

**PRODUCTION AND
CHARACTERIZATION OF MELAMINE-
FORMALDEHYDE ADHESIVE**

BY

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NOVEMBER, 2004.

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**In Partial Fulfillment of the Requirement for the Award of the
Bachelor of Engineering (B. ENG) degree.
(Chemical Engineering)**

**Department of Chemical Engineering, School of Engineering
and Engineering Technology, Federal University of
Technology, Minna, Nigeria**

NOVEMBER, 2004.

DECLARATION

I, Itebeni Ununotovo Anthony, declare that this project is solely the result of my work and has never been submitted anywhere for any degree. All literature cited have been duly acknowledged in the reference.

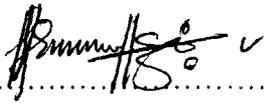
Itebeni

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Itebeni Ununotovo Anthony

29/11/04
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DATE

CERTIFICATION

This project titled 'PRODUCTION AND CHARACTERIZATION OF MELAMINE FORMALDEHYDE ADHESIVE' by ItEBeni Ununotovo Anthony meet the regulation governing the award for the Degree of Bachelor of Engineering (Chemical Engineering) of Federal University of Technology Minna and is approved for its scientific contribution to knowledge and literary presentation.



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HEAD OF DEPARTMENT

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EXTERNAL SUPERVISOR

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DATE

DEDICATION

This project work is dedicated to my loving parents Mr. And Mrs. Warson Ogagaruba Itebeni for giving me sound education.

ACKNOWLEDGEMENTS

My sincere thanks go to Almighty God for my life and for seeing me through this programme.

My profound gratitude goes to all my lecturers in the department of Chemical Engineering, especially my supervisor Dr. M.O.EDOGA who despite his commitments devoted his attention, helpful advice, provision of materials and encouragement towards the completion of this work.

I give God the glory for giving me , my family who were loving, caring and understanding during this period; they are Glory Itebeni, Joy Itebeni, Omovigho Itebeni, Efe Itebeni, Enejeta Itebeni, Edwin Itebeni and the entire Itebeni's family. God bless you all, especially Joy for her financial support as well as an instrument of encouragement in my life.

And to all my friends who stood by me when things were rough, you were truly friends indeed especially Ala Ayodeji, Kolawole S. Olanrewaju, Kingsley Igboamalu, Manfred Illogo, Mavis Ogbogolo, Oche Martins Igoche, Paul Yakubu, Dayo, Charles, Nath, Victorial Effiong, Iyabo, Vivian Obi, Otuwe Idika-mba. Thank you all and God bless you all. My gratitude goes to all the graduating students of 2003/2004 session.

To crown it all, I again thank my parents Mr. And Mrs. Warson Ogagaruba Itebeni for their support . I love you dad and mum.

ABSTRACT

The study was based on the production and characterization of Melamine-formaldehyde adhesive.

The synthesis of Melamine-formaldehyde adhesive was carried out in a water jacketed reactor at formaldehyde to melamine (F/M) ratio of 1.5, a pH range of 8.30-8.50, at an operating temperature of 95-100°C and at atmospheric pressure.

The physicochemical properties such as pH range of 8.3, viscosity of 34.98 cp for sample A and 38.54 cp for sample B, refractive index of 1.5 and molecular weight of 2829.28 and 52.35 for sample's A and B were obtained.

Analysis of IR showed that there is presence of amine group (N-H) at 3369.34 cm⁻¹ in Sample A and 3383.82 cm⁻¹ in sample ^B respectively.

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NOMENCLATURE

C = Viscometer constant [$c = 0.0882$]

t = Time for a fixed volume of a liquid to flow by gravity through the u-capillary.

μ_l = Viscosity of liquid

ρ = Density

N_1 = Weight of specific gravity bottle

N_2 = Weight of specific gravity bottle + sample's weight

N_3 = Weight of sample

V = Volume of the sample

μ_i = Viscosity of the polymer solution

μ_o = Viscosity of the solvent (Acetone).

$(\mu)_l$ = Limiting viscosity number

M_A = Neat melamine-formaldehyde resin

M_B = Melamine + urea formaldehyde (mixed)

K and a = parameter that depend on the solvent and polymer.

CHAPTER ONE

1.0 INTRODUCTION

Before 1930, the basic adhesives were based on animal glue, casein, clays, mastic, Pitches, asphalt, bitumen, starch, blood and resins. But today there has been a series of adhesives in the market, and the types of materials available are constantly being proliferated by new exotic materials that solve problems with greater ease and at less cost.

There are two important classes of amino resins *namely* the condensation products of urea and that of melamine with formaldehyde. Considering the two resins, they have similarity in their production and applications, but melamine resins are hydrolytically more stable than the urea formaldehyde. Melamine-formaldehyde adhesive when compared with urea formaldehyde is more expensive but possesses better mechano-chemical properties that qualifies for exterior structural applications

The melamine formaldehyde resin was first introduced into the market in 1936 shortly (about ten years) after the urea formaldehyde product came into the market. The product made with melamine-formaldehyde resin were very similar to those based on urea but with some superiority as has been pointed out above. Melamine resin unlike urea resin has limited uses.

Melamine formaldehyde resin being a petrochemical product is used for the production molding powder for electrical fittings and accessories and laminates, due to its much better water resistance and outdoor weatherability than moldings made from the urea formaldehyde resin. Principally melamine resin is used for the production of adhesive, which is largely used for plywood and furniture manufacture. This is because the resin gives excellent, boil-resistant bonds but for economy is usually blended with the ureas. (Malcolm P. Steven, 1990) The good

stability of the symmetrical triazine rings makes the melamine formaldehyde polymers very resistant to chemical change once the resin has been cured to the insoluble cross-linked state.(Irving Skeist,1990)

In spite of all these excellent qualities of melamine resin coupled with the fact that Nigeria is a petroleum-producing nation that has the raw materials for the production of melamine resin has not made any attempt towards producing melamine resin.

The objective of this work was therefore to develop melamine-formaldehyde adhesive that would be hydrolytically stable and would be used for bonding plywood and wood panels.

