

# A review on the preparation of natural adhesive from natural liquid of plants and animals

Kiflom Gebremedhin

**Abstract** - Three samples are readily to be studied. Starch extracts from plants, animal blood as well as cow's milk were used to be reviewed in this work. In each sample used how to prepare the glue from each samples. Starch extracted from plants using a corresponding procedure and it becomes gelatinization next acidification and mixing steps was allowed so to become ready for usage. Animal blood was also taken to and prepared using the manifested procedure and its efficiency was checked by series tests such as viscosity test, test for jelly strength, apparent moisture content, neutrality foam, odor and keeping qualities grease, ashes and other miscellaneous materials wood-joint tests. Casein was the main protein found in cow's milk which is responsible for preparation of glue from cow. Several procedures are listed below how to prepare with its check up efficiency mechanism.

**Keywords** - adhesiveness, glue, Casein, viscosity test, animal blood, Starch, preparation of adhesive

## I. INTRODUCTION

Glue is a type of adhesive that is capable of holding materials together in a functional manner by surface attachment that resists separation [1, 2]. "Adhesive" as a general term that includes cement, mucilage, glue and paste [1-3]. But we can also used interchangeably for any organic material that forms an adhesive bond. Adhesives are gluing materials which are directly extracted either from natural source like bone, gums and starches or synthetically derived from chemicals like urea-formaldehyde [1,2, 4].

The Knowledge and the use of natural adhesives glue are not new. The ancient Egyptians have used the mixture of Mud, clay and camel's dung as natural adhesives to attach decorations to wood, to build huts and to bond wooden together arbitrary. In the 1930s with advancement of chemical and plastics industry, new adhesive glues were developed for commercial uses [5, 6].

Glues have a wide application in furniture, leather, shoes, printing and textile industries [6, 7]. They serve to fix, bind or attach solid things together.

The most common glues is animal glue which is usually made from the hides and bones of cattle, horses, and sheep and is usually classified as either hide or bone glue [6-8]. Besides, natural blood glue produced in Addis Aaba Ethiopia Abbiatores which produces a modest quantity of glue for domestic consumption.

Now days a number of industries like leather, wood working industry, shoes industry, which use glue is increasing with a large quantity in every year [7, 8, 9]. In our country Ethiopia due to the growth of different manufacturing and construction sector, particularly the present housing construction activities, wood working and furniture sectors highly demand for glue. The stockholders who work in the woodwork, plywood industry, textiles, leather, glass, metal, bookbinding, construction and the packaging industry are faced in cost and availability of glue.

In order to use this glue for fixation of their solid materials, they loss their money for purchasing which lead high wastage as raw materials. Inline the above importance of glue, Researchers have tried to convert wastes (plant and animal by-products) as filler materials in both thermoplastic and adhesive composites [10-13].

Natural Adhesive can also prepared from cereals or roots such as corn, wheat, tapioca, sogo, etc. The basic constituent is polysaccharide which on hydrolysis yields long chain glucose units. Variations can occur with the use of different food materials and with changes in hydrolysis methods [14].

Moreover, adhesiveness can also prepare from the cow's milk. Because of the cow's milk mainly contains Casein (the main protein found in milk) has been used as a glue since the days of ancient Egypt, Greece, Rome, and China. It is mixed with sodium carbonate and calcium hydroxide, and then dissolved in water. [15]

Therefore, the main aim of this review paper is to elaborate the nature of adhesiveness with the mechanism of preparation from different natural plant as well as animal raw materials so as to facilitate for the next finding.

## II. OBJECTIVES OF THE PROJECT

### *General objective*

The general objective of this study is to review on the preparation or production of natural adhesive from natural liquid of plants and animals.

### *Specific objective*

- To determine the preparation of adhesive from plants liquid material
- To explain the preparation of adhesive from animals blood.
- To show the preparation of adhesive from cow's milk.

