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Secondary Nucleation in Emulsion Polymerization: A Review

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Abstract: ***One of the most important aspects of particle formation in emulsion polymerization systems with monomer emulsion feed is of secondary nucleation. It is one such aspect that is not well understood and has fascinated the research community. Understanding secondary particle formation is vital for production of synthetic latexes. On one hand, secondary particles might ruin surface-coating properties of latexes while on the other hand, secondary nucleation contributes to PSD (particle size distribution) broadening and its advantage can be taken to produce high solids content latexes by introducing a new crop of small particles that increases the solids content but prevents the resulting high viscosity. Despite all the extensive work on seeded emulsion polymerization, the available literature on secondary particle formation is scarce. The aim of the present work was to explore the research done on secondary nucleation as it occurs inside the seeded emulsion polymerization systems. The particle nucleation mechanism and the prediction of conditions leading to secondary nucleation for seeded batch emulsion polymerization has been analyzed by a few researchers (Hansen and Ugelstad (1978-1979), [1,2], Morrison and Gilbert, (1995) [3]). This review paper investigates the work of those scientists & researchers to the present-day advances in the field. Some of these models also predict the effect of different variables on particle evolution and the situations in which secondary nucleation can be safely ignored. However, one consideration to be kept in mind is that all such explanations are often based on a large number of unknown parameters and lack physical transparency.***

Keywords: ***Secondary nucleation, emulsion polymerization, particle formation, particle size distribution, latex***

I. INTRODUCTION

The products of the emulsion polymerization are widely used in the industries to manufacture large latex quantities for a multitude of applications such as surface coatings (paints, adhesives…) synthetic rubbers (SBR, neoprene…), various grades of plastics and has a number of practical advantages. An ab initio emulsion polymerization involves the dispersion of one or more water insoluble monomers in a continuous aqueous phase which is stabilized by the droplets of a surfactant. This is followed by the addition of a persulfate initiator to start the reaction. The final product is a latex consisting of colloidal dispersion of polymer particles in water. The most significant procedure in an emulsion polymerization reaction scheme is that of particle formation. It has been the topic of a substantial investigation in the past few decades. It is a process that creates new interfacial area and leads to the generation of a new phase (on top of stabilized monomer droplets and the continuous phase). Particle formation though can also occur in seeded systems (where a pre-existing population of polymer particles is polymerized further), which is known as secondary nucleation. Therefore, by controlling this process, the total particle number, the particle size distribution (PSD) and many other properties of the final product latex can be managed. Particle formation usually occurs via two governing mechanisms – homogeneous nucleation and micellar nucleation. Both of these can contribute to secondary nucleation, depending on the conditions involved. Secondary nucleation leads to a broad particle size distribution (PSD), improves rheological properties and increases the solids content of latexes *[4-6]*. Latexes with high solids content are generally cheaper in terms of production and shipping cost per unit. In the usual emulsion polymerization without secondary particle formation, the solids content of the latex particles is finite because of the high viscosity. However, despite the advantages, in some cases secondary nucleation is undesirable. The presence of a bimodal particle size distribution (PSD) also complicates reaction modeling and in the case of multi-component systems (i.e. the seed polymer and new polymer have different chemical compositions) secondary nucleation leads to 'phase separation' on a sub-micron scale. Also, in manufacture of surface coatings latex, secondary particles can ruin important coating properties *[7]*. It poses vast complexity and its true mechanism is still largely unknown. Therefore, secondary nucleation mechanism in essence could make or break the product latex and needs to be dealt with great care. Generally, polymerization conditions are categorized by two distinct environments – monomer starved and monomer saturated feed conditions *[8]*.

