THE DEVELOPMENT AND MODIFICATION OF UREA -FORMALDEHYDE ADHESIVE USING AGRICULTURALWASTES

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NIGERIA.

A RESEARCH WORK SUBMITTED IN PARTIAL
FULFILMENT OF THE REQUIREMENT FOR THE
AWARD OF BACHELOR OF ENGINEERING DEGREE
IN THE DEPARTMENT OF CHEMICAL
ENGINEERING, FEDERAL UNIVERSITY OF
TECHNOLOGY MINNA, P.M.B 65, MINNA, NIGER
STATE OF NIGERIA.

MARCH 2000

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DECLARATION

I hereby declare that this research work is my original work. To the best of my knowledge, it has never been presented in any symposium, seminal or elsewhere in any form for the award of diploma or degree.

_____   _____

OLADUNJOYE M. ABIODUN   Date

CERTIFICATION

This is to certify that I have supervised, read and approved this project report, which I found adequate both in scope and quality for the partial fulfillment of the requirement for the award of bachelor of engineering (B.ENG) degree in chemical Engineering.

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EXTERNAL SUPERVISOR   DATE

DEDICATION

I solemnly dedicate this project work to my beloved parents Mr. S. O. and Mrs. A. Oladunjoye, for their immense support and contribution throughout this programme.

Moreso, to my project supervisor Dr M. O. Edoga under whose supervision, guidance and assistance this study was done.

ACKNOWLEDGEMENT

My acknowledgement goes to the Almighty God for given me sufficient grace, strength, knowledge and understanding throughout this programme and my parent's whose unrelenting efforts have contributed so much into my educational pursuit.

I also use this opportunity to thank all my lecturers for the knowledge they have impacted on me.

Finally, my appreciation is due to my brothers, Mr Oluwasanmi Oladunjoye, Mr Blessing Oladunjoye and my Sister Jumoke Oladunjoye. My profound gratitude goes to all my friends most especially Femi Akintola, Shola Adesanya, Wale Yusuff, Wale Adegboye, Wale Adewale,Toyin Adedokun, Dele Dada and Akin Aina for their contribution and support during the course of my educational pursuit.

ABSTRACT

This research work was aimed at developing urea formaldehyde adhesive and the modification of the resin with extract (furfural) from agricultural waste such as rice husk and maize cob. The synthesis of the resin was carried out in a reactor at pH 7.5 – 8.0. temperature of 65 – 70°C and pressure of 1 atmosphere. The ratio of urea to formaldehyde was 1:1.5. The neat UF was divided into three equal parts; one part of the resin was modified with furfural from rice husk, while the second part was modified with furfural from maize cob. The third part is the neat resin . Another resin was produced and modified with furfural from each of the agricultural waste during the synthesis.

The physicochemical properties of the resin was determined as well as the NMR cum IR analysis of the samples were carried out. The IR spectra show that the same functional groups were present in the structure of the samples except sample A, which has no ether linkage due to the fact that it was not modified with furfural. The NMR signals revealed the complexity of structure of the samples. Moreso, it showed a chemical shift of proton of the samples except for sample A (neat UF resin). This indicates a change in the structural constitution of the samples (i.e the furfural – m,odified UF resins) and hence signifies the presence of furfural in the modified samples which is the aim of the research work.

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NOMENCLATURE

W_1 =Weight of specific gravity bottle.

W_2 =   Weight of specific gravity bottle + weight of sample

W_2 = Weight of sample.

V = volume of the sample

          = Viscousity of the polymer solution

visousity of solvent (Acetone)

The limiting viscousity number or intrinsic.

Viscometer constant.

Kinematic viscousity

Density

Time for a fixed volume of a liquid to flow through the U – tube capillary.

A   =   Sample of neat –urea-formaldehyde resin

B   =   Sample of resin modified with rice husk extract during synthesis.

C   =   Sample of resin modified with rice husk extract after synthesis.

D   =   Sample modified with maize cob extract after synthesis.

M_0 =   Weight of aluminum dish.

M_1 = M_0 + weight of sample.

M_2 =   Weight sample = $M_1 - M_0$

M_3 = M_0 + weight of sample after drying.

M_4 =   Weight of water and other impurities being vapourized.

M_5 =   Weight of dried resin.

TDS   =   Total solid content.

CHAPTER ONE

INTRODUCTION

1.0   UREA – FORMALDEHYDE ADHESIVE

Adhesives are substances which are capable of holding materials together by surface attachment. Such adhesives are cements, glues, mucilage and pastes. The choice of a specific adhesives depends on the materials to be bonded, their applications, chemical composition, stresses, cost, suitability and other conditions to which the bond will be subjected.

The bond formed by adhesive is either chemical or mechanical. In a chemical bond the adhesives acts chemically on the molecules at the surfaces of the objects to be joined and causes bonding by intermolecular attraction. In a mechanical bond the adhesives flows into the pores of the bonded materials and lock them together mechanically [1].

Adhesive are classified into a number of groups such as:
1.   Thermoplastic adhesives.
2.   Thermosetting adhesives.
3.   Contact adhesives or cements.
4.   Hot-melt adhesives.
5.   Pressure-sensitive adhesives and
6.   Remoistenable adhesives. [2]

Urea- formaldehyde as an adhesive is a polycondensation reaction project of urea with formaldehyde in alkaline solution. The urea-formaldehyde resins are colourless and can be coloured with pale pigments. [3]

Urea-formaldehyde adhesives are used chiefly for bonding wood, especially plywood, chipboard, and solid wood joints. UF resins are cheap, show no glue line, and are used extensively in furniture or wood industry. The hardness, colourabily, low cost and solvent resistance makes it the most important adhesives used by the industry.

UF, being a condensation polymer depend upon a chemical cross linking reaction to form it's adhesive bond.

Resins with greater flexibility than the adherends lessen the tendency to stress the glue line and cause peeling; resins with minimal shrinkage have less tendency to pull away from the glue line, inert fillers act to reinforce the glue line. The glue ought to be kept as thin as possible to lower the tendency for cohesive failure, and water or solvent should be allowed to evaporate before joining impervious adherends. Hygroscopic filler such as cellulose, asbestors or certain clays, is added to absorb the last trace of moisture [3]

However, the aim of this research work is to develop UF adhesive that will have low flexibility, minimal shrinkage as well as no free formaldehyde by incorporating maize cob extract into the UF resin structure.

The entire work of the research would include the development of neat urea-formaldehyde resin and the modification of UF resin by fortifying the resin with maize cob extract and the determination of physiochemical properties of both NMR and IR of neat and modified UF resin.

CHAPTER TWO

LITERATURE REVIEW

2.0   UF RESIN

Urea-formaldehyde resins are products of polycondensation reaction of formaldehyde and urea. It belongs to the aminoplast family. UF resins are the utmost important commercially when compared with other amino-plastics. The resins are colourless, odourless, and because of their properties such as hardness, colourability, solvent resistance and no glue line makes the UF suitable for various applications in the industry.

Urea-formaldehyde resins accounts for about 80% of production of adhesives while melamine and a few other amino-plastics constitutes the remainder.

2.1   BACKGROUND

The primary reaction products of urea and formaldehyde were investigated as early as 1884. The intensive study of UF resins did not begin until the early 1920s. The first polymer to achieve commercial importance, in about 1930, was a urea **thiourea-formaldehyde** resin. The production, properties, and fabrication of urea-formaldehyde resin into finished articles was studied by H. John (1918). He boiled 5 part of a 40% by volumes of formalin solution with 1 part of urea (a dilute formic acid medium) and distilled until about half of the liquid was removed. The result was a water-soluble, clear, very sticky, and highly viscous residue, which he suggested as an adhesive for glass and metal. He further proposed pigmentation of this colloidal resin solution and use as a filling cement for root canals in dentistry. Later on, he discovered that these water-clear compositions could be cured by heat to give better properties. He also suggested the impregnation of textile fabrics with such colourless, water–soluble resins and even believed that the partially cured, gelatinized products would find use as a rubber substitute.

These observations and suggestions set the pace and direction for the development of urea-formaldehyde resins for use as adhesives and casting compositions.

H. John was the first to suggest that clear, colloidal, sticky solutions of urea-formaldehyde resins could be used as adhesives. I .G farbenindustries A.G took up this idea and develop wood glues for hot and cold cure that were water resistant. These caused a revolution in the technique of glueing in the wood-fabricating industry, particularly in plywood production.

UF adhesives for lamination became available first in Germany and Switzerland about 1934 by I.G farbenindustries A.G under the trade name kaurit, but soon on a world wide basis. World War II also helped to introduce these adhesives

rapidly and all the bellingerents used them for the manufacture of airplanes, some of which were at that time constructed of wood.

The application of urea-formaldehyde resins for gluing purposes is based on the fact that excellent control of the condensation reaction is possible by variation of the pH. [5]

2.2   RAW MATERIALS FOR U-F RESINS PRODUCTION

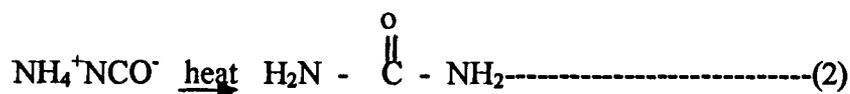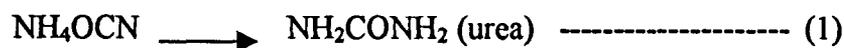The basic raw materials for the manufacture of UF resins include;

1.Urea

2. Formaldehyde

2.2.1   UREA

Urea was discovered in urine by Rouelle in 1775. Between 1828 and 1850 organic compounds were synthesized from sources that were clearly "inorganic". The first of the compounds to be synthesized in the laboratory was urea and was accomplished by Friedrich Wohler, a German chemist in 1828 by the isomerization of ammonium cyanate though an intramolecular rearrangement. (equation 1) [5]

Wohler found that the organic compound urea could be made by evaporating an aqeous solution containing the inorganic compound ammonium cyanate (equations 2).

$$NH_4OCN \longrightarrow NH_2CONH_2 \text{ (urea)} \text{ -------------------- (1)}$$

$$NH_4^+NCO^- \xrightarrow{\text{heat}} H_2N - \overset{\overset{\textstyle O}{\|}}{C} - NH_2 \text{------------------------(2)}$$

Urea is also formed by first reacting carbondioxide with ammonia at 140-160^{0}c and 700 – 1400 PSI leading to an equilibrium mixture containing about 40 – 50% urea and ammonium carbamate.

$$CO_2 + 2NH_3 \longrightarrow NH_2CONH_2 + H_2O \rightleftharpoons H_2NCOONH_4$$
(Ammonium carbamate)

$$NH^+_4 (O.CONH_2)^- \rightleftharpoons CO(NH_2)_2 + H_2O \uparrow$$
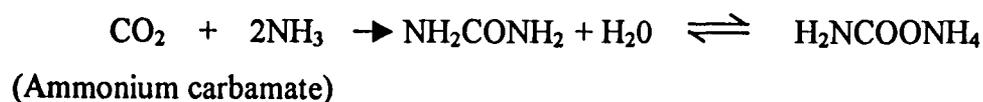
On heating urea to 132^{0}C it loses ammonia and resolidified to 'biuret':

$$2CO(NH_2)_2 \longrightarrow NH_2.CONH.CONH_2 + NH_3$$
biuret
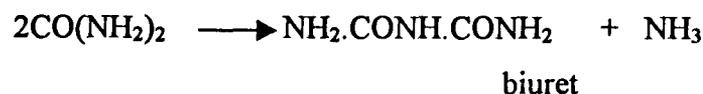
Cyanuric acid is also formed along side (NHCO)$_3$. [3].

