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Synthesis of High Solid Content Acrylic Resin by Emulsion Polymerization used as a Binder in Surface Coating

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Abstract: ***The achievement of high solid content acrylic latex at a low viscosity obtained by copolymerization of methylmethacrylate (MMA) and butylacrylate (BA) via emulsion polymerization method. It was found that, for the semi continuous copolymerization of methylmethacrylate and butylacrylate with 63% solid content resin can be obtained through micro emulsion polymerization in presence of potassium persulphate (KPS) as a initiator. Water was used as solvent. The effect of the initiator concentration and monomer to co-monomer ratio on solid content was studied. The copolymer was characterized by Fourier Transform Infrared (FTIR) spectroscopy. Thermal stability of synthesized resins was studied by Thermo Gravimetric Analyzer (TGA). The high solid content acrylic polymer mostly used as a binder in paint industry because of its weatherproof& high thermal stability, productivity and economic factor.***
Keywords: high solid content, acrylic latex, emulsion polymerization, copolymerization.

I. INTRODUCTION

From the environmental protection point of view, water borne paints has been an important topic for research throughout the world. The result of this effort is vast application of waterborne coatings such as acrylic emulsions. In emulsion polymerization heat transfer is very efficient and the viscosity build-up of the polymerisation mass is quite low as compared to other techniques. So emulsion polymerisation is widely used for paint and adhesives. The polymerisation proceeds at the micelle, where the surface/volume ratio is very high, the rate of polymerisation is quite high. Lowest particle size achieved as compared to other polymerisation techniques. Emulsion system generally utilizes water soluble initiator such as persulphates. Emulsion polymerisation yield high conversion in shorter duration.

The micro emulsion synthesis of PMMA with high solid contents via a modified emulsion polymerization method i.e. the semi-continuous emulsion polymerization in the presence of water soluble initiators and a trace of surfactants is reported. PMMA latex with solid contents up to 63% were successfully fabricated. The latex can be directly applied in many fields, which is very attractive for practical production.

The possibility of obtaining high-solids-content microlatexes was investigated. It was found that, for the semi continuous copolymerization of methylmethacrylate and butylacrylate coagulum-free 45.20% solid content latexes can be obtained through micro emulsion polymerization using Dowfax 2A-1 surfactant. The degradation starts around 220°C though for D it is at 260°C and 30% degradation is observed at 420°C. This is a typical degradation pattern of acrylate polymers.[5]

The high solid content nano composites based on poly (methylmethacrylate-co-butylacrylate)/nanosilica was synthesized via mini emulsion polymerization in a semi-continuous operation. Oleic acid was used to act as a coupling agent between silica surfaces and polymer. Latexes with solid content of 42% were obtained, containing 5% by weight nano-SiO_2 with respect to polymer. It may be observed that the glass transition temperature of the nanocomposite (Tg = 26℃) is higher than that of the pure acrylic latex (Tg = 13℃). [3]

It was aimed to investigate the usage of pure waterborne poly (acrylate) resins, in which methyl methacrylate (MMA) was used as the main monomer, as binder in paint industry. The film formation structure and properties of resins, which were synthesized systematically, were investigated in order to determine the properties of monomers in acrylic resin structure which characterize properties of binders. The emulsion polymerization was carried out for 3 h with 200 rpm shaking rate at a temperature of 70±1◦C.

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The selected polymers have low Tg values (between 21 and 37.5˚C) showing that synthesized polymers have moderate flexibility. [7]

To achieve a 100 µm dry film thickness with 30% by volume solid thermosetting coating, it is necessary to apply a wet film thickness of 330 µm. To achieve the same 100 µm dry film thickness with the 80% by volume solid coating a wet film thickness of 125 µm is required. [9]

In the present process we thoroughly investigated the effect of synthesis parameter i.e. initiator concentration, monomer to solvent ratio on solid content and properties of latex. The initiator plays a dominant role in the free radical polymerisation of high solid acrylic based resins. High solid content with low viscosity exhibits excellent property for binder which also takes care of environmental safety by formulating solvent free coatings.

