is capping - a partial packaging process, also called pre-packaging, since additional packaging steps are required later. Several companies, like Analog Devices, Inc., have been capping accelerometers for a number of years -- but the caps are passive, with no electrical paths. The passive cap cannot interfere with chip bond wire bonding and this requires caps smaller than the MEMS device. The common solution is separately singulate the caps in a manner that leaves the MEMS bond pads exposed. The capped cavity is hermetic, but a getter can be applied to the interior for better atmosphere control and reliability assurance

Full WLP – The entire package can be constructed with the devices are still in wafer form and many believe that this is the future – the ultimate package. We predict that MEMS will eventually evolve to WLP and this contention is supported by the rapid increase in issued patents as well as the large base of patent applications filed during this decade. The WLP can be hermetic, although many low-cost processes using polymers have been proposed [x]. Regardless of the materials, WLP is an excellent format for getters that can be applied to the wafer by any of several methods.

PACKAGE ATMOSPHERE

The full-hermetic package has more controlled interior atmosphere than the other types, but it is not absolute. Even a metal package that presents an extraordinary barrier to the environment can have a varying atmosphere. The device, the package, and added materials, such as adhesives and RF absorbers, can change the atmosphere over time. Die attach adhesives can outgas organic materials, and metal, especially plated, can evolve hydrogen gas that is known to poison certain devices. It is also difficult to remove all moisture before sealing a package. MEMS devices, that are particularly sensitive to even the tiniest particles, can become the source of contamination due to wear. But MEMS devices may also function optimally within a specific humidity range. Volatile lubricants and anti-stiction agents (more later), may also be needed for MEMS to perform satisfactorily. The best assurance for the full-hermetic package is to use atmosphere control agents and getters.

1.0 Device Reliability Issues [Mike, so you want to add here?]
- 1.1 Device Defects
- 1.2 Package Assembly Defects
- 1.3 Degradation caused by Chemical Reactions
- 1.4 Particle-Induced failures (CMOS) – Is particles another paper?
- 1.5 Package induced defects – Stiction? [Add from MEMS paper]
- 1.6 Influence of package atmosphere & atmosphere during manufacturing (Vacuum, Nitrogen, etc).

2.0 Chemical Reactions within a package
- 2.1 Moisture effects
- 2.2 Halides
- 2.3 Other contaminants

2.3.1 Oxygen – OLED

3.0 Getters

3.1 Definitions

Getters: *agents that counteract harmful contaminants within a sealed package; this includes solids, liquids, gases and combinations. These materials are MOLECULAR SCAVENGERS that guard and control package environment over an extended time. Getters can interact with gases, liquids or solids as well as combinations.*

Getters can be as simple as ceramic substrate that is pre-dried before package sealing. But they are usually more complex additives like the hydrogen getters that adsorbs the gas, converts it to water by reaction with a compound, and then adsorbs the water with a moisture getter contain in the same composite. Getters are not limited to gases and vapors. Particle getters can attract and hold onto tiny solids are dislodged or those that are generated by wear of MEMS devices. Combinations of getter agents can also be used and multi-action products are available.

MODERN GETTERS

Today's getters for electronic packages can be designed for high selectivity and capacity. Materials are available that absorb gases, liquids and even solids. Some convert a contaminant to a species that can be more easily trapped. The present list of commercial getters includes moisture, particle, oxygen, and hydrogen, but additional getters can be designed as the need arises. Getters can use both physical and chemical mechanisms and can be specific to a single molecule like hydrogen or water. Others, such as particles getters, can be very general. Table 1 lists getter classes and mechanisms while Table 2 shows the physical form and status of specific products. Each type of getter will be discussed in the next sections.

