PRODUCTION AND CHARACTERISATION OF POLYVINYL ACETATE FOR EMULSION PAINTS

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(JANUARY, 2010)

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A Project Report Submitted in Partial Fulfillment of the Requirement for the Award of

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of Technology Minna, Nigeria.

(JANUARY, 2010)

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DECLARATION

I hereby declared that this project entitled 'Production and Characterisation of Polyvinyl acetate for Emulsion paints' is an authentic work of mine and has not been presented for award of any degree elsewhere.

All quotations are indicated and sources of information are specifically acknowledged by means of reference.

20-01-2010.

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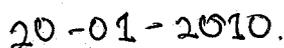
STUDENT SIGNATURE   DATE

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CERTIFICATION

This research project by Akindiya Martin Akinwale (2004/18566EH) has been examined and certified under the supervision of Engr. Dim. P. E. to the adequate in scope and quality for the partial fulfilment of the requirement for the award of Bachelor of Engineering (B.ENG) in Chemical Engineering.
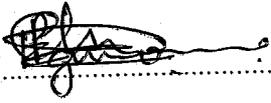
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(PROJECT SUPERVISOR)

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Engr. J. O. OKAFOR   DATE

HOD (CHEMICAL ENGINEERING)

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EXTERNAL EXAMINER   DATE

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DEDICATION

This research project work is dedicated to the Almighty God, the I AM THAT I AM, the King of Kings, the creator of heaven and earth for his love and continuous protection over me.

ACKNOWLEDGEMENT

All praise and adoration goes to the I AM THAT I AM, the invisible God, the doer and the performer of all actions and reactions that takes place in my life, the Almighty God. You are all that I am.

My warmest thanks goes to my mum, dad and stepdad, Mrs A. R. Imarahi, Mr M. A. Akindiya and Mr S. A. Imarahi for their love, care, unflinching financial and moral support throughout my existence in life, especially my schooling years. Furthermore, my sincere gratitude goes to my uncles, aunts, siblings Margret, Dominic, Benjamin, Barbie, Tito and cousins for their continuous concern and support during the course of time.

My profound gratitude to my well experienced supervisor Engr. Dim P. E. for his helpful criticism, comments and corrections which helped in achieving the objective of this project. May the Almighty God grant him his heart desires as well as his families.

I appreciate the effort of my Guardian, Mrs A. J. Shittu for her word of advice, support in times of trouble and to my friends off and on campus for making my days in this reputable institution a memorable one. Finally, a sincere vote of thanks to my one true friend Miss Ekundayo A. O. for her support at all times. I pray the good Lord bless you all and your families. Amen.

ABSTRACT

The aim of this research work is to produce polyvinyl acetate using vinyl acetate monomer (VAM), vinyl alcohol and sodium laurel sulphate (SLS) among others using polymerization process and thus note the effect of variation of sodium laurel sulphate on polyvinyl acetate produced. The yielding of the product polyvinyl acetate was ascertained through a decrease in temperature. From the results with variation of sodium laurel sulphate (an emulsifier) which enables the fast rate of polymerization and minimizes coagulation or fouling (i.e at reduction) while vinyl acetate monomer causes a decrease in temperature which enables formulation of polymer until the growing chain terminates at 60°C and reaction is complete. The pH results, density, conductivity and resistivity obtained after the variation was been able to be compared with that of its standard values.

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CHAPTER ONE

1.0 INTRODUCTION

Polyvinyl acetate is a colourless, odourless, rubbery synthetic polymer. Prepared from vinyl acetate monomer (VAM). Preparation of polyvinyl acetate is as a result of the complete or partial hydrolysis of polymer. It has been noted that 89% to 90% of polyvinyl acetate (PVA) is converted from hydrolyzed alcohol. Discovered in Germany in 1912 by Dr. Fritz Klatte on an industrial scale just before the World War I. As an emulsifier with water, PVA serves as an adhesive for porous materials such as wood, paper   and clothes. As wood glue, known as "white glue" and "carpenter glue " or aliphatic resin emulsion been the most commonly wood glue used and the first successful synthetic binder used in substantial volume. Mostly used in book binding and book arts due to its flexibility, strong bond and its non-acidic nature (unlike many other polymers).

PVA as a copolymer with more expensive acrylics used extensively in paper, paint and industrial coatings, known as vinyl acrylics. It can also be use to protect cheese from fungi and humidity. It is slowly attacked by alkali, forming acetic acid as a hydrolysis product. Boron compounds like boric acid and borax will form tackifying precipitates by causing the polymer to cross links.

Commonly recommended for use in making leather handcrafted works and paper mache. The typical emulsion paint is a synthetic resin e.g. Polyvinyl acetate emulsified in water. Other unemulsifiable binders are oil, resins, oil vanishes, rubber and bitumen. While other ingredients are usually stabilizer, which ensures that coagulation is prevented. The drying action of the paint is as a result of evaporation of the emulsifying liquid (Roscher, 2007).

The paint films are initially or permanently permeable making this feature very useful. This makes some suitable for decorating new plaster and other damp surface for external use. PVA is alkali resistant and so may be used on lacquer and cement concrete, asbestos cement and plaster in polymerized form for plastic masses and films.

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PVA emulsion is a stable colloidal suspension as milk, consisting of an immiscible liquid dispersed and held in another liquid by a substance called emulsifier. In an emulsion polymerization, the surfactant is dissolved in water until the critical micelle concentration (CMC) is reached. The interior of the micelle provides the necessary sites for polymerisation. A monomer (vinyl acetate) and a water soluble free radical initiator are added and the whole batch is shaken or stirred. Emulsion polymerizations are always performed free radically. Anionic and cationic chain end would be rapidly quenched by the water. The product of an emulsion polymerization is called Latex paint (Rosen and John, 1993).

1.1 Aims and Objectives

The aim of this project is to produce and characterise polyvinyl acetate through polymerization using vinyl acetate monomer, vinyl alcohol and potassium persulfate and thus observing the effect of variation of monomers on the quality of polyvinyl acetates produced.

1.2 Scope of Work

This project will cover the formulation of polyvinyl acetate and to carry out physiochemical properties like pH test and density etc of the various samples produced based on variation in monomers used.

1.3 Justification

The justification of this research work is to improve the quality of polyvinyl acetate to ascertain its conformity to standard value of composition and ratio of reagents.

1.4 Limitations

In the course of this study the limitations encountered are lack of materials, equipment and source of fund.