Emphasis would also be placed on the modification of the melamine-formaldehyde with urea to produce melamine-urea-formaldehyde resin

Finally, the physico-chemical properties and infrared spectroscopy (IR) of the resins (neat and modified) would also be determined.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Adhesive

An adhesive is a substance that has the capability of holding materials together. The manner by which adhesive are able to serve this function is due to a surface attachment that is resistant to separation. A bond occurs when the adhesive molecules adsorb onto a solid surface and chemically react with it. Cement, mucilage, glue and paste are organic materials that form adhesive bonds.

Natural adhesives have been known to be in existence since ancient Egypt. Egyptian carving dating back 3,300 years depict the gluing of a thin piece of veneer (a thin layer of fine wood or in making plywood) to what appears to be a plank of sycamore. Beeswax, tree pitches (a dark sticky substance made from trees) and bitumen (a natural substance that contains hydrocarbons i.e. coal) were used as protective coatings and adhesives. Egg whites were used to bind manuscripts at one time and wooden objects were bonded with glues made from fish, horn and cheese. During the 18th century, the technology of animal and fish glues advanced. In the 19th century rubber and nitrocellulose-based cement were introduced.

Adhesive materials are made up of polymers. Polymers are huge molecules or macromolecules that are formed by the linking of thousands of simple molecules known as monomers. When a polymer is formed the chemical reaction that take place is called polymerization. Polymerization and adhesive bond formation take place at the same time creating the means to keep surface together.

Natural adhesive are primarily of animal or vegetable origin. Animal glue is prepared from mammalian collagen, the primary protein of skin, bones and muscle. By dissolving a protein from milk in an alkaline solvent one can make

casein glue. Casein glue was often used to glue together wood. Today it is to improve the adhering characteristics of paints and coatings

Serum albumen, a component in blood obtainable from either fresh animal blood or dried soluble blood powder was also used as glue when added with alkaline. Today glue products made from blood are used in the plywood industry. Corn, wheat, potatoes or rice contain starch and dextrin extracts are soluble in water and are obtainable from plant sources all over the world.

2.2 Adhesive Composition

An adhesive is composed of basic raw material which is called binder and which determine its adhesiveness (adhesion) and its internal strength (cohesion) and of frequently necessary auxiliaries, which establish particular endues, and processing characteristics. The adhesiveness of an adhesive, its internal strength after setting and its processing characteristics are the functional properties that determine its suitability for use in forming adhesive joints. Adhesive joint are the joints formed between substrates and adherent using adhesives.

The binder used for adhesive is primarily high polymer having optimal strength properties. High internal strength is essential if the adhesive in an adhesive joint is to be able to transmit forces from one adherent to the other. In organic polymers, such as the various types of weatherglass are used only to a very limited extent.

Previously the only binders available were natural polymer of vegetable and chemical origin, such as internal resins, starch and particularly protein (gluten from hides and bones, blood albumen, casein and milk). Subsequently cellulose derivates and product based on natural rubber were also used. Over last 40 years the development of plastic and synthetic resins has produced a very wide range of

binders of adhesive. Virtually any standard poly adduct may be used, provided they can be applied as solutions, dispersions emulsions or melt.

Adhesive may also be classified based on their application and setting, chemical composition cost and suitability for various adherents and end product.

2.3 Advantages of Adhesive Bond

Adhesive bonding has many advantages to the construction industry over other methods of joining materials; these include

1. Thin films, fibers and small particles that could not be combined as well or at all by other techniques are readily bonded with adhesives.

Types of such uses are:

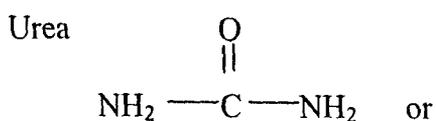
- (a). Laminates of plastic films, aluminum foil, fabrics and paper.
 - (b). Glass wool insulation and fiberglass mat composites.
 - (c). Abrasive wheels, sandpaper, emery cloth and brake lining
 - (d). Tires reinforced with rayon, nylon, polyester, glass fiber and steel.
 - (e). Corrugated board, paper bags, labels, tapes, stamps and envelopes.
 - (f). Veneer furniture.
 - (g). Particleboard.
2. Stresses are distributed over wider areas; making possible lighter and stronger assemblies than could be achieved with mechanical fastening. For example, airplane wings, tails and fuselages may be constructed of sandwich panels comprising a honey comb core bonded to thin faces of aluminum or magnesium; consequently the possibility of fatigue failure is decreased. Glued floors, wood framing and entire room modules, factor- prebuilt for economy, have tensile, flexural, and impact strength to resist the rigors of transportation and hoisting into place. In reinforced plastics and advanced composites, a glass fiber is adhered to

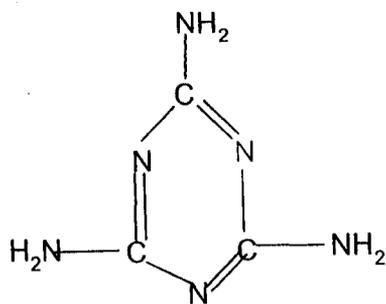
the unsaturated polyester matrix or graphite fiber to epoxy matrix with the aid of functional silanes and other coupling agents.

3. The glue line provides electrical insulation in capacitors, printed circuits, motors, potted resistor etc.
4. The glue line can be a moisture barrier, sealing window panels in certains wall construction.
5. The strength to weight ratio and dimensional stability of anisotropic materials can be improved by cross bonding. Thus wood, inherently nonuniform and water sensitive is converted into warp-resistant, water resistant plywood. Nonwoven fabrics having the same properties in all directions are made by lightly bonding a random web of fiber.
6. Dissimilar materials can be joined e.g. aluminum-to-paper, iron-to-copper. When two metals are bonded, the adhesive separates them and prevents corrosion. When the two adherents are markedly different in coefficient of thermal expansion, a flexible adhesive lessens the stress due to temperature change. Laminates of dissimilar materials can give combinations superior to either
7. Finally, what is often the key consideration: adhesive bonding may be faster and cheaper than the weaving of cloth; soldering, brazing or welding of metals; or mechanical fastening of rivets, bolts or nails.(Ivor H. Updegraff,1985)

2.4 Amino Resin

Amino resin (referred to as aminoplast or aminoplastic) is type stage resin made by the reaction of an amine or an amide with an aldehyde or exceptionally with a ketone. The majority of commercially importantly amionresins are of either





melamine (2,4,6-triaminotriazine)

Although resins based upon other amines and amide have been described. Other amines amide from which resins can be made include thiourea, guanamide, guanidine, cyanamide, dicyandiamide, aniline, p-diamino benzene, pyroles, amino acids, protein and urethanes.