Table 1

TYPE OF GETTER	PRINCIPLE
Moisture; H_2O	**Desiccant; physical and reactive**
Oxygen; O_2	**Active metal**
Carbon Dioxide; CO_2	**Lithium; use to form vacuum by purging with CO_2**
Hydrogen; H_2	**Palladium, Palladium oxide, organic compounds**
Particle	**Tacky polymer**
Organic vapors	**Activated carbon**
Multipurpose	**Combinations of above**

Table 2

GETTER	FORM	STATUS
Moisture; H_2O	**Film, paste, container**	**Commercial**
Particle	**Film, paste**	**Commercial**
Hydrogen; H_2	**Film, paste, thin film, plating**	**Commercial**
Oxygen; O_2	**Strip, paste, thin film**	**Commercial**

Humidity range	Film, paste, fluid?	Feasible

4.0

Moisture

A major concern is *chemistry within the package*. Chemical reactions will cause changes that are generally unintended and undesirable. Some metals will oxidize and corrode. Joints can undergo changes that disrupt electrical connections. Solid-state devices can undergo change in the presence of “air gasses”, especially oxygen and water vapor. In fact, water is the most significant molecule in terms of potential damage to devices and the package. Water can create two different problems. H_2O is a medium for ions and a catalyst for many reactions, especially metal corrosion. This is why aircraft are stored in dry desert locations. But water in the package builds pressure during heating and it can become a “bomb” ready to literally explode under high temperature conditions like those found in soldering. But metal and ceramic enclosures can usually contain the pressure while organic materials may not. Future plastic hermetic packages will be more concerned with vapor pressure however. Water can also cause special problems for MEMS by aggravating stiction, and raise havoc with optical systems, especially MOEMS.

Types of Desiccants

Physical desiccants are materials that can adsorb water vapor by causing these polar molecules to adhere to special surfaces by physical interactions. These bonding actions involve very weak surface bonds such as Van der Waals forces. Hydrogen bonding can also play a role. Molecular sieves, or zeolites, are common getter physical desiccants. Their main advantages are their low cost, safety, and wide availability. Water capacities can be moderate to large, but the total amount of absorbed moisture tends to eventually reach a plateau that is a function of the equilibrium pressure of water over the zeolite surface. Since the water absorption value is temperature-dependent, capacity decrease with temperature. This means that the water absorption is reversible and high temperatures can cause water to re-enter the package atmosphere. Finally divided carbon, especially activated carbon, can absorb water, but is more commonly used to trap organic vapors, such as those released from adhesives.

The zeolite particles can be distributed in a porous, or “breathing” binder or matrix for versatility, easy handling, reduced inventory and automated application to packages. Physical getter materials are widely available and can be use to make both film and paste getters, but there are some limitations. Although the water adsorption capacity can be large, the maximum amount of adsorbed water can reach a plateau as determined by the equilibrium pressure of water over the zeolite surface. The specific value will vary with temperature; a temperature increase reduces water-holding capacity. But there is a more serious limitation. Since zeolite-water bonds are physical and rather weak, the reaction is reversible. This means that physical desiccants can release water under higher temperature conditions that could be found in some packages. A new water-vapor equilibrium pressure is established when the temperature changes. However, physical getters still find many applications and remain popular products today. It is important to understand getter properties and conditions that the package will experience.

Chemical desiccants represent a totally different class of water sorbing desiccants. These materials form stable compounds when they react with water vapor, thus making water removal irreversible under most operating conditions. This second class of getters chemically reacts with water, but also with other molecules that include oxygen, hydrogen and compounds such as CO_2 and SO_2. Metal elements including calcium, form oxides that are very effective moisture getters. Other Group IIa metals (alkaline earth metals) that form moisture-gettering oxides are magnesium (Mg), barium (Ba), and strontium (Sr).These oxides react with water according to the following reaction:

$$MO + H_2O \rightarrow M(OH)_2$$; where M can be Ba, Mg, Sr or Ca.

The theoretical capacity of oxides can be large since a stoichiometric water absorption capacity of is about 1/3rd the weight of the metal oxide. Since the water-combining reaction is favored by an increase in temperature, water is not released inside the package during operation as can occur with physical adsorbents.