CHAPTER TWO

2.0 LITERATURE REVIEW

Polyvinyl acetate (PVA) (Vinyl Acetate Homopolymer) comprises polymers of all molecular weights found from the free radical polymerisation of vinyl acetate monomer, sold as latex, emulsion of spray dried solids. The homopolymers as spray dried polyvinyl acetate emulsion, can be reconstituted in water, mixed with other adhesive emulsions or mixed with dry ingredients where they have the ability to be used as a binder in dry mix formation.

The PVA emulsions are basically the major form of polyvinyl acetate used in the adhesive market. PVA emulsion exhibits excellent compatibility with many modifying resins, lending themselves to a broad range of applications through formulation. In addition to compatibility, molecular weight (or grade) and the amount and the type of protective colloid used to produce the emulsion affected adhesive properties. Variations in type and quantity of protective colloid used in producing the PVA emulsion have a major impact on the performance of the adhesive film. Vinyl acetate adhesives can vary in moisture sensitivity by changing the content and type of protective colloid (TCQGI, 2008).

In an emulsion which is a type of radical polymerization that usually starts with an emulsion incorporating water, monomer and surfactants. The most common type of emulsion polymerization is an oil-in-water emulsion, in which droplets of monomers (the oil) are emulsified (with surfactants) in a continuous phase of water. Water-soluble polymers, such as certain polyvinyl alcohols or hydroxyethyl cellulose, can also be used to act as emulsifier/stabilizers; the surfactant is dissolved in water until the critical micelle concentration (CMC) is reached. The interior of the micelle provide the site necessary for polymerisation. Monomer vinyl acetate and a water soluble free radical initiator are added and the whole batch is shaken and stirred. Emulsion polymerisation is always performed free radical. Anionic and cationic chains end would be rapidly quenched by the water. The product of an emulsion polymerisation is called latex; "latex paint". Once everything (Surfactant and water) is thrown in the pot, the monomer can be found in three different places. Firstly, it can be in large monomer

droplets floating around aimlessly in the water. Secondly, though unlikely, some of the monomer may be dissolved in water. Lastly, the monomer may be found in micelles, which is exactly where we require it. Initiation takes place when an initiator fragment migrates into o a micelle and reacts with a monomer molecule. Water soluble initiators, potassium persulfates are commonly used in order to prevent polymerisation in the big monomer droplets. Once polymerisation starts, the micelle is referred to as a particle. Polymer particles can grow to extremely high molecular weight, especially if the initiator concentration is low. That makes the radical concentration and the rate of termination low as well. A time chain transfer is added to the mix to keep the molecular weight from getting too high (Odian, 1991).

Monomer migrates from the large monomer droplets to the micelle to sustain polymerisation. On average, there is one radical per micelle. For this reason, there is no much competition for monomer between the growing chains in the particles, so they grow to nearly identical weights and the polydispersity is very close to one. Practically all the monomer is consumed in emulsion polymerisations. Meaning the latex can be used without purification. This is important for paints and coatings, each micelle can be considered as a mini bulk polymerisation. Unlike traditional polymerisations, there is no unreacted monomer left over, and no thermal "hot spot" formed. In bulk polymerisations (here, described as no solvent. Just monomer and initiator), thermal hot spot causes degradation; discolouration and chain transfer broadens the molecular weight distribution. Increases in temperature sometimes cause the rate of polymerisation to increase explosively. The water here acts as a heat sink for all those mini reactors and keeps them from blowing up (Rose and John, 1993).

In addition it protect colloids, PVA homopolymers typically contain functional additives such as wetting agents and plasticizers such as dioctlphthalate or dibutylphthalate. Such modifiers impact adhesion, open times, speed of task, water resistance and emulsion stability.

There are three major types of stabilization mechanisms used in the manufacture of PVA homopolymers, polyvinyl alcohol (PVOH), hydroxyl-ethyl cellulose (HEC), and surfactants.

Although PVA films produce good aging characteristics due to there resistance to properties to UV and oxidation, Vinyl acetate is a hard polymer and is water sensitive. It is for this reason that polymers are generally formulated with plasticizers to grow the proper flexibility. Also it is also the reason why PVA polymers are generally viewed as inappropriate for exterior uses. PVA polymers are the lowest cost emulsion while possessing good adhesion to many porous surfaces such as wood and paper.

Packaging and furniture application involving paper and wood substrates consist over 90 % of the usage of PVA emulsion adhesives. The balance of the usage involves a wide variety of applications, including consumer white glue. The packaging applications include box board manufacture, paper bags, paper lamination, and tube winding and remoisten able labels. In construction, PVA is used in prefab construction, including flooring and panel installation. PVA is not generally used as a primary fastener where great strength is needed.

Alternative systems, such as vinyl acetate/acrylic copolymers and/or vinyl acetate ethylene copolymers (VAE), limit the growth of PVA in applications requiring properties such as moderate water resistance, flexibility, low temperature adhesion or specific adhesion to non porous surfaces e.g. vinyl or aluminium. This resin classification market of polyvinyl acetate (vinyl acetate homopolymers) estimates 2003 demand with a historical perspective back to 1998 as well as forecasts through 2008 within the Europe/European Adhesives (Gilbert, 1996).

2.1 Properties of Polyvinyl acetate

The degree of polymerization of polyvinyl acetate typically is 100 to 5000. The ester groups of the polyvinyl acetate are sensitive for alkali and will slowly convert PVAc into polyvinyl alcohol and acetic acid.

1. It is a colourless liquid.

2. It has a boiling point of 72.7 ^{0}C.

3. It has a melting point of -93 ^{0}C, 180 ^{0}K, -135 ^{0}F.

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4. It has a molar formula of $C_4H_6O_2$.

5. It has a molar mass of 86.09 g/mol.

2.1.1 Uses of polyvinyl acetate

1. It is used as an adhesive. Wood glue, bookbinding and clothes

2. It is used as water based paints.

3. It is used as paper coatings.

4. It is used for consolidates for porous building stones, in particular sand stones.

2.1.2 Preparation of vinyl acetate

Polyvinyl acetate (PVA or PVAc) is a rubbery synthetic polymer.

- (Homo) polymers are prepared by polymerization of vinyl acetate monomer.

- Copolymers are vinyl acetate (VAM) based polymers internally plasticized with for example ethylene (VAE) or acrylic (VAA).