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II. PARTICLE FORMATION MECHANISMS

Particle formation refers to the formation of stable particles which are the primary sites of nucleation. Although several extensive models for particle formation have been proposed, the mechanism of particle formation in emulsion polymerization has remained a controversial topic, the reasons being the small size of initial particles involved which makes experimentally assessing them using transmission electron microscopy (TEM) difficult and also because particle nucleation is not an easily reproducible process. That being said three commonly accepted mechanisms – micellar nucleation, homogeneous nucleation and droplet nucleation developed over the years are discussed below *[9,10,11]*. Both micellar and homogeneous routes involve propagation in the aqueous phase (as initiators are typically water soluble) with the slight amount of solubilized monomer. The third potential nucleation mechanism – droplet nucleation where the initiation occurs within a monomer droplet is a rare phenomenon.

1) *Micellar Nucleation*: This mechanism is generally held to apply to any system where the aqueous-phase surfactant concentration is above the critical micelle concentration (CMC). Postulated by *Harkins, 1946 [12]* and quantified by *Smith & Ewart, 1948 [13]*, the particle formation includes entry of radicals generated in the aqueous phase, into the monomer swollen micelles. The nucleation is complete when all the micelles have been transformed into polymer particles or have given up their monomer and emulsifier to growing particles. The rapid propagation will result in a latex particle. *Min and Gostin [14]* furnished an academic study for secondary particle formation through micellar nucleation. They studied the evolution of bimodal PSD in vinyl chloride semi-batch seeded emulsion polymerization with monomer saturated conditions. They demonstrated that as micelles formed during the reaction, the second crop of particles also formed.
2) *Homogeneous Nucleation*: Here, the aqueous-phase surfactant concentration is below the CMC. It was proposed independently by *Priest, 1952 [15]* and *Jacobi, 1952 [16]* and further developed by *Fitch and Tsai, 1971 [17]*, the radicals generated in aqueous phase, add monomer molecules and further propagate until the oligomer radicals exceed their solubility in the aqueous phase and precipitate. The precipitating radicals either nucleate a particle by absorbing monomer molecules or flocculate among themselves or with a pre-nucleated particle. Flocculation continues until a critical surface potential develops to prevent further flocculation. The radical end is in a monomer enriched environment, thus rapid propagation results and a particle forms. In the absence of surfactant, charged end-groups from the initiator (e.g. $-SO_4^{-\bullet}$) provide colloidal stability.
3) *Coagulative Nucleation:* This is a relatively recent development and can be considered as a subset of homogeneous nucleation. This mechanism has been proposed by *Lichti et al. [18]*. It occurs in two steps. The first step involves the formation of colloidally unstable precursor particles via homogeneous nucleation. This is followed by their coagulation to form stable, mature particles. In a work done on vinyl chloride emulsion polymerization by *Hugo et al. [19]*, it was found that the onset and extent of secondary nucleation can be determined not only by rates of homogeneous nucleation but also by particle coagulation.

III. CONDITIONS FOR SECONDARY NUCLEATION

Investigation of conditions for onset of secondary nucleation was primarily done by *Morrison and Gilbert, 1995 [2]*. Their treatment of secondary nucleation is as follows, the aqueous phase kinetics of seeded emulsion polymerization are based on the theory of homogeneous nucleation proposed by *Fitch and Tsai, 1971 [17]* but also updated to recent works in aqueous phase kinetics field. It was pointed out that a new radical formed from initiator in the aqueous phase will go through some polymerization with aqueous-phase monomer, but must have three possible subsequent routes: (i) termination in the aqueous-phase, (ii) entry into a pre-formed particle, or (iii) creation of a new particle. The emulsion kinetics are based on modified HUFT (Hansen, Ugelstad, Fitch & Tsai) theory *[20]* for successful entry of the radical which states that radical entry (and subsequent formation of particles) occurs only in the systems where the surfactant concentration is kept fairly below the critical micelle concentration (CMC) (i.e. homogeneous nucleation). Although whichever particle formation mechanism is dominant, the process stops when the overall radical entry rate exceeds the rate of creation of new particles. In fact, secondary particle formation is difficult to avoid if micelles are present, since the rate of entry of surface-active oligomeric radicals into micelles is extremely fast, and this results in particle formation by same means. *Coen, 1998 [21]* extended the work of *Morrison et al. [2]* and experimented with a model on PSD, particle number, particle size and secondary nucleation for styrene/persulfate/Styrene dodecyl sulfate (SDS) emulsion polymerization and predicted a general observation that secondary particle formation occurs readily in systems stabilized by polymeric surfactant. The experiments suggested that such surfactants reduce the rate of entry into latex particles and further that the radicals which are unable to enter may instead form new particles. *Prescott et al. [22]* and *Butucea et al. [23]* established the conditions for avoiding secondary nucleation altogether. Seeded emulsion polymerization is generally run in a semi-batch reactor under monomer-starved conditions *[8]*. In the reaction, the monomer gets consumed as fast as it is added. This makes sure that after primary nucleation, entire polymerization occurs under Interval III where there are no monomer droplets present.