Urea is a colourless, odourless, solid, with melting point of 132^{0}C and it is slightly soluble in ether, soluble in alcohol and insoluble in dichloroform. It has molecular weight of 60.06

The ureas cure between 70^0F and 225^0F (57^0C and 143^0C). Standard ureas are distinctly moisture-resistant and are immune to mold and fungi attacks. [1]

2.2.2 FORMALDEHYDE

Formaldehyde is an example of organic compound which have a trigonal planar arrangement of groups around the carbonyl atom. The carbon atom is an SP^2 hybrid. The bond angles of formaldehyde are 118^0 and 121^0 i.e

Formaldehyde polymerizes in as water solution to give a solid long-chain polymer called **Paraformaldehyde** or poly-"oxymethylene". The application 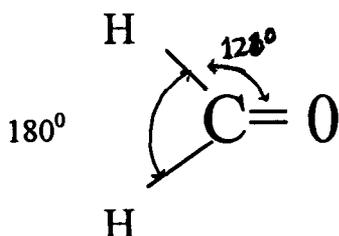of strong heat to this material reverts it to formaldehyde. This is therefore, a convenient source of gaseous formaldehyde. In the presence of dilute acid, paraformaldehyde yields the solid trimer trioxymethylene (melting point 6 1^{O}C).
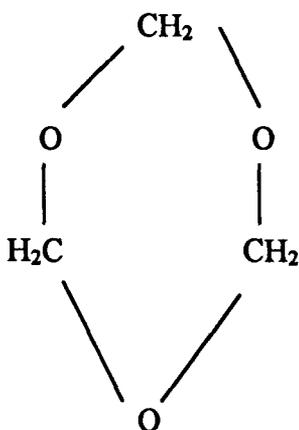
Long chain formaldehyde polymers have become very important as plastics in recent years. [3]. Formaldehyde, CH_2O, is produced in very large quantities from methanol by partial oxidation with air.

$$CH_3OH \xrightarrow[O_2]{air} HCHO + H_2O$$
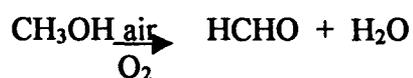
A mixture of air and methanol vapour is passed over a heated platinum wire catalyst and the resulting crude product containing water, formaldehyde and methanol is purified by fractional distillation.

Formaldehyde is a gas at ordinary temperatures and pressures, all other aldehyde are liquids and solids. It has a boiling point of -21^0C, density of 0.8153 at -20^0C, pungent smelling, poisonous gas, highly reactive, with a molecular weight of 30.03. It is readily soluble in water forming hydrate called methylene glycol.

$$CH_2O + H_2O \longrightarrow HOCH_2OH$$
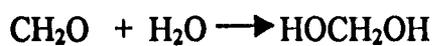
When formaldehyde is marked as a 40% aqueous solution "formalin" it is used in the preservation of biological specimen. Formaldehyde polymerizes easily even in aqueous solution, particularly at higher concentration, as a result, about 30% of the commercial solution is stabilized with 6-10% methanol to prevent the precipitation of polymer. [5].
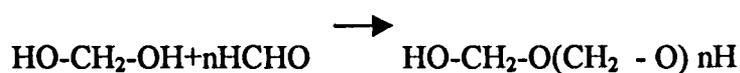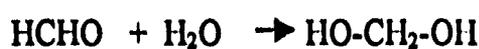
The reactivity of formaldehyde to form methylene glycol is as follows

$$HCHO + H_2O \longrightarrow HO\text{-}CH_2\text{-}OH$$

$$HO\text{-}CH_2\text{-}OH + nHCHO \longrightarrow HO\text{-}CH_2\text{-}O(CH_2 - O)\, nH$$

This reaction continues to produce chains of poly oxymethylene glycol and to prevent the precipitation of the polymer (paraformaldehyde), methyl alcohol is added to stabilized the solution. The major industrial use of formaldehyde is in the production of resins with phenol (bakelite) and urea [3].

2.2.3 MAIZE COBS

The maize cob is the central rachis to which the grains are attached and which remains as agricultural water after threshing. The major extract from maize cob is furfural which was used to fortify the UF resin so produced. The cob consist principally of cellulose 35%, pentosans 40% and lignin 15%. The agricultural and industrial use of maize cobs are as follows:-

Agricultural uses:- it is used as litter for poultry and other animals, mulch and soil conditioner, animal and poultry feeds, and when ground to fineness, it is used as dilutes and carriers for insecticide and pesticides.

Industrial uses:- those based on physical properties are found in vinegar manufacture, for cleaning, burnishing, polishing and soft grit blasting. It is also used in the manufacture of asphalt shingles and roofing, fillers for explosives, plastics, glues, adhesives, rubber compounds and tyres.

Industrial uses based on chemical properties include, manufacture of furfural, manufacture of fermentable sugars, solvents and liquid fuels; also used for the production of charcoal, gas and other chemicals by destructive distillation [6]

2.2.4 RICE HUSK

Rice husk is an agricultural waste and it is the outer most cover of the rice seed (i.e. it envelops the rice). An oil known as furfural is extracted from it by using a solvent (benzyl alcohol) and this oil was used to fortify the UF adhesive produced.

Furfural is a colourless liquid heterocyclic aldehydes $C_5H_4O_2$, obtained by the distillation of the pentose sugars occurring in corn cobs, oat hulls, rice husks and other agricultural waste products. It is widely used as solvent and reagent in the dyestuffs, plastics and other industries. [7] . It is obtained by the digestion of corn cobs or oat hull with dilute mineral acid. A wide variety of agricultural by-products also yield furfural if treated in a similar manner; thus, the potential supply of this highly reactive aldehyde is virtually limitless. When pure, it boils at 161.7^0C and it is sometimes called furfuraldehyde, fural, 2-furaldehyde or 2-furnancarboxyaldehyde.

Furfural was first produced on a commercial scale in 1922, and it is been used as a general synthetic intermediate in the preparation of chemicals, many of which compete with the same chemicals derived from coal and petroleum. Large amount of furfural are also used in the preparation of molding resins and other polymers of value to the plastic industry. Its unusual solvent properties make it useful in the refining of vegetable and lubricating oils and in extracting certain components such as butadiene, from cracked refinery gases. Furfural is also been used as an insecticide, herbicide furgicide and embalming fluid.[8]

2.3 CHEMISTRY OF REACTION

The chemistry of urea with formaldehyde involves both polyaddition and polycondesation reactions, depending on the medium of reaction.

The reaction of urea and formaldehyde was studied many years ago by amongst other, Goldschmidst in 1896. This investigator used various amount of urea and formaldehyde in acid solutions of various strengths. He obtained insoluble white, granular deposits, which were analysed and found to correspond to the empirical formula $C_5H_{10}N_4O_3$.

However, this so-called "Goldschmidt's compound" was later made with varying amounts of formaldehyde and was therefore different from it's original composition. Its formula was given as ($CH_2 = NOCHNCH_2NHCONHCH_2OH)_2$.

It was believed that the $-N=CH_2$ group was polymerized to form a high molecular-weight substance[1]. Einhorn and Hamburger in 1908 made it a point in their experiment to use only mild reaction conditions.

$$
\begin{array}{c}
O \\
\parallel \\
C \\
\diagup \quad \diagdown \\
HOH_2CN \qquad NCH_2OH \\
\mid \qquad\qquad \mid \\
H_2C \qquad\quad CH_2 \\
\diagdown \quad \diagup \\
O
\end{array}
\qquad (1)
$$
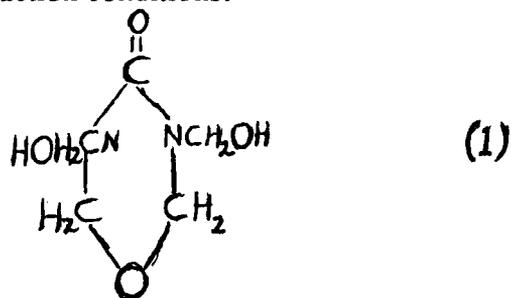
They condensed urea with formaldehyde in alkaline solution; by neutralization and drying they isolated various white, crystalline, easily soluble products, that melted at about 126^0C, it formed amorphous substance on further heating at 137^0C, and finally decomposed at 260^0C. These substances were given formulas (ii) and (ii)

NH$_2$CONHCH$_2$OH   CO(NHCH$_2$OH)$_2$

(ii) methylolurea   (iii) N,N^1 - dimethylolurea

De Jong and De Jonge have conducted a very interesting series of investigations of the kinetics and mechanism of the urea formaldehyde reaction. These investigation have rendered additional evidence that the condensation products of urea and formaldehyde are formed by a step wise polycondensation that finally leads to methylene bonds between urea fragments. This stands in contradiction, however, to the polymerization scheme of Marvel.