Polyvinyl acetate is also the raw material to make polyvinyl alcohol. Polyvinyl acetate is partially or completely hydrolysed.

The major industrial route involves the reaction of ethylene and acetic acid with oxygen in the presence of a palladium catalyst.

Chemically,

Ethylene + acetic acid + water, $[C_2H_4 + C_2HCOOH + 2H_2O \longrightarrow C_4H_6O_2]$
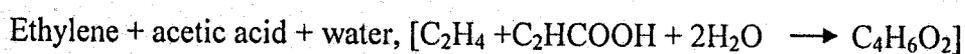
Vinyl acetate is also prepared by the gas-phase addition of acetic acid to acetylene (Roscher, 2007).

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Structurally represented as thus:
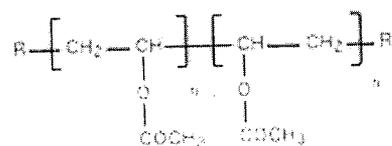
2.1.3 Polymerization

It can be polymerized, either by itself to make polyvinyl acetate or other monomers to prepare copolymers such as ethylene-vinyl acetate. Due to the inability of the radical, attempts to control the polymerization via most 'living/controlled' radical processes have proved problematic. However, RAFT (or more specifically MADIX) polymerization offers a convenient method of a xanthate chain transfer agent.

2.1.4 Other derivatives

Vinyl acetate undergoes many of the reactions anticipated for an alkene and an ester. Bromine adds to give the dibromide. Hydrogen halides add to the 1- haloehtyl acetate, which cannot be generated by other methods because of the non availability of the corresponding halo-alcohols. Acetic acid adds in the presence of palladium catalyst to give ethylidene diacetate, $CH_3CH(OAc)_2$. It undergoes transesterifiation with a variety of carboxylic acids. The alkene also undergoes Diel-Alder and 2+2 cycloadditions (Roscher, 2007).

2.2 Emulsion Polymerization

Emulsion polymerization is a radical polymerisation that usually starts with an emulsion incorporating water, monomer, and surfactant. The most common type of emulsion polymerisation is an oil-in-water emulsion, in which droplets of monomer (the oil) are emulsified (with surfactants) in a continuous phase of water. Water soluble polymers, such as certain polyvinyl alcohols or hydroxyethyl cellulose, can also be used to act as emulsifiers/stabilizers. The name "emulsion polymerization" is a misnomer that arises from a historical misconception.

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Rather than occurring in emulsion droplets, polymerisation takes place in the latex particles that form spontaneously in the first few minutes of the process. These latex particles are typically 100mm in size, and comprises of many individual polymer chains. The particles are stopped from coagulating with each other because each particle is surrounded by the surfactant; the charge o the surfactant repels other particles electro statically. When water-soluble polymers are used as stabilizers instead of soap, the repulsion between particles arises because these water-soluble particles form a "hairy layer" around a particle that repels other particles, because pushing particles together would involve compressing these chains (Odian, 1991).

Emulsion polymerization is used to manufacture several commercially important polymers. Many of these polymers are used as solid materials and must be isolated from the aqueous dispersion after polymerisation. In other cases the dispersion itself is the end product. A dispersion resulting from emulsion polymerisation is often called latex (especially if derived from a synthetic rubber) or an emulsion (even though "emulsion" strictly speaking refers to dispersion of liquid in water). The emulsions find application in adhesives, paints, paper coatings and textile coatings. They are finding increasing acceptance and are preferred over solvent based products in these applications as a result of their eco-friendly characteristics due to the absence of VOCs (Volatile Organic Compounds) in them.

2.2.1 Advantages of emulsion polymerization

1. Higher molecular weight polymers can be made at fast polymerization rates. By contrast, in bulk and solution free radical polymerization, there is a trade off between the molecular weight and polymerization rate.

2. The continuous water phase is an excellent conductor of heat and allows the heat to be removed from the system, allowing many reactions method to increase their rate.

3. Since polymer molecules are contained with the particles, viscosity remains close to that of water and is not dependent on molecular weight.

4. The final product can be used as it is and does not generally need to be altered or processed.

2.2.2 Disadvantages of emulsion polymerization

1. Surfactants and other polymerization adjuvant remain in the polymer or are difficult to remove.

2. For dry (isolated) polymers, water removal is an energy intensive process.

3. Emulsion polymerization is usually designed to operate at high conversion monomer to polymer. This can result in significant chain transfer to polymer.

2.3 History

The early history of polymerization is connected with the field of synthetic rubber. The idea of using an emulsion monomer in an aqueous suspension or emulsion was first conceived by workers at Bayer, before World War 1, in an attempt to prepare synthetic rubber. The impetus of this development was the observation that natural rubber is produced at room temperature in dispersed particles stabilized by colloidal polymers, so the industrial chemist simply tried to duplicate these conditions. The Bayer workers used natural occurring polymers such as gelatine, egg albumin and starch to stabilize their dispersion. By today's definition, these were not true emulsion polymerization, but suspension polymerizations.

The first "true" emulsion polymerizations, which used a surface-active agent and polymerization initiator, were conducted in the 1920s to polymerize isoprene, Over the next twenty years, through the World War 2, efficient method for production of several forms of synthetic rubber by emulsion polymerization were developed, but relatively few publications in the scientific literature appeared: most disclosures were confined to patent or were kept secret due to war time needs.

After World War II, emulsion polymerization was extended to the production of plastics. Manufacture of dispersions to be used in latex paints and other products sold as liquid dispersions commenced. Ever more sophisticated processes were devised to prepare products that replaced solvent-based materials. Ironically, synthetic rubber manufacture turned more and more away from emulsion polymerization as new organometallic catalysts were developed that allowed much better control of polymer architecture. (Wilby et al, 1933).

2.4 Theory

The successful theory to explain the distinct features of emulsion polymerization was largely developed by Smith, Ewart and Hawkins in the 1940s, Based on their studies on polystyrene, Smith and Ewart arbitrarily divided the mechanism of emulsion polymerization into three stages or intervals. Subsequently, it has been recognized that not all monomers or systems undergoes these particular three intervals. Nevertheless, the Smith-Ewart description is a useful starting point to analyze emulsion polymerizations.