Of the aldehyde, which will react with amines or amides, form resins, the most widely employed is formaldehyde.

Aminoplast belong to the group of thermosetting resins, as the soluble and fusible condensation products on heating are converted into insoluble and infusible materials. The product of the first stage condensation of formaldehyde with amines takes the form of aqueous syrup solutions or water-soluble fine-grained powder or may be amorphous. Their form depends on the reaction conditions, the pH of the reaction medium, the proportion of formaldehyde to amine, and the temperature.

The principal attractions of amino resin are: water solubility before curing (which allows easy application to many substrates and with other material), colourless (which permits a colourless glue line as well as unlimited colourability with dyes and pigments) good solvent resistance, hardness, and high heat resistance, as well as low cost. A limitation of amino resins is the release of formaldehyde during curing and in some cases after curing. Outdoor weatherability is poor for products made with formaldehyde resin, but products made with melamine formaldehyde resins have good water resistance and outdoor weatherability.(Irving Skeist,1990).

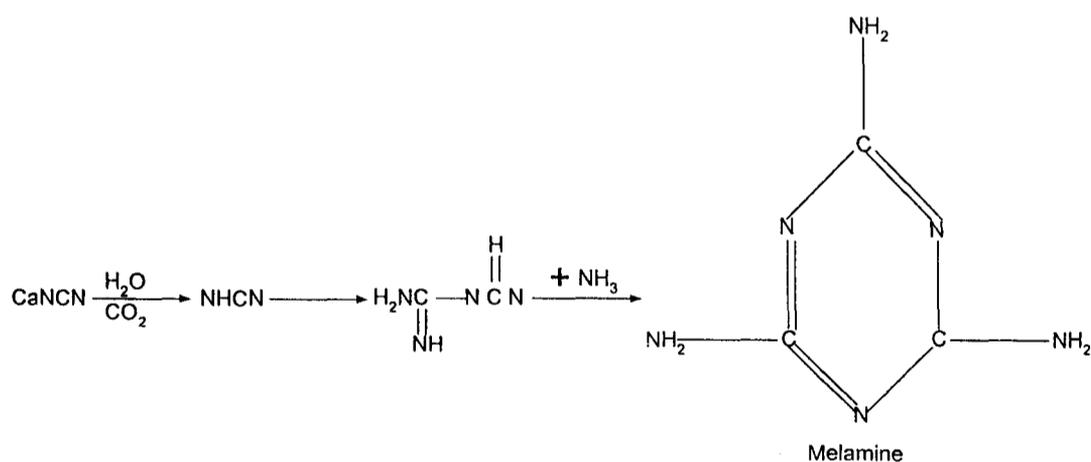
2.5 Raw Materials for Melamine Resin Production

The basic raw material for M-F resin manufacture include:

- I. Melamine
- II. Formaldehyde

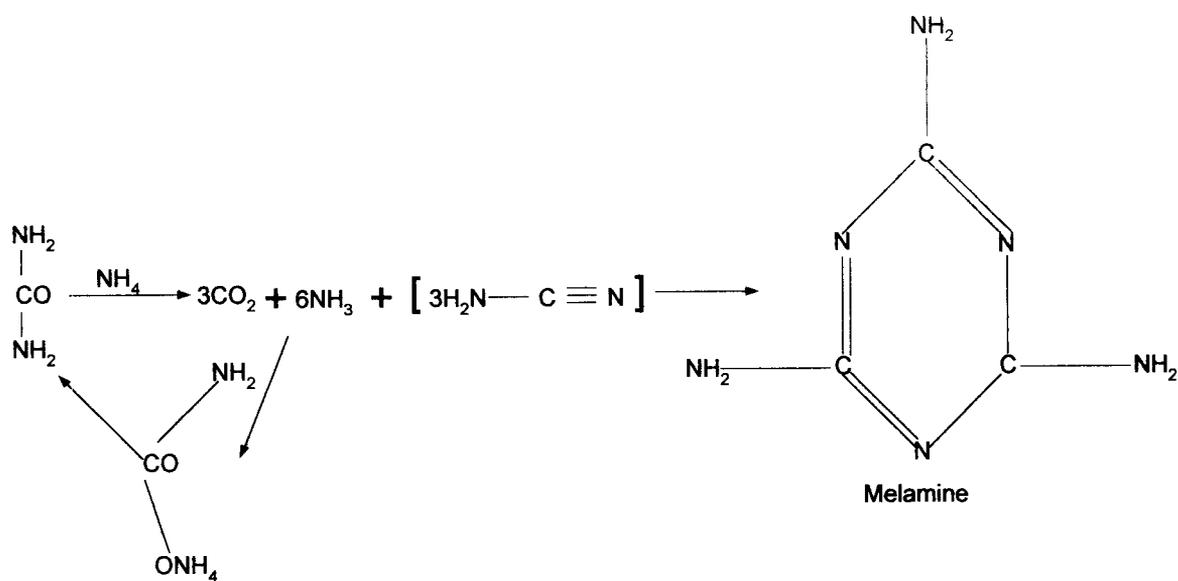
2.5.1 Melamine

Melamine ($C_3H_6N_6$) whose common name is 2,4,6-triamino-1, 3,5-triazine, is a white crystalline compound that is slightly soluble in water, melts at $354^{\circ}C$ and is a cyclic trimer of cyan amide; it was synthesized early in the history of organic chemistry but remained a chemical curiosity until it was found to react with formaldehyde to form a useful amino resin. This compound, the most valuable of all the triazine, had been investigated by Liebig as early as 1834. It almost forgotten, however, because no use had been found for it until the discovery of the melamine resins about 1935. It was produced first by converting calcium cyanamide, which in turn dimerised to dicyandiamide (cyan guanidine) and this last substance was reacted in the presence of ammonia and under pressure to form melamine. (Encyclopedia of Polymer Science and Technology, 1984)



REACTION SCHEME FOR THE FORMATION OF MELAMINE FROM CALCIUM CYANAMIDE.