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IV. RADICAL ENTRY MECHANISM

One of the most disputed issues over the years in the field of emulsion kinetics is that of radical entry *[10,24,25]*, reasons being the lack of accurately measured experimental data of radical entry rate coefficients and model building while minimizing the number of adjustable parameters. Radical entry mechanism is the process by which radicals move from the aqueous phase into the particle interior. Many models for a successful radical entry have been proposed and not all give the same picture. *Fitch and Shih [26]* presented the 'diffusive entry model', according to which the diffusion of radicals from aqueous phase to particle surface is the rate-determining step for an entering radical. But this conclusion was later discarded as it predicted the value of 2nd order entry rate coefficient to be much higher than the experiments *[7]*. *Yeliseeva [27]* suggested the desorption of surfactant molecules from the particle surface to be the rate determining step for radical entry. Later this model was also refuted due to the lack of experimental proof. The work done by *Adams et al. [28]* demonstrated that the entry mechanism did not depend directly on any event occurring on the particle surface.

Presently the well-accepted model is that given by *Maxwell and Morrison [29]*. They developed the model for persulfate-initiated styrene emulsion polymerization. According to them, an initiator deprived radical was too hydrophilic to directly undergo entry; aqueous phase propagation and termination before entry would have to be considered. The addition of a sufficient number of monomer units to an initiator deprived radical (until the radical achieves a critical degree of polymerization z) so that the oligomer becomes surface active; the entry process of radical is assumed so fast as to be diffusion controlled (suggesting entry into a particle was the only probable fate). The mechanism comprises of the following equations:

Initiator decomposition: $\text{Initiator} \xrightarrow{fk_d} 2\dot{\text{I}}$ E-1

Initial propagation step: $\dot{\text{I}} + \text{M} \xrightarrow{k_{pi}} \text{I}\dot{\text{M}}$ E-2

Subsequent propagation: $\text{I}\dot{\text{M}}_{i-1} + \text{M} \xrightarrow{k_{pw}} \text{I}\dot{\text{M}}_i\ ,\ i < z$ E-3

Termination: $\text{I}\dot{\text{M}}_\text{I} + \dot{\text{T}} \xrightarrow{k_{tw}}$ dead products, $i < z$ E-4

Entry: $\text{I}\dot{\text{M}}_\text{z}$ + latex particle $\xrightarrow{\rho}$ entry E-5

Here $\dot{\text{I}}$ is the derived radical from initiator having dissociation rate coefficient k_d with efficiency *f*. M is a monomer unit, $\dot{\text{T}}$ is any aqueous phase radical, $\text{I}\dot{\text{M}}_\text{I}$ an aqueous-phase oligomer containing *i* monomer units and $\text{I}\dot{\text{M}}_\text{z}$ a surface-active oligomer. k_{pw}, k_{tw} and ρ are kinetic coefficients for propagation, termination and entry (all in aqueous phase).

This model implies that the only chemical fate the z-mer undergoes will be entry as soon as the critical degree of polymerization is attained. The value of z depends on the monomer and initiator end group while k_{pw} depend upon the degree of polymerization. This model by *Maxwell and Morrison [15]* has no adjustable parameters. To this date, it has provided agreement with all studies involving electrostatically stabilized latex systems and is yet to be refuted.

