



Review on Opacifying Polymeric Pigment: Reconceive Hiding

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Abstract: A hollow core-shell latex particle synthesized through sequential semi-continuous emulsion polymerization method has served as a promising substitute to white inorganic pigments useful for the coating applications. Incorporating more amount of Titanium dioxide in the paint is a costly measure with diminishing returns. Severe paint defects such as phase separation, agglomeration or settling arises due to incompatibility between inorganic pigments and organic resins. Opaque polymer helps in minimizing the cost of Titania in surface coating formulations. It provides white appearance and hiding due to diffraction of incoming light in different directions. It has gained widespread importance over the years due to its unique structure and morphology. It has potential applications in other technologies such as micro-encapsulation, paper coatings and controlled release of drugs. Osmotic swelling – the most prominent approach involves the synthesis of an ionizable core particle which is encapsulated by another polymer functioning as shell, followed by neutralization with the addition of suitable alkali. Significant techniques have been developed including hydrocarbon encapsulation and water-in-oil-in-water emulsion in this field.

Received on 30-08-2018
Accepted on 29-10-2018
Published on 12-11-2018

Keywords: Core-Shell, Titanium Dioxide, Latex, Opacity, Paint.

DOI: <https://doi.org/10.6000/2369-3355.2018.05.02.4>

1. INTRODUCTION

Energy and material costs are rising for the multibillion-dollar architectural coatings market, yet tough competition between industry leaders prevents passing on increasing manufacturing costs to consumers. Almost one third to half of the cost for a typical latex paint is titanium dioxide (TiO₂), which is used as a pigment to whiten the coating or increase its opacity. Moreover, paint comprises of latex polymer binder which provides strength and impermeability, water as a liquid medium in case of waterborne paints and additives designed to aid film formation or boost product shelf life.

In coatings industry, acrylic technology has expanded in the form of acrylic solution polymers precursor to emerging acrylic emulsions. Market acceptance of acrylic emulsion as coating binders is mainly due to its outstanding properties like color stability, transparency, and resistance to weathering and aging. Resistance to hydrolysis and lack of absorption of ultraviolet light (which is the high-energy portion of the light spectrum most responsible for degradation) are the factors which increase the weathering resistance of acrylic polymers.

Pigments are incorporated as colorants and fillers in materials such as paints, cosmetics, and drugs. Conventionally several inorganic pigment particles such as

TiO₂, barium sulfate and calcium carbonate have been employed in paint compositions. TiO₂ induces an exceptionally high opacifying effect which is derived from high light scattering coefficient, a consequence of its fine particle size and a high index of refraction ($n=2.5-2.8$). There are four naturally occurring sources of TiO₂: rutile, anatase (TiO₂), ilmenite (FeTiO₃) and leucosene (TiO₂/FeTiO₃), the latter of which is a weathered form ilmenite. Out of the four forms only rutile and anatase are used as pigments, with rutile being approximately 20% better than anatase at scattering light. Although rutile and anatase have the same chemical composition, they vary in their densities, lattice structure and refractive indices.

A desirable latex paint composition combines a pigment or an air void that provides opaque characteristics with a binding agent. Opacity or hiding power is an important optical property of white paint coating, resulting from multiple scattering of incident light due to interactions with pigment particles. High opacity develops due to large contrast in refractive indices between pigment and the surrounding medium [1, 2]. The difference of the refractive index between the polymer shell (e.g. $n_{\text{polystyrene}} = 1.46-1.68$; $n_{\text{PMMA}} = 1.49$) and the ($n_{\text{air}} = 1.0$) inside the voids, produces intensive scattering of light, thereby accelerating the intensity of the diffracted light (i.e. diffuse light) and lowering the intensity of the reflected light (i.e. peculiar light). This results in improving the hiding ability of the core-shell particle.

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An opaque pigment will impart desirable properties to a paint formulation by allowing the paint to completely hide a substrate with a thin film. Pigments need to be stable, safe and insoluble in water and solvents, have a high refractive index and be suitable for production in an optimized colloidal particle size. The opaque polymer is a non-film forming, water-based emulsion polymer that forms microscopic air voids on drying, as the water diffuses through the polymeric shell. These micro voids of fine and narrow particle size distribution behave like a primary pigment, thereby influencing efficient dispersion of TiO₂. On drying, the liquid irreversibly evaporates out of the void and gets replaced by air, thus yielding a small particle with the capacity of internal reflection and scattering of light. Hollow Latex Particle (HLP) has gained great commercial value as a plastic pigment due to its excellent hiding ability and low density. In addition, the opaque polymer particles have a relatively low specific surface area compared to equivalent volumes of TiO₂. The dry opaque polymer has a low product density and moderates the specific gravity of the coating.

For the past decades, the control on morphology and design of latex particles has been a crucial area of research in polymer science [3, 4]. These composite latex particles possess unique colloidal and physical properties which are different from homogeneous and solid particles. It has gained importance due to its superior features such as deformation performance, low density, versatility and good stability. Hollow polymeric microsphere with exceptional structure and morphology is a kind of latex particle enhancing hiding ability [5, 6].

General core-shell structure plays a crucial role in fabricating emulsion particles with unique morphology due to interpenetrating networks and ionic bonding between core and shell particles. Compared to simple copolymer/polymer blend, particles with core-shell structure can enhance properties like abrasion resistance, water-resistance, weather-resistance, stain-repellence, anti-radiation performance, tensile strength, impact strength, adhesive strength and remarkably reduce the minimum film forming temperature of the polymer emulsion [7].