However, melamine was first manufactured from dicyandiamide, but it is now made from urea, a much lower-cost starting material. In this process the urea is dehydrated which terminates to melamine. The reaction is carried out at high pressure of 1050^uC which terminates to melamine. The reaction is carried out at high pressure of 1050^uC in the presence of ammonia to suppress the formation of deamination products. Ammonium carbamate is also formed in the reaction and must be recycled to convert it back to urea.



Reaction for the formation of melamine by dehydration of urea

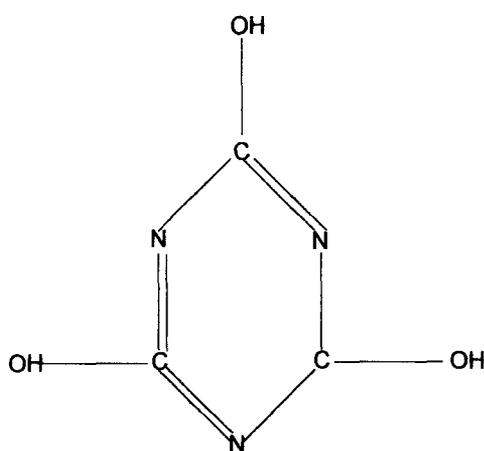
When pure, well-dried dicyandiamide is used in an autoclave at an elevated temperature of 200^oC and pressure of (800-1400 psi) or about 160^oC between 4000-5000 psi, melamine is obtained in a yield of 97-99%.

On a laboratory scale, Smolka and Friedrichs have suggested a very simple method of making melamine using no ammonia pressure. Dicyandiamide or Cyanamid is fused in an open container with a guanidine salt or with biguanide, whereupon these rapidly form melamine. However a great proportion of unreacted by-product is present in the crude melamine obtained in the way, so purification is necessary.

One major problem associated with all these processes is corrosion, particularly in the reaction for the formation of melamine by dehydration of urea, in the presence of acid deamination product such as cyan uric acid and as such corrosion-resistant metals and alloys have been suggested and experimented although not always satisfactory. Stainless steel of different composition alloyed with chromium, nickel, vanadium, rare metals, super purified aluminum, titanium and its alloys, silver and gold and platinum metals or their alloys have been suggested and patented for this use.

Pure melamine (formula weight 126.13) crystallizes in colourless, monoclinic prisms that melt at about 350°C , at this temperature it decomposes slightly and the remainder sublimes, which can be reclaimed unchanged. In the presence of ammonia or in high vacuum, small quantities of melamine can be sublimed with almost no decomposition, so that this method has proven useful for the quantitative analysis of melamine in crude melamine. The solubility of melamine in water at 20°C is about 0.3g/100ml and at $98-100^{\circ}\text{C}$ is about 5g/100ml. Melamine is also soluble in organic solvent, but is soluble to some extent in ethylene glycol, ethanolamine and triethanolamine.

Heating melamine over 300°C for a long time causes the amino group to be split off in the form of ammonia with the formation deamination products which posses a remarkable resistant to heat e.g. Mellon may be heated to red heat with further decomposition. When hydroxyl groups gradually hydrolyze the amino groups of melamine, the hydrolysis products of melamine are obtained.



Hydrolysis product of melamine.

The low solubility of melamine, its greater stability at higher temperature (compare to the high almost unlimited, water solubility of urea) and its low decomposition point (about 130⁰ C) are very probable reason for the better water resistance and heat stability of the melamine formaldehyde resins. In addition to the fact that the melamine has three amino groups are present as against two in urea obviously offers the possibility of a high degree of cross-linking in the final condensation of melamine formaldehyde resins due the higher functionality thus producing a network with more inter-connection.

2.5.2 Formaldehyde (HCHO)

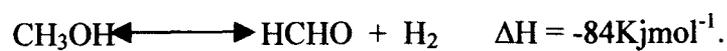
Formaldehyde is a petrochemical product, which is an important compound in the chemical industry. Its Synthesis can be divided into two groups namely:

- I. Silver contact process
- II. Formox process

I. Silver Contact Process

In the silver contact process, methanol is partially oxidized and dehydrated to formaldehyde. A mixture of air and methanol vapour is passed over a heated

platinum wire catalyst at a temperature of about 600⁰C. The hydrogen, which is formed during the dehydration, is burned to give water.



II. Formox Process

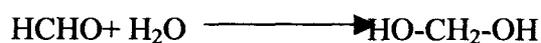
In this process, formaldehyde is formed from methanol by oxidation using iron III and molybdenumoxide as catalysts at a lower temperature of 270-380⁰C. The reaction is exothermic and the yield of formaldehyde is nearly quantitative.

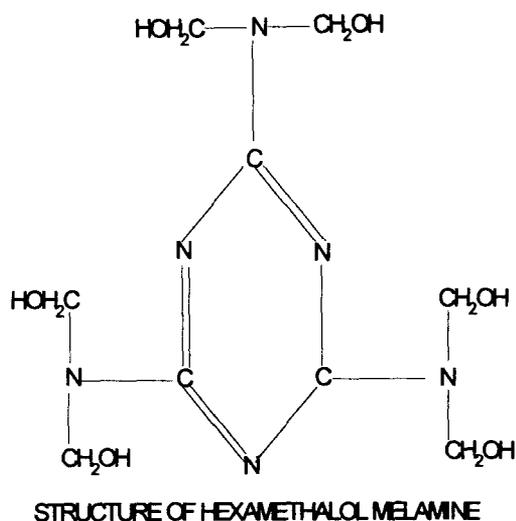
In both processes the formaldehyde is isolated by absorption in water and the formaldehyde content of these aqueous solution (formalin) can be increased by distillation.