### III. REVIEW OF RELATED LITERATURES

#### *Overview of adhesiveness*

#### **ADHESION THEORY**

Several theories of adhesion exist which are based on surface-chemical phenomena. It is generally considered that there is no generalised, unified theory of adhesion since the phenomenon is known to exist between a great diversity of material types. In some special cases, either pure adsorption, or electrical or diffusion attractive forces are found at an adhesive-bound interface. More frequently, one finds adhesion to be a synergistic combination of all of these driving, attractive forces. This is especially true in the case of practically all adhesive bonding situations [14, 15].

#### **Adsorption theory**

In adsorption theory the attractive forces between materials is interpreted in terms of the chemisorbed and physisorbed atomic and molecular species that exist at an interface. Essentially this theory regards adhesion as one particular property of a phase interface where in polar molecules or groupings will be orientated in an ordered way. The forces are initially involved in this mechanism are the van de Waals' forces - the orientation, induction and dispersion effects. If a molecule, which is large enough to contain a polar group and a non-polar part as separate and distinct entities, approaches an interface at which the dielectric constant changes it will orientate itself. It will move so that its non-polar part will be in the medium of lower dielectric constant and its polar part in the medium of high dielectric constant. This is the process that takes place in adsorption and must really take place if an adsorption theory is valid [14, 15].

#### **Electrical theory**

This theory explains adhesive attraction forces in terms of electrostatic effects at an interface.

This is based on the phenomenon of an electrical double layer formed at the junction of two materials. At any boundary an electrical double layer is produced and the consequent coulombic attraction might account for the adhesion and resistance to separation.

#### **Diffusion theory**

In this theory adhesion is attributed to intermolecular entanglements at the interface.

This is applied to the union of high polymers. The fundamental concept is that adhesion arises through the interdiffusion of the adherend and the adhesive. It is based upon the chain nature of the structure with the consequent flexibility and the ability of the chains to undergo Brownian movements on a sub-molecular scale. When the adhesive is applied in solution (most probably) and if the adherend is sensibly soluble in the solvent the substrate molecules will also diffuse to an appreciable extent into the adhesive layer. Overall the clean-cut boundary between the adherend and the adhesive disappears and is replaced by a layer representing a gradual transition from one polymer to the other. A major difference in this theory is that it implies a three dimensional volume process rather than a two dimensional surface process.

#### **Practical view-point**

From these preliminary remarks it can be seen that adhesives are scientifically and technologically diverse subjects encompassing the fields of polymeric materials, rheology, surface chemistry, engineering mechanics and process technology. Adhesion on the other hand is a specific interfacial phenomenon pertaining to the degree to which the surface of two different materials is attracted to each other. The molecular basis of adhesion is rarely studied in practice; one resorts to secondary means of determining the forces of adhesion (contact angle, contact potential, adhesive joint strength). In particular, one must make a clear distinction between the forces of adhesion and adhesive joint strength. The latter is in the realm of engineering mechanics and is required for engineering design purposes; adhesive joint strength is therefore the most important engineering property of an adhesive material [14, 15].

#### **Adhesive types**

Adhesives can be classified into three main types given below. There are of course several products that are combinations of these three types but essentially all adhesives can be grouped into these categories.

#### **Chemical reactive types**

Basically an adhesive of this type is supplied in a low molecular weight form and after application a polymerization reaction is allowed to take place. This polymerization can be achieved by:

#### **Two component pack**

Supply the produce as a two component pack, i.e. base plus hardener. Examples of this type are:

- Epoxy adhesives based on epichlorhydrin bisphenol. Cured with amines or polyamide.
- Phenolics adhesives i.e. a nonvalac type with hexamethylene tetramine.
- Unsaturated polyesters using an organic peroxide, i.e. M.E.K. peroxide and cobalt naphthenate.
- Polysulfide with lead dioxide or an isocyanate.
- Polyurethanes with isocyanate.
- Silicone polymers utilizing a metal salt of an organic acid, e.g. lead octoate.
- Reactive acrylics - rely on peroxides or amines.