Core-shell, hemispherical, or inverted core-shell particles (where polymer at the second step is located at the center and the seed polymer resides at the periphery of the particle) are examples of particle morphologies which can be designed through modification of thermodynamic and kinetic factors.

1.1. History of Innovation

Void structured spherical polymer particles were first produced by Kowalski and Vogel. They developed a process for the preparation of hollow latexes based on Osmotic Swelling principle which has become a prominent synthetic approach to synthesize hollow particles. This technique was subsequently improved by Vanderhoff and Okubo.

Osmotic swelling is the most suitable method for developing commercialized polymeric pigments. In this method, a carboxylic acid group which acts as a core (containing low molecular weight oligomer) gets encapsulated by shell polymers. Acid groups get ionized and form polyelectrolytes on neutralization with appropriate alkali. The increased inner osmotic pressure due to electrolytes leads to the absorption of water which ultimately results in swelling [2, 9].

Rohm and Haas [8] - pioneers in this field focused on optimizing these particles to function as an opacifying agent. Dow scientists have discovered better ways to hide the surface coatings over past 50 years. They had successfully developed the world's first synthetic hollow spherical pigment for paints. Presently, Ropaque-Opaque Polymer is manufactured in 17 countries across six continents. It has been accurately engineered to optimize the air void, thereby continuing to maintain the industrial standards for its remarkable quality, reliable supply and on-going innovation in opaque polymer technology. Conclusively, Dow, Arkema, Ashland, Interpolymer, Visen, Hankuck, Junneng and Indulor are the leading manufacturing companies of opaque polymer today, market been well established over the regions of North America, South America, Europe, Africa, Middle East, and Asia-Pacific.

1.2. Phenomenon Responsible for Hiding Power

Paint film is composed of pockets of air termed as voids, following are the types: Intra particle voids which develops within pigment particles, Intra resin voids that are present within the resin and Inter coating voids which are located at the pigment particles-resin interface [10]. Air voids can aid opacity in the paint and coating films via three mechanisms: Air voids that scatter light, small air voids which reduce the refractive index of the binder, thereby increasing the light scattering ability and foams which scatter light at the air-polymer interface [11].

Preparation of HLP begins with polymerization of highly swollen seed particles with the monomer. The small void is formed when the stress concentration of polymerization shrinkage occurs at the interface of the seed polymer inside the cross-linked polymer particle.

1.2.1. Theory of Scattering

The opaque polymer provides white appearance and hiding because of scattering of light randomly at all angles. When an incident beam of electromagnetic radiation within the visible region interacts with a particle having a diameter close to the wavelength of radiations, non-selective scattering radiations are produced. Bohren and Huffman revised the mathematical explanation of light scattering for spherical particles which was first described by Gustav Mie [12, 13].

Mie Theory describes scattering over the entire spectrum of light, ranging from infrared to visible spectrum, stretching up to ultraviolet region. The Mie scattering efficiency is

dependent on the following factors: Shape and size of the particle, the refractive index difference between medium and particle, the wavelength of light, and the number of particles which behave as scattering centers [14, 15].

Apart from scattering due to refraction, direct scattering from the surface of the particle termed as Rayleigh scattering is observed in hollow particles. The Rayleigh scattering is inversely proportional to the fourth power of the wavelength of light. Blue shade may be imparted by Rayleigh scattering if the optimization of particle size is inappropriate since the blue light has the smallest wavelength. Therefore, the particle size shouldn't exceed the upper limit to obtain the desired opacity or a lower limit to minimize the blue shade. Several studies and investigations were carried out for determining the optimum size of hollow particles. It was calculated that the optimum diameter size of the hollow pigment and the void should be between 0.5 and 0.6 μm and 0.25 and 0.3 μm , respectively [63].

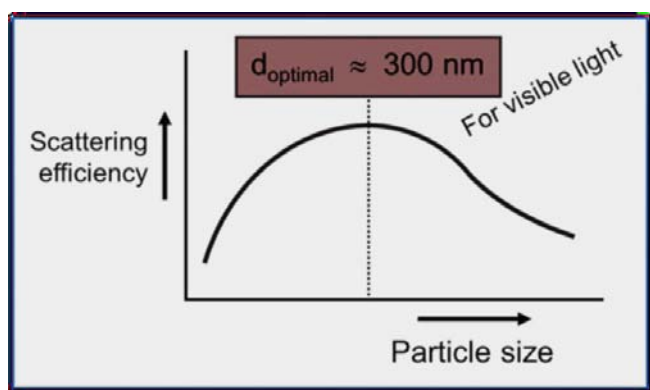


Figure 1: Scattering of Light by Particles in Coatings.

Taking into consideration the refractive index of conventional polymeric binders which ranges between 1.3–1.7, the optimum size of air-filled hollows which provides the maximum scattering intensity and consequently enhances hiding power of paints extends from 350 to 850 nm, as calculated from the below equation [64].

$$D = \frac{1.45\lambda}{\pi(N-1)}$$

Where: D– is the hollow diameter, λ - is the wavelength, N- stands for the refractive index of the binder

2. INFLUENCE OF PIGMENT ON PAINT PROPERTIES

The composition of modern water-borne architectural coatings strongly depends on the desired application properties and therefore on the pigment volume concentration (PVC). In general, paints consist of thinner/diluent (water/solvent), a polymeric binder, pigments and filler particles. Additionally, additives like coalescents, thickeners, dispersants and defoamers are added to enable a sufficient stability and obtain good application properties.