V. MAXIMUM SECONDARY NUCLEATION RATE BY HOMOGENOUS NUCLEATION MECHANISM

The derivation shown for the determination of maximum rate of secondary nucleation in a seeded emulsion system was originally published in PhD thesis of Bradley Morrison, University of Sydney, 1994. This work was never published in a peer reviewed journal, it is replicated here for the benefit of the reader.

This is essentially an extension of the *Maxwell and Morrison [15]* model. The equations from E-1 to E-5 can be extended up to the degree of polymerization j_{crit} whereby the oligomer is completely water-insoluble and precipitates out of solution by undergoing a coil-to-globule transition (Fig. 2.). When length j_{crit} is reached, a new particle is formed and between z and j_{crit} oligomers can propagate, terminate or undergo an entry into a pre-formed particle. The relevant equations are:

$\text{I}\dot{\text{M}}_{i-1} + \text{M} \xrightarrow{k_{pw}} \text{I}\dot{\text{M}}_{i+1}\ ,\ i \geq z$ E-6

$\text{I}\dot{\text{M}}_\text{i} + \dot{\text{T}} \xrightarrow{k_{tw}}$ dead products, $i \geq z$ E-7

$\text{I}\dot{\text{M}}_\text{z}$ + old particle $\xrightarrow{\rho}$ entry, $i \geq z$ E-8

$\text{I}\dot{\text{M}}_{j_{crit}-1} + \text{M} \xrightarrow{k_{pw}}$ new particle E-9

Applying steady state approximations to the above two sets of equations, the following expressions are obtained

$$[\text{I}\dot{\text{M}}_1] = \frac{2\ fk_d\ [\text{I}]}{k_{pw}\,[M]_w + 2\,k_{tw}\,[\dot{T}]_w} \quad \text{E-10}$$

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$$[\dot{IM}_i] = \frac{k_{pw}\, C_w\, [\dot{IM}_{i-1}]}{k_{pw}\, C_w + 2\, k_{tw}\, [\dot{T}]_w}\,,\ 1 < i < z \qquad \text{E-11}$$

$$[\dot{IM}_j] = \frac{k_{pw}\, C_w\, [\dot{IM}_{j-1}]}{k_{pw}\, C_w + 2\, k_{tw}\, [\dot{T}]_w + k_e \frac{N_{seed}}{N_A}}\,,\ z \leq j \leq j_{crit} \qquad \text{E-12}$$

$$\rho = k_{pw}\, C_w\, [\dot{IM}_{z-1}]\, \frac{N_A}{N_p} \qquad \text{E-13}$$

Rate of generation of new particles:

$$\frac{dN_{new}/N_A}{dt} = k_{pw}\, C_w\, [\dot{IM}_{j_{crit}-1}] \qquad \text{E-14}$$

Using iterative substitution into E-14, we can arrive at the final expression

$$\frac{dN_{new}/N_A}{dt} = \frac{2\, k_d\, [I]\, (k_p\, C_w)^{j_{crit}-1}}{(k_p\, C_w + 2\, k_t\, [\dot{T}])^z\, (k_p\, C_w + k_e\, \frac{N_{seed}}{N_A} + 2\, k_t\, [\dot{T}])^{j_{crit}-z-1}} \qquad \text{E-15}$$

Here C_w is the concentration of monomer in aqueous phase, $[\dot{T}]_w$ total aqueous phase radical concentration. N_{seed}, N_{new} and N_p represent the total number of particles of seed, new particles and final particles respectively. k_p is the rate coefficient of propagation at the long chain limit, k_t is the termination rate coefficient and N_A is the Avogadro's number.

VI. SPECIFIC VARIABLES IN SECONDARY NUCLEATION

It is to be noted secondary nucleation involves a large number of variables; the major ones available in the literature with significant work done upon are covered.