#### **Moisture**

Polymerisation can be achieved by relying on moisture either on the surface of the adherend or in the atmosphere to effect a cross-linking mechanism on some other "natural" component.

In this case the adhesive is supplied as a single component. Examples are:

- Polyurethane containing an isocyanate group.
- Cyanoacrylates. These are the instant bond adhesives.

- Silicones containing an acetylene group. These are the common R.T.V. silicones which with moisture releases acetic acid causing a cross-linking of the paste to an elastomeric.
- Anaerobic which rely on absence of oxygen.

### **Heat**

The final method of curing a chemical reactive type is by utilizing heat to polymerize the adhesive components. Examples are:

- Epoxies with the catalyst incorporated in the adhesive in a latent form, e.g. dicyandiamide which will require a temperature of 175<sup>o</sup> C to affect a cure.
- Phenolics of the resole type.
- Polyvinyl acetates which are based on polyvinyl alcohol reacted with an aldehyde. The conversion is normally about 80% and on heating after application the cross linking is completed.
- Urethanes incorporating a blocked isocyanate. The free isocyanate groups are all reacted with a temporary blocking agent such as phenol which is stable up to 150<sup>o</sup>C.

The problems associated with the above three types of adhesives are:

- Two components types - difficult to ensure correct and adequate mixing of the two components (often by unskilled personnel or in adverse conditions).
- Moisture curing types - poor shelf life even when stored in sealed containers. Once container is opened the life will drop rapidly.
- Heat curing types - again poor shelf life plus the problem of heating the adhesive or adherend.

### **Thermoplastic type**

Basically the adhesives in this class are thermoplastic in nature which means they are heated to a sufficient temperature where they will flow and wet the substrates and then set and develop the bulk strength on cooling. The ideal Hot Melt adhesive is a solid up to a temperature of 80<sup>o</sup> C (as a minimum) but will then melt sharply to give a low viscosity fluid that is easily applied and capable of wetting the adherend followed by rapid setting upon cooling. They normally contain a base high molecular weight polymer together with tackifying resins and viscosity depressants.

Examples of polymers that are used as the base for Hot Melt adhesives are:

- Ethylene vinyl acetate - a polyethylene chain containing the highly polar acetate group.
- Ethylene-ethyl acrylate which has an ethyl acrylic grouping.
- Ionomers - derived from ethylene acrylic acid copolymers but including a metal cation or some of the pendant carboxyl groups. The metal cation is free to cross-link with the anionic side groups similar to a thermosetting resin but the reaction is thermally reversible.
- Phenoxies - similar chemical structure to epoxides.
- Polyamides of low to intermediate molecular weight based on the unsaturated dibasic acids of vegetable origin.
- Polyesters (saturated).
- Vinyl resins such as polyvinyl acetate, polyvinyl butyral and polyvinyl ethers – used in various special areas.

### **Evaporation or diffusion types**

In adhesives of this class the adhesive polymers is essentially in its final form however, wetting of the adherend is achieved by dissolving or dispersing the polymers in a suitable solvent.

#### *Solvent Based Systems*

- Rubber adhesives - usually based on an elastomeric which is either natural or synthetic.
- The synthetic rubbers that are used in adhesives are polychloroprene nitrile (a copolymer of butadiene and acrylonitrile) butyl (a copolymer of isobutylene and isoprene) and styrene butadiene rubber. Natural rubber is essential isoprene.
- Normally resins, usually phenol-formaldehyde based, are incorporated.
- Phenolic or resorcinol formaldehyde resins dissolved in a solvent.
- Vinyl resins such as polyvinyl acetate, polyvinyl chloride, polyvinyl ether etc.
- Acrylic resins based on methyl methacrylate, ethyl acrylate, acrylic acid etc.
- Miscellaneous resins such as cellulose acetate and polyamides.