Formaldehyde is highly reactive with a pungent smell is poisonous it is a gas liquid at -20⁰C with a density of 0.8153 and molecular weight of 30.03. aqueous formaldehyde solution is used for amino resin production because formaldehyde dissolves very easily in water by forming a hydrate called methylene glycol.



In amino plastic manufacture, aqueous solution formalin contain 36-37% w/w formaldehyde is used. Both high and low methanol content formalin is used according to the needs of the manufacturer. The low methanol content formalin was more reactive but less stable (polymerizes easily) and must be used soon after its production. For this reason, resin manufacturers prefer to use formalin with a high (7-10%) methanol content for stabilization.





2.6.1 Industrial development of M-F resin.

U-F and M-F resins are the most commonly used amino resins. They are produced domestically by adding formaldehyde (HCHO) to urea (NH_2CONH_2) or melamine $\{\text{C}_3\text{N}_3(\text{NH}_2)_3\}$ to form methylol monomer units and subsequent condensation of these units to form a polymer. M-F resins are used for high-pressure laminates such as counter and tabletops.

The basic operations that may be used in M-F resins manufacture are shown in figure 1 Amino resins generally are produced in a batch reactor but some are produced in closed continuous systems. The first reaction of the process, the addition of formaldehyde to the amino compound to form methylol compound is carried out under alkaline conditions. Caustic, formaldehyde and amino compound are charged to the heated reaction vessel.

Next the reactor conditions are altered to favour the second reaction, the condensation of the methylol compounds to form a polymer resin. The condensation reaction is carried out under acidic conditions and is stopped at the desired degree of polymerization by lowering the temperature and raising the pH.

At high degree of polymerization, a solid polymer is produced. At low degree of polymerization stable syrup is produced that can be used as an adhesive or laminating resin. The syrup can be combined with a filler to make a molding

compound or used with other polymers in coating formulations. The syrup can also be sprayed dried to form a powder for convenient storage and handling.

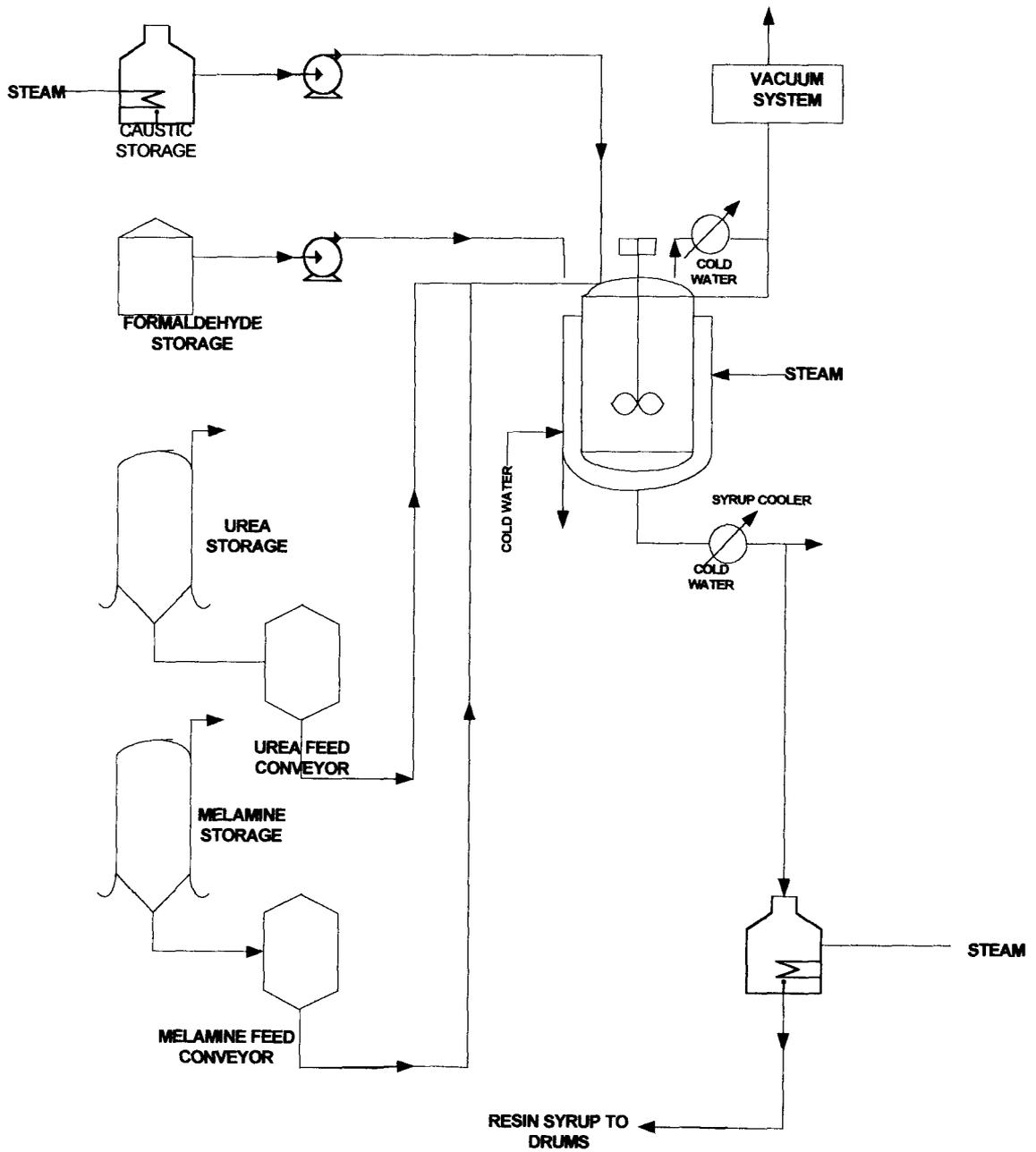


Fig.1 Basic operations for urea-formaldehyde and melamine-formaldehyde resins manufacture.