II. EXPERIMENTAL WORK

A. Materials

Methyl methacrylate (MMA) (LobaChemie, Mumbai, India) and butyl acrylate (BA) (Otto Chemie, Mumbai, India) were purified by treating with 10% Sodium hydroxide (NaOH) (LobaChemie, Mumbai, India) solution followed by washing with De-ionized water (Aquapath, Mumbai, India) to remove inhibitor. Potassium persulfate (KPS) (LobaChemie, Mumbai, India) of extra pure grade were used without further purification, Sodium lauryl sulfate (SLS) (LobaChemie, Mumbai, India) surfactant was used as received.

B. Methodology

The polymerization reaction is a chemical aspect. In this system, polymerization system, catalyst system and the solvent system includes. This refers to the physical aspects of polymerization reactions which decide whether the monomer is polymerized in its condensed or gaseous state. It is polymerized as such or along with other inert components such as solvents and non-solvents, a factor such as the nature of the monomer and the type of polymerization mechanism chooses.

The experimental apparatus consisted of a 2 liter cylindrical four neck flask made of glass. Standard Four neck flask provided with a high speed stirrer. It is equipped with motor and with external jackets for heating and cooling. Proper arrangements are provided for the control of reaction temperature and the speed of the stirrer.

Emulsion polymerization was carried out in four neck flask with a mechanical stirring at 200 rpm to 300 rpm, under constant nitrogen supply. Temperature of reactor system was kept constant at 55 ^{0}C ± 5 ^{0}C. Pre-weighed surfactant (SLS) and water were charged in the reactor and the addition of MMA and BA monomer by certain time interval was followed. N_2 gas supply is mandatory to ensure absence of oxygen into reactor. Agitation was start at rate of 200 rpm and simultaneous purged the N_2 gas into reaction mixture. After one hour of agitation the aqueous KPS solution was then added from the top and the polymerization was initiated. During the polymerization, adequate of the reaction mixture were withdrawn from the reactor at different time interval to check viscosity.

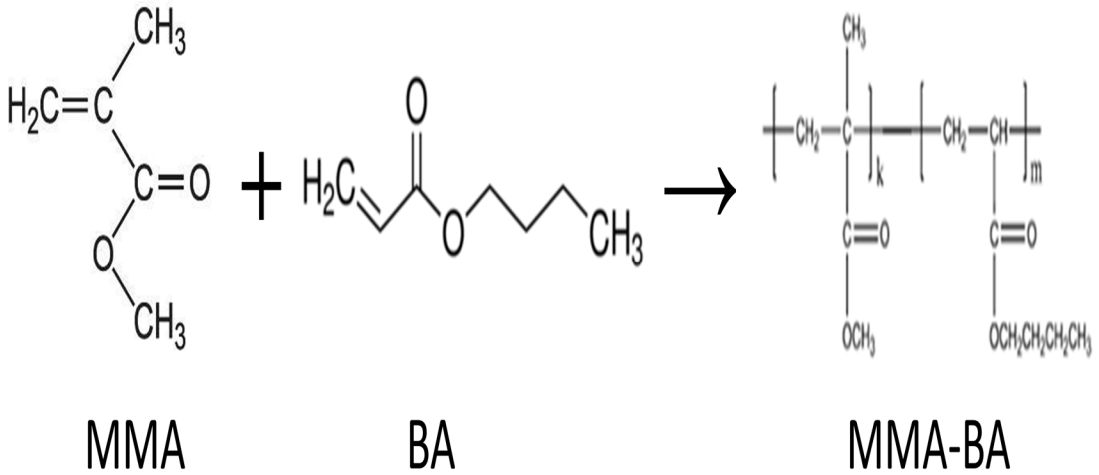

Fig. 1: Reaction of synthesis of MMA-BA

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Recipes used in the semi continuous polymerization of Methyl methacrylate (MMA) and butyl acrylate (BA) are given in ***Table 1.***