De Jong and De Jonge first examined by kinetic studies the reaction of urea and formaldehyde in 0.1M aqueous solution within a pH range of 2 to 11 in an attempt to elucidate the production of mono-and di-methylolurea (see fig.1). They found that the reaction producing both substances showed a closed resemblance to each other. In both cases an equilibrium is reached from both sides that is independent of the pH of the solution. Although the formation of both substance appears to be a bimolecular reaction, the decomposition of dimethylolurea proved to be a mono-molecular reaction. The reaction rates of both were found to be directly proportional to the concentration of the hydroxyl and hydrogen ions, which have a catalytic influence.

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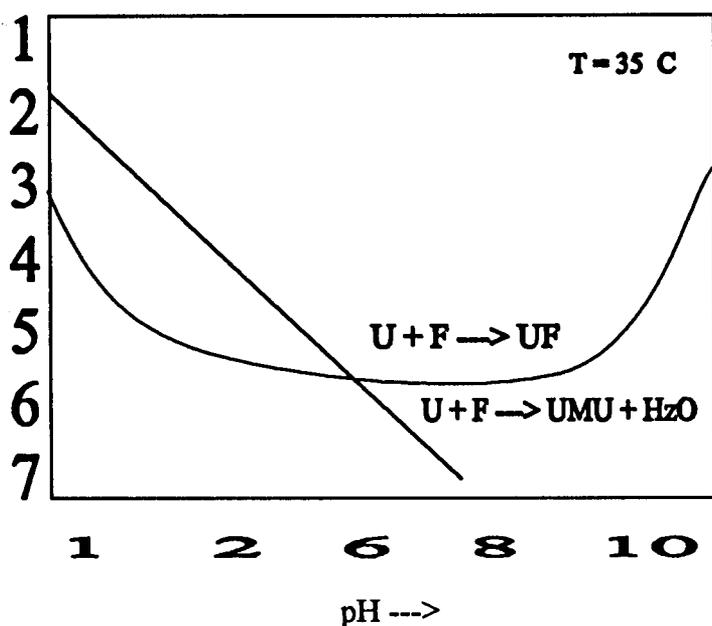
Fig.1   Influence of pH on the addition reaction of urea and formaldehyde and on the condensation reaction. U is urea, F formaldehyde, and M a methylene group.

An investigation by the same authors referring to the "kinetics of the formation of methylene linkages in solution of urea and formaldehyde" as applied to 1-3M aqueous solutions with a pH of 4.1 to 4.4 strongly indicated that the reactions involved are all of one type, namely bimolecular, hydrogen-ion catalysed reactions, between an aminomethylol group and an amino group, leading to the formation of methylene linkages between urea fragments. (equation 3). These findings indeed seem to confirm the validity of equation 5,6, and 7

$$- NHCH_2OH + - NH_2 \rightarrow -NHCH_2NH - +H_2O \text{ ------------(3)}$$

Other investigators (Scheiber et al, 1928) then found that in acid solution these methylolurea are converted into insoluble substances,similar to Goldschmidt's compound.   From monomethylolurea in glacial acetic acid they isolated low molecular weight polymethylolurea (iv) and polymethylolurea acetate (v)

$$(CH_2 = NCONH_2)_{12} . H_2O \qquad\qquad (CH_2 = NCONH_2)_{12} CH_2 COOH$$

$$\text{(iv)} \qquad\qquad\qquad\qquad \text{(v)}$$

All research now indicates that the further increase of molecular size is very probable caused by the following reactions, all of which occur with the simultaneous evolution of water and in some cases, of formaldehyde.

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1. The formation of unsaturated azomethine groups, e.g from monomethylolurea. This unsaturated group supposedly polymerizes easily to polymethylarurea (equation 4)

$$XNH_2CONHCH_2OH \rightarrow (NH_2CON = CH_2)_2 + XH_2O \text{ -------------(4)}$$

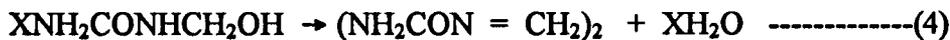2. The formation of methylene bridges as in equation 5, between methylol and amino groups of neighbouring molecules.

$$RNHCH_2OH + NH_2R^1 \rightarrow RNHCH_2NHR^1 + H_2O \text{ -----------(5)}$$

3. The formation of ether bridges between two methylol groups of two neighbouring molecules (equation 6).

$$RNHCH_2OH + HOCH_2NHR^1 \rightarrow RNHCH_2OCH_2NHR^1 + H_2O \text{ - (6)}.$$

4. The formation of methylene bridges between two methylol groups by the splitting off of water and formaldehyde (equation 7)

$$RNHCH_2OH + HOCH_2NHR^1 \rightarrow RNHCH_2NHR^1 + CH_2O \text{ -------------(7)}$$

Molecular weight may vary from a few hundred to a few thousand, with a wide distribution of molecular size. According to equations 5,6,7 these molecules are built up by the splitting off of water at random from between reactive groups of neighboring molecules, thus increasing their size.

Marvel et al. holds that primary reaction product of urea and formaldehyde leads to the formation of methyleneurea ($NH_2CON = CH_2$), which polymerizes instantly to it's trimer, forming a ring of the trimethylenetriamine type. In a second stage, by the formation of methylene bisamides, the ring would produce the polymeric urea-formaldehyde resin (equation 8). The formula for this cured resin is given in the structure below (equation 8). The probability of a rather irregular constitution in such cured urea – formaldehyde resin is suggested by the fact that well cured urea-formaldehyde resin do not give a well defined X-ray diffraction pattern.

$$3(NH_2CON=CH_2) \rightarrow$$

NH——————————CH₂——————————NH
| |
CO   CO
| |
N   N
/   \   /   \
CH₂   CH₂   CH₂   CH₂
| | | |
—NHCON   N — CO   CO —N   NCONHCH₂—
\ | | \   /
CH₂   NH   NH   CH₂
        | |
        CH₂   CH₂
        | |
        NH   NH   CH₂
        | | /   \
—NHCON   CH₂   \ | CO —N   NCONHCH₂—
     \   \   N — CO | |
      | | CH₂   CH₂
     H₂C   CH₂   \   /
       \   /   N
         N |
         | CONHCH₂⁻
       CONHCH₂
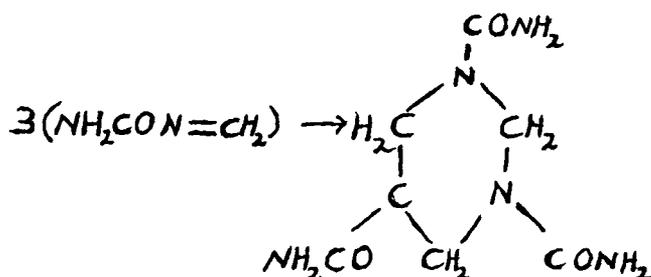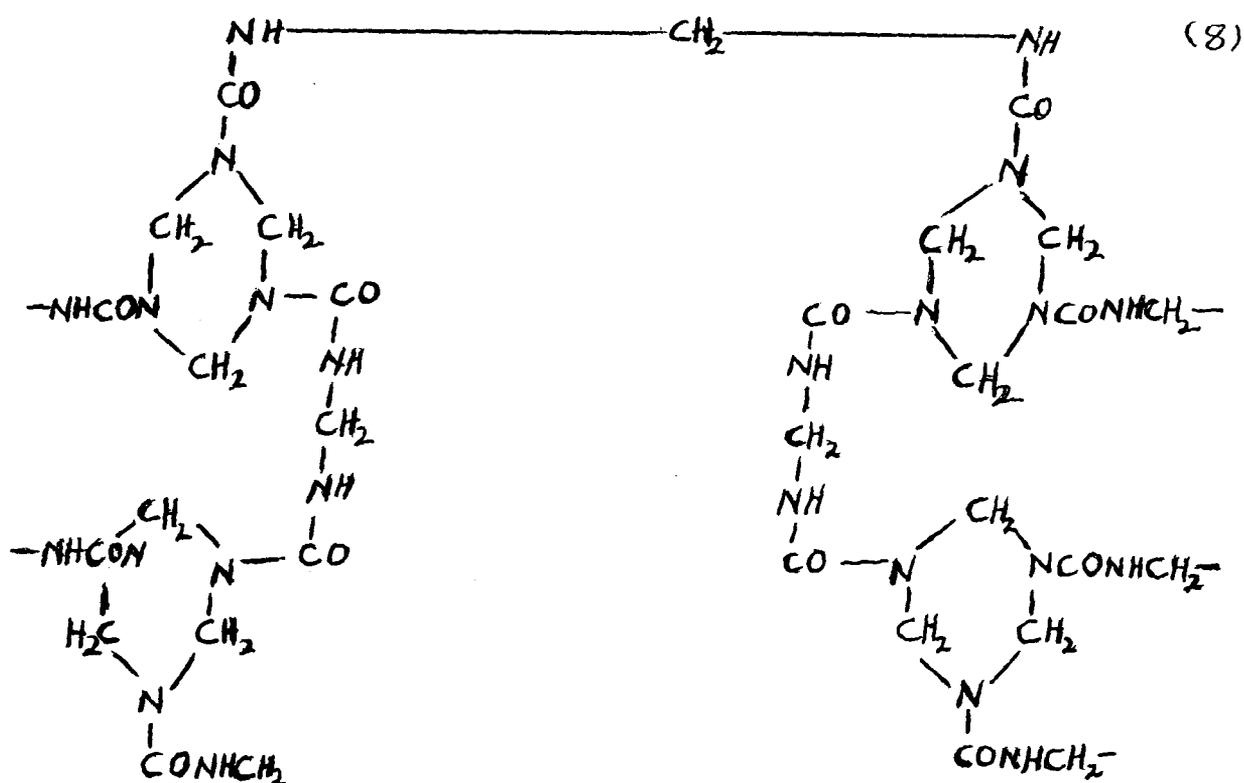
Staudinger et al. were interested in the constitution of urea –formaldehyde, thiourea-formaldehyde, and substituted urea-formaldehyde condensation products. They found that the high viscousity of these solution was based on the association of dialyzable intermediate condensation products. They were able to dissolve the normally insoluble, powdery condensation products in the following solvents: urea-formaldehyde in aqueous solutions of lithium bromide, lithium iodide,or magnesium perchlorate; and thiourea-formaldehyde in dimethylformamide or ecaprolacium.Molecular-weight determinations by cryoscopic and end-group methods proved that these "insoluble" urea-formaldehyde powders were composed of only six to eight urea-formaldehyde fragments, and that the corresponding thiourea-formaldehyde powders were composed of only four to five thiourea-formaldehyde fragments.