An opaque polymer is a special type of hiding pigment that can replace the most crowded and least efficient portions of TiO_2 in the paint. The hiding strength of the paint is highly dependent on the following factors: differences of refractive indices between the pigment particles and medium, particle size and dispersion of the pigment (i.e. particle shape and degree of aggregation of the particles) & the composition of pigment in the resin and the thickness of the applied film.

Some factors that could affect the hiding power of white pigments:

- **Particle Size:** If the particle size is too small, wavefront passes through & around it. Thus, no scattering occurs & the dispersion is transparent.
- **Pigment Dispersion:** For obtaining an efficient dispersion, wetting the pigment in a good dispersion medium is important along with breaking down of the larger particles through milling.
- **Concentration on the Paint Film:** With the high concentrations of pigment, crystal particles become more compact, resulting in loss of efficiency of dispersion & hiding power.
- **Porosity of the Film:** Porosity contributes positively to increase the hiding power.

Hiding power relies mainly on prime pigments. Extender and anticorrosive pigments have minimal effect on hiding power.

Underlying substrate is invisible to observer in case of pigment & visible with use of extender. Pigment enhances hiding power, while extender results in poor opacity

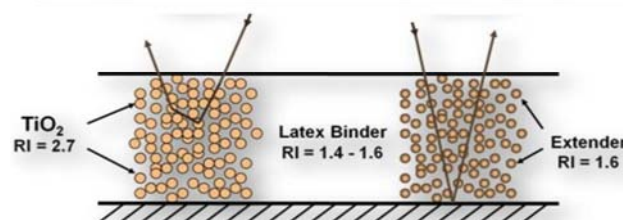


Figure 2: Influence of Pigment & Extender on Opacity.

2.1. Role of Pigment Volume Concentration and Critical Pigment Volume Concentration in Paint Formulation

PVC is one of the key parameters describing paint properties. It strongly determines application properties such as gloss, scrub resistance, tensile strength in modern water-borne architectural coatings. Homogeneous distribution of the pigments is essential in order to obtain maximum hiding power with the small amount of costly TiO_2 . The pigment distribution is determined by the colloidal interaction of the TiO_2 particles, which tend to aggregate and form clusters in the paint. Cluster formation can result in a higher surface roughness of the film along with minimal hiding power due to reduced light scattering efficiency. The scattering efficiency is strongly dependent on the dispersion state of TiO_2 particles

within the paint film. By using a combination of cheap filler material such as Calcium Carbonate and small amounts of TiO_2 , high PVC is achieved in flat paints. A high portion of filler reduces desired opacity and gloss but increases surface roughness. The polymeric binder content reduces within the paint when the portions of pigment and filler particles are increased. Opacity increases along with increase in PVC, to a certain point, after which, the opacity starts decreases with an increasing PVC. This arises from crowding of the pigment particles, where multiple particles acting as one large particle is effective at scattering light. Properties of a coating change abruptly as the PVC increases. These changes occur at the point termed as Critical pigment volume concentration (CPVC).

The CPVC was first defined by Asbeck and Van Loo in 1949 [16, 17]. CPVC is the PVC at which the binder concentration is just hardly adequate to completely wet pigments and fillers. Furthermore, binder occupies the interstitial spaces between the particles. The pigments and fillers are very closely packed. Above the CPVC, the porosity of the coating increases rapidly. The locus of the CPVC is strongly dependent on the particle size, the particle size distribution, and the shape of the pigment and filler particles. Latex paints have a CPVC of about 60%.

2.2. Effect of Pigment Dispersion in Paints

The incompatible nature of inorganic opaque pigments results in weaker interaction with organic resins & polymers in which they are embedded. In addition, higher densities of inorganic pigments form sediments due to gravitational effect. The physico-chemical incompatibility and high-density differences between inorganic pigments and organic resins results in paint imperfections such as phase separation, clusters and flocculation.

In order to increase compatibility of inorganic pigments and overcome dispersion problems some methods were proposed in literature. By reducing the size of pigments, the decreased dimensions reduce the surface tension, prevent flocculation and provide higher dispersibility. According to Stokes-Einstein equation, sedimentation rate of pigments decreases dramatically with reduction in the size & diameter.

However, decreasing the size has unfavourable effect on scattering efficiency where white appearance shifts to blue color according to Rayleigh scattering and with even further reduction pigments become transparent. The optimum size of the commercial TiO_2 lies between 0.25 and 0.45 μm . Modifying the surfaces of inorganic pigments and encapsulating them with polymers in a core shell structure is an interesting method. Encapsulation yields compatibility with resin however it is not a solution to the high-density problem.

In solvent-borne systems, a sterical barrier controls the problem of re-agglomeration whereas a water-borne system requires the ionic mechanism of electrostatic repulsion, accomplished through the usage of dispersants, thereby preventing pigment settling. Stabilizing the well-dispersed regions and avoiding re-agglomeration is the primary task of the dispersing agent [18, 19].

Uneven distribution and clustering of pigment particles have a detrimental impact on application properties such as gloss and hiding power. Nature of emulsion and type of dispersants play an important role in influencing the pigment distribution. HLP has proved to be an excellent opacifier and overcome the problems associated with low and high concentrations of TiO_2 in paint formulations [20].