Commercial Moisture Getters

Moisture getters use compounds that absorb and bind water molecules. Zeolites and certain metal oxides are effective and popular. A special polymer matrix can be used as the "breathable" binder, such as Staystik 415 and 482 (StayDry SD1000 and SD800 respectively).

Chemical type getters are popular in many applications, especially those where low, predicable moisture limits are preferred. Cookson's STAYDRY - HiCap2000 is a high capacity moisture getter based on metal oxide in a polymer matrix. This material is a high capacity moisture getter designed for use in a variety of high performance/high reliability, hermetically sealed electronic/optic packages. A thermoplastic dissolved in solvent is used as the carrier or matrix so that the product can be needle-dispensed on the inside surface of lids or other package areas. Once dried, the deposited getter becomes a non-tacky film that functions primarily as a moisture getter by absorbing H_2O, but also CO_2. The adsorption capacity is 15% based on the dry weight of applied getter. A 1 inch x 1 inch film that was 3 mils thick would absorb about 11 mg of water. Graph 1 shows moisture gain vs. time using a 3 mil film of HiCap2000 as a range based on many samples [how many samples or how is chart range obtains?] under JEDIC Level 1 conditions; 85^{o}C at 85% relative humidity. Chart 2 shows the same material under JEDEC Level 2 conditions where relative humidity is set at 60%.

Chart 1

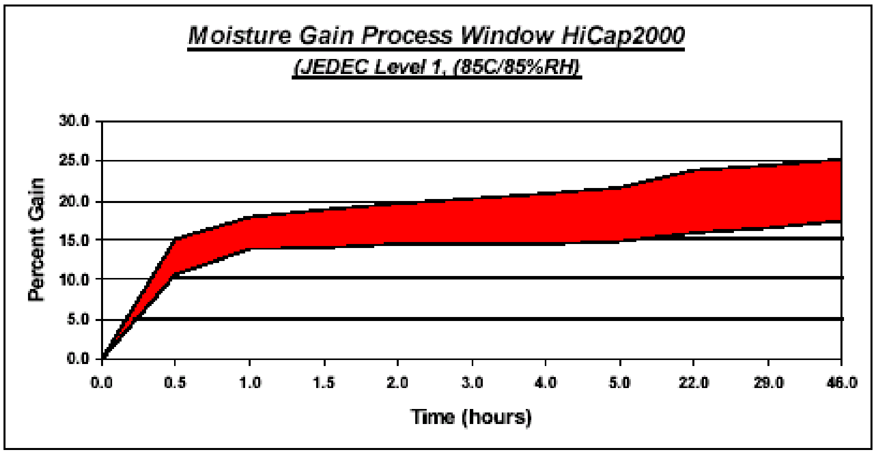
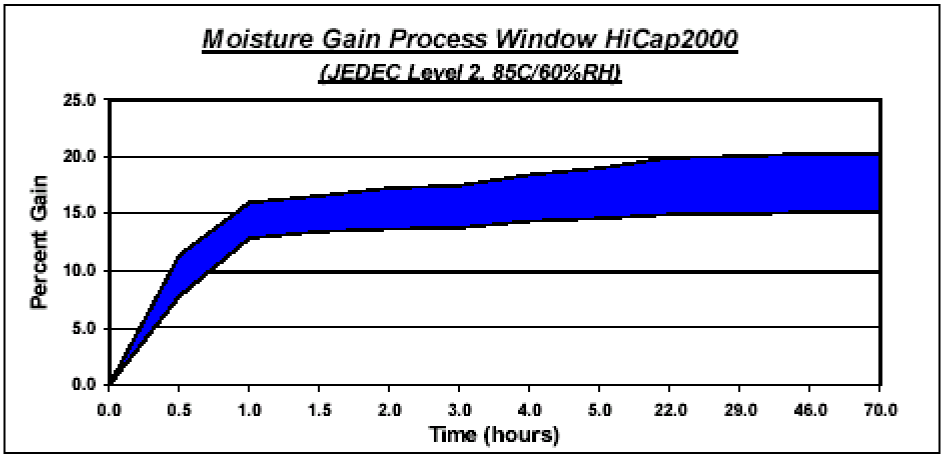
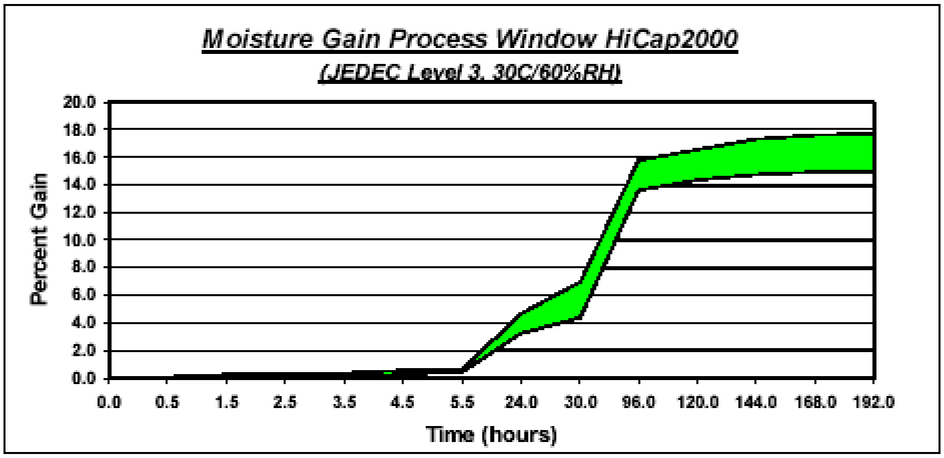