The Smith-Ewart-Hawkins theory for the mechanism of free radical emulsion polymerisation is summarized by the following steps:

- A monomer is dispersed or emulsified in a solution of surfactant and water forming relatively large droplets of monomer in water.
- Excess surfactant creates micelles in water.
- Small amount of monomer diffuse through the water to the micelle.
- A water soluble initiator is introduced into the water phase where it reacts with monomer in the micelles. (This characteristic differs from suspension polymerization where an oil-soluble initiator dissolves in the monomer, followed by polymer formation in the monomer droplets themselves.) This considered Smith-Ewart interval 1.
- The total surface area of the micelles is much greater than the total surface of the fewer, larger monomer droplets; therefore the initiator typically reacts in the micelle and not monomer droplets.

- Monomer in the micelle quickly polymerizes and the growing chain terminates. At the point the monomer-swollen micelle has turned into a polymer particle. When both monomer droplets and polymer particles are present in the system, this is considered Smith-Ewart interval 2.

- More monomer from the droplets diffuses to the growing particle, where more initiators will eventually react.

- Eventually the free monomer droplets disappear and all remaining monomer is located in the particles. This is considered Smith- Ewart interval 3.

- Depending on the particular product and monomer, additional monomer and initiator may be continuously and slowly added to maintain their levels in the system as the particle grow.

- The final product is a dispersion of polymer particles in water. It can also be known as a polymer colloid, a latex, or commonly and inaccurately as an 'emulsion'.

Smith-Ewart theory does not predict the specific polymerization behaviour when the monomer is somewhat water-soluble, like methyl methacrylate or vinyl acetate. In this case, homogeneous nucleation occurs: particles are formed without the presence or need for surfactant micelles.

High molecular weights are developed in emulsion polymerization because the concentration of growing chains within each polymer particle is very low. In conventional radical polymerization, the concentration of growing chains is higher, which leads to termination by coupling, which ultimately results in shorter polymer chains. The original Smith-Ewart-Hawkins mechanism required each particle to contain either zero or one growing chain. Improved understanding of emulsion polymerization has relaxed that criterion to include more than one growing chain per particle. However, the growing chain per particle is still considered to be very low.

Because of the complex chemistry that occurs during an emulsion polymerization, including polymerization kinetics and particle formation kinetics, quantitative understanding of the mechanism of emulsion polymerization has required extensive computer simulation (Smith and Ewart, 1948).

2.5 Process

Emulsion polymerization has been used in batch, semi batch, and continuous process. The choice depends on the properties desired in the final polymer or dispersion and on the economics of the product. Modern process control schemes have enabled the development of complex reaction processes, with ingredients such as initiator, monomer and surfactant added at the beginning, during or at the end of the reaction.

Early Semi-batch recipes (SBR) are examples of true batch process: all ingredients added at the same time to the reactor. Semi-batch recipes usually include a programmed feed of monomer to the reactor. These enable a starve-fed reaction to insure a good distribution of monomers into the polymer backbone chain. Continuous processes have been used to manufacture various grades of synthetic rubber.

Some polymerizations are stopped before all the monomer has been reacted. This minimizes chain transfer to polymer. In such cases the monomer must be removed or stripped from the dispersion.

Colloidal stability is a factor in design of an emulsion polymerization process. For dry or isolated products, the polymer dispersion must be isolated, or converted into solid form. This can be accomplished by simple heating of the dispersion until all the water evaporates. More commonly, the dispersion is destabilized (sometimes called "broken") by addition of a multivalent cation. Alternatively, acidification will destabilize dispersion with a carboxylic acid surfactant. These techniques may be employed in combination with application of shear to increase the rate of destabilization. After isolation of the polymer, it is usually washed, dried and packaged.

By contrast, products sold as dispersion are designed with a degree of colloidal stability. Colloidal properties such as particle size distribution and viscosity are of critical importance to the performance of the dispersions.

2.6 Raw Materials

2.6.1 Monomer

Typical monomers are those that undergo radical polymerization, are liquids or gaseous at reaction conditions, and are poorly soluble in water. Solid monomers are difficult to disperse in water. If monomer stability is too high, particle formation may not occur and the reaction kinetics reduces to that of solution polymerization.

Ethylene and other simple olefins must be polymerized at very high pressures (up to 800 bars).

2.6.2 Co-monomers

Co-polymerization is common in emulsion polymerization, the same rules and commoner pairs that exist in radical polymerization operate in emulsion polymerization. However, copolymerization kinetics is greatly influenced by the aqueous solubility of the monomers. Monomers with greater aqueous solubility will tend to partition in the aqueous phase and not in the polymer particle. They will not get incorporated as readily in the polymer chain as monomers with lower aqueous solubility. This can be avoided by a programmed addition of monomer using a semi-batch process.

Ethylene and other olefins are used as minor co monomers in emulsion polymerization, notably in vinyl acetate copolymers. Small amount of acrylics acid or other ionisable monomers are sometimes used to confer colloidal stability to dispersion (Odian, 1991).

2.6.3 Initiators

Both thermal and redox generation of free radicals have been used in emulsion polymerization. Persulfate salts are commonly used in both initiator modes. The persulfate ion readily breaks up into sulphate radical ion above 50 °C, providing a thermal source of initiator. Redox initiator takes place when an oxidant such as persulfate salt, a reducing agent such as glucose, rongalite,

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or sulphite, and a redox catalyst such as an iron compound are all included in the polymerizations that take place below 50 °C.

Although, organic peroxides and hydroperioxides are used in emulsion polymerization, initiators are usually water soluble and partition into the water phase. This enables the particle generation behaviour described in the theory section. In redox initiator, either the oxidant or the reducing agent (or both) must be water soluble, but one component can be water-insoluble (Odian, 1991).

2.6.4 Surfactants

Selection of the correct surfactant is critical to the development of any emulsion polymerization process. The surfactant must enable a fast rate of polymerization, minimize coagulum or fouling in the reactor and other process equipment, prevent an unacceptable high viscosity during polymerization (which leads to poor heat transfer), and maintain or even improve properties in the final product such as tensile strength, gloss, and water absorption.

Anionic, non-ionic and cationic surfactants have been used, although anionic surfactants are by far most prevalent. Surfactants with low critical micelle concentration (CMC) are favoured; the polymerization rate shows a dramatic increase when the surfactant level is above the CMC, and minimization of the surfactant is preferred for economic reasons and the (usually) adverse effect on the physical properties of the resulting polymer. Mixtures of surfactants are often used, including mixture of anionic with non-ionic surfactants. Mixtures of anionic and cationic surfactants form insoluble salts and are not useful.