3. SYNTHESIS OF CORE-SHELL LATEX PARTICLES VIA DIFFERENT ROUTES

3.1. Osmotic Swelling

A low molecular weight carboxylic acid group (usually methacrylic acid/ acrylic acid are preferred) containing core polymer is synthesized inside micelles through Oil-in-Water (O/W) emulsion polymerization. After the addition of monomer and subsequent polymerization, the core which usually contains 10-30% ionizable compound is encapsulated by shell polymer. The carboxyl groups form polyelectrolytes on neutralization with the suitable alkali resulting in increased osmotic pressure inside the shell polymer [9]. The obtained polymeric latex delivers much higher osmotic pressure than the non-neutralized acidic polymer. The osmotic pressure expands the core, and upon removal of water, the void is created inside the shell. The hard shell must be thermally

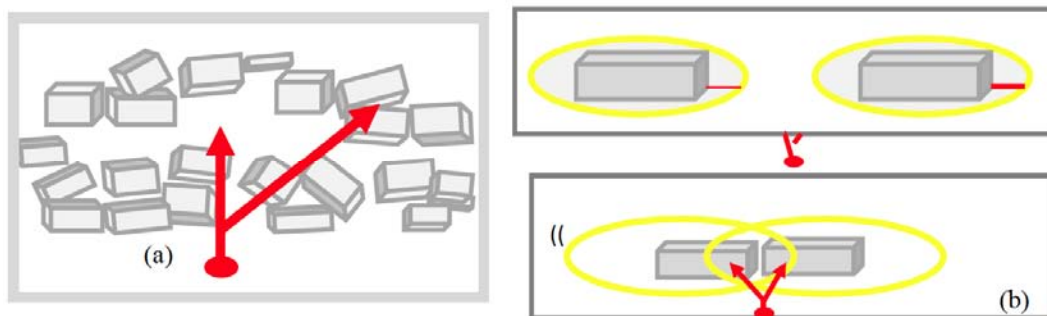


Figure 3: (a) Random Distribution of TiO_2 in Classic Paint Formulation, (b) Inefficiencies of TiO_2 - Gaps develop when concentration is low, overlapping reduces its performance when concentration is high.

stable and permeable to water. Thermoplastics such as styrene, styrene-methyl methacrylate copolymer are usually used in the preparation of shell. The shell can be coated with another layer such as with silica nanoparticles which improves the mechanical properties and allows functionalization [21, 22].

Preparation of hollow latex – HL based on osmotic swelling approach, includes many factors such as polymerization recipe, feeding mode in each step and post-treatment condition. The amount of unsaturated carboxyl monomer used is the crucial parameter for the generation of the hollow structure. The presence of acid-functional unsaturated monomer in the shell polymer is useful for stabilization of the multi-stage emulsion polymer and assuring permeability of the shell with the swelling agent.

3.1.1. Core Development

In the HL preparation, the build-up of osmotic pressure from carboxyl groups in the alkali post-treated process is the driving force to form void structure, implying that increasing content of unsaturated acid improves the swelling degree and gives a larger void. The high level of carboxylic acid when incorporated in emulsion copolymer has several disadvantages. Copolymers of polar materials don't absorb surfactants effectively, leading to instability and coagulation. The further partition can significantly lead to the formation of oligomeric species which act as dispersants or flocculants. Proper encapsulation of structured particles with a core containing carboxylic acid copolymer becomes problematic. The core tends to remain at the polymer-water interface. Rohm and Haas developed technology which doesn't depend on osmotic swelling related to co-polymerised ionic monomers. In this case, they imbibe low molecular weight organic acids such as benzoic acid or acid anhydrides into the cores for later encapsulation followed by ionization with a base [23, 24]. Alternative approach involves incorporation of acrylate and methacrylate ester comonomer which has the capacity to hydrolyse and swell at higher temperatures after particle formation. In this case, prior to swelling, the cores are

encapsulated with a tie coat followed by an outer shell of styrene copolymers. Following this type of methodology, a strongly alkaline medium under pressure is required at high temperatures around 150°C for expansion to occur [25, 26].

3.1.2. Influence of Monomer Feeding Style and Core Diameter on HLP

Core Size and type of Monomer Feeding Mode employed are important factors determining the efficiency of core encapsulation in the multistep emulsion polymerization. Bigger core particles contain more amounts of carboxyl groups, implying that stronger driving forces which develops during alkali post-treatment process, produces collapse structures. In the monomer addition, the emulsion polymerization process becomes unstable due to coagulation while in the pre-emulsion addition; coagulation is prevented by pre-emulsified monomer mixture fed into the reaction system. Core particles obtained from the monomer addition are usually interconnected and exhibits less spherical structure. "Long Hair" like appearance is found on the surface of latex particles which leads to entanglement and aggregation of core particles as monomer droplets are flexible to migrate in the aqueous phase in absence of surfactant. Unbalanced swelling forces during the alkali post-treatment, certainly gives rise to muddled morphology on the final latex particles. This problem is solved with the development of uniform morphology and narrow size distribution through pre-emulsion addition mode. Stability of latex is achieved due to constant ratio maintained between surfactant and monomer during particle growth stage [27].