Furthermore, staudinger et al. Considered that all higher molecualr-weight condensation products of urea-and thiourea-formaldehyde consist of intractable mixtures of condensates of various constitution.

Generally, the factors to be considered for better product during the reaction of urea with formaldehyde are as follows:

1.The molecualr proportion of urea to formaldehyde is very important, as the relative amounts of the reactants determine to a large extent, the properties of the product.

2. The reaction product also differ very much when lower or higher condensation stages are compared, especially with respect to solubility and viscousity, both of which depend on the molecular weight. The same urea formaldehyde condensation

product may have different applications which demand higher or lower viscousity. It is therefore essential to define the resins as to their extent of condensation.

3.Temperature is another factor to be considered as the reaction temperature; ambient, medium, or high temperatures produces resins with different properties.
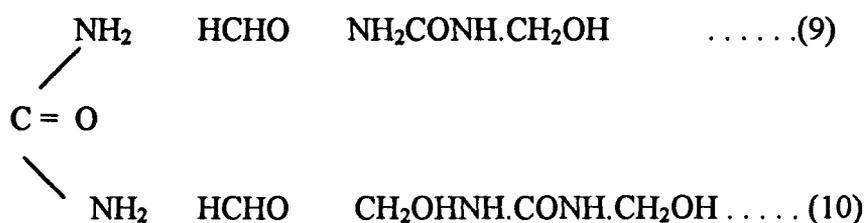
4.Also, another factor worth considering in determining the kind and quality of condensation product is the pH.

When investigating a new reaction, one of the first factors to be considered is the pH, and thereafter the optimum range of pH to obtain the best results.'

2.4 THEORIES OF RESINIFICATION

Urea-formaldehyde resins are one of the group of amino resins which are usually prepared by a two stage reactions. The precise control of these reactions bring about the success in making and using amino resins.

The first of the stage is primarily concerned with the manufacture of the resin. At this stage, formaldehyde is added to urea to introduce the hydroxyl-methyl group, which is also known as methylol group. The reaction is either carried out under neutral, or acidic, or alkaline condition leading to the production of mono and dimethylol ureas. See the equations of reaction below.

$$NH_2 \quad HCHO \quad NH_2CONH.CH_2OH \quad \ldots\ldots(9)$$
$$C = O$$
$$NH_2 \quad HCHO \quad CH_2OHNH.CONH.CH_2OH \ldots\ldots(10)$$

Equation 9 → monomethylourea

Equation 10 → dimethylolurea

The ratio of mono to dimethylol compounds depend strictly on the ratio of urea- to –formaldehyde and it is very important that the amount of formaldehyde should be much in the reaction to allow for some dimethylolurea formation.

The second stage of the process is the combination of methylol group with an active hydrogen to release a molecule of water forming a dinner, a polymer chain, or a

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vast three-dimensional polymer network. This reaction is known as cure, polymerization or methylene bridge formation.

If the product of the first stage, which in practise contains unreacted urea and formaldehyde, the reaction is then subjected to acid conditions at elevated temperatures. The event observed during the second stage follows these sequences.

1. A solution is produced from which, if cooled, a white precipitate would be obtained.

2. As heating proceeds, the temperature at which precipitation occurs drops progressively until a stage is reached when the condensation products remain in solution at room temperature.

3. With further heating there is an increase in velocity with which the syrup sets to an insoluble and irreversible gel which eventually converts, with the evolution of water and formaldehyde to hard, colourless, transparent and infusible mass.[5]

For technical purpose, it is often convenient to arrest the reaction prior to gelation by changing to a slightly alkaline pH and to remove some, if not all of the water. The first hardening reaction may then be carried out when desired by changing once again to an acid pH.

2.5 CHEMICAL PROPERTIES OF FURFURAL

Furfural has the structural formula C_4H_3OCHO. It contains not only an aldehyde group but also an ether linkage (C-O-C) and a system of alternating single and double bonds (diene structure). These provides several site in the moleculars, for reaction with other compounds. It is similar to benzaldehyde in most of it's reaction as an aldehyde and it has the ability to undergo substitution reactions for hydrogen atoms on the ring.

Resin formation can take place by reaction at the aldehyde group or through the diene-aldehyde systems (also known as resinophore grouping). Three general routes to furfural derivatives are employed in the chemical industry.

1. It react as an aldehyde of phenols, ketones, esters and other materials to produce resins and compounds valuable as plasticizers

2. The catalytic removal of the aldehyde group from furfural gives furan, C_4H_4O, which can be hydrogeneted to tetrahydrofuran. The latter is a widely used solvent and also as an intermediate in the preparation of polytetramethylene ether glycol, an important ingredient of a variety of polyurethane elastomers and spandex type fibers.

3. Catalytic hydrogenation of furfural gives furfuryl alcohol and tetrahydrofurfuryl alcohol. The former is used in the preparation of resins and the latter can be converted to dihydropyran. Dihydropyran is either hydrogenated to give tetrahydropyran which resembles tetrahydrofuran in it's solvent properties or converted directly to polymeric materials and chemical important to the industry. [8]

2.6 PROPERTIES OF UREA-FORMALDEHYDE RESINS

The major properties which makes urea-formaldehydes one of the most useful resins in the wood industry are.

1. It posses good electrical insulation properties with particularly good resistance to tracking.

2. It is a colourless compound and this property permit a colourless glue line as well as unlimited colourability with dyes and pigments.

3. It is odourless i.e it do not impact taste and odour to food stuffs and beverage with which they come in contact.

4. Low cost.

5. Hardness and heat resistance.

6. It is soluble in water before cunning and this create easy application to many substrates and with many other materials.

7. It has a good solvent resistance.

8. It has a low storage capacity.

2.7 PREPARATION OF UREA-FORMALDEHYDE ADHESIVES

In the preparation of urea-formaldehyde resins, formaldehyde is first neutralised to a pH of 7.5 with addition of caustic soda (NaOH) and urea is then dissolved into it in a mole ratio 1:2 i.e U-F molar ratio 1:2. To regulate the pH, sodium formate may also be added as a buffer. Heat is then applied for about 15 minutes to boiled the mixture under reflux and this give rise to dimethylolurea and other low molecular weight products. Formic acid is then added to conveniently acidified the resin to a pH of 4, and the mixture is allowed to react for another 5-20 minutes. The resulting resin is then stabilized by neutralizing to a pH 7.5 with alkaline to give a water-soluble resin within approximately 50% solid content. For the resin to be in aqeous solution, vacuum distillation is used to partially dehydrate the resin and this gives a 70% solid content.

When making the pH adjustment a pH meter is used since formaldehyde interferes with the universal indicator. A standard hardener is used to text for the reactively of the final product and the solid content, pH value, density, specific gravity, refractive index and viscousity is also tested for.

CHAPTER THREE

3.0 MATERIALS AND METHODOLOGY

3.1 MATERIALS AND EQUIPMENT

The main materials and equipment used for this research work / investigation includes:

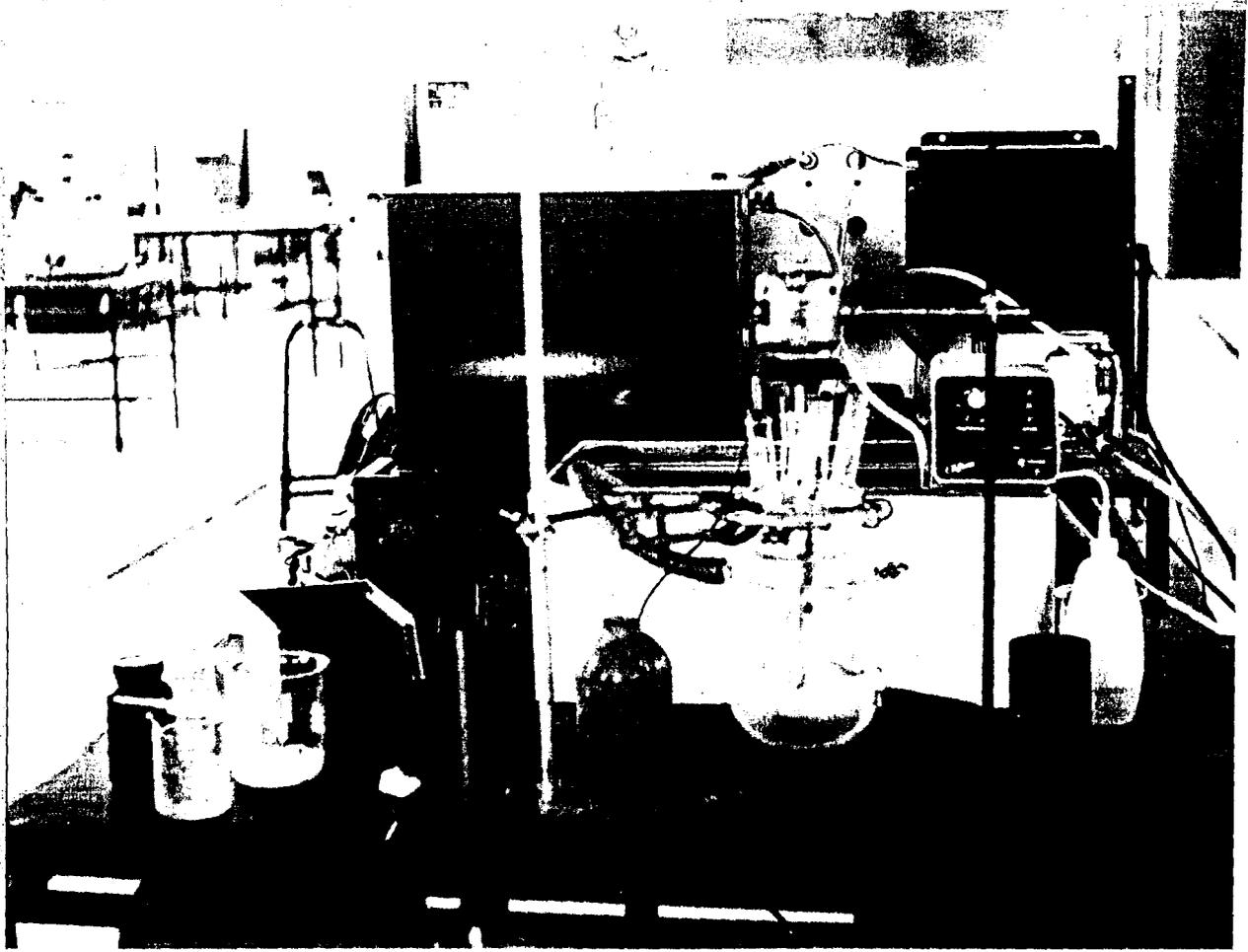| S/NO	MATERIALS
1.	Urea.
2.	Formaldehyde (37 - 40% concentration).
3.	Monosodium dihydrogen phosphate.
4.	Sodium hydroxide 50% concentrated solution.
5.	Sulphuric acid 50% concentrated solution.
6.	Rice Husk (furfural).
7.	Maize cob (furfural).