Sample ID	Polymer	Monomer(w/w)	Monomer:Solvent	Solvent(w/w)	Surfactant(w/w)	Initiator (w/w)	Solid Content (%)
Sample-A	Poly(MMA/BA) 1:1	36.20	1:1.6	60.3	3.37	0.13	54
Sample-B	Poly(MMA/BA) 1:1.5	37.5	1:1.5	57.56	4.56	0.38	73
Sample-C	Poly(MMA/BA) 1:1.5	40	1:1.4	56	3.66	0.44	60
Sample-D	Poly(MMA/BA) 1:0.3	39	1:1.54	60.25	0.3	0.45	63
Sample-E	Poly(MMA/BA) 1:1	35	1:1.677	58.72	5.81	0.47	75
Sample-F	Poly(MMA/BA) 1:1	35	1:1.67	58.67	5.76	0.57	77.68
Sample-G	Poly(MMA/BA) 1:1.4	46.77	1:1	46.77	5.87	0.58	66.57

Table 1: Sample recipes with solid contents

III. RESULTS AND DISCUSSION

A. *Total Solid Content*

The solid content is calculated as per ASTM D2834 at 75^0C temperature for 60 minute.

$$Solid\ Content = \frac{W3 - W1}{W2 - W1} X100$$

Where,

W1 is the weight of petridish; W2 is weight of petri dish along with sample before heating whereas W3 is weight of petri dish and sample after heating.

In the series of reactions, to optimize the initiator concentration, initiator concentration was varied between 0.1 to 0.6 with the monomer to co monomer concentration. Very little difference was observed in solid content with variation in initiator concentration around 54-77%. At lower and higher concentrations of initiator, coagulum formation was observed. To improve the percentage of solid in the latex, monomer to co monomer concentration was varied from 1:0.3 to 1:1.5 At higher concentrations of monomers to co monomer ratio coagulum formation was observed because of reduced stability of the latex. With increase in ionic concentration of the continuous phase, solid percent was improved from 54 to 77.8. At 77.8% solid content the initiator concentration was 0.57, whereas at 54% it was 0.13.

B. *Effect of Initiator Concentration On High Solid Content*

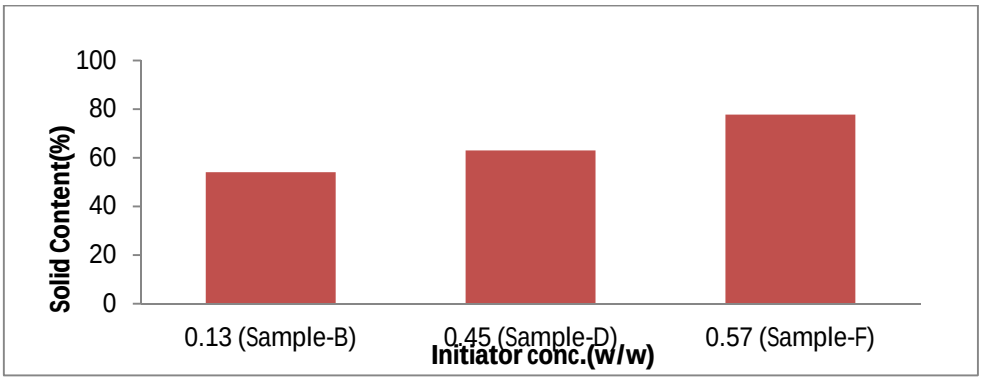

Fig. 2: Initiator conc. v/s Solid content

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Above Graph shows that when initiator concentration increases with constant reaction temperature then high initiator concentration leads to excess generation of free radical which increases rate of initiation of polymerization hence solid content will increase.