2.7 Infrared (IR) Analysis

IR absorption spectroscopy is the measurement of the amount of radiation absorbed at various frequencies by compounds having covalent bonds (whether organic or inorganic) with the infrared region of the electromagnetic spectrum. The IR region of the electromagnetic spectrum lies at the vibrational portion with wavelength (λ) between 2.5 μm and 15 μm , which correspond to frequencies between, 4000 and 650 cm^{-1} (waves numbers).

Infrared spectrophotometer is the instrument that determines the absorption spectrum for a compound. It determines the absorption spectrum for a compound. It determines the relative strengths and positions of all determine the relative strengths and positions of all the absorption in the IR region and plots this on a piece of calibrated chat paper. This plot of absorption intensity (% transmittance) on the vertical scale from 100% being at the top of the spectrum to 0% at the bottom versus wave number or wavelength is referred to as infrared spectrum of the compound. An IR spectrum can be divided into two portions for examination. The region 4000 – 1500 cm^{-1} is useful for the identification of various functional groups while the region 1500-600 cm^{-1} (finger prints region) is useful for comparing two compound for identification. The absorption of radiation at different wave numbers corresponds to the excitation of molecules from a low (usually the lowest) vibrational energy level to the next higher vibrational energy level.

A strong absorption throughout a narrow range of frequencies causes a sharp “peak” or “line” in the recorded spectrum. Absorption peaks are not always narrow and sharp because each vibrational energy level has superimposed upon it an array of rotational energy levels; therefore a particular vibrational transition is really the superposition of transitions from many vibrational rotational levels.

Fourier transform infrared spectroscopy (FTIR) is a widely used method in which the electromagnetic radiation is split into two beams. One is made to travel a longer path than the other. Recombination of the two beams creates an interference pattern (interferogram) and the mathematical (Fourier transform) of this interference pattern by a computer converts it into the usual IR spectrum. The advantages of FTIR are that the whole spectrum is measured in a few seconds and high resolution is obtained.

A drop of the liquid sample is placed in the center of the lower window and the second plate is placed carefully on top, spreading the drop into a thin film. The nuts or screws are tightened firmly but not excessively and placed in the holder provided in the instrument. The cell was disassembled after obtaining the spectrum and the windows are rinsed well with a dry, violent solvent (CH_2Cl_2 hexane etc). This procedure is run as neat using Genesis II FTIR spectrometer.

Infrared spectra could be obtained on cured resins. About 1 to 2 mg of the sample is mixed with 50 to 100 mg of dry potassium bromide (KBr) powder. The particle must be reduced by grinding the mixture with mortar and pestle or pounding action of a miniature ball mill for 30 seconds at full speed or a pellets press may be used.

CHAPTER THREE

3.0 EXPERIMENTAL PROCEDURE

3.1 Materials and Equipment

To carry out production of melamine formaldehyde, many instruments and materials were used. The main materials and equipment setup are presented briefly in this chapter.

Table 3.1: Materials used for the experiment.

Materials	Structure	code	Comment.
Formaldehyde	CH ₂ O	UN1198	37% _{w/v}
Melamine	C ₃ H ₆ N ₆	Andrich chem	White powder
Sodium Hydroxide	NaOH	UN1165	Alkaline (36% _{w/v})
Distilled water	H ₂ O	NA	Liquid

The experimental procedures were divided into four stages which included synthesis the melamine resins; modification and formation of melamine resins into adhesives; IR and characterization of the physico-chemical properties of the melamine resin, modified melamine resin and adhesive; and application of the M-F resin adhesive for plywood, solid wood joints manufacture. Conventional names of the materials are used in this presentation and shown in Table 3.1. The various equipment employed throughout the investigation are described in Table 3.2.

Table 3.2: Equipment used in the experiment.

EQUIPMENT	SOURCE	CODE	COMMENT
Water bath regulator	Clifton England	CE 94	At 90-100 ⁰ C
Beaker	Pyrex England	NA	Glass apparatus
Conical flask	Pyrex England	NA	Glass apparatus
Electric motor stirrer	Gallenkamp England	NA	Continuous stirring
Double-jacketed reactor	Quick fit England	NA	Glass apparatus
Retort stand	P.H & Co. England	NA	Steel
Thermometer	Zeal England	NA	Mercury in glass
Weighing balance	Ohaus, U.K	NA	Digital display
Stop watch	Armfield England	NA	For timing
Density bottle	Pyrex England	NA	Glass apparatus
pH meter	Kent in. Ltd. Eng,	NA	Digital display
Pump	Charles pumps Ltd. Eng.	NA	

3.1.2 Melamine formaldehyde reactor

M-F reactor is a double-jacketed glass type with openings at the outer part of the reactor (one at the bottom and the other at the upper part) for hot water passage at the bottom and goes out at the upper part. A positive displacement diaphragm pump is used to pump water through this reactor. The reactor has a lid with five necks, one for electrically driver mechanical stirrer inserted at the center of the reactor while others are for pH electrode, thermometer and the remaining two spaces for charging in the reactants and prepared solutions the reactor was connected to a water bath. The water bath was used to keep the temperature of the

reaction at the desired value. Melamine and Formaldehyde were charged into the reactor at once. The stirrer aided in ensuring proper mixing and dissolution of Melamine. The pH meter electrode and thermometer were used to determine the pH value and temperature of the reaction mixture, respectively.

Fig. 1 shows the system comprising of different apparatus used in the preparation of melamine formaldehyde resin. The water bath is used to keep the temperature of the reaction at the desired value. Melamine and formaldehyde were charged into the reactor at once. The stirrer aids to ensure proper mixing and dissolution of melamine. The pH meter electrode and thermometer are used to determine the pH value and temperature of the reaction mixture respectively.