The instruments/apparatus used to carry out the research work are listed below.

S/NO	EQUIPMENTS
1.	Semi-batch reactor.
2.	Stop watch.
3.	Thermometer.
4.	pH meter/electrode.
5.	Dessicator.
6.	Ubbelhode viscometer.
7.	Weighing balance.
8.	Water bath regulator.
9.	Aluminium dish.
10.	Electric ovum.

11.   Refractometer.

12.   Conical flask.

13.   Specific gravity bottle.

14.   Beakers.

15.   Measuring cylinder.

16.   Electric motor/stirrer.

17.   Retort stand.

18.   Water bath.

19.   Pump.

20.   IR spectrometer.

21.   NMR spectrometer.

3.1.1 DESCRIPTION OF MAJOR APPARATUS USED

Fig. 1 shows the set-up system for the preparation of UF adhesive. The apparatus used during the synthesis of UF includes, thermometer and pH meter electrode which are used to determine the temperature of the reaction mixture and the pH.value respectively, the water bath was used to keep the temperature of the reaction at the desired value say 65^0C, while the stirrer was used to ensure proper mixing and dissolution of urea with formaldehyde.
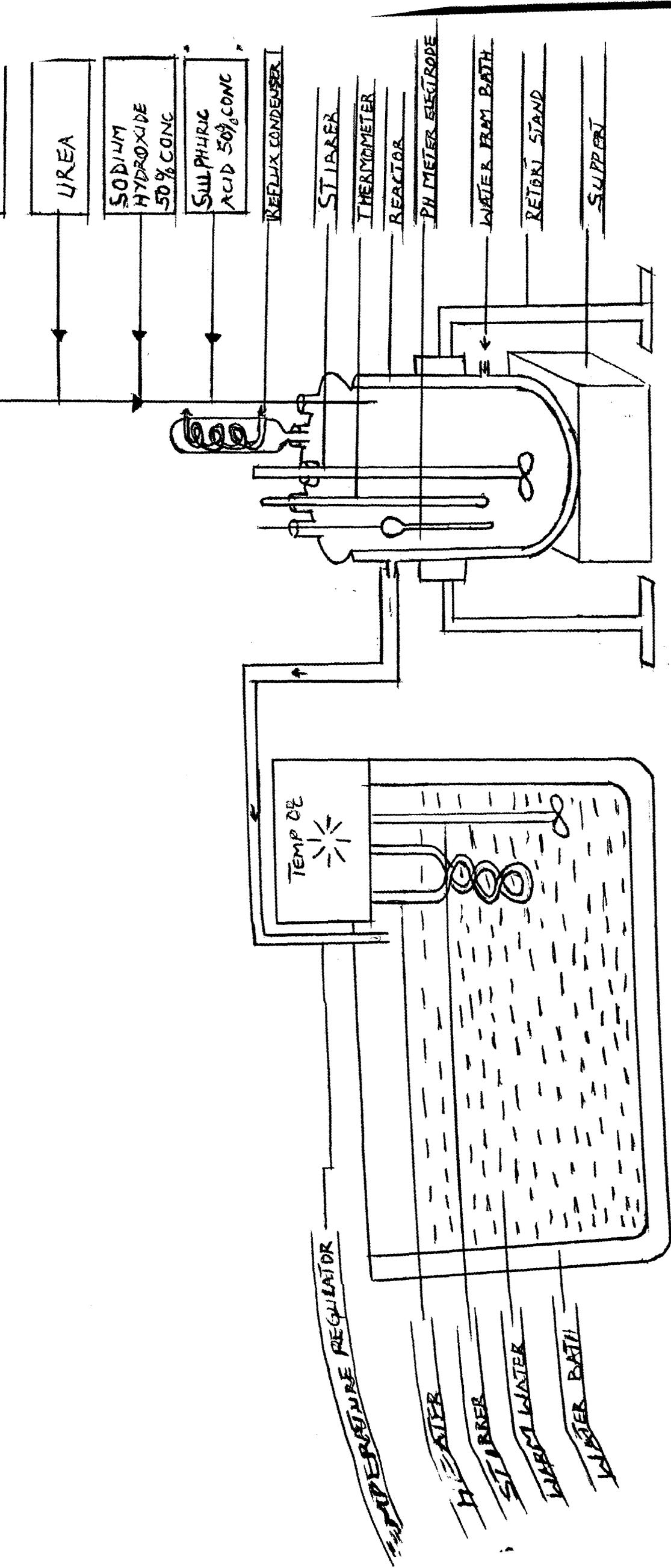
UREA

SODIUM HYDROXIDE 50% CONC.

SULPHURIC ACID 50% CONC.

REFLUX CONDENSER

STIRRER

THERMOMETER

REACTOR

PH METER ELECTRODE

WATER FROM BATH

RETORT STAND

SUPPORT

TEMP °C

TEMPERATURE REGULATOR

HEATER

STIRRER

WARM WATER

WATER BATH

FIGURE 1: SET-UP SYSTEM FOR PREPARATION OF UREA FORMALDEHYDE ADHESIVE

3.2 EXPERIMENTAL PROCEDURES

3.2.1 EXTRACTION OF FURFURAL FROM MAIZE COB

The process of extracting furfural from maize cobs involves three stages. The first stage involves the drying of the maize cobs to constant weight using oven. The maize cob is then grinded after obtaining a constant weight into a powdery form.

The second stage involves the use of benzyl-alcohol to extract the furfural from the agricultural waster (maize cob). A known quantity of the powdered maize cob (20g) was weighed into a beaker, after which the solvent (benzylalcohol) was added to cover the sample. The mixture was stirred with a glass rod and heat was supplied for 10 minutes. The resulting mixture was filtered and the solution collected into a beaker.

The third stage involves the separation of the furfural from the mixture. The apparatus need is a distillation apparatus. The solvent distilled off and the extract was collected into a bottle.

3.2.2 EXTRACTION OF FURFURAL FROM RICE HUSK

The extraction of Fufural from Rice husk involves three stages . All the steps involved in the extraction of Fufural from maize cob was followed and the solvent used is benzyl alcohol.

3.2.3 PREPARATION OF UREA-FORMALDEHYDE RESIN (NEAT)

In the preparation of urea-formaldehyde resin, $135cm^3$ of formaldhyde solution (37-40% aqueous) was measured into the reactor by measuring cylinder. The pH of formalin was then adjusted to a pH in the range of 7.5-8.0 using sodium hydroxide (50%conc.) by adding it drop by drop until the pH meter stabilizes in the range 7.5-8.0. 60g of urea was weighed and then added to the formalin in the reactor step-wisely and the mixture was stirred with the aid of electric motor stirrer to dissolve the urea.

After the dissolution of urea, the mixture was heated at a temperature of 65^0C under reflux for 15 minutes, after which the pH of the reaction mixture was adjusted to 4.5-5.0 with 50% concentrated H_2SO_4 ($0.5cm^3$). After this, the mixture was further heated under reflux and aliquots was been removed by pipette at approximately 5

minutes intervals. The refluxing was stop when the aliquots give rise to a precipitate on addition to a large excess of water. This takes 30 minutes, and the resulting mixture was stabilized by adjusting the pH to 7.5-8.0 with IM sodium hydroxide (50%conc.). The resulting resin liquor was concentrated by distillation at a temperature of 50-60°C, until it attains a syrup-like consistency monodosium dihydrogen phosphate was added to stabilize the pH.

3.4 PREPARATION OF UREA-FORMALDEHYDE RESIN WITH ADDITION OF FURFURAL EXTRACT EITHER MAIZE COB OR RICE HUSK DURING THE SYNTHESIS.

$2cm^3$ of furfural was added to $135cm^3$ of formalin (1.2mole) measured into the reactor. The solution was well stirred and the pH was adjusted to 7.5-8.0. 60g of urea (1.0mole) was weighed and added to the solution in the reactor and the mixture was well stirred to dissolve the urea. The mixture was heated at a temperature of 65°C under reflux for 15 minutes after which the reaction mixture was adjusted pH 4.5-5.0 with 50% concentrated sulphuric acid ($0.5cm^3$) and the mixture was further heated for 30 minutes. The resulting resin was stabilized by neutralizing to pH 7.5-8.0 with $0.5cm^3$ of sodium hydroxide (50% concentration). Monosodium dihydrogen phosphate is then added to stabilize the pH after which the resin is concentrated by distilling at a temperature of 50-60°C

3.5 PREPARATION OF UREA-FORMALDEHYDE RESIN WITH ADDITION OF FURFURAL EXTRACT FROM MAIZE COB OR RICE HUSK AFTER THE SYNTHESIS.

$135cm^3$ of aqueous formalin (37-40%solution) was measured into the reactor and the pH was adjusted to 7.5-8.0. 60g of urea (1.0mole) was weighed and added step-wisely into the reactor. The mixture was well stirred to dissolve the urea, after which the mixture was heated for 15 minutes under reflux at 65°C. The pH was then adjusted to 4.5-5.0 with sulphuric acid (50% conc.) and the reaction mixtures was further heated at reflux for 30 minutes, after which the pH was adjusted to a pH 7.5-8.0 with sodium hydroxide (50%conc). The resin was concentrated by distilling the resin at 50-60°C, after which furfural from either maize cob or rice husk was mixed with the resin so produced. This is known as physical mixing.

3.6 THE PHYSIOCHEMICAL PROPERTIES

3.6.1 DETERMINATION OF REFRACTIVE

Some quantity of pre-heated resin was introduced into the prison chamber of through the provision make for it, and allowed to stabilized for sometimes.

The refractometer reading was then taken by turning the compensation ring of the refractometer until there was a shary division between the dark portion of the sample. The accurate refractometer reading was taken as the whole number and the decimal with shown on the micrometer screw gauge.