C. FTIR Analysis

Infrared spectra of the samples were obtained by a FTIR 1-S Affinity from 400 - 4000 cm^{-1} range. Michelson interferometer (30° incident angle) Equipped with dynamic alignment system sealed interferometer with auto dryer with Diamond as an ATR crystal and DLATGS detector equipped with temperature control mechanism.

Fourier Transform Infrared (FTIR) Spectroscopy is only supporting tool for identification of structures. $-CH_3$ & $-CH_2$ aliphatic group is between 2990-2850 cm^{-1} because MMA-BA copolymer has long aliphatic chain of Butyl Acrylate, CH_3 aliphatic compound is between 1465-1440 cm^{-1} because MMA-BA copolymer has CH_3 group, C=O aldehydes is between 1740-1720 cm^{-1} and C-O-C ether is between 1240-1070 cm^{-1} because both MMA and BA has C=O and C-O-C group, the presence of MMA and BA monomer can be predict by intensity of C-H peak for alkenes. In the Fig.3 both the spectrum C-H peak is weak with very short intensity hence the concentration of monomer is negligible.

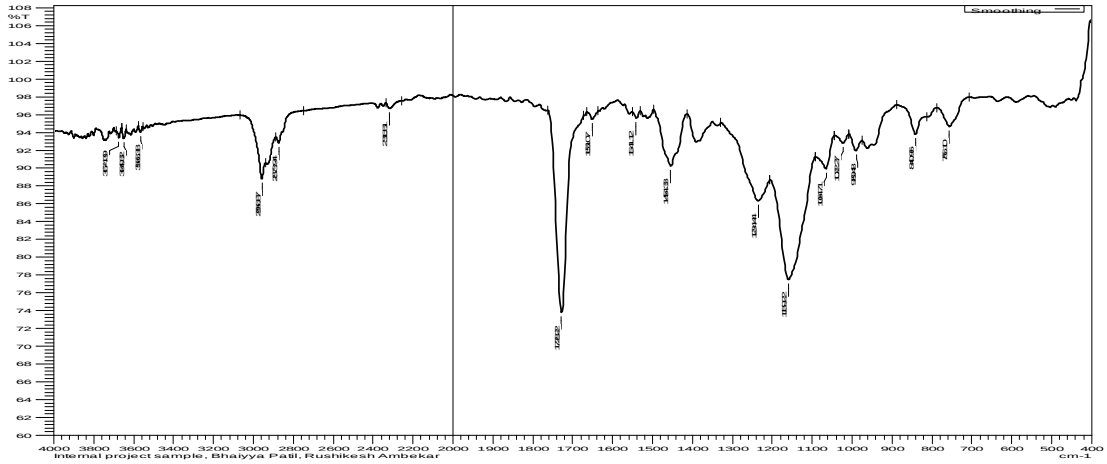

Fig. 3: FTIR of Sample-D

D. Thermo Gravimetric Analysis (TGA)

TGA curves determine that degradation process which goes along with the weight reduction, started just after the thermal decomposition. Thermo Gravimetric Analyzer (TGA) was carried out on TGA-50 (Shimadzu, India) under nitrogen atmosphere. The rate of heating was 10˚C/min and the samples were heated up to 600˚C. Fig.4 and Fig.5 shows the TGA thermograms of acrylic latex. The TGA thermogram investigated by peak of sample-A (Fig.4) at 478.54°C for the derivative of the weight loss for acrylic latex up to 95.19%. While in the case of sample C (Fig.5), peaks at 423.1°C, for the derivative of the weight loss 90.92%.

The presented peaks are close to that observed for TGA analysis. When monomer concentration was increase in the polymerisation system then thermal stability will also increases. The Fig.4 & 5 distinguish when monomer to solvent ratio is 1:1.65 then weight loss start from 142˚C and when monomer to solvent ratio is 1:1.4 then weight loss start from 249.8˚C because the concentration of solvent is less therefore thermal stability is more. The final residual weight percents at high temperatures (600°C) are listed.