#### *Water Based Systems*

There are very few polymers of sufficient molecular weight to be attractive as adhesives that will dissolve in water. However, dispersions or emulsions are very important. Examples are:

- Rubber latices - again either natural or synthetic such as polychloroprene, nitrile or styrobutadiene rubber.
- Vinyl resins, where polyvinyl acetate emulsions are very widely used.
- Acrylic resins which offer some advantages over PVA types such as water and solvent resistance.

The problems associated with evaporation type adhesives are fairly straightforward.

- Elimination of the dispersing medium which could be toxic or inflammable or slow to leave the adherend.
- A large percentage of the adhesive is basically waste and non-recoverable.
- Possible damage to the adherend by the dispersing medium.

The disadvantages of Hot Melt adhesives are of course the heating associated with their application and possible thermal degradation if held at a high temperature for a long time and the thermoplastic nature of the polymer. Also the stress concentrations built up by the actual covering and shrinking process [15].

### **Preparation of adhesive glue from plant starch**

#### **Preparation of starch from plant extracts**

The plant paste obtained was collected in a fine filter bag and it will be preserved using sodium azide. 10 mg of the paste was weighed and 1ml of 20% HCl and incubated for 90 minute at room temperature (20-25<sup>0</sup>). An aliquot (0.8 mL) will be mixed with 4mL of 90% ethanol and stored at -20<sup>0</sup>c overnight to precipitate the starch. After centrifugation (10min, 12000g), the starch pellet was washed three times with 90% ethanol. Then the yield will be dried [6].

#### **Gelatinization**

The base material i.e. the starch is gelatinized in the reactor using caustic soda. Heating in water is the simplest method of breaking up starch extract. On heating in water, starch first swell and then burst open with a resulting thickening of the suspension. The temperature at which this thickening of the suspension occurs is called the gelation temperature. For most starches in pure water, gelation occurs between 57 and 72°C. In this form, the starch is not a true solution but a colloidal suspension.

The heating process can take one of two forms. In the first, salts (usually the chlorides of metals such as calcium, magnesium and zinc) are added to a suspension of the starch in water, and the adhesive is produced by controlling temperature and the time of stirring. In the second and primary method, caustic soda is added to the starch suspension; the product is neutralized with hydrochloric acid later in the process [7]

The starch paste now has a high viscosity and acts as an adhesive. If the concentration of the starch is above 7%, then the cooked paste is very viscous and difficult to pump. Above 15% starch solids content, the cooked paste forms an immobile rubbery mass on cooling. Suspensions with a higher amylose/ amylopectin ratio will have a higher viscosity.

Pregelation starch is produced by physical modification of the starch to impart the ability to form a paste easily in cold water. The process consists of heating the starch slurry to a temperature above the gelation temperature and then quickly drying the starch before retardation can occur. The main process equipment used is a heated-drum drier or hot roll. Unmodified starches, such as those produced by the steps outlined previously, come in powder form (Pregelation) or as high-viscosity, low-solids content pastes that do not show a stable viscosity with time. Therefore, several treatments have been developed to provide liquid adhesives that are not subject to retrogradation and have a viscosity and rheology more suitable for many applications. These treatment methods include alkali treatment, acid treatment and oxidation.

The gelation temperature can be lowered by the addition of an alkali, such as sodium hydroxide, to the starch suspension. If sufficient alkali is added, the starch can be induced to gel at room temperature [12].

#### **Acidification**

The gelatinized starch is acidified to normalize its PH. A pre-determined quantity of acid is sprayed on the gelatinized starch by means of an atomizer jet to give the required PH. Additional catalysts such as inorganic salts may be added at this stage. Acid modification of starch is achieved by heating the starch at 49-54°C with small amounts of aqueous mineral acid, followed by neutralization with a base. This tends to make for a much thinner solution at the same solids content when compared to unmodified starch. Starches prepared in this manner are often known as thin-boiling or high-fluidity starches. Acid modification is often used when applications require higher solids content but a controlled, lower viscosity [7].