3.6.2 VISCOSITY MEASUREMENT

The viscosity of the resin was measured using the viscometer both and U-tube viscometer with capillary inserted into the viscometer bath.

A known quantity of the sample was poured into the U-tube viscometer with capillary and then corked. The U-tube was then suspended into the viscometer bath containing water until the temperature of the bath was 32^0C. 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. The viscosity of the sample was than calculated using the result obtained.

3.6.3 pH MEASUREMENT

A pH meter /electrode was used to measure the pH of the resin produced. About $50cm^3$ of the UF resin prepared was collected into a beaker and the pH meter was inserted into the beaker to the determine the PH of the resin. the value of the PH of the resin was then read from the instrument after a couple of minutes.

3.6.4 SPECIFIC GRAVITY MEASUREMENT

To measure the specific gravity of the resin produced. An empty specific gravity bottle was weighed and it's weight recorded. This bottle was than filled with UF sample and weighed and the weight was recorded also. The density between the weight of the specific gravity bottle when filled with the sample and the weight of the empty specific gravity bottle, then divide by the weight of equal volume of water.
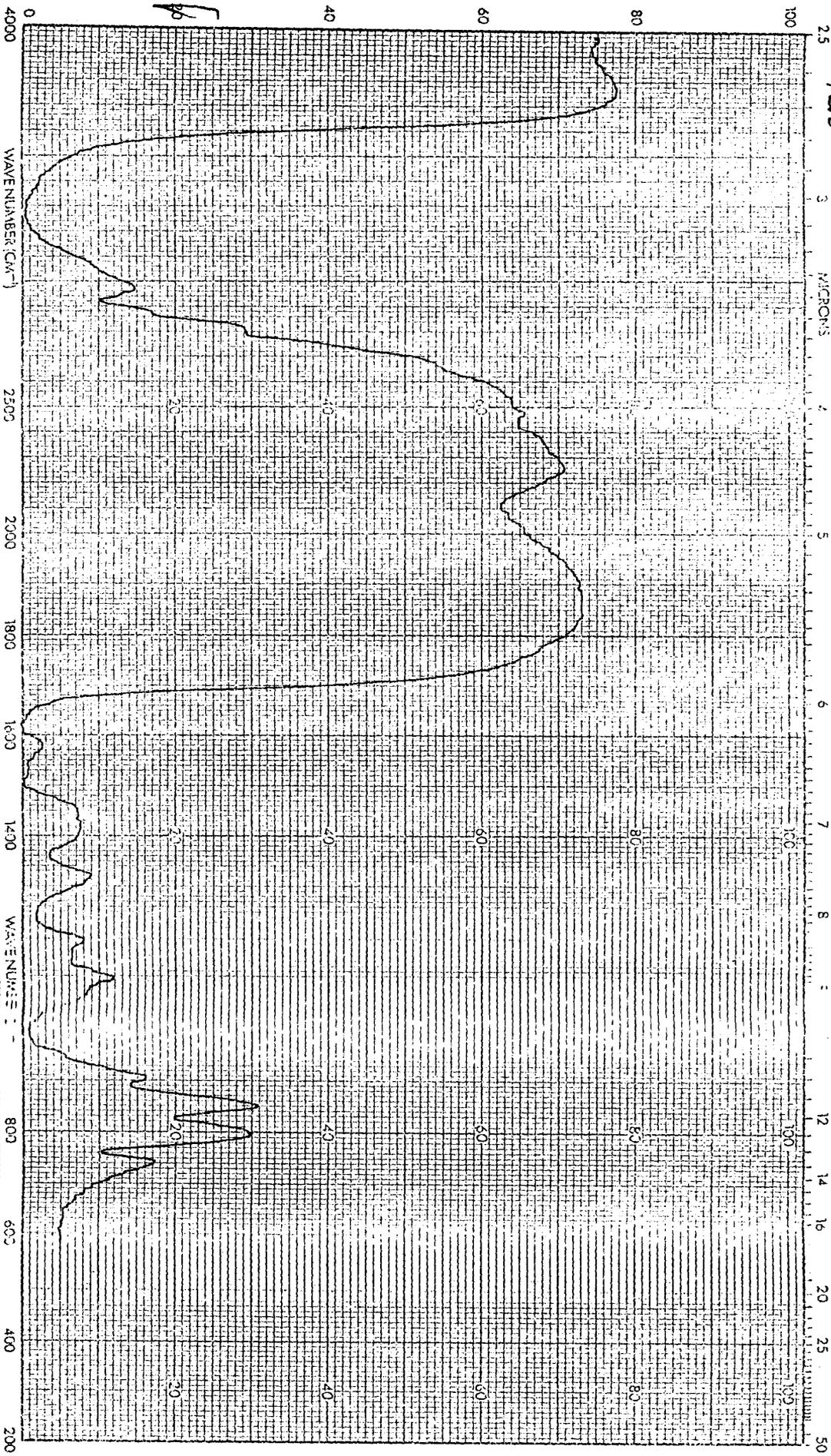
CHAPTER FOUR

4.0   RESULTS

Table 1.0 shows the results (i.e. properties) obtained from the analysis of the samples. These are, the values of the density, viscousity, refractive index, pH, total solid content and the molecular weight of the samples.

Table 1.0

PROPERTIES AND THE TEMPERATURE (^{0}C) AT WHICH THEY ARE DETE RMINED	SAMPLE A	SAMPLE B	SAMPLE C	SAMPLE D	LITERATURE VALUE
SPECIFIC GRAVITY (g/cm^3 at 30)	1.41	1.51	1.46	1.36	1.47 – 1.52
VISCOUSITY (Cp) (at 32)	37.31	41.95	38.89	32.39	-
REFRACTIVE INDEX (at 32)	1.48	1.52	1.53	1.59	1.54 – 1.56
SOLID CONTENT (TDS %) 100	67	64.57	63.0	60.7	-
OPERATING PRESSURE (ATM)	1.0	1.0	-	-	-
OPERATING TEMPERATURE	65.70	65.70	29	29	-
MOLECULAR WEIGHT	3041.56	3469.42	3186.53	2594.19	-
pH at 30	8.20	7.4	7.6	8.0	7.5 – 9

Fig. 3A

25

F638

CHART 5199-1042

MICRONS

2.5   3   4   5   6   7   8   9   10   12   14   16   20   25   50

TRANSMISSION (%)

100   80   60   40   20   0

WAVE NUMBER (CM⁻¹)

4000   2500   2000   1800   1600   1400   800   600   400   200

WAVE NUMBER (CM⁻¹)

SAMPLE

REF. NO.

26

ABSCISSA	ORDINATE	SCAN TIME 3 mins	REP. SCAN _____ SINGLE BEAM IR. Perkin Elmer
EXPANSION 0.5	EXPANSION 0.5	MULTIPLIER _____	TIME DRIVE 3 mins
SUPPRESSION _____	% T _____ ABS _____	SLIT PROGRAM _____	OPERATOR Ken Oi. DATE 7/3/2000
SAMPLE B (UF)	REMARKS O.K	SOLVENT _____	CELL PATH _____
ORIGIN _____		CONCENTRATION _____	REFERENCE _____

Fig 3c

CHART 5199-1042

	ABSCISSA		ORDINATE		SCAN TIME	3mins	REP. SCAN		SINGLE BEAM
EXPANSION	0·5	EXPANSION	0·5 mins	MULTIPLIER		TIME DRIVE	3mins	
SUPPRESSION		%T	ABS	SLIT PROGRAM		OPERATOR	Ken Ogi	DATE
SAMPLE	C (u.f)	REMARKS	O.K.		SOLVENT		CELL PATH	
ORIGIN					CONCENTRATION		REFERENCE	

EM360/390 NMR SPECTROMETER

varian instrument division   palo alto, california

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PART NO. 950209-04

LOCK POS. _____ ppm	SPECTRUM AMPL. 107	SWEEP TIME 2 min	NUCLEUS H	SAMPLE: A (uf) OPERATOR J.A Deggi
LOCK POWER _____ mG	FILTER 0.05 sec	SWEEP WIDTH 20 ppm	ZERO REF. Tmf	DATE 7-3-2000
DECOUPLE POS. _____ ppm				
DECOUPLING POWER _____ mG	RF POWER 0.05 mG	END OF SWEEP _____ ppm	SAMPLE TEMP. _____ C	SOLVENT: SPECTRUM NO. _____

