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# Impact of Organic Additives and Contaminants in Electroplating Baths on Solder Wetting Characteristics

**Giridharan VM, Dr. Ranga Nagendra Babu**

Scholar, Department of Mechanical Engineering, Sunrise University, Alwar, Rajasthan, India

Research Supervisor, Professor, Department of Mechanical Engineering, Sunrise University, Alwar, Rajasthan, India

**ABSTRACT:** The solderability of Cu–Sn–Pb electroplated coatings is critically influenced by the presence of organic additives and unintended contaminants in the electroplating bath, as these species directly affect deposit morphology, surface chemistry, and interfacial reactions during soldering. Organic additives such as brighteners, levelers, suppressors, and grain refiners are intentionally introduced to control deposition kinetics, improve surface smoothness, and refine grain structure. However, their concentration, decomposition, and interaction with metal ions can significantly alter the electrochemical environment, especially under varying current density conditions. Excessive or degraded additives may become incorporated into the deposited layer, leading to carbonaceous inclusions, increased internal stress, and microstructural heterogeneity. These effects often manifest as surface roughness, porosity, or organic residue films that inhibit proper flux action and reduce solder wettability. In addition to intentional additives, contaminants such as breakdown products, oil residues, metallic impurities, and particulate matter can accumulate in the plating bath over time. These contaminants can adsorb onto the cathode surface, disrupt uniform nucleation, and promote the formation of defects such as nodules, pits, and dendritic structures. From a soldering perspective, such surface irregularities and chemical residues increase the contact angle of molten solder, resulting in poor spreading, dewetting, or non-wetting phenomena. Furthermore, the presence of organic residues at the metal interface can hinder the formation of stable intermetallic compounds (IMCs) between solder and substrate, which are essential for metallurgical bonding and long-term reliability. The degradation of solder wetting characteristics is also exacerbated by post-plating oxidation, which may be accelerated by certain additive chemistries or contaminants that alter surface reactivity. Over time, these effects contribute to variability in solder joint quality, increased defect rates, and reduced reliability of relay components.

**KEYWORDS:** Electroplating Bath Chemistry, Organic Additives, Brighteners and Levelers.

## I. INTRODUCTION

The performance of electroplated coatings in electronic components is critically dependent on their ability to form reliable solder joints, and solderability remains one of the most important quality indicators for Cu–Sn–Pb finishes used in relay terminals and similar applications. Among the numerous process variables governing solderability, the role of organic additives and unintended contaminants in electroplating baths has emerged as a complex and often underappreciated factor influencing wetting behavior. Electroplating baths are rarely composed of simple metal salt solutions; instead, they contain a carefully engineered mixture of organic additives such as brighteners, levelers, suppressors, and grain refiners that are introduced to control deposit morphology, improve surface smoothness, and enhance overall appearance. While these additives are essential for achieving desirable physical and aesthetic properties, their presence also introduces variability in electrochemical reactions at the cathode surface, particularly when their concentration, decomposition, or interaction with other bath constituents is not tightly controlled. This variability can significantly affect the surface chemistry and microstructure of the deposited Cu–Sn–Pb coatings, ultimately influencing solder wetting characteristics.

Organic additives function primarily by adsorbing onto the cathodic surface during deposition, modifying the kinetics of metal ion reduction and influencing nucleation and growth mechanisms. For instance, brighteners tend to accelerate localized deposition, leading to finer grain structures, whereas suppressors can inhibit deposition in certain regions, promoting uniform thickness distribution. However, fluctuations in additive concentration, often caused by consumption, breakdown, or drag-out during processing, can lead to inconsistent deposition behavior. When additive levels exceed optimal ranges, excessive adsorption may occur, resulting in the incorporation of organic residues within the plated layer. These residues can become trapped at grain boundaries or on the surface, forming a thin organic film that is not easily removed during subsequent rinsing or drying steps. Such films act as barriers to solder wetting by preventing direct संपर्क between the molten solder and the metallic substrate, thereby increasing contact angle and promoting non-wetting or dewetting phenomena. Conversely, insufficient additive concentrations can lead to coarse, uneven deposits with higher surface roughness and porosity, which also negatively impact wetting by creating non-uniform solder spreading and localized void formation.