Examples of surfactants commonly used in emulsion polymerization include fatty acids, sodium lauryl sulphate and alpha olefin sulfonate (Odian, 1991).

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2.6.5 Non-surfactant stabilizers

Some grade of polyvinyl alcohol and other water soluble polymers can promote emulsion polymerization even though they do not typically form micelles and do not act as surfactants (for example, they do not lower surface tension). It is believed that these polymers graft onto growing polymer particles and stabilize them.

Dispersions prepared with such stabilizers typically exhibit excellent colloidal stability (for example, dry powder may be mixed into the dispersion without causing coagulation). However, they often result in products that are very water sensitive due to the presence of the water soluble polymer (Odian, 1991).

2.6.6 Others

Other ingredient found in emulsion polymerization includes chain transfer agents, buffering agents, and inert salts. Preservatives are added solid products as liquid dispersions to retard bacteria growth. These are usually added after polymerization, however (Odian, 1991).

2.7 Applications

Polymers produced by emulsion polymerization can be divided into three categories.

> Synthetic rubber

- Some grades of styrene-butadiene
- Some grades of Polybutadiene
- Polychloroprene (Neoprene)
- Nitrile rubber
- Acrylic rubber
- Fluoroelastomer (FKM)

➤ Plastics

- Some grade of PVC

- Some grades of polystyrene

- Some grades of PMMA

- Acrylonitrile-butadiene-styrene terpolymer (ABS)

- Polyvinylidene fluoride

- PTFE

➤ Dispersions (i.e. polymers sold as aqueous dispersions)

- Polyvinyl acetate

- Polyvinyl acetate copolymers

- Latexacrylic paint

- Styrene-butadiene

- VAE (Vinyl acetate – ethylene copolymers)

2.8 Statistical Analysis of Polymers

When dealing with millions of molecules in a tiny droplet, statistical methods must be employed to make generalizations about the characteristics of the polymer. It can be assumed in polymer synthesis, about the characteristics of the polymer. It can be assumed in polymer synthesis, each chain reacts independently. Therefore, the bulk polymer is characterized by a wide distribution of molecular weights and chain lengths. The degree of polymerization (DP) refers to the number of repeat units in the chain, and gives a measure of molecular weight. Many important properties of the final result are determined primarily from the distribution of chain lengths under varying conditions.

2.8.1 Statistical Polymer Growth

In other to characterize the distribution of polymer lengths in a sample, two parameters are defined: number average and weight average molecular weight. The number average is just the sum of individual molecular weights divided by the number of polymers. The weight average is proportional to the square of the molecular weight. Therefore the weight average is always larger than the number average. The following graph shows a typical distribution of polymers including the weight and number average molecular weights.
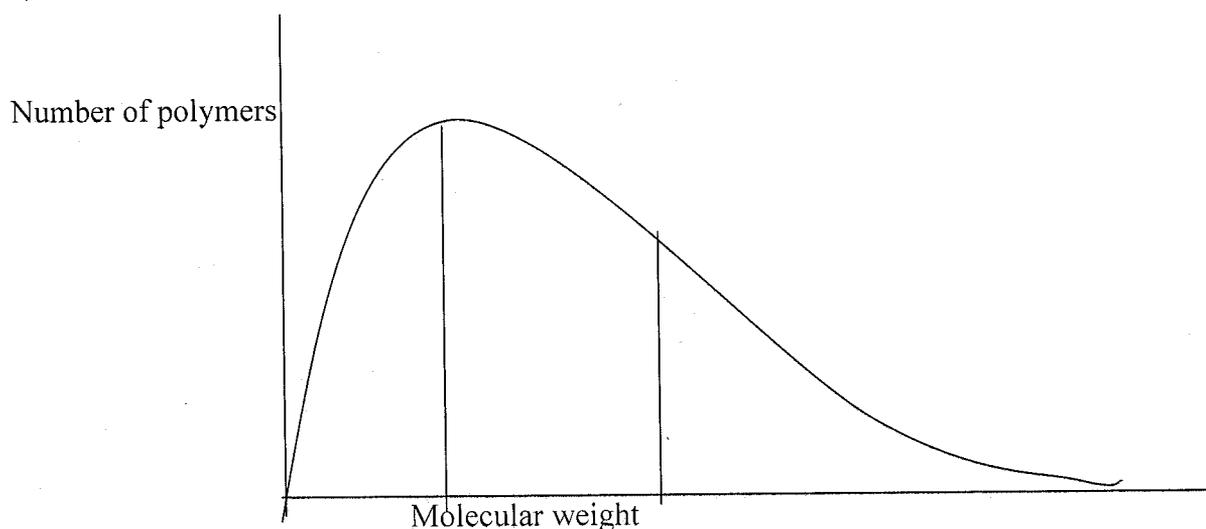

Illustration: line 1 is the number average and line 2 is the weight average.

The molecular weight of a polymer can be represented by the viscosity average molecular weight. This form of the molecular weight is found as a function of the viscosity of the polymer in solution (viscosity determines the rate at which the solution flows - the slower a solution moves, the more viscous it is said to be, and the polymer molecular weight influences the viscosity). The following simulation allow you to calculate the viscosity of a polymer solution, and use the data you find to produce the viscosity average molecular weight (Odian, 1991).

The molecular weight of a polymer can also be represented by the viscosity average molecular weight. This form of molecular weight is found as function of the viscosity of the polymer in solution (viscosity determines the rate at which the solution flows – the slower a solution moves, the more viscous it is said to be – and the polymer molecular weight influences the viscosity).

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The following simulation allows you to calculate the viscosity of a polymer solution, and use the data you find to produce the viscosity average molecular weight (Odian,1991).

EFFECT OF RAW MATERIALS ON POLYVINYL ACETATE

The raw materials used in producing polyvinyl acetate for emulsion paints are divided into five categories. All five categories are responsible for individual purposes and are also sub-divided:

1. Monomers

2. Co monomers

3. Surfactants

4. Initiators

5. Other Surfactant Stabilizers

Note:

In this study, we are concerned with the effects and variation of co monomers, surfactants, initiator and other surfactant stabilizers on the final polyvinyl acetate produced.

- **Co monomers :**

  Sodium lauryl sulphate: Also serves as a surfactant and atimes a non surfactant.