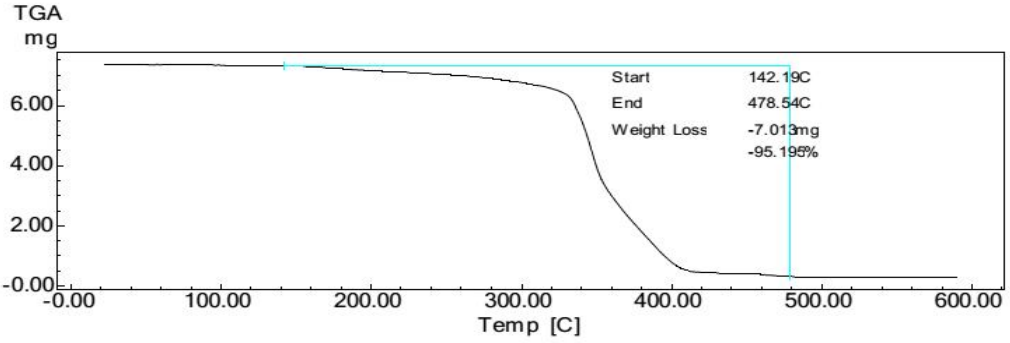

Fig.4: TGA curve for sample A

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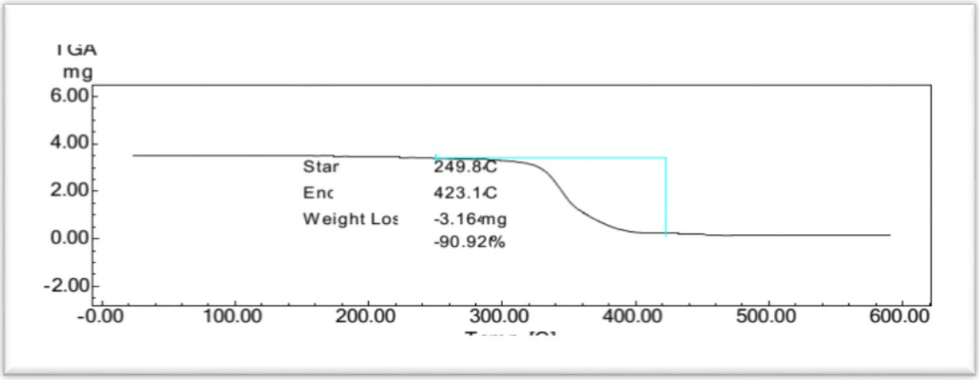

Fig.5: TGA curve for sample C

1) *Determination of Viscosity:* The viscosity was determined by B ford cup. The cup was filled up to the mark with a given fluid. The nozzle was closed and kept it on the vertical stand. The nozzle was open and time was noted in seconds. It determines by the formula: $\eta = 48.5 / B$

Where, η is viscosity in poise and B is flow time for test liquid. Flowing table shows the viscosity for different compositions.

Sample ID	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F	Sample G
Viscosity(poise)	1.89	2.16	1.78	1.24	2.27	2.51	2.34

Table 2: Viscosity of different samples

From Table 1 & 2 Sample B,E & F has observed the solid content is more than 70% i.e. got the high solid content but from table 2 these samples has observed the viscosity is more than 2 poise. Sample A, C & D shows the low viscosity value. Amongst this samples D has the lowest viscosity with 63% solid content. So this sample will be more appropriate binder for surface coating due to its optimum solid content with low viscosity.

IV. CONCLUSION

Acrylic monomers that control the flexibility and hardness of the resin which are butyl acrylate (BA) and methylmethacrylate (MMA) respectively. Optimization of emulsion polymerization process with regard to initiator concentration and monomer co monomer ratio is done with different combinations. The all samples are tested successfully and it is found to have satisfactory appearance and physical properties to be used as binder in the paint industry. Synthesized binder exhibits high solid content, low viscosity, high transparency and excellent film forming ability.