In addition to intentionally added organic compounds, electroplating baths are susceptible to contamination from a variety of sources, including degradation products of additives, impurities introduced through raw materials, environmental exposure, and carryover from preceding process steps such as cleaning or etching. Over time, organic additives undergo electrochemical and thermal decomposition, producing byproducts that may have different adsorption characteristics and electrochemical activity compared to the original compounds. These degradation products can accumulate in the bath and interfere with deposition processes in unpredictable ways. For example, some breakdown products may preferentially adsorb onto the cathode, inhibiting metal deposition and leading to thin or poorly adherent coatings, while others may promote the formation of nodular or dendritic structures that compromise surface integrity. Furthermore, contaminants such as oils, surfactants, or residual cleaning agents can alter the surface energy of the deposit, significantly affecting its wettability. Even trace amounts of such contaminants can lead to the formation of hydrophobic regions on the plated surface, which resist solder spreading and contribute to incomplete wetting.

The impact of these organic species on solderability is closely linked to their influence on the microstructure and composition of the electroplated layer. The presence of organic inclusions within the deposit can modify grain size, crystallographic orientation, and defect density, all of which play a role in determining how the surface interacts with molten solder. Fine-grained deposits produced under optimal additive conditions generally exhibit improved wettability due to their higher surface energy and more uniform composition. However, when organic contamination is present, these benefits can be negated by the formation of surface films or internal defects that disrupt the continuity of the metallic phase. Additionally, organic residues can act as sites for oxidation, further degrading solderability. Oxide layers formed on contaminated surfaces are often more stable and difficult to reduce during soldering, requiring higher temperatures or more aggressive fluxes to achieve adequate wetting. This not only increases process complexity but also raises the risk of thermal damage to sensitive components.

## II. RESEARCH OBJECTIVES

The research on the impact of organic additives and contaminants in electroplating baths on solder wetting characteristics, particularly for Cu–Sn–Pb plated systems used in relays and electronic interconnections, is driven by the need to understand, quantify, and control the subtle chemical and electrochemical interactions that ultimately determine solderability performance and long-term reliability. The primary objective of this study is to systematically investigate how various organic additives—such as brighteners, levelers, suppressors, grain refiners, and wetting agents—introduced intentionally into electroplating baths influence the surface chemistry, microstructure, and morphology of the deposited Cu–Sn–Pb coatings, and how these changes translate into measurable variations in solder wetting behavior, including wetting force, spreading rate, contact angle, and incidence of non-wetting or dewetting defects. A key focus is to establish a direct correlation between additive concentration, adsorption kinetics, and electrochemical behavior at different current densities, with the resulting deposit characteristics such as grain size distribution, crystallographic texture, inclusion content, and surface roughness, all of which are known to significantly affect solder wettability. In addition to beneficial additives, the study aims to identify and characterize the role of unintended organic contaminants—originating from bath degradation, breakdown products of additives, carryover from upstream cleaning processes, or environmental exposure—which may accumulate over time and adversely impact plating quality by promoting porosity, organic inclusion entrapment, carbonaceous residues, or surface passivation layers that inhibit proper solder wetting. Another important objective is to evaluate the synergistic and antagonistic interactions between different classes of additives and contaminants, recognizing that electroplating baths are complex, dynamic systems in which multiple species compete for adsorption sites on the cathode surface, thereby altering local current distribution, nucleation rates, and growth mechanisms. The research further seeks to quantify how these interactions influence the formation of intermetallic compounds (IMCs) at the solder/coating interface, especially Cu–Sn phases, which play a critical role in determining both initial wetting performance and long-term joint reliability; particular attention is given to whether additive-derived impurities or contaminants act as diffusion barriers or accelerants for IMC growth. A parallel objective is to investigate the effect of bath aging and operational history on the evolution of additive chemistry and contaminant buildup, including the use of analytical techniques such as cyclic voltammetric stripping (CVS), high-performance liquid chromatography (HPLC), total organic carbon (TOC) analysis, and mass spectrometry to monitor chemical changes in the bath over time, and correlate these with observed variations in solderability test results such as dip-and-look, wetting balance, and spread tests. Furthermore, the study aims to examine how process parameters—such as current density, temperature, agitation, and filtration—modulate the influence of additives and contaminants, potentially amplifying or mitigating their effects on deposit quality and wetting behavior, thereby enabling the identification of critical process windows that ensure consistent solderability. Another key objective is to assess the impact of post-plating handling and storage conditions, including exposure to air, humidity, and elevated temperatures, on the interaction between residual organic species on the coating surface and oxidation processes, which may lead to the formation of organic-oxide composite films that further degrade solder wetting performance.