EM360/390 NMR SPECTROMETER

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PART NO. 950209-04

interferences.
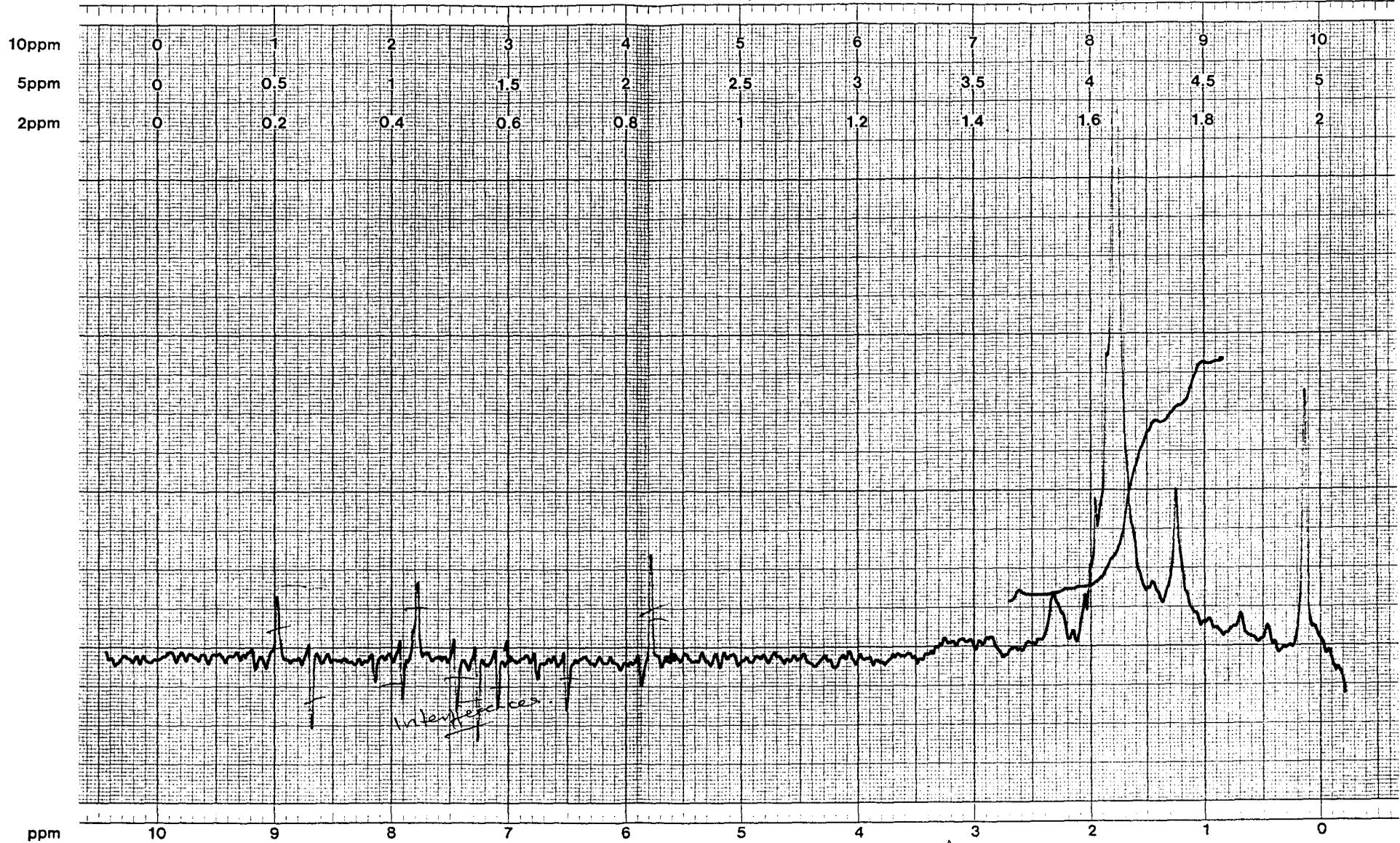
LOCK POS. _____ ppm   SPECTRUM AMPL. _1006_   SWEEP TIME _2_ min   NUCLEUS _¹H_   SAMPLE: B (Ut)   OPERATOR _Tot Deson_

LOCK POWER _____ mG   FILTER _0.05_ sec   SWEEP WIDTH _10_ ppm   ZERO REF. _TMS_   DATE _7-8-20__

DECOUPLE POS. _____ ppm

DECOUPLING POWER _____ mG   RF POWER _0.05_ mG   END OF SWEEP _0_ ppm   SAMPLE TEMP. _____ C   SOLVENT: _____   SPECTRUM NO. _____
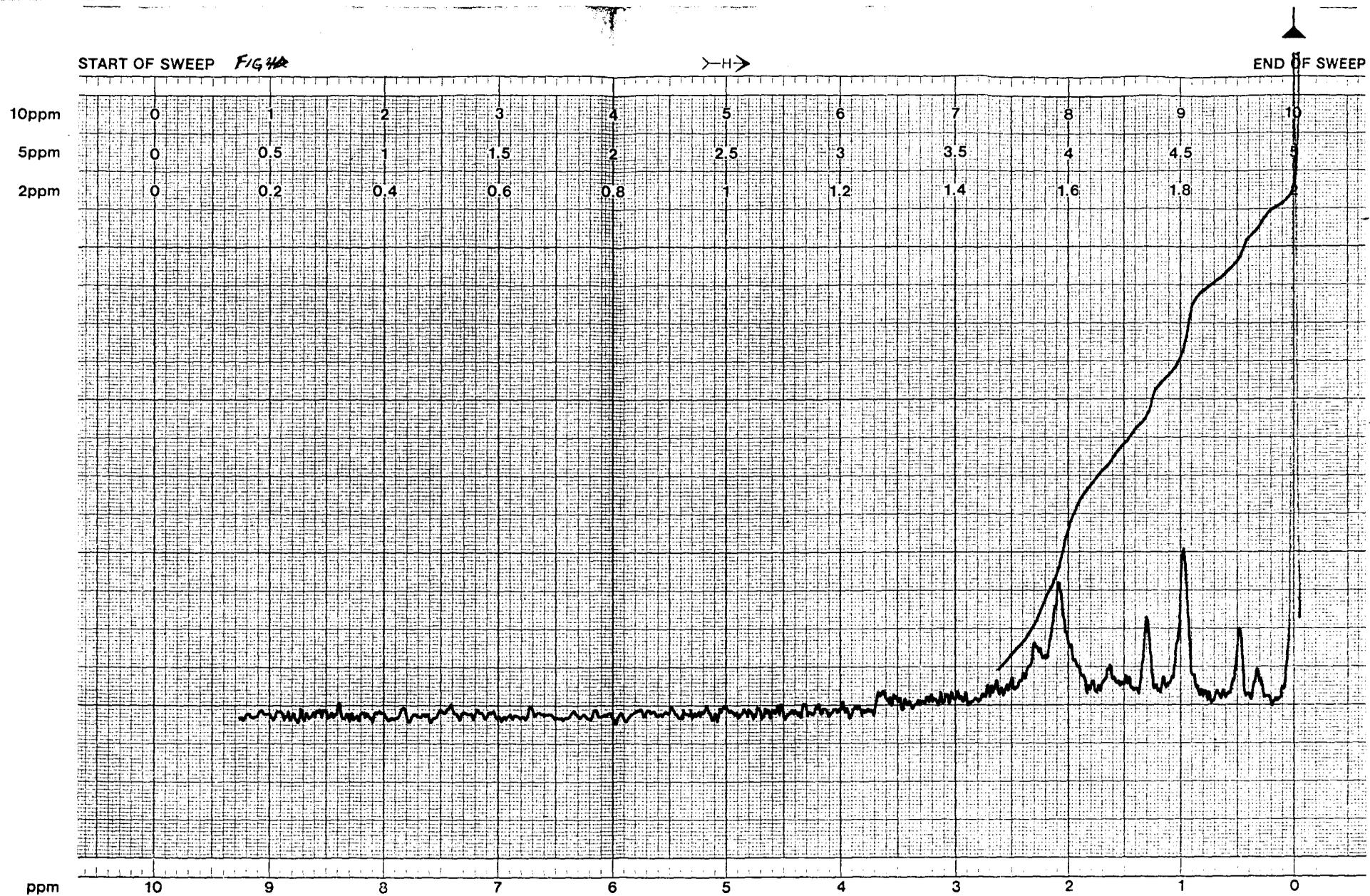
10ppm 0   1   2   3   4   5   6   7   8   9   10

5ppm 0   0.5   1   1.5   2   2.5   3   3.5   4   4.5   5

2ppm 0   0.2   0.4   0.6   0.8   1   1.2   1.4   1.6   1.8

ppm   10   9   8   7   6   5   4   3   2   1   0

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PART NO. 950209-04

EM360/390 NMR SPECTROMETER

LOCK POS._____ppm   SPECTRUM AMPL._1007_   SWEEP TIME_____2_____min   NUCLEUS_____H_____   SAMPLE: ⟨ (CuF) OPERATOR J.A Dago

LOCK POWER_____mG   FILTER____0.05____sec   SWEEP WIDTH___20___ppm   ZERO REF.___(cm)___   DATE 7-3-2000

DECOUPLE POS._____ppm

DECOUPLING POWER_____mG   RF POWER___0.04___mG   END OF SWEEP____0____ppm   SAMPLE TEMP._____C   SOLVENT: SPECTRUM NO._____

DMSO

4.1   DISCUSSION OF RESULT

The values of the properties of the samples as obtained from the analyses of the physio-chemical properties was tabulated as shown in table 1.0

From the table, the specific gravities of the samples are 1.41, 1.51, 1.46 and 1.36 g/cm^3 respectively. the literature value is between the range 1.47 – 1.52g/cm^3 and only the value of sample B falls within this range. The values of samples A, C and D are very close to the literature value. Therefore, only sample B confirms with the literature values, and due to the fact that other values are very close to the literature value, the result obtained is said to be valid.

The viscousities of samples A,B,C, and D are 37.31, 41.95, 38.89, and 32.39cp respectively. this results shows that the value of sample A,C, and D close to each other in comparison to that of sample B. The outrageous value of sample A, is due to the fact that the visiousity was not determined at the same time i.e sample A was kept in the refrigerator till the synthesis of the other samples was completed. The difference is attributed to the fact that polymerization reaction often continue at room temperature and in consequence, increase in the molecular mass, which has direct effect on viscousity.

The refractive index of samples A, B, C, and D are 1.48, 1.52, 1.53, and 1.59 respectively. These value are very close to the literature value, only the value of sample A shows a difference of 0.06 which is still within the limit of the experimental error. As a result the values are considered to be valid in comparison to the literature value.

The values of the total solid contents for each of the samples A,B,C, and D are 67%, 64.57%, 63.0%, and 60.7% respectively. These values are very close to each other and this shows that the results obtained agrees with each other. Although the literature value for the total solid content is not known, and since the value for each samples is within the same range, the result obtained is valid.

The molecular weight of samples A,B, C and D are 3041.56, 3469.42, 3186.53, and 2594.19 respectively. it can be seen that the value of sample B is higher than the other values and this can be attributed to the fact that sample B has undergone certain extent of polymerization reaction at room temperature after the termination of the reaction. As a result of this, sample B is said to have a better mechanical properties, whence it's a polymer with good thermal properties. Sample D has the lowest molecular weight, and this is due to the fact that the analysis was carried out immediately after the synthesis of sample D and hence, no extent of polymerization reaction is possible.

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Also, the pH value of samples A,B,C, and D are 8.20, 7.4, 7-6, and 8.0 respectively. These values are considered to be valid since, the pH of the resins was brought to alkaline medium after the synthesis. (i.e. 7.5 – 8.0).

4.2   INFRA RED SPECTRA

Fig. 3A shows the infra-red spectra of sample A. There is absorption at region 760 – 890 cm^{-1}, this region shows a peak with two bond which is a characteristic indicating the presence of alkene (C-H)group. The absorption at region 1200 – 1320 shows the presence of Amine (C – N) groups and between the region 1320 – 1430 cm^{-1}, the absorption shows C - H stretching which indicate the presence of Alkenes. There is a sharp and broad peak at the region 1640 – 2125cm^{-1} which indicate the presence of Alkenes (C = C) groups and also the absorption at the region 2125 – 2907 indicate the presence of Alkynes (C = C) groups. Lastly, there is N – H (amine group) stretching at 2925 – 3825cm^{-1} and   -NH bending at 3825 – 3975 cm^{-1} (RCONH$_2$). Hence, the groups indicate the structure of urea – formaldehyde.