1) *Surfactant*: It plays an important role in particle formation in emulsion polymerization. The moment of introduction of additional surfactant and its amount is crucial for the formation of secondary particles as demonstrated by *Chern et al. [30] and Chu et al. [31]* while experimenting with butyl methacrylate (BMA)/methacrylic acid (MAA)/sodium dodecyl sulfate (SDS) system. They formed a bimodal-disperse latex by adding one shot of surfactant at the beginning of the feed. Latex products with bimodal PSD show minimum viscosity. The point at which minimum viscosity is achieved for bimodal PSD-Latices corresponds to the best particle packing efficiency. This property is crucial for producing concentrated polymer dispersion products and is highly desirable in industry. Temperature control is considered an advantage of emulsion polymerization. During a research done by *Mayer et al, [32]*, it was found that momentary addition of emulsifier during high solids emulsion polymerization leads to secondary nucleation with improved temperature control scheme as compared to regular high solids polymerization. Another important surfactant addition method is charging all surfactant into the reactor for whole initial batch seeding period. In this case *Šňupárek Jr et al. [33]* believed that no secondary particles were formed. Amount of surfactant is another variable. It has been shown that by keeping the surfactant concentration less than that of CMC, secondary nucleation in seeded emulsion polymerization with micellar nucleation can be avoided *[34]*. Also during the study of vinyl chloride emulsion polymerization (with micellar nucleation) by *Min et al. [14]*, it was found that at a constant surfactant concentration (above CMC), a system using seed with large surface coverage ratio produced less secondary particles.
2) *Seed*: *Min et al. [14]* reported that the degree of secondary particle formation was inversely linked with seed solids content. By increasing the solids content of the seed, the surface area of seed was increased as number of seed particles increased which decreased the seed surfactant coverage and promoted oligo-radical entry. *Ferguson et al. [35]* in their investigation of secondary nucleation in a surfactant-free core-shell latex system concluded the same results. Besides it was also found that at a given seed solids content, increasing seed particle size decreases number and surface area of seed particles, promoting the formation of secondary particles. *Cheong and Kim [36]* investigated the effect of surface charge density of seed particles on emulsion kinetics and eventually on secondary nucleation. They carried out three emulsifier-free seeded emulsion polymerizations of methyl methacrylate (MMA) using monodispersed seed particles with different surface charge densities, prepared from the styrene (St) and sodium styrene sulfonate (NaSS) comonomers using the two-stage shot-growth process. The results were as follows, the electrostatic repulsion between highly charged seed particles reduces the rate of adsorption of growing oligomeric radical in the emulsifier-free seeded emulsion polymerization which in turn reduces the average number of particles and leads to slow polymerization rates. This limiting polymerization results in a large number of secondary particles being formed in early stages. They proposed a mathematical model to explain these effects by establishing modified Smolchowski equation and the DLVO (Deryagiun-Landau-Verwey-Overbeek) theory *[37]*.