The research also intends to develop mechanistic models that describe how organic molecules adsorb, desorb, decompose, and incorporate into the growing metal layer under varying electrochemical conditions, and how these mechanisms influence macroscopic properties such as wettability and defect formation. In addition, a practical objective of the study is to establish threshold limits for critical contaminants and optimal concentration ranges for key additives, beyond which solderability degradation becomes significant, thereby providing actionable guidelines for bath maintenance, replenishment strategies, and contamination control in industrial electroplating operations. The study also seeks to explore mitigation strategies, including advanced purification techniques such as carbon treatment, dummy plating, and membrane filtration, to remove detrimental organic species and restore bath performance. Ultimately, the research aims to bridge the gap between electrochemical bath chemistry and end-use soldering performance by integrating insights from materials science, surface chemistry, and process engineering, thereby enabling the development of robust, contamination-tolerant electroplating processes that consistently produce Cu–Sn–Pb coatings with superior and reliable solder wetting characteristics suitable for high-reliability relay applications.

## III. METHODOLOGY

A rigorous methodology to investigate the impact of organic additives and contaminants in electroplating baths on solder wetting characteristics of Cu–Sn–Pb coatings should be designed to systematically isolate, control, and quantify the influence of each variable while maintaining strong reproducibility. The study begins with the preparation of standardized copper substrates, typically high-purity Cu coupons (e.g., 99.9%) with controlled dimensions. These substrates must undergo a strict surface preparation protocol to eliminate variability arising from surface contamination. The cleaning sequence includes mechanical polishing using progressively finer abrasive papers, followed by ultrasonic cleaning in acetone, rinsing in deionized water, acid pickling (commonly dilute $H_2SO_4$ or HCl), and final rinsing and drying in nitrogen. This ensures a reproducible, oxide-free, and contaminant-free starting surface, which is critical because even minor surface variations can significantly affect both electroplating quality and subsequent solder wetting behavior.

Following substrate preparation, the electroplating bath is formulated based on a conventional Cu–Sn–Pb plating chemistry. The baseline bath composition includes metal ion sources such as copper sulfate, tin sulfate or stannous salts, and lead salts, along with supporting electrolytes like sulfuric acid. To this baseline, controlled quantities of organic additives are introduced. These additives typically include brighteners (e.g., sulfonated organics), levelers (e.g., polyethers), grain refiners, and wetting agents. Each additive is selected based on industrial relevance and prior literature evidence of its impact on deposit morphology. The experimental design should employ a structured Design of Experiments (DOE), such as a factorial or Taguchi approach, to vary additive concentrations at multiple levels (e.g., low, nominal, and high concentrations relative to supplier recommendations). In parallel, specific contaminants are deliberately introduced into separate bath samples to simulate real-world degradation conditions. These contaminants may include organic breakdown products, oils, chloride ions, metallic impurities, or carbonaceous residues. Their concentrations should reflect both acceptable limits and worst-case scenarios observed in industrial plating lines.
Electroplating is then performed under tightly controlled conditions using a laboratory-scale plating cell equipped with a temperature controller, agitation system, and a regulated DC power supply. Key process parameters such as current

density, bath temperature, pH, agitation rate, and plating time are held constant to isolate the effects of additives and contaminants. Current density is typically selected based on industrial practice (e.g., 1–5 A/dm$^2$), and uniform current distribution is ensured through proper electrode geometry and shielding. During plating, parameters such as voltage response and bath stability may also be monitored to detect any anomalies caused by additive interactions or contamination. After deposition, the coated samples are rinsed thoroughly and dried under controlled conditions to prevent post-plating oxidation.