  1. It serves a co monomer and confer colloidal stability to dispersion.

  2. Enables low viscosity through it's ability to allow poor heat transfer

  3. Minimum film formation temperature.

  4. Affects or a major determinant in rate of film coalescence of vinyl acetate (Vinyl acrylic latex).

  5. Fast rate of polymerization and enables thickening.

6. Affects polarity of vinyl acrylic (polarity) i.e polarity of polymers.

- **Sodium Benzoate: (Non-Surfactant)**

1. Also benzoate of soda, due to its soluble ability in water. It grafts unto polymer particles and stabilizes them. (Stabilizer).

2. Dispersions prepared with such stabilizers typically exhibits excellent colloidal stability, i.e. doesn't cause coagulation.

- **Potassium persulfate (An initiator)**

    1. Enables stability of monomers in water.

    2. Affects and enables redox initiator and concentration.

    3. Determines reaction time.

Characterisation would involve the determination of the:

- pH

- Density

- Conductivity

- Resistivity

CHAPTER THREE

3.0 METHODOLOGY

This research work is carried out with the aid of materials and equipments listed below:

3.1 Materials and Equipment

Table 3.1: List of Materials used

MATERIALS	SOURCE	COMMENT
Vinyl acetate monomer (VAM)	Shangai Sunshine Chemicals Co. Ltd China.	A colourless liquid with sweet smell in small quantities, pleasant fruity, characteristic odour.
Potassium persulphate ($K_2S_2O_2$)	ECEM B. V Netherlands. www.ecem.com	Powder
Vinyl alcohol (PVOH)	Shangai Sunshine Chemicals Co. Ltd China.	Liquid
Sodium laurel sulphate (SLS)	Spectrum Chemicals Mfg. Corp, USA	Powder
Gohesenol	Continental Chemicals USA.	Powder
Sodium benzoate	Spectrum Chemicals Mfg. Corp, USA	Powder

De-ionized water   Chemistry Lab.   Liquid

Table 3.2 List of Equipment used

EQUIPMENT	SOURCE	COMMENT
Erlenmeyer flask	England	25 ml transparent Pylex glass
Thermometer	England	A long transparent glass
Measuring cylinder	England	Ex 20^oC 100ml + 1ml transparent
Beaker	England	Transparent glass
Weighing Balance	United States of America	
Heat mantle with magnetic stirrer	Mumbai – 400053 India	
Stop watch	China	HQ 3268Adustable quartz
Water bathe	England	SWM 345 220V

3.2 EXPERIMENTAL PROCEDURE

4ml of de-ionized water was measured into the flask and heated to 60 ^oC for 10 minutes. 17 g of gohesnol was added into the flask and heated until temperature of 80 ^oC was attained and heating was stopped. When temperature falls back to 76 ^oC, the following ingredients were placed into the flask. Drop of potassium persulfate free radical initiator, 10 g sodium benzoate, 10 g of sodium laurel sulphate and heating continues for 15 minutes until temperature of 80 ^oC, 10 ml of vinyl alcohol emulsifier was added and heating continues until 90 ^oC was attained. At this temperature, 5 ml of vinyl acetate monomer was added at every time intervals of 20 minutes and various values of temperature were taken at this time value. The flask was shaken vigorously to form emulsion. The emulsion was placed for 30 minutes in an oil bath to cool. The emulsion was removed from the flask and cooled to room temperature. The procedure was repeated four more times with variation in sodium laurel sulphate in a fixed composition of other reagents. Amount varied were thus: 5 g, 7.5 g, 12 g and 15 g. With the variation of sodium laurel sulphate,

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acetate produced had a continual thickening characteristic as the amount increased. 10ml of distilled water was added at every increment of sodium laurel sulphate in other to achieve a form that can be characterised easily.

3.3 Characterisation of Samples

3.3.1 Determination of pH.

10ml of the sample was weighed and put into a beaker. 5ml of distilled water was also weighed and poured into the beaker. The content of the beaker was stirred to have uniformity of solution. The pH meter was calibrated and standardized with 2 buffers, pH 7 and pH 9 respectively. The electrode was dipped into individual samples and the readings were taken down.

3.3.2 Determination of conductivity

Equipment consists of a box like figure called a bridge and a cup like figure as well called a cell, both of which work together to arrive at a value of conductivity. The sample was poured into the cell. The cell was fitted to the bridge by 2 pin like clips. The reading was recorded on two scales (Manual and Automatic) after the on button was pressed. This was done for all 5 samples and the different conductivity values were noted.

3.3.3 Determination of density.

Density bottle of 25ml was washed and dried for use. Empty density bottle was weighed and recorded. The sample was poured into the density bottle and weighed. This was done for another 4 samples and recorded.

3.3.4 Determination of resistivity.

This is the inverse of value obtained in conductivity.

CHAPTER FOUR

4.0 RESULTS

This chapter includes all the results obtained in the present study and the results are presented as follows:

Table 4.1: Temperature variation

Temperature of Reactant (°C)	Time (Minutes)	PVOH (ml)	VAM (ml)	$K_2S_2O_3$
80	00.00-20.00	10.00	-	-
95	20.00-40.00	-	5.00	-
71	40.00-60.00	-	5.00	Drop
64	60.00-80.00	-	5.00	Drop
59	80.00-100.00	-	5.00	Drop
54	100.00-120.00	-	5.00	Drop