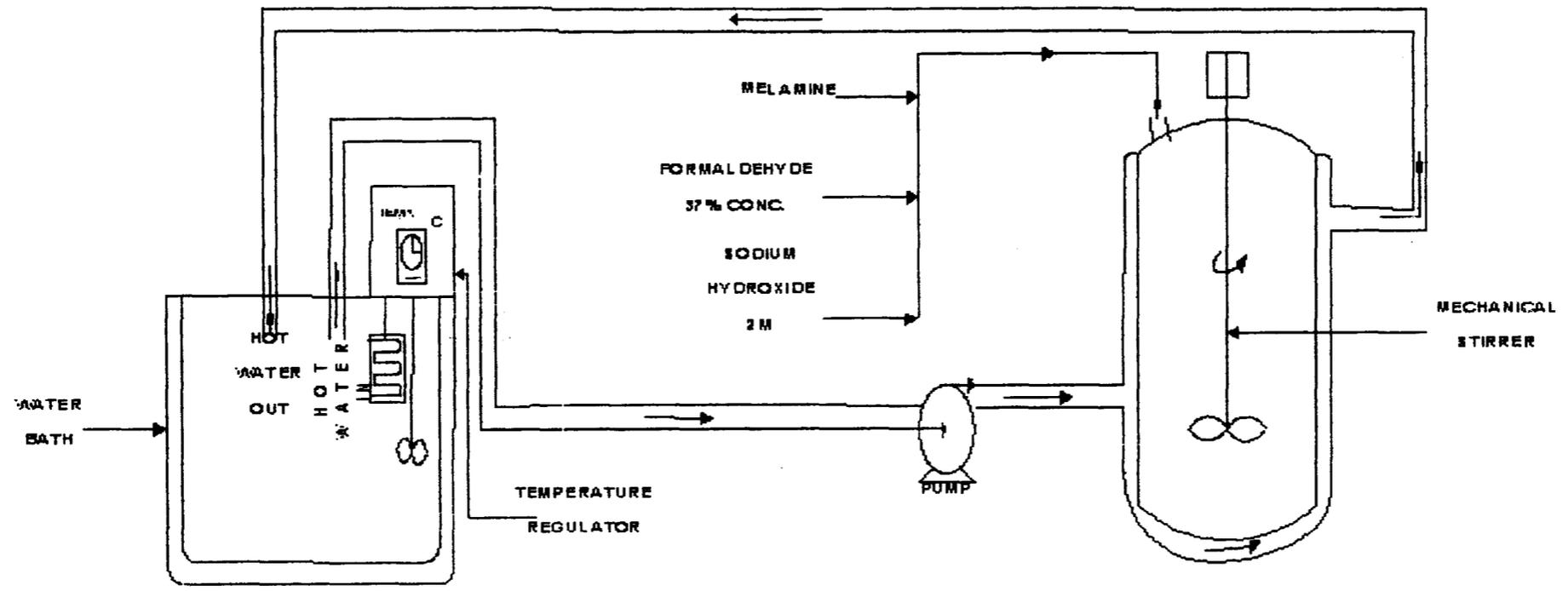


FIG.2: LABORATORY SET-UP FOR THE DEVELOPMENT OF MELAMINE FOR FORMALDEHYDE ADHESIVE

3.1.3 Preparation of M-F Resin

To prepare a suitable M-F resin, formaldehyde was charged into a reactor equipped with stirrer and thermometer. The pH of the formaldehyde was adjusted to 8.00-8.20 with 2M NaOH and melamine then dissolved into it (M-F molar ratio 1:2). The mixture was boiled under reflux for about 30 minutes to give a trimethylmelamine and other low molecular weight products. The resulting resin was then stabilized to a pH of 8.2 to give a water soluble resin which was approximately 50% solid content. When the resin was used in aqueous solution, as was normally the case, was then partially dehydrated to give a 75% solid content by vacuum distillation. The viscosity, specific gravity and pH of the M-F Resin was determined as would be described later in this section

The finished product is checked for viscosity, specific gravity, pH value (which must be in the range of 8.0-8.40)

3.2 Characterization of M-F Resin Samples

3.2.1 Determination of refractive index (n_d)

The prism assembly cover was opened cleaned with alcohol and then with distilled water. The mode selector was turned to the desired position and the sample solution was applied to the measuring prism surface using a glass dropper. The prism cover was closed and the exposed face partially or fully illuminated. The dispersion correction wheel is turned so that the crosshair adjustment access hole is at the six o'clock position.

The adjustment control was rotated counter clockwise to position the shadow line at the bottom of the field of view. The eyepiece was rotated to bring the crosshair into focus and at the retrace. Eliminate any red or green colour at that edge of the shadow line by rotating the dispersion correction wheel. The

adjustment control knob was turned so that the shadow line is centered at the crosshair

Turn the mode selector switch to the negative index (n_D) and obtain the n_D by depressing the read button. The temperature of the sample can be known by depressing the temperature button.

3.2.2 Viscosity measurement

The standard method of viscosity determination was employed using the viscometer bath and U-tube viscometer with capillary inserted into the viscometer bath.

75.3g of the sample was poured into the U-tube viscometer with capillary and corked. The U-tube was suspended into the viscometer bath containing water and the temperature of the bath was taken. The cork was removed and the time taken for the content to run up starting from the top mark to the middle mark was noted using a stopwatch.

From this result, the viscosity of the sample was calculated.

3.2.3 Specific gravity measurement

The empty specific gravity bottle was weighed and its weight was recorded. The same specific gravity bottle was filled with M-F sample and was weighed, and its weight was recorded. The difference in weight between the specific gravity bottle filled with the resin and the empty specific gravity bottle gives the density.

The ratio of the density of the resin at ambient temperature to that of water at 4⁰C gives the specific gravity.

3.2.4 IR measurement

IR spectra were obtained with Genesis II FTIR mode spectrometer with about 2mg of the melamine resin (modified/unmodified) synthesized at certain thermodynamic condition (section 2.7). the resin samples were frozen immediately after synthesis and until time of analysis.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

Table 4.1: Properties of the various samples of melamine-formaldehyde resin produced.