The characterization of the electroplated coatings is a critical step in linking bath chemistry to solder wetting behavior. Surface morphology is examined using scanning electron microscopy (SEM) to identify features such as grain structure, roughness, porosity, nodules, and dendritic growth. Energy-dispersive X-ray spectroscopy (EDS) is used to confirm elemental composition and detect the incorporation of impurities or additive residues within the coating. Surface roughness measurements can be performed using profilometry or atomic force microscopy (AFM), as roughness plays a significant role in wetting dynamics. Additionally, X-ray diffraction (XRD) may be used to analyze crystallographic texture and phase composition, particularly to identify intermetallic compounds or preferred orientations induced by additives. To assess the presence of organic residues, surface-sensitive techniques such as X-ray photoelectron spectroscopy (XPS) or Fourier-transform infrared spectroscopy (FTIR) may be employed.

## IV. BACKGROUND

The solderability performance of electroplated Cu–Sn–Pb coatings is critically dependent on the physicochemical condition of the plated surface, which in turn is strongly influenced by the composition of the electroplating bath. Among the many variables governing plating quality, the presence and behavior of organic additives and unintended contaminants play a particularly decisive role in determining final solder wetting characteristics. Organic additives—such as brighteners, levelers, suppressors, and grain refiners—are deliberately introduced into electroplating baths to control deposit morphology, improve surface smoothness, and enhance aesthetic and functional properties. However, their concentration, breakdown products, and interactions with metal ions can significantly alter the microstructure, surface chemistry, and ultimately the wettability of the deposited layer. In parallel, contaminants—whether introduced through bath aging, environmental exposure, or inadequate process control—can further complicate deposition behavior and degrade solderability. Understanding the combined impact of these factors is therefore essential for diagnosing solderability failures in Cu–Sn–Pb electroplated relay components.

Organic additives function by adsorbing onto the cathode surface during electrodeposition, modifying local electrochemical kinetics and influencing nucleation and growth processes. Brighteners, for example, are typically sulfur-containing organic compounds that promote fine-grained, reflective deposits by accelerating nucleation rates. While this can improve surface uniformity, excessive incorporation of sulfur or decomposition by-products into the deposit can lead to increased impurity levels at the grain boundaries. These impurities may subsequently oxidize or react during storage or thermal exposure, forming surface films that inhibit solder wetting. Similarly, levelers are designed to preferentially adsorb on high-current-density regions, reducing thickness variations and producing smoother coatings. However, overuse or imbalance of levelers can suppress deposition excessively in certain regions, leading to non-uniform grain structures and localized defects such as microvoids or porosity, which negatively impact solder spreading behavior.

Suppressors, often polymeric compounds such as polyethylene glycol derivatives, act by inhibiting metal ion reduction in specific regions, thereby improving throwing power and deposit uniformity. Yet, these large organic molecules can become entrapped within the growing metal layer, particularly under conditions of high current density or insufficient agitation. Entrapped organics may not be fully removed during post-plating rinsing and can later decompose, leaving carbonaceous residues on the surface. These residues act as barriers to flux activity during soldering, preventing effective oxide removal and reducing the wettability of the surface. Grain refiners, another class of additives, are used to control crystallographic orientation and reduce grain size, which can enhance mechanical properties. However, extremely fine-grained structures may exhibit higher grain boundary density, increasing the likelihood of impurity segregation and oxidation, both of which are detrimental to solder wetting. In addition to intentionally added organics, electroplating baths are susceptible to contamination from a variety of sources. Organic contaminants may originate from degraded additives, breakdown products formed under prolonged electrochemical operation, or external sources such as oils, greases, and cleaning residues introduced during handling. Over time, these contaminants accumulate in the bath and can adsorb onto the cathode surface alongside functional additives, disrupting the intended balance of

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electrochemical reactions. This often results in inconsistent deposition, increased roughness, and incorporation of non-metallic inclusions within the coating. Such inclusions can act as nucleation sites for oxide formation, further impairing solderability.

The presence of organic contaminants also influences the electrochemical double layer at the cathode interface, altering charge transfer kinetics and mass transport behavior. This can lead to localized variations in current density and deposition rate, producing heterogeneous microstructures across the plated surface. Regions with higher impurity concentration may exhibit increased resistivity and reduced thermal conductivity, which can affect heat transfer during soldering and lead to uneven wetting. Furthermore, organic residues on the surface can reduce the effectiveness of flux by limiting its ability to chemically reduce oxides and promote solder spreading. As a result, even if the bulk composition of the coating is within specification, the surface condition may still be unsuitable for reliable solder joint formation.