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3) *Monomer Composition*: Water soluble monomers can be used to originate secondary nucleation. *Urretabizkaia et al. [4]* during the high solids emulsion copolymerization of vinyl acetate (VA), methyl methacrylate (MMA), acrylic acid (AA) and butyl acrylate (BA) showed that the formation of secondary particles was observed once the feed began in systems with ≈15 mole% VA and ≈2 mole% AA in monomer emulsion feed. Similarly, *Gaboyard et al. [38]* detected secondary particles in copolymerization of BA, MMA and acidic phosphonated methacrylate (MAPHOS) system with above 6 mole% MAPHOS in monomer feed composition. Monomer composition can also lead to bimodal particle size distribution (PSD). *Pedraza and Soucek [39]* found this by dynamic light scattering (DLS) at ≈ 23 mole% 2-Hydroxyethyl methacrylate (HEMA) in core monomer composition in a functionalized core–shell latex, proposing that HEMA-rich oligo-radicals show secondary nucleation through homogeneous nucleation. *Moayed et al. [40]* while synthesizing bimodal latexes from acrylic monomers established that the richer the aqueous phase in monomer is, the larger the number of secondary particles present
4) *Monomer Hydrophobicity*: *Ocepek et al. [41]* by varying the 2-Hydroxyethyl methacrylate (HEMA) content in emulsion polymerization system with BA/MMA/HEMA latexes, observed the effect of monomer hydrophobicity on secondary nucleation. They proposed a link between hydrophobicity of BA and hydrophilicity of HEMA that affects secondary nucleation in HEMA-rich latexes The BA to MMA ratio in monomer feed composition was varied to determine the monomer hydrophobicity. Further transmission electron microscopy (TEM) was used to detect the signs of secondary particles when HEMA content was above 10 mole%, regardless of BA to MMA ratio. In the absence of BA, no secondary nucleation was observed.
5) *Monomer Feed*: The monomer feed rate has an intense effect on the growth of secondary particles and subsequently on the PSD. *Zeaiter et al. [42]* pointed out that secondary nucleation was reduced and a mono-dispersed PSD was achieved with a high monomer feed rate (4.5×10^{-4} mol/s) while homogeneous nucleation promoted secondary particle formation at low monomer feed rates (2×10^{-4} mol/s). Thus, the latex poly-dispersity index could be easily manipulated by varying monomer feed rate. The smaller sized particles appearing in TEM micrographs are an indication of secondary nucleation. Another related situation is the input feed of monomer emulsion stream instead of pure monomer, *Sajjadi and Brooks [43]* suggested that monomer emulsion feed resulted in a bimodal PSD in BA latex system via homogeneous secondary nucleation. *Sajjadi et al [44]*. examined the conditions for secondary nucleation and particle coagulation in seeded systems of BA under monomer starved conditions and found interesting results: (i) particle coagulation occurred if the particle surface coverage (q_{cr1}) dropped below q_{cr1}=0.25±0.05; (ii) secondary particle formation occurred above a critical surface coverage of q_{cr2}=0.55±0.05, indicating that the presence of micelles in the reaction vessel is not the only prerequisite for micellar nucleation to occur; (iii) the number of polymer particles remained approximately constant if the critical surface coverage was within (q_{cr1}=0.25)< q<(q_{cr2}=0.55),and; (iv) this surface coverage band is equivalent to the surface tension band of 42.50±5.0 dyne/cm that is required to avoid particle formation and coagulation in the course of polymerization.

VII. OTHER IMPORTANT WORKS IN LITERATURE CHARACTERIZING SECONDARY NUCLEATION

1) *Vorwerg et al. [43]* work's in measuring exit and entry rate coefficients in using poly-styrene (PSt) seed particles electro-sterically stabilized with poly(acrylic acid) was complicated when vast amounts of secondary nucleation were observed under conditions where new particle formation should not be possible and it was shown that the amount of secondary nucleation was a function of pH. Therefore, an extensive electrosteric stabilizer reduced the entry rate coefficient for radical entry and for radical desorption, inducing secondary particle nucleation.
2) *Hammond et al. [44]* also faced similar issues as *Vorwerg [43]* while performing similar experiments on polystyrene (PS) latexes stabilized with poly(ethylene oxide) (PEO). Huge discrepancies were observed between theoretical and experimental model. The only probable explanation was that there must be another nucleation mechanism acting in these systems.
3) *Ferguson et al. [35]* in an experiment to find conditions for avoiding secondary nucleation in vinyl acetate and styrene system (described by homogeneous nucleation) to produce core shell morphologies found that it is almost impossible to avoid the secondary nucleation and subsequently core shell particles were unlikely to occur. However, it should be possible to produce the desired morphology using large seed particles and inverse core shell morphology. Secondary particle formation was suppressed by decreasing seed radius, by increasing solids content, and by starved-feed conditions.

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VIII. CONCLUSION

This review paper has covered all the major aspects of secondary nucleation research done so far. Technical and economic problems arising from secondary particle formation concerned scientists and researchers to look for methods for controlling this phenomenon. Nowadays with the advancements in the field of microscopy and imaging especially like those of Transmission electron microscope (TEM) and Dynamic light scattering (DLS), characterization of secondary nucleation and finding its occurrence in various emulsion systems is accessible. The true mechanism and kinetics of secondary particle formation still to this day largely remains a disputed topic. Although several efforts have been made to understand the secondary growth of particles, none claims to have established a set of conditions that generalize this nucleation mechanism. Most experiments provide results for one monomer emulsifier combination that doesn't necessarily hold valid for other combinations. Understanding secondary nucleation remains a critical aspect for defining the properties of the final products of the emulsion polymerization systems.