Table 4.2: Physiochemical Properties of PVAc

Sodium laurel Sulphate (g)	pH	Conductivity $(\times 10^2 \mu\text{mohs})$	Density (g/cm^3)	Resistivity $(\times 10^{-4} \mu\text{omhs}^{-1})$
5.0	5.83	29	1.29	3.448
7.5	6.02	34	1.32	2.941
10.0	6.77	40	1.34	2.500
12.5	7.67	52	1.35	1.923LS
15.0	7.83	59	1.37	1.695
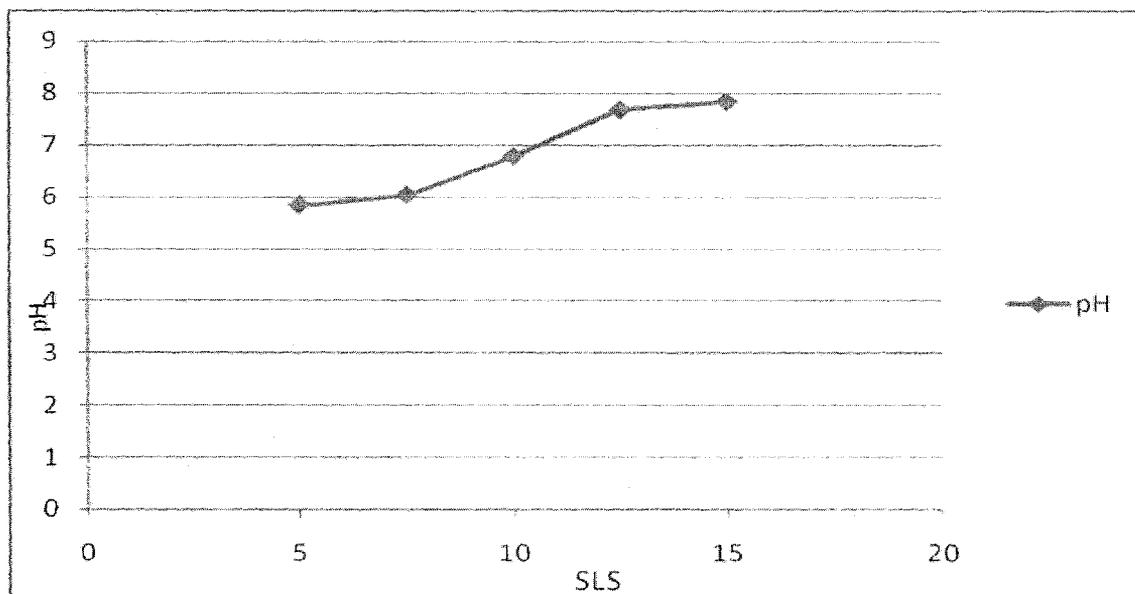
Figure 4.1: pH against SLS
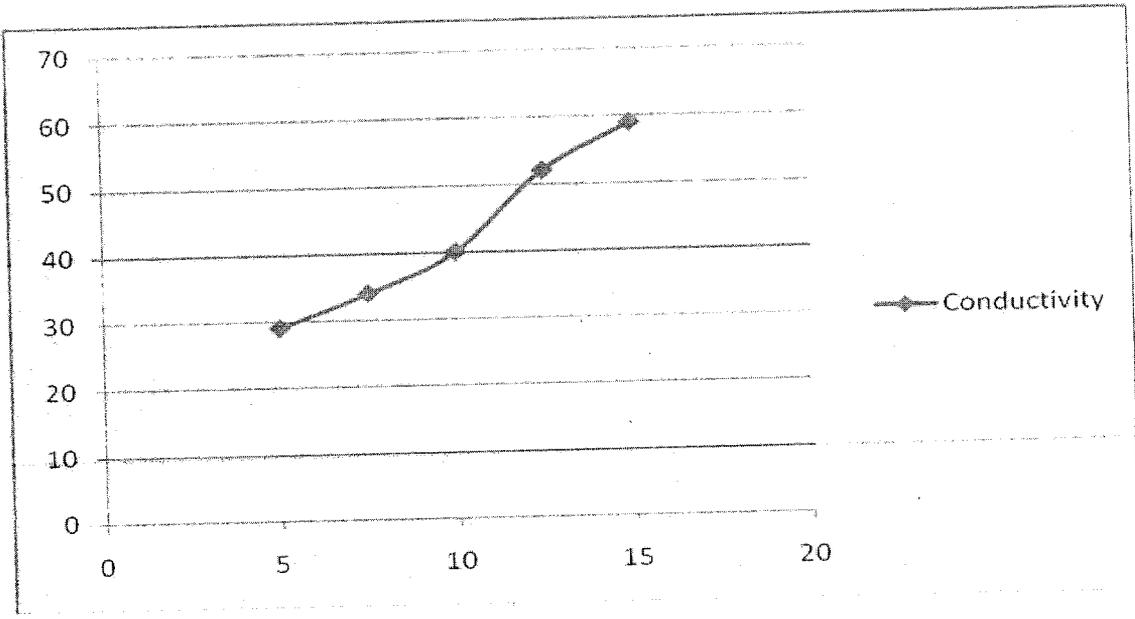
Figure 4.2: Conductivity against SLS
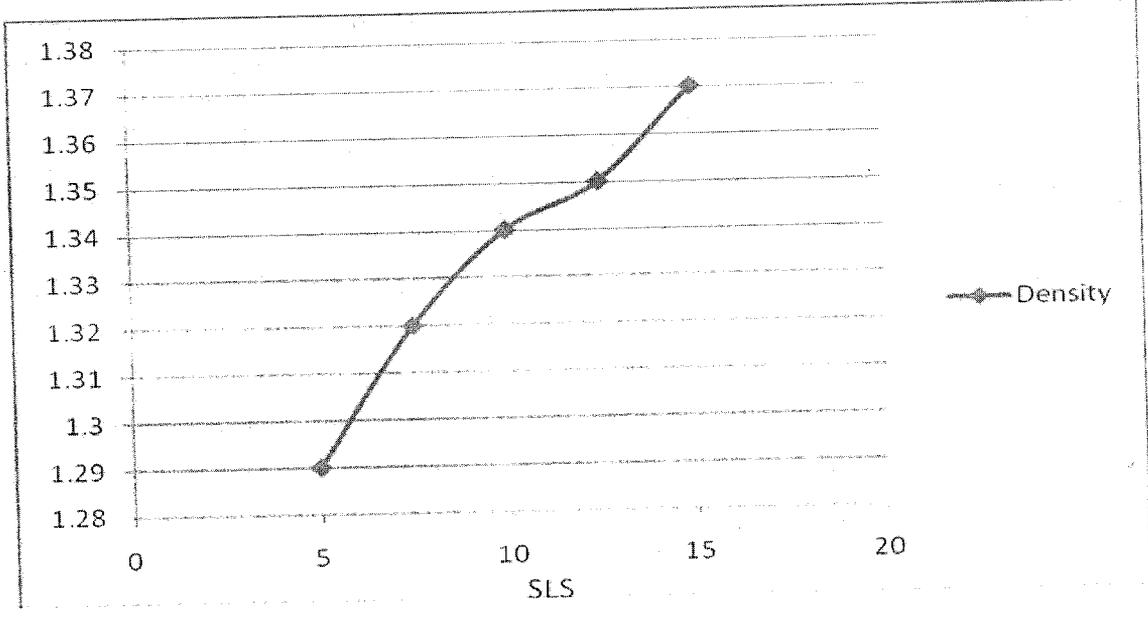