## V. LITERATURE REVIEW

Electroplating is a critical surface engineering process widely used in microelectronics, especially for Cu–Sn–Pb and related metallization systems where solderability is a key functional requirement. Among the various factors governing deposit quality, the role of organic additives and contaminants in electroplating baths has received considerable attention due to their profound influence on microstructure, surface chemistry, and ultimately solder wetting behavior. Organic additives are intentionally introduced into plating baths to control deposition kinetics, while contaminants—either introduced unintentionally or generated during operation—can degrade coating performance. Understanding their combined effects is essential for addressing solderability failures.

Organic additives typically consist of suppressors, accelerators, and levelers, each playing a distinct role in modifying electrodeposition. These additives adsorb onto the cathode surface and influence nucleation and growth processes, thereby controlling grain size, morphology, and surface roughness. For example, additives such as polyethylene glycol (PEG), bis(3-sulfopropyl) disulfide (SPS), and other organic compounds are widely used in copper electroplating to achieve uniform and defect-free deposits. Their adsorption behavior alters local current density and promotes fine-grained microstructures, which are generally favorable for solder wetting. However, excessive or imbalanced additive concentrations can lead to abnormal deposition behavior, including roughness, inclusions, and void formation .

One of the key mechanisms through which organic additives affect solderability is impurity incorporation. During electrodeposition, additive molecules or their decomposition products can become entrapped within the growing metal layer. These impurities may segregate at grain boundaries or accumulate at the surface, altering both the chemical composition and physical structure of the deposit. Studies have shown that such additive-derived impurities can significantly influence the formation of intermetallic compounds (IMCs) and the integrity of solder joints. In particular, impurity-rich regions at the interface can act as nucleation sites for voids during soldering or thermal aging, thereby degrading wetting and joint reliability .In addition to impurity incorporation, organic additives strongly affect surface morphology and roughness, which are critical determinants of wetting behavior. A smooth, uniform surface promotes better solder spreading, whereas rough or porous surfaces can trap flux residues and oxides, inhibiting wetting. Additives such as saccharin, thiourea, and various surfactants are commonly used as brighteners and leveling agents to improve surface finish. These compounds modify the electrochemical polarization behavior and suppress dendritic growth, leading to more homogeneous coatings. However, improper control of additive concentration or breakdown products may result in localized defects, such as nodules or pits, which negatively impact wettability .

Another important aspect is the interaction between organic additives and inorganic contaminants present in the plating bath. Industrial electroplating baths often contain trace metallic impurities such as iron, zinc, or chloride ions, which can interact synergistically or antagonistically with organic additives. These interactions influence deposition kinetics, current efficiency, and coating quality. For instance, certain organic additives are known to mitigate the adverse effects of metallic impurities by modifying cathodic reactions and improving deposit uniformity. Conversely, some impurity–additive combinations can lead to increased porosity or dendritic growth, which compromises solder wetting . Contaminants can also arise from additive degradation over time, especially under conditions of high current density and elevated temperature. Organic molecules may undergo electrochemical or thermal decomposition, producing by-products that accumulate in the bath. These degradation products can adsorb onto the cathode surface or co-deposit with the metal, altering the deposit's chemical composition. The difficulty in accurately controlling additive concentration further exacerbates this issue, as conventional analytical techniques may not fully capture the dynamic changes occurring in the bath . As a result, maintaining bath stability and cleanliness is crucial for consistent solderability performance.

## VI. DISCUSSION

The influence of organic additives and contaminants in electroplating baths on solder wetting characteristics is a critical yet often underappreciated factor in determining the reliability of electronic assemblies, particularly for Cu–Sn–Pb plated components such as relay terminals. Electroplating baths are rarely composed of pure metal salts alone; instead, they are complex chemical systems containing a variety of organic additives, including brighteners, levelers, suppressors, grain refiners, and wetting agents. These additives are intentionally introduced to control deposit morphology, improve surface finish, and enhance throwing power. However, their behavior is highly sensitive to process conditions such as current density, temperature, agitation, and bath age. When not properly controlled, these same additives can become sources of contamination or can decompose into by-products that adversely affect solderability, particularly by altering surface chemistry and inhibiting proper wetting.