For commercial applications the essential requirements inherent to HL made by osmotic swelling are as follows: The swellable core particles capable of expansion should be of sufficient volume relative for the formation of a micro-void which can scatter light efficiently. The diameter of the void and thickness of the shell defines scattering efficiency. The void volume fraction of commercial hollow products ranges from 30 to 50%. The shell with appropriate transport properties, composition, and network structure facilitates the

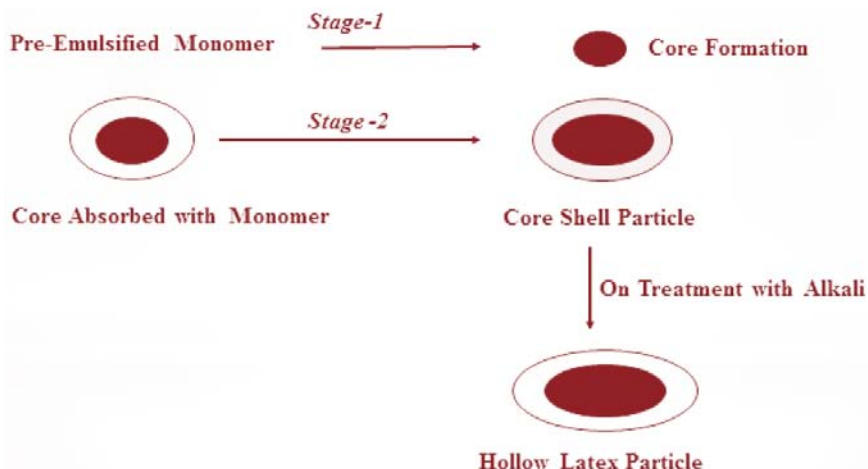


Figure 4: Mechanism of Osmotic Swelling Technique.

transport of water into the interior of the particle. The shell must have thermoplastic flow properties at the expansion temperature, sufficient cohesive forces and uniform morphology to retain the integrity of the particle.

3.1.3. Investigations Reported for Osmotic Swelling Technique

Preparation of core-shell polymer particles by two-stage emulsion polymerization is the simplest technique reported in the literature [22, 28]. In this method, seeded emulsion polymerization is adopted to prepare the hydrophobic core with some amount of carboxyl groups and hydrophilic shell polymer latex. On neutralization with base osmotic pressure builds up in the shell latex as core expands, thereby developing opaque hollow polymer microspheres. The final latex particle size is controlled by the short nucleation stage at the start of the reaction and by the stabilization of the nuclei during the growth stage. Nucleation depends on the formation of radicals. The addition of seed particles at the start of the reaction removes the variability in the nucleation step. The polymerization rate and particle size can be easily controlled. Seeded polymerization provides less reactor build up, reduces pebbles and improves the stability of the emulsion.

Okubo and Mori [29, 30] prepared different kinds of core-shell polymer particles. Moreover, they developed a dynamic swelling method for the preparation of many multiform core-shell particles. They used a styrene-Methacrylic acid copolymer. In the first step, by addition of aqueous base potassium hydroxide, pH was maintained between 7-13. Heating was provided for 3 hours at 75°C, followed by rapid cooling to room temperature. In the second step same heating and the cooling pattern was followed but pH was reduced to 2.2 by addition of hydrochloric acid. Apparently, considerable control can be exercised over the nature of the microvoids by the variables applied to this two-step treatment.

Structural factors such as composition, core/shell mass ratio, and crosslinking level are critical parameters contributing to the morphology and properties of the core-shell hollow latex particles. Vanderhoff *et al.* [31] synthesized soft hydrophilic core, interlayer with moderate polarity and hard hydrophobic shell latex particles. Interlayer was incorporated for effective encapsulation of hydrophilic core with the hydrophobic shell. Further, optimization of kinetic and thermodynamic factors was done to achieve the preferred morphology. Choi *et al.* [32] demonstrated that the proper encapsulation and morphology uniformity of the core/shell latex particles could be improved by the introduction of the crosslinking structure along with progressively reducing the hydrophilicity from the inner to the outer part of the shell particle.

The influence of several factors such as: Core/shell emulsion polymerization techniques, feeding methods of shell comonomers and alkalization swelling conditions on size, morphology and volume expansion are important for

formation of stable, uniform sized, clear structured hollow polymer microspheres [33-35].

A.K. Khan [36] studied on optimizing shell composition of core-shell particles for developing extreme hiding. A series of core-shell latexes were synthesized at multiple ratios comprising poly (n-butyl acrylate-co-methyl methacrylate-co-methacrylic acid) as core and poly (styrene-co-acrylonitrile), poly (butyl acrylate-co-methyl methacrylate) as shell. The core-shell emulsion of shell composition (styrene: acrylonitrile at 60:40 ratio) showed the best optical properties useful for decorative coatings.

A series of core-shell polymeric particles with poly (n-butyl acrylate-co-methacrylic acid-co-ethylene glycol dimethacrylate-EGDMA) as core and poly (styrene-co-methyl methacrylate) as shell were prepared by Lakhya J Borthakur [37]. EGDMA used as crosslinking agent avoided the probability of gel formation and bonded core and the shell phase together. The spherical morphology was achieved at 60:40 core/shell monomer ratio. These particles were applied as a pigment/binder in emulsion paint, paint properties like a gloss, rock hardness and opacity were compared with the standard sample. Reduction of TiO₂ in the paint formulation up to 17% was possible with similar hiding power by the above core-shell latex.