Fig. 3B, this shows the infra-red spectral of sample B. There is absorption at region 770 – 890 cm^{-1} which indicate the presence of aromatic rings, this is due to the introduction of furfural (C$_4$H$_3$OCHO). The absorption at the region 1600 – 2125 cm^{-1} indicates the presence of esters. This is likely due to the displacement of the formaldehyde from UF resin by furfural. UF being hydrophylic in nature is modified to hydrophobic resin by the furfural being introduced into sample B. There is absorption of hydrogen-bonded alcohols (broad) at the region 3225 – 3850 cm^{-1}. This is due to the presence of furfural in the sample.

Fig. 3c gives the infra-red of sample C, the absorption is observed at the region 770 – 890cm^{-1}, which indicate the presence of aromatic rings. At peak of 890 – 1110cm^{-1}, the region shows the presence alkenes (C – H) groups which is as a result of the formaldehyde. The region 1200 - 1470cm^{-1} shows the presence of Amines (C – N) from urea, and at the region 1630 - 2900 cm^{-1} there is the presence of esters (C = O group as a result of the furfural introduced into the sample. At the region 2900 - 3850cm^{-1}, there is the presence of carboxylic acids (C = O) which is a broad characteristic, this groups confirm then presence of furfural in sample C.

Fig. 3D, shows the infra-red of sample D. There is absorption at the region 770 - 910cm^{-1} which shows the presence of aromatic rings C – H. At peak 920 - 1120cm^{-1} the intensity of the absorption is not sharp and a bit small, this indicate the presence of alkenes (C - H) groups and the absorption at the region 1650 – 2900cm^{-1} indicates the presence of Alkenes (C = H) group. The peak here is very broad and a

bit sharp. At peak $2900 - 3800cm^{-1}$, the peak shows the stretching of carboxylic acids (C = O) group. This confirms the presence of furfural in the sample.

4.3 NUCLEAR MAGNETIC RESONANCE SPECTRA (NMR)

Fig. 4A, shows the nuclear magnetic resonance spectra of sample A. The spectra line is not all that clear to aid in the interpretation of the nuclear magnetic resonance of the sample. This might be due to the fact that too much of the sample was placed on the equipment for analysis which did not actually give room for the machine to analyse the sample.

Fig. 4B shows the nuclear magnetic resonance spectra of sample B. the figure shows that the sample has 3 peaks with chemical shift of the first one in the range 0.1-0.2ppm, the within the standard range (1 - 3ppm) given for the aromatic proton. Standard assumption state that a compound is aromatic if the NMR absorption peak of the hydrogen atoms attached to the carbon atoms of the ring are at low field just as shown in figure 4B. The spectra shows interference's at 5.7 - 9.0ppm range. This might be due to the presence of impurities in the sample.

Fig 4D shows the nuclear magnetic resonance spectra of sample D. This has 3 peaks in the range 0.5 - 1.4ppm and it confirms the presence of cyclopropane, primary and hydroxylic group protons. There is a chemical shift from

1.8 - 2.5ppm, which give hydroxylic proton. Hence this confirms the presence of furfural in the sample.

CHAPTER FIVE

5.0 CONCLUSION

From the analysis of the infra – red spectra and nuclear magnectic spectra, it can be deduced that sample B, C, and D contains furfural. Therefore the aim of the thesis which is to modified the urea formaldehyde with furfural is achieved.

The new product is said to exhibit certain degree of water resistance; urea formaldehyde is hydrophilic in nature, but the introduction of furfural into the samples displaced the hydrogen ions thereby making the resin to be hydrophobic in nature. As a result, samples, B,C, and D have good water resistance and good weatherability as compared to sample A (neat urea formablehyde).

Also, the resin produced by the introduction of the modifier during syntheses (sample B) has good properties as compared to the resin produced by the introduction of the modifier after synthesis (sample C and D). This can be as a result of proper cross linking between urea, formaldehyde and the modifier during the synthesis of the resin.

5.1 RECOMMENDATION

Further work should be carried out on the co-polymerization of melamine with UF as the product (urea-melamine-formaldehyde) has good adhesive properties due to the fact that the presence of melamine in the product increases bond durability and imparts water resistance to the bond, speed cure rate, and reduces potential formaldehyde release.

Analysis, such as impact strength, curing temperature, tensile strength, elasticity, % elasticity at break should be carried out to give a concrete detail of both the physiochemical properties and mechanical properties of the resin.

Also, the production/synthesis of the UF resin in powdery form should be embark upon in the subsequent project work.

Moreso, the addition of other ingredient such as: extenders, fillers, plasticizers e.t.c. should be considered so as to improve the properties of the resin.

Lastly, the department should to make available all the necessary equipment that will enable the students to carryout their research work so as to enhance adequate and a valid result. Unavailability of equipment is a major constraint that delay this work. It is unfair for the student to be running to other department to carryout their experiment when we have our own laboratory. I think, it is high time for the department to look into this in other to save from embarrassment in other department.

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APPENDIX

(A) CALCULATION OF DENSITY, KINEMATIC VISCOUSITY, VISCOUSITY AND MOLECULAR WEIGHT

Let the weight of the specific gravity bottle = W_1

Weight of specific gravity bottle + sample = W_2

Weight of sample $W_3 = W_2 - W_1$

ρ(density) = $\dfrac{\text{Mass}}{\text{Volume}}$

υ (Kinematics viscousity) = C x Time

Where C = Viscometer constant

μ (Viscousity) = υ x ρ

$[\mu]$ Limiting Viscousity Number = $\dfrac{\mu_I - \mu_0}{\mu_0 \text{ x } C}$

and $[\mu_I] = KM_I^a$ [13]

For sample A

$W_1 = 9.95g$

$W_2 = 80.69g$

$W_3 = W_2 - W_1$

   = 80.69 – 9.95 = 70.74g

ρ_A (density) = $\dfrac{W_3}{V}$ . . . . . (1)

But V (Volume of sample) = 50ml(cm^3)

∴ $\rho_A = \dfrac{W_3}{V} = \dfrac{70.74}{50} = 1.4148$g/cm^3 ≈ 1.41g/cm^3

To Calculate Kinematics Viscosity

Using υ(Kinematics viscousity) = C x t . . . . . (2)

Where C = 0.0882 and t = 300s (i.e. the time taken by the sample to run through the capillary tube) we have,

υ_A = 0.0882 x 300 = 26.46 stokes

To calculate Viscousity

The Viscousity is given as $\mu = \upsilon$ x ρ . . . . (3)

∴ μ_A = 26.46 x 1.41 = 37.31 Cp

$[\mu]$ Limiting Viscousity Number = $\dfrac{\mu_I - \mu_0}{\mu_0 \text{ x } C}$ . . . . (4)

Where μ_0 (Viscousity of solvent, Acetone) = 0.42 and C = 0.7

Hence, $[\mu_A] = \dfrac{37.31 - 0.42}{0.42 \text{ x } 0.7} = 125.48$

To calculate Molecular weight

The molecular weight of M_A is obtained from the relationship $[\mu]_I = KM_I^a$ -----(5)

where $K = 9.2 \times 10^{-2} cm^3/g$ and $a = 0.9$

by making M the subject of the formular we have,

$$M = (\frac{[\mu]}{k})^{\frac{1}{a}}$$

$$= (\frac{125.48}{9.2 x 10^{-2}})^{\frac{1}{0.9}} = 3041.56$$

By using the same method for the determination of density, kinematic viscosity, viscosity and molecular weight as shown above, the parameters for sample B,C,and D are obtained as follows:

FOR SAMPLE B

$W_1 \quad = 9.95g$

$W_2 \quad = 85.24g$

$W_3 \quad = 85.24 - 9.95$

$\quad \quad = 75.29g$

$V \quad = 50cm_3$

Therefore $\rho_B = \frac{75.29}{50} = 1.51 g/cm^3$

$t_B \quad = 315s$

$\upsilon_B \quad = C \times t_B = 27.78$ stokes

$\mu_B \quad = \upsilon_B \times \rho_B = 41.95cp$

$[\mu]_B = \frac{41.95 - 0.42}{0.294} = 141.26$

Then, with $a = 0.9$ and $k = 9.2 \times 10^{-2}$ by using equation 5

$M_B \quad = 3469.42$

FOR SAMPLE C

$W_1 \quad = 9.95g$

$W_2 \quad = 82.76g$

$W_3 \quad = 82.76 - 9.95 = 72.8g$

$V \quad = 50cm^3$

$\rho_C \quad = \frac{72.81}{50} = 1.46g/cm^3$

With $t_c = 3023$ we have

$\upsilon_c \quad = 0.0882 \times 302 = 26.04$ stokes

$\mu_c \quad = 26.04 \times 1.46 = 38.89cp$

$[\mu_c] = 130.85$

with $a = 0.9$ and $k = 9.2 \times 10^{-2}$ using equation 5 we have,

$M_2 = 3g$

$M_3 = 27.137g$

$M_4 = M_1 - M_3 = 1.063$

$M_5 = M_2 - M_4 = 1.937g$

Therefore, $\% \text{ TDS} = \dfrac{1.937}{3} \times 100 = 64.566$

$\approx 64.57\%$

FOR SAMPLE C

$M_0 = 25.2g$

$M_1 = 28.2g$

$M_2 = M_1 - M_0 = 3g$

$M_3 = 27.09g$

$M_4 = M_1 - M_3 = 1.11g$

$M_5 = M_2 - M_4 = 1.89g$

The $\% \text{ TDS} = \dfrac{1.89}{3} \times 100 = 63g$

FOR SAMPLE D

$M_0 = 25.2g$

$M_1 = 28.2g$

$M_2 = M_1 - M_0 = 3g$

$M_3 = 27.21g$

$M_4 = M_1 - M_3 = 1.18g$

$M_5 = M_2 - M_4 = 1.82g$

The $\% \text{ TDS} = \dfrac{1.82}{3} \times 100 = 60.66\%$

≈ 60.7