From a mechanistic standpoint, solder wetting is governed by surface energy relationships and is often evaluated through parameters such as contact angle and wetting time. A clean, oxide-free metallic surface promotes low contact angles and rapid spreading of molten solder. Organic additives, however, can adsorb onto the cathode surface during electrodeposition, becoming incorporated either physically or chemically into the deposited Cu–Sn–Pb layer. At optimal concentrations, certain additives contribute to fine-grained, smooth deposits that can actually improve solderability. For instance, grain refiners can increase the density of grain boundaries, which may facilitate uniform intermetallic compound (IMC) formation during soldering. However, when additive concentrations exceed their optimal window or when breakdown products accumulate, they can form insulating or carbonaceous residues on the plated surface. These residues act as barriers to metallurgical bonding, leading to increased contact angles, delayed wetting, or even complete non-wetting and dewetting defects.

One of the most critical issues associated with organic additives is their tendency to decompose under electrochemical conditions. High current densities, localized heating, and prolonged bath usage can lead to the breakdown of complex organic molecules into smaller fragments, some of which may be more strongly adsorptive or less soluble. These decomposition products can co-deposit with the metal, resulting in inclusions within the plating layer or forming thin organic films on the surface. Such films are often not completely removed during standard rinsing or post-plating cleaning processes. During soldering, especially in flux-limited or no-clean processes, these residues can inhibit flux activity, preventing effective oxide removal and thus degrading wetting performance. In severe cases, they contribute to the formation of voids or non-wetted regions at the solder interface, compromising joint integrity.

## VII. CONCLUSION

The impact of organic additives and contaminants in electroplating baths on the solder wetting characteristics of Cu–Sn–Pb coatings is both profound and multifaceted, influencing not only the immediate solderability performance but also the long-term reliability of electronic assemblies. Organic additives—such as brighteners, levelers, suppressors, and grain refiners—are intentionally introduced into electroplating baths to control deposit morphology, improve surface smoothness, and enhance overall coating appearance. Under controlled conditions, these additives play a beneficial role by promoting uniform nucleation, refining grain structure, and reducing surface roughness, all of which contribute positively to solder wetting by enabling better spreading and lower contact angles. However, the delicate balance of additive concentration, breakdown products, and interactions with other bath constituents introduces a significant source of variability. When current density fluctuates or bath maintenance is inadequate, these additives can decompose or become incorporated into the deposit in undesirable ways, leading to organic inclusion within the plated layer. Such inclusions act as barriers at the metal surface or within grain boundaries, inhibiting metallurgical interaction between the solder and substrate, thereby degrading wettability. One of the most critical consequences of organic contamination is the formation of surface films that are not easily removed during standard fluxing operations. These films, often composed of decomposed additive residues or absorbed organic molecules, create a chemically inert layer that prevents proper wetting by molten solder. As a result, defects such as non-wetting, dewetting, and solder beading can occur, particularly in fine-pitch or high-reliability applications like relay contacts. Moreover, these organic residues can promote localized oxidation by trapping moisture or reacting with environmental species during storage, further compounding solderability issues. The presence of carbon-rich contaminants detected through surface analytical techniques such as XPS or AES has been strongly correlated with increased contact angles and reduced solder spread, highlighting the direct link between organic contamination and wetting degradation.

In addition to intentional additives, unintended contaminants—such as oils, greases, cleaning residues, or breakdown products from anode bags and filtration systems—can enter the plating bath and significantly alter deposition behavior. These contaminants often adsorb onto the cathode surface during plating, disrupting the electrochemical reduction process and leading to heterogeneous deposition. This results in microstructural inconsistencies such as porosity, voids, and rough or nodular growths, which negatively impact solder wetting by creating uneven surfaces and trapping flux residues. Furthermore, contaminants can interfere with the adsorption-desorption dynamics of functional additives, effectively "poisoning" their intended action and leading to unpredictable deposit characteristics. This is particularly problematic in high-throughput manufacturing environments where bath composition may drift over time without rigorous monitoring and control.

Another important aspect is the influence of organic additives and contaminants on intermetallic compound (IMC) formation during soldering. A clean and well-prepared Cu–Sn–Pb surface facilitates the formation of a uniform and adherent IMC layer, which is essential for strong metallurgical bonding. However, the presence of organic residues can delay or inhibit IMC nucleation, resulting in weak or discontinuous interfaces. In some cases, excessive additive incorporation can lead to the formation of brittle or irregular IMC layers, which compromise joint integrity and increase susceptibility to failure under thermal or mechanical stress. Additionally, organic contaminants can contribute to void formation at the solder–substrate interface, particularly through mechanisms such as outgassing during reflow, which further degrades joint reliability.