The analysis was carried out to understand the effect of the composition of the unsaturated acid monomer on particle morphology. Methacrylic acid – MAA gave better results instead of acrylic acid while the synthesizing three-layer core/shell latex particles with a hydrophilic core and hydrophobic shell. An interlayer with moderate polarity was inserted between core/shell molecules for effective encapsulation. Fine pores existed inside the alkali-treated particles when 12.2 wt. % of MAA was used for core preparation. With MAA content increased from 20 to 30 wt. %, particle morphology changed from hollow to collapse structures. When the concentration of MAA was further increased to 40.0 wt. %, it was difficult to prepare uniform multistage particles [38].

Based on the osmotic swelling method and the previous research on the three-layer core/shell latex, a four-layer core/shell polymer latex – sequentially consisting of High carboxyl soft-core, a transition layer, rigid supporting layer, and an outermost film forming layer was designed by Xinyi Huang [39]. The effect of crosslinker content (Divinylbenzene) on the four-layer core/shell latex and the final HL was investigated.

Nausaen [40] carried out a comparative study to estimate the opacity level of HLP consisting of poly (methyl methacrylate-co-divinyl benzene-co-acrylic acid) and solid particles comprising of poly (styrene-co-acrylic acid) and poly (styrene-co-methyl methacrylate-co-acrylic acid). The coated film of HL showed better hiding efficiency with multiple scattering compared to solid particles. Chitosan was incorporated into HLP, which served as an opacifying agent for special indoor

coating applications due to the good dispersion of the pigments. The capacity to chemically adsorb the indoor air pollutant formaldehyde provides HL-Chitosan molecules a platform to use it as a special white pigment.

3.2. Hydrocarbon Encapsulation

The principle in the literature defining hydrocarbon encapsulation method to create hollow or voided particles through emulsion polymerization technique is less researched for most commercial applications. A vacuum or steam stripping step is required to recycle the hydrocarbon. The need for a recycle stream can be inherently compatible with the infrastructure of an existing plant producing commercial quantities of latex. Thereby, few capital requirements may inhibit the commercial development of a hydrocarbon-based process. In non-solvent encapsulation method, low molecular weight polymers are swollen with a hydrocarbon. Shell monomer and hydrocarbon should have good compatibility however its polymer is incompatible with it. Shell monomer gets polymerized after swelling of micelle with non-solvent. While polymerization proceeds, phase separation occurs and shell polymer moves to hydrocarbon micelle interface. Single hollow polymer particle is formed after stabilization of structure with the removal of non-solvent and crosslinker [41].

3.2.1. Selection Criteria for Suitable Solvents

One distinction that can be made with this technology is on basis of introduction of hydrocarbon during post-treatment of the latex particle or encapsulation during the polymerization. With the former approach, a core particle is formed and swollen in a good solvent along with subsequent polymerization of shell polymer on the swollen core. It is suggested that shell polymer is cross-linked and has different polarity compared to the core polymer. Non-polar solvent i.e. hydrocarbon, which is selected should have minimal solubility in the shell polymer for swelling action [42].

A general approach for obtaining hollow particle that provides particles of both emulsion and suspension size diameters was explained by the Japanese Synthetic Rubber Company [43].

3.2.2. Parameters for Choosing Anti-Solvents

Encapsulation of a non-solvent for the polymer being formed through emulsion polymerization has also been investigated. Thermodynamic and kinetic factors governing this approach have been modelled and published [41]. The process relies on the polymerization kinetics as well as solution thermodynamics within the dispersed particles to achieve encapsulation. Hence, structured particles and a swelling stage are not required. Further, it specifically requires a non-solvent hydrocarbon for the polymer being formed, thereby eliminating the need for polymers of different polarities to undergo phase separation.

3.2.3. Working Principle of Hydrocarbon Encapsulation

A low molecular weight seed is swollen with a solvent and monomer mixture. The polymerization of the monomer leads to the formation of a polymer which has different polarity from the seed polymer. The incompatibility of the two polymers in a common solvent leads to the phase separation and encapsulation. A unique feature of this process technology is that the seed particle can be eliminated and a polymer gets solubilized in the monomer. Thus, by manipulation of the solution thermodynamics of a polymer–monomer–solvent mix within a dispersed particle, it is possible to achieve encapsulation in a multistage process. Normal shear mixing conditions are required for this encapsulation process which proceeds in form of seeded, semi-continuous emulsion polymerization. A seed concentration is optional in defining the final particle size. The hydrocarbon mixture becomes a poorer solvent for the polymer being formed, as the monomer is consumed, leading to phase separation within the domain of the particle.

This initially occurs at the water–dispersion interface forming a desired shell concentration of polymer. Crosslinking monomer and second monomer charge are introduced to stabilize the morphology established during the encapsulation stage. The morphology of the particle can vary from hollow to micro-domain depending on the conversion rate at the beginning of the second monomer charge. When the degree of conversion reaches 30–40%, the polymer phase separates throughout the particle, and this polymer matrix becomes the locus for subsequent polymerization process [44].