Chart 2



It can be seen that the two charts are similar under these two somewhat similar conditions. But JEDEC Level 3, where the temperature is close to ambient at 30°C, behaves differently. Water absorption begins at a much slower rate than for the elevated conditions. In fact, maximum water removal requires several days as shown in Chart 3.

Chart 3



1.1.1 Reactive materials (We do not offer metal oxides so do we want to mention them?)

1.2 Oyxgen Getters – combined Water & Oxygen for OLED
1.3 Organic Absorbers – combined Water & Organic

2.0 Manufacturing with Getters & Barrier Sealants
2.1 Liquids/Paste advantages

3.0 Barrier Sealants
3.1 Solder pre-form (AuSn)
3.2 Seam seal
3.3 Glass frit
3.4 Polymers – We have all kinds of data on current product
3.4.1 Difference between polymer, technologies (UV, thermal epoxy, LCP, etc.)

4.0 Getters & Barrier sealants

Applications Requiring Getters

There are several areas where getters are used as enabling technology or a means of extending lifetimes and boosting reliability. Traditional areas include telecommunications, especially aerospace, military, optoelectronics and micromechanical packages. Micro-Electro-Mechanical Systems (MEMS) and optical-MEMS, also known as MOEMS (Micro-Opto-Electro-Mechanical Systems) represent newer markets for getters. Table 3 lists needs for the micromechanical packaging.

MEMS/MOEMS Needs List

- **Getters**
  - **Moisture**
  - **Organic vapor absorbers**
  - **Vacuum-producing**
  - **Particle**
  - **(Hydrogen)**
  - **Other**
    - **Humidity control agents; 30 – 50%**
    - **Anti-friction, anti-stiction, anti-wear agents**

REFERENCES

(1) Rose, George M. Jr., US patent 2,538,593, assigned to RCA, filed April 30, 1949.

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(3) Gilleo, K., The NHP Factor, EP&P, 11/1/2002; http://www.edn.com/index.asp?layout=article&articleid=CA256053

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