Figure 4.3 : Density against SLS
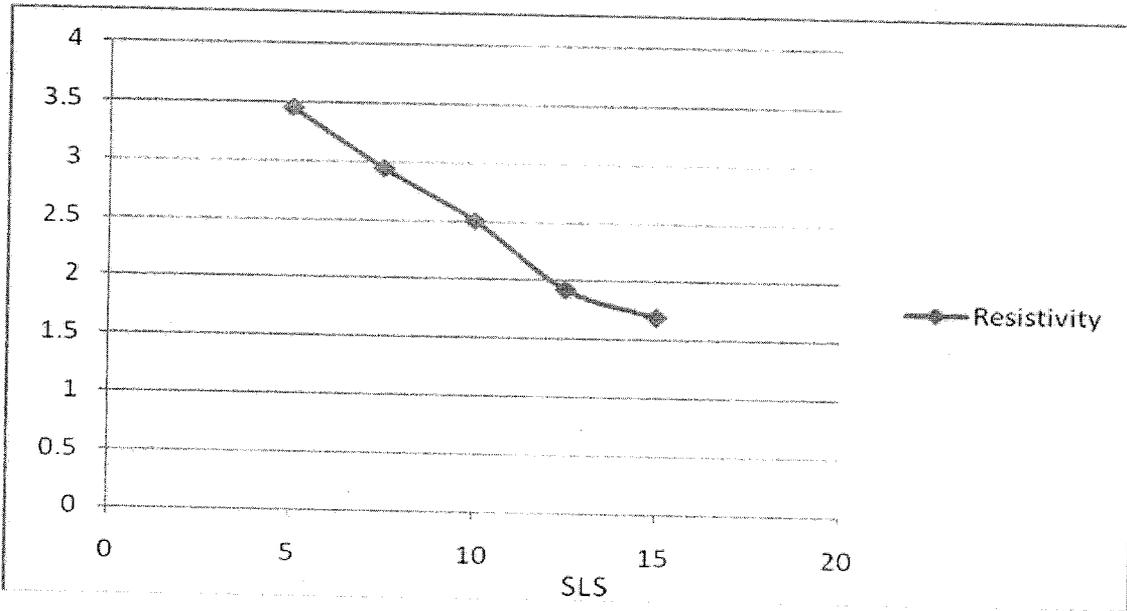
Figure 4.4 : Resistivity against SLS

Standard Properties of PVAc at 25°C and 100kPa includes:

- Density $0.934g/cm^3$

- Conductivity $24 * 10^2 \mu mohs$

- Resistivity $4.18 * 10^{-4}(\mu mohs^{-1})$

CHAPTER FIVE

DISCUSSION OF RESULTS, CONCLUSION AND RECOMMENDATION

5.0 Discussion of Result.

The result of this research work indicated above, shows an increase in temperature from 80 °C to 95 °C, though temperature was added until it was 90 °C. An extra increase of 5 °C was attained in the system due to the presence of vinyl alcohol which enables a fast rate of polymerization and thus is responsible for its exothermic nature. It also (PVOH) prevents high viscosity during polymerization and minimizes coagulation as well. A sudden decrease in temperature of 71 °C was attained as vinyl acetate monomer starts to react due to the fact that vinyl acetate monomer is an excellent conductor of heat which at this point takes heat from the system. The temperature continues to decrease until the growing chain of the monomer terminates and reaction is complete.

Table 4.2 shows the effect of sodium laurel sulphate on the polyvinyl acetate formed with variation in amount of sodium laurel sulphate added when characterised and thus enables the comparation of physical properties obtained and that of the standard value recognised worldwide.

5.1 Conclusion

In conclusion, formulation of polyvinyl acetate has been done using vinyl acetate monomer, an emulsifier and initiator. The result and graph obtained shows that vinyl acetate monomer has a low solubility due to an increase in temperature when reaction starts and a sudden decrease in temperature as reaction continues and then terminates when polymer is formed. Sodium laurel sulphate as a surfactant and a co monomer which is responsible for various properties observed ranging from been a thickener to having effects on conductivity, pH level, resistivity, density and viscosity compared to the standard values.

5.2 Recommendation

Having established the fact that (Homo) polymers are prepared by polymerization of vinyl acetate monomers (VAM). Ethylene (VAE) or acrylic (VAA) should be used as plasticizers for comparison of after effect.

Polyvinyl acetate should be used partially and completely hydrolysed and thus observe the effects.

Other reagents should be varied in the production of polyvinyl acetate (PVAc) and effects monitored.

REFERENCE

Fitch, R. M., 1971. Polymer Colloids, Pleum and Sons Inc, New York.

German patent 250690 September 12, 1909.

Gilbert,R. G., 1996. Emulsion Polymerization: A Mechanistic Approach Academic Press Publishers, London.

McCabe, W. L., Smith C. J. and Harriot, 1993, Unit Operation of Chemical Engineering, 5th Ed. Mc Graw hill book Company, Singapour.

Odian, .G. 1991. "Principles of Polymerization" 3rd Ed., John Wiley and Sons, Inc., New York.

Roscher,.G. 2007. Vinyl Esters in Ullmann's Encyclopedia of Chemical Technology, John Wiley and Sons, Inc., New York.

Rosen, S. L., 1993. "Fundamental Principles of Polymeric Materials" 2nd Ed., John Wiley and Sons, Inc., New York.

Smith, W. V, Ewart, R. H. J. Chem. Phys, 1948, 16, 592.

The Chem. Quest Group, Inc. TCQGI, 2008.

Whitby, G.S., Katz, M. 1933. Ind.Eng. Chem, PP 25, 1338, Wiley Interscience, Publication, New York.

APPENDIX

All conversions made on a basis of 50 ml Erlenmeyer flask.

Total monomer added = 0.49 x 50 ml = 25 ml.

Initial addition of 5 ml and a total intermittent addition of 20 ml (i.e. 25 ml).

Volume of emulsifier used = 0.2 x 50 ml = 10 ml.

Total volume of initiator used = 0.00147 x 50 ml = 0.0735

Buffer is added intermittently to regulate the pH, buffers of pH 7 and pH 9 were used.

Density is calculated with the formula = Mass/Volume in g/cm^3.

Constituent	Proportion (Parts)	Volume (ml)
Vinyl acetate monomer	0.4900	25
Emulsifier (PVOH)	0.2000	10
Initiator	0.00147	0.0735