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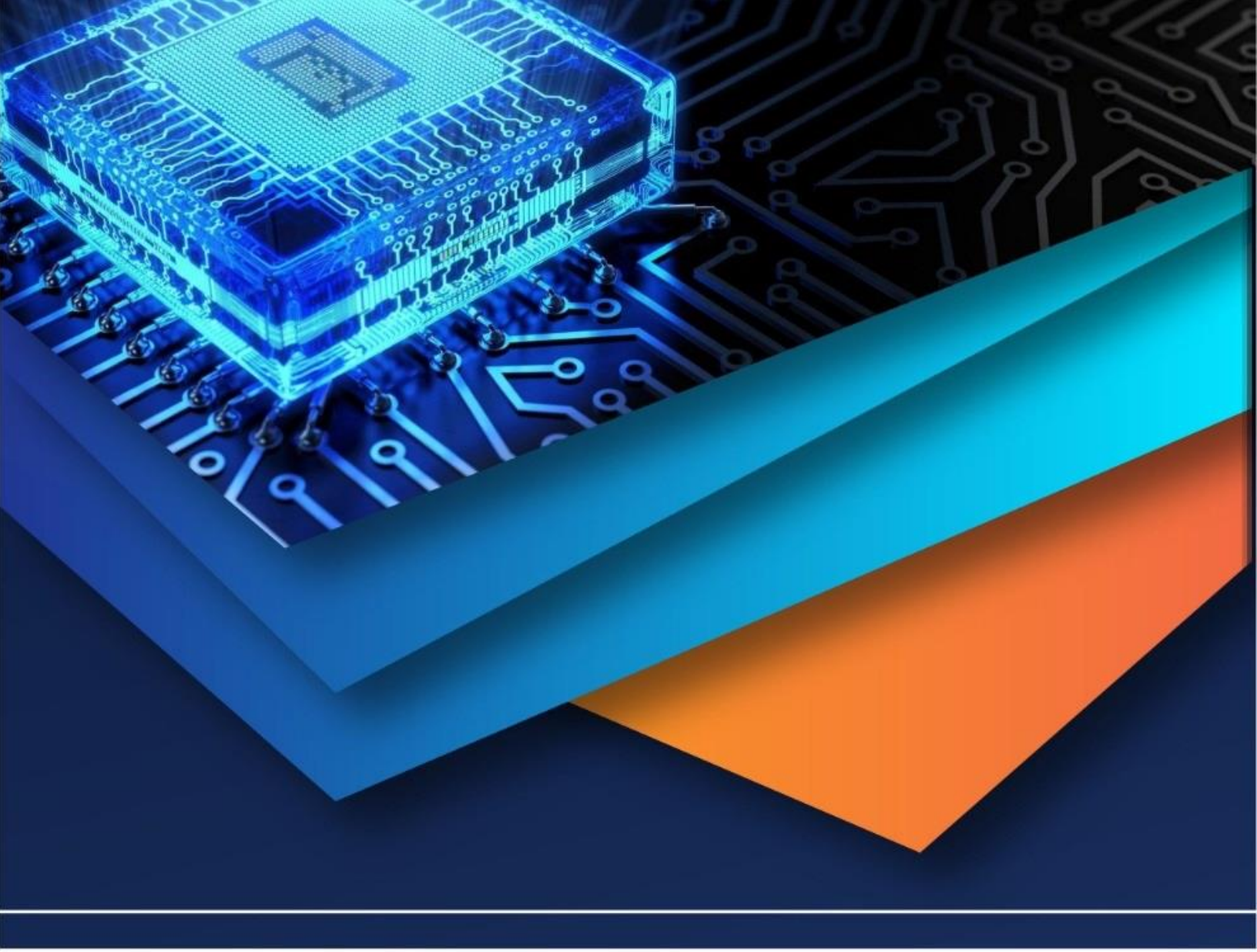

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