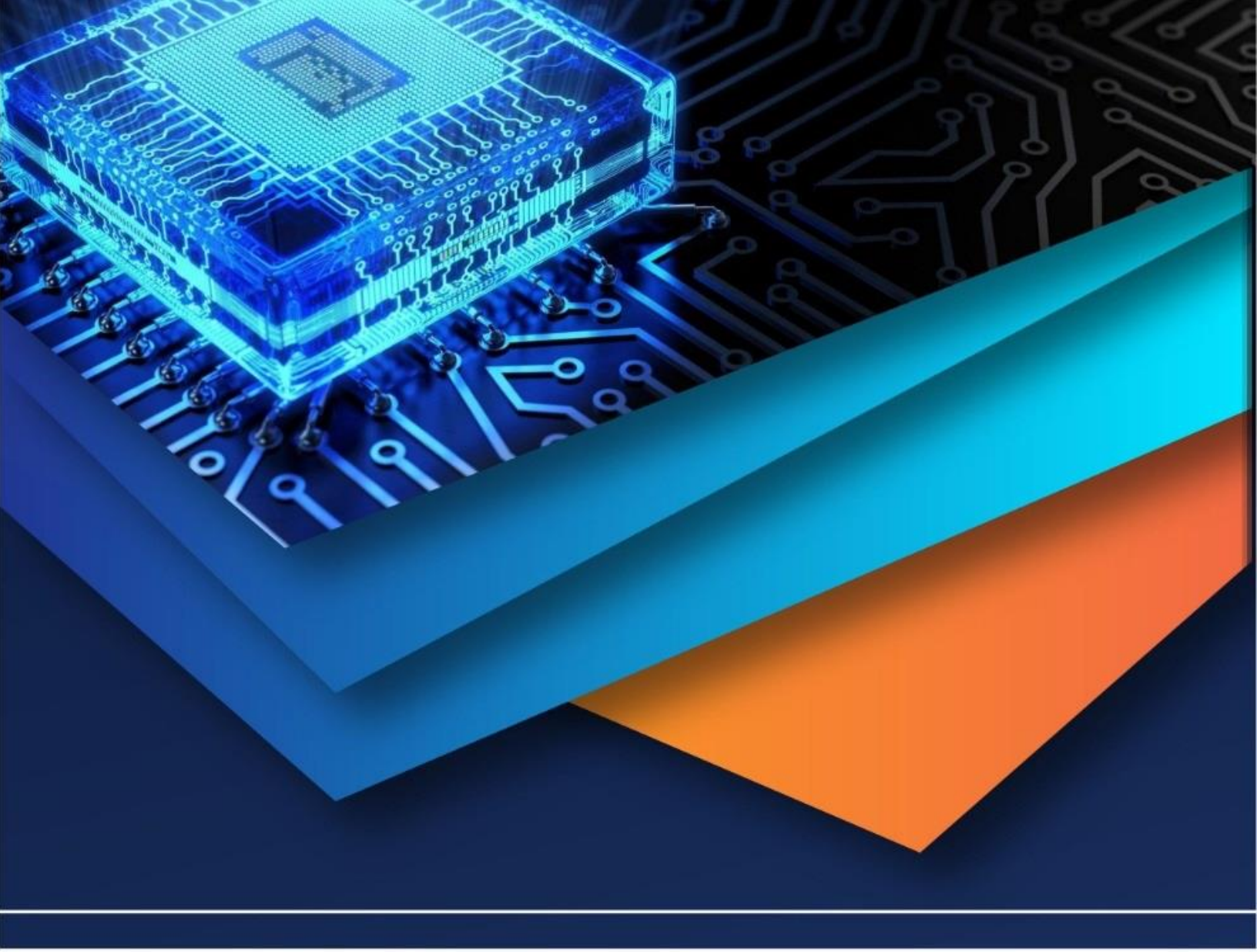
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