Properties and temperature [$^{\circ}$ C] at Which they were determined.	Sample A	Sample B	Literature value
pH [at 32° C]	8.30	8.50	7.50 – 9.50
Viscosity C_p [at 32° c]	34.98	38.54	
Specific gravity [g/cm^3 at 32° C]	1.47	1.51	1.47 – 1.52
Refractive index [at 32° C]	1.50	1.53	1.52 – 1.58
Molecular weight	2829.28	3152.35	
Operating temperature	95 – 100	95 - 100	
Operating pressure [atm].	1.0	1.0	

Table 4.1 gives the results of the physico-chemical characterization of the neat and modified resin. The pH values of the sample A and sample B are given as 8.30 and 8.50 respectively. These values are considered reasonable as compared to the pH values obtained from the literature (7.50 – 9.50) for standard melamine-formaldehyde resin.

The specific gravity of samples A and B are 1.47 and 1.51 g/cm^3 respectively. The values of the two samples fell within the range given in the literature, which is between $1.47 - 1.52$ g/cm^3 .

The viscosity of sample A and B are $34.98C_p$ and $38.54C_p$ respectively. The result shows that the value of samples A and B are closer in comparison to each other. The little variation in the values can be attributed to the fact that their values were not determined at the same time. This was because the knowledge of polymerization shows that the reaction often continues at room temperature and this lead to increase in molecular mass, which has direct effect on viscosity.

The molecular weight result shows that sample B has the highest value of 3152.35 while that of sample A has 2829.28. The molecular weight difference can be considered as a result of the fact that sample B had undergone certain extent of polymerization at room temperature after the termination of the reaction.

The refractive index of sample A and B agreed to some extent. Sample A is 1.50 and that of sample B is 1.53. Although sample A is out of the range given in the literature, but that of sample B agreed with the standard range of 1.52 – 1.58.

Analysis of the infrared spectra

An analysis of the spectrum of sample A for structural information on functional groups in fig.1. (Neat M-F) shows that there is absorption at frequency 3369.34cm^{-1} . The peak shows only one band which is characteristic indicating the presence of secondary amine (N-H) groups. At peak 2923.08 cm^{-1} , the intensity of the absorption is between medium and strong (m-s), which is an indication of C-H stretching vibration. Thus CH_2 group is confirmed present.

The absorption at region 1641.81cm^{-1} is medium and strong (m-s) but is a bit small. The region shows that there is N – H band, therefore confirming the presence of amines.

Fig.2 gives the infrared spectra of sample B. It is observed that there is absorption at region 3383.82 cm^{-1} the peak of the region is a bit broad in nature and the intensity of the absorption is medium which is an indication of N-H stretching vibration. This shows the presence of secondary amine group.

The absorption at region 1818.00 cm^{-1} is very strong. This region shows that there is a C = O stretching vibration, while at peak 1735.87 the absorption indicates the presence of an aldehyde.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION

The work reported here focused on the development and characterization of melamine formaldehyde resins at pH of 8.30, F/M ratio of 1.5, temperature of 95⁰C and at atmospheric pressure. The result of the physico-chemical characterization and IR analysis support that melamine formaldehyde resin was obtained by polycondensation of melamine and formaldehyde at the above stated thermodynamic conditions. The work further indicates that Urea shows good promise as modifier.

5.2 RECOMMENDATION

To enhance the validity of this work, further analysis should be carried out to determine some important properties like the softening glass transition temperature, impart strength, curing temperature and tensile strength etc.

Unavailability of some basic equipment is one of the major constraints that delayed this work. The department should try and set up a polymer-processing laboratory in other to ease the difficulty encountered by students in trying to carry out some test in other departments. Also the use of other chemical is recommended in order to substitute melamine since it is highly expensive and scarce.

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APPENDIX

(A) SAMPLE CALCULATION.

(I) Kinematics viscosity, viscosity, Density And Molecular Weight.

For Sample A

$$V = 50 \text{ ml}$$

$$t_A = 270 \text{ s}$$

$$\mu_A = c \times t_A = 0.0882 \times 270 = 23.8 \text{ stokes}$$

$$N_1 = 12.20 \text{ g}$$

$$N_2 = 85.70 \text{ g}$$

$$N_3 = N_2 - N_1$$

$$N_3 = 73.50 \text{ g}$$

$$\rho_A = 73.50/50 = 1.47 \text{ g/cm}^3$$

$$\mu_A = \mu_A \times \rho_A = 23.8 \times 1.47 = 34.98 \text{ Cp}$$

$$(\mu_A)_i = \frac{\mu_A - \mu_0}{\mu_A \times c} = \frac{34.98 - 0.42}{0.42 \times 0.7} = 117.57$$

$$(\mu_A)_i = 117.57$$

From the relationship of $(\mu_A)_i$ and molecular weight [i.e.] $(\mu_A)_i = kM^a$

Where $k = 9.2 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$ and $a = 0.9$

So, $M_A = [(\mu_A)_i / k]^{1/a}$

$$= [117.50/9.2 \times 10^{-2}]^{1/0.9}$$

$$= 2829.28$$

$$M_A = 2829.28.$$

Sample B.

$$t_A = 290 \text{ s}$$

$$\mu_B = c \times t_B$$

$$= 0.0882 \times 290 = 25.52 \text{ stokes}$$

$$\mu_B = 25.52 \text{ stokes.}$$

$$N_1 = 12.20$$

$$N_2 = 87.70$$

$$N_3 = N_2 - N_1$$

$$= 87.70 - 12.20 = 75.50 \text{ g}$$

$$N_3 = 75.50 \text{ g}$$

$$\rho_B = N_3 / V$$

$$= 75.50 / 50 = 1.51 \text{ g/cm}^3 \text{ at } 32^\circ\text{C}$$

$$\mu_B = N_B \times \rho_B$$

$$= 25.52 \times 1.51 = 38.54 \text{ Cp.}$$

$$(\mu_B)_1 = \frac{\mu_B - \mu_0}{\mu_0 \times c} = \frac{38.54 - 0.42}{0.42 \times 0.7} = 129.66.$$

$$= 129.66$$

From the relationship of $(\mu_B)_1$ and molecular weight [i.e.] $(\mu_B)_1 = kM^a$

Where $k = 9.2 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$ and $a = 0.9$

$$M_B = [(\mu_B)_1 / k]^{1/a}$$

$$M_B = [129.66 / 9.2 \times 10^{-2}]^{1/0.9} = 3154.35.$$