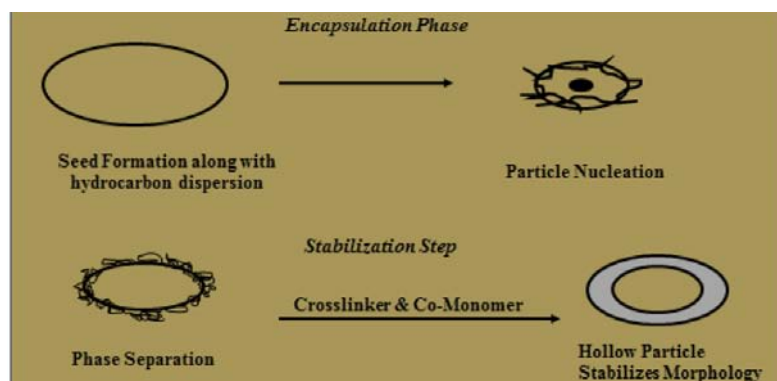


Figure 5: Schematic Diagram of Non-Solvent Encapsulation.

3.3. Water-in-Oil-in-Water (W/O/W) Emulsion

“Oil” term is generally referred to any organic liquid which is immiscible in water. In Water in Oil (W/O) emulsion, water is the inner phase and oil is the continuous outer phase. W/O/W emulsions are mainly used in controlled drug delivery systems, food processing, and cosmetics [45-47]. Conventionally surfactant oil solution is prepared in the first step, followed by addition of water to the oil phase dispersed with proper mixing methods like mechanical agitation or ultrasonic homogenization. Alternative methods are reported in the literature, such as, (i) Low-energy emulsification and High internal phase emulsification (HIPE)

Low-energy emulsification comprises of: “Phase Inversion Temperature” and “Catastrophic Inversion” techniques. In Phase Inversion Temperature method, the temperature has to be maintained properly, the hydrophilic-lipophilic nature of surfactant is varied and this effect results changing O/W emulsion to W/O emulsion [48, 49]. Catastrophic Inversion method indicates the abrupt increase of the volume fraction of dispersed phase. Water is gradually added inside the pre-emulsified monomer. After a critical volume fraction is attained, O/W emulsion switches to W/O emulsion [50]. Moreover in HIPE method; the volume fraction of dispersed phase is much more than W/O emulsions. Through the following volume of water, the shape of droplets get distorted and divided into a film of the continuous phase [51, 52].

Emulsion stability is a key feature for producing multi-hollow structured particles by means of W/O/W emulsion polymerization. The nature of the monomer phase, the diameter of water droplets, type and structure of surfactants, the viscosity of monomer, and the density difference between water and monomer directly affects the stability [53, 54]. Creaming, Coalescence, Oswald Ripening, Phase Inversion Sedimentation, and Flocculation are the mechanisms contributing to the destabilization of the emulsion system.

Recent synthetic methodology incorporated with W/O/W emulsion technology is the production of a new generation opaque polymer pigment with multi-hollow structure applicable for surface coatings. In comparison to single hollow particles, multi-hollow polymer pigment improves the scattering efficiency and imparts improved hiding power. Asmaoglu [55] synthesized multi-hollow structured polymer particles by suspension polymerization of W/O/W emulsion system, where Methyl Methacrylate and EGDMA monomer mixture was used as the oil phase. In this case, water droplets are dispersed in the monomer phase inside the spherical micelles by using a hydrophobic surfactant.

High-speed mixing and ultra-sonication were employed. The effects of surfactant and cosurfactant composition in terms of “Hydrophilic-Lipophilic balance- (HLB)” on the stability of the W/O emulsion and the size of water droplets were studied. “Span 80 and Tween 80” surfactant mixture at an HLB value of 8 provided optimum stability and lower droplet sizes. The

surface morphology and hollow structure of polymer pigments were analyzed by scanning and transmission electron microscopy techniques. The opacity values were evaluated by contrast ratio measurements.

4. TESTING PROCEDURES FOR CORE-SHELL LATEX PARTICLES

A standard characterization of the physical properties is a difficult task for HLP due to the presence of an air void. The measurement related to the percentage of solids serves misleading while analyzing the rheological performance of a coating formulation. Thus, the volume fraction and the weight fraction of the particles in a formulation are considerably different. Percentage of solid content is measured carefully. The effective weight solids for a given voided particle can be calculated simply by treating the encapsulated water as a solid material.

The particle size distribution and dimensions of the void within the particle are crucial parameters for characterization. Most standard particle-sizing techniques depend on density or light scattering for the detection of particle diameter. Electron Microscope is the most reliable equipment to determine the dimensions of the void, the thickness of the shell and the overall particle size. It requires drying the sample, which may sometimes result in shrinkage.

Coopper and Devon [56] have reported mathematical equations regarding the use of a disc centrifuge for characterizing the dimensions of HLP, thereby helping to solve the particle density and particle size. Strawbridge and Hallet have made significant contributions explaining the application of light scattering techniques of hollow coated particle [57].

Cryogenic Scanning Electron Microscopy reveals the changes in microstructure. It occurs when latex coating containing hollow particle is dried. The spherical nature of core-shell latex is confirmed by Scanning Electron Microscopy, to understand the morphology, Transmission electron microscopy is appropriate.

Opacity is the level of how opaque a substance is, commonly referred to hiding power, and most often measured employing contrast ratios. Contrast ratios are usually measured using a spectrophotometer, where YB and YW are the lightness of the paint, using the XYZ color system, over a black and white background.