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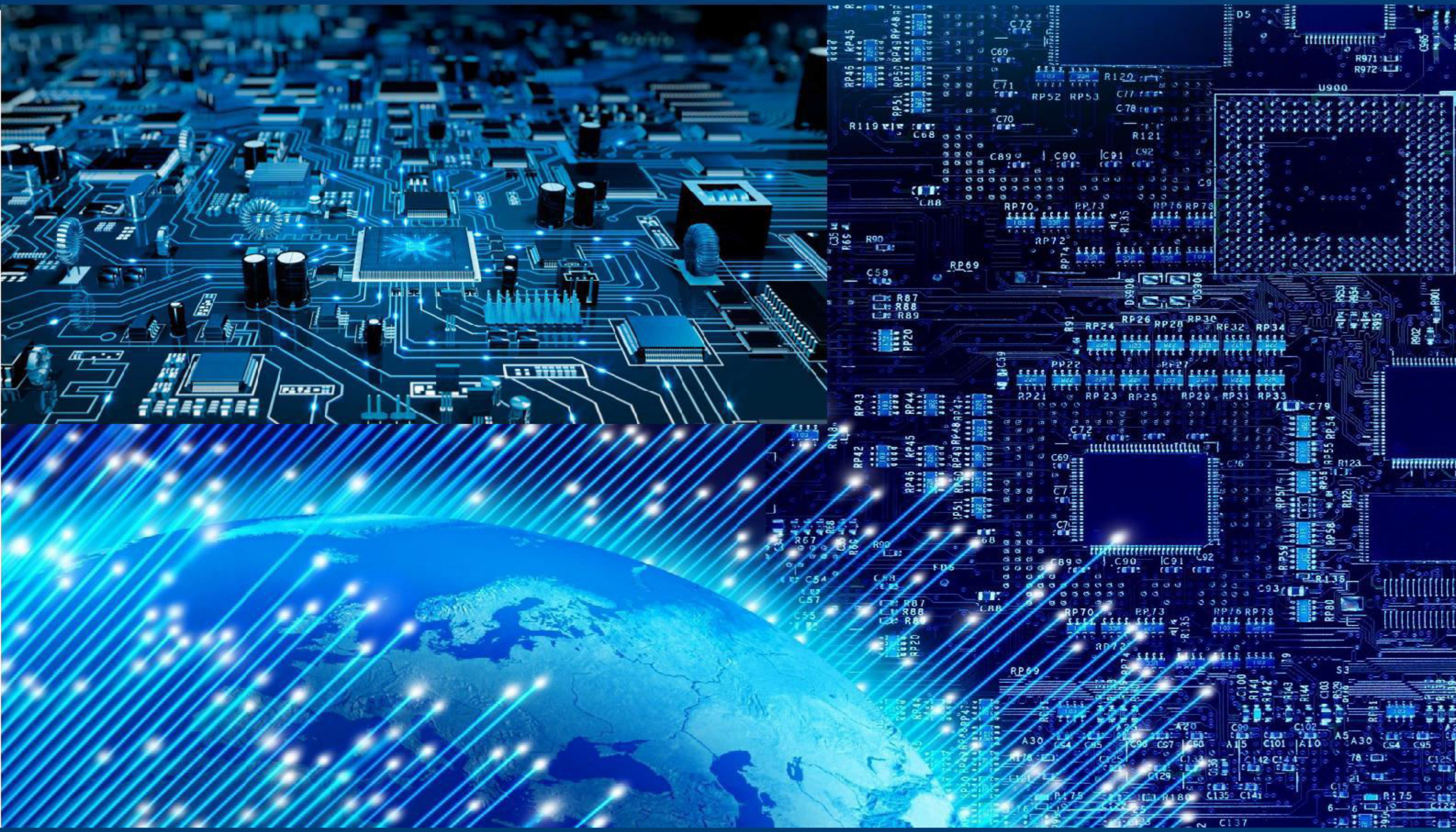

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