Opacity occurs when the light is refracted; the level the light refracted is quantified by the refractive index [58].

$$\text{Contrast ratio} = 100 * YB / YW$$

Particles that have a higher refractive index will refract light to a greater degree than particles with a lower refractive index. Scattering occurs at the interfaces of two substances that have different refractive indices. Scattering will occur multiple

times within a paint film, due to contact of the scattered light with multiple pigment particles and interfaces. This leads to complete reflection before the light reaches the substrate, indicating that a pigment with a higher refractive index will have a greater probability of ensuring good opaque film. Coating thickness plays an important role in film opacity, targeting manufacturers to engineer a film that will give complete opacity to save resources and reduce formulation costs.

5. APPLICATIONS OF EMULSIFIED OPAQUE POLYMER PARTICLES

5.1. Architectural Coatings

Hollow emulsified particles have served as a synthetic pigment contributing to opacity in architectural coatings due to its effective light scattering properties. The pigment is a very crucial ingredient in architectural coatings capable of imparting color, hiding the substrate, and modifying the performance of a coating, e.g. Functional pigments improve corrosion resistance [59]. Opaque Polymer engineered by experts provides exterior performance benefits such as, improved dirt-pickup resistance, excellent durable film, and superior tint retention. The coating industry recognized the utility of an air void as a hiding ingredient for paint. The opacity of a paint film will not be effective by extender pigments unless they are used at higher levels [60]. The commercial products developed in the coating industry have a uniform particle size, typically between 0.4 and 0.5 micrometers along with void volume fraction ranging from 25–40%. Percentage of solids is typically between 35–40%. HLP has proved to be a suitable and cost-effective replacement for the introduction of air voids inside the paint film without increasing the porosity of the film. By reducing levels of TiO₂, hiding, brightness, and wet scrub resistance improve whereas gloss and viscosity are unaffected in paint formulations.

5.2. Paper and Paper Board Coatings

5.2.1. General

Coating for paper and board is primarily done to improve properties like color, opacity, gloss for the surface of the product, relating in terms of rate of drying, moisture sensitivity and response to printability. Traditionally binders for pigments for coating paper and boards were prepared from natural raw materials: Carbohydrates such as starch, protein casein, and gelatine of animal origin. Over the years with the development of polymerizable vinyl and styrene-based monomers, synthetic resins have replaced the natural sources for synthesizing paper coatings.

5.2.2. Latices for Paper Coatings

HLP has been developed for paper coating applications through the technique which involves a shrinkage mechanism during polymerization. Two types have been developed,

'Plastic Pigment' and 'Binder-Pigment' latex particles. Paper coatings with excellent hiding power, gloss and brightness are achieved by these latices. Paper properties are highly dependent on particle size and a void volume of HLP. The presence of a void within the particles reduces the density of hollow particles contributing to the increased opacity [61].

Whiteness and micro-porosity of paper coating are dependent on particle diameter and chemical composition of polymer latices. Studies have been reported for acrylic and vinyl copolymer, notably in typical formulations with kaolin/ Calcium Carbonate as fillers. With the increase in particle size, both the properties improved but tear strength of paper reduced, indicating that tear strength is an important factor for selection of polymeric binder and pigment [62].

5.2.3. Printing Operation of Paper Coatings

Coated paper and paperboard are usually printed and the coating must exhibit a suitable level of smoothness and opacity along with sufficient strength to withstand the printing operation. High-speed application of tacky inks to the coating surface under shear conditions is frequently involved in printing. Tacky inks help in removing the small undesirable pieces of the coating from a weak coating, thereby leaving unprinted spots on the printed product; this phenomenon is known as "picking". Surface sizing increases pick resistance for paper coating. Abrasion resistance, linting resistance, and folding resistance are other important properties related to the strength of the coating. Performance of a final product is decided by the choice of binder used for paper coating application. Features like: surface strength, compressibility, gloss, opacity, brightness, and ink receptivity are affected by the selection of polymeric binder and pigment.

5.2.4. Processing of Paper Coatings

The gloss of paper coatings is enhanced by influencing the mechanical properties of HLP with high pigment volume concentration during the calendaring of the coating. When the calendaring process is employed, the shell polymer being thermoplastic in nature will deform under application of stress. Reutilization of HLP will produce less severe processing conditions during the coating process. HLP improves the brightness and opacity of paper coating due to the effective light scattering capability of these particles, indicating that a small number of particles get deformed during the calendaring process. The ultimate finishing properties of coated paper are dependent on overall composition, the dimension of voids and processing conditions. The effective solids determine the rheological characteristics of the formulations.

6. CONCLUSION

Opaque Polymer has attracted great attention and strong commercial interests owing to its unique properties: low density, opacity, fine particle size and unique morphology. It has served as a new dimension to latex technology and

developing applications in low TiO₂ paints, diagnostics, drug delivery system, paper coatings, removal of pollutants, micro-encapsulation and stimuli-responsive systems. The coupling of structured latex technology and an expansion process based on osmotic swelling is the most prominent method for obtaining sub-micron size hollow polymer particles, invented by Kowalski and his colleagues later on commercialized by Rohm and Hass Company and its competitors.

However, due to the high cost of TiO₂, deteriorating resources and an energy-intensive manufacturing process which yields undesirable by-products, substitutes are required to maintain a source of white pigment in the future, thereby abiding with trending sustainability regulations. Opaque polymer pigment has revolutionized in the field of emulsion polymerization and proved as a benchmark for partial replacement of white inorganic pigments up to 15-25% in the paint industry.

ACKNOWLEDGEMENTS

Authors would like to thank the Department of Polymer and Surface Engineering, Institute of Chemical Technology, Mumbai for the support provided.

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