#### **Mixing**

Oxidization of starch is usually obtained by treatment with aqueous alkaline hypochlorite. A starch suspension at pH 8-10 is treated with hypochlorite (5-10% Cl based on starch) for a long enough time to produce the desired viscosity. Acid is liberated during the reaction, so base must be added to maintain the pH for optimum reactivity. Dried oxidized starch is generally whiter than unmodified starch. Because of the low color, these starches are often used for the sizing and coating of printing papers. These oxidized or chlorinated starches behave similarly to acid-modified starches. However, the oxidized starch has greater tack and adhesive character and, thus, is often used in adhesive applications.

Preservatives and extenders are added and the mixture mixed thoroughly to obtain homogeneous product. Solution of preservative such as formaldehyde is added to the mixture to obtain homogeneous product. To prevent conversion of the adhesive proceeding further than desired, it is immediately discharged from the mixer and cooled [12].

#### ***Preparation of adhesive glue from animal blood.***

Many petroleum-based adhesives such as phenol formaldehyde, urea formaldehyde, resorcinol formaldehyde, and poly (vinyl acetate) are widely used in the production of plywood, composite wood panels, and furniture [16]. However, the rising cost of petrochemical- based products and growing awareness of environmental protection have prompted the development of "green" products from inexpensive and renewable resources [17]. For example, California Air Resources Board (CARB) has recently set strict limits on formaldehyde emission from composite wood products [18]. This has cost, compliance, testing, and certification requirement implications to the wood products industry. Therefore, protein-based adhesives have gained renewed attention and consideration [19–21]. During the past decade, research on protein-based adhesives has been largely directed toward soy protein. However, despite the low cost and plentiful availability soy proteins, adhesives prepared from soy proteins suffer from poor water resistance characteristic [17–19]. Several methods have been reported for preparing adhesives from animal blood since 1930s [21–23]. However, those methods require using dried blood powder. Since drying is an energy intensive process, blood adhesives produced using the past methods have not become economically viable alternatives to synthetic adhesives. Unlike polyol- based natural polymers, blood proteins are complex macromolecules and contain a number of chemically linked amino acid monomers, which form polypeptide chains and constitute the primary structure[17,18]. These structural features can be changed by physical, chemical, or enzymatic treatments. Such treatments alter secondary, tertiary, or quaternary structures of the proteins without breaking the covalent bonds and lead to protein denaturation. It is well known that the native structure of proteins can be modified to increase the bonding strength of protein-based adhesives. Unfolded protein molecules have increased surface area and hence afford improved interaction with substrates [19–21]. Accordingly, the performance of blood protein adhesives is dependent on the dispersion and unfolding of the protein in solution. The advantages of animal blood-based adhesives include: (1) animal blood is

abundantly available and inexpensive because blood from slaughterhouses is mostly discarded, (2) blood glue is easy to handle because of its relatively low viscosity, and (3) blood glue can be applied using both hot and cold presses [22]. It has been shown that wood products bonded with blood protein adhesive are more water resistant than those bonded with plant protein adhesives [23]. The objectives of this research were to (1) prepare an adhesive from fresh cow blood without first drying it, (2) evaluate physico-chemical properties of the adhesive prepared, and (3) determine bonding strength of the adhesive as a function of its alkaline pH.

### **Methodology of adhesive preparation from animal blood**

#### **Chemicals and solvents used for preparation of adhesive from blood**

Fresh cattle blood, EDTA, Lime water, sodium azide ( $\text{NaN}_3$ ), NaOH, Sodium Silicate ( $\text{NaSiO}_3$ ) Aluminum dihydrogen ( $(\text{Al}_5(\text{P}_3\text{O}_{10})_3)$ ), Ammonia ( $\text{NH}_3\text{H}_2\text{O}$ )

#### **Blood Sample collection**

Fresh cattle blood will be collected from Mekelle municipal abattoir. During the blood collection, the age and body condition scoring of each cattle will be recorded. The age of the animals will be determined on the basis of the dental dentitions as described by Kelly<sup>9</sup> and two age groups will be considered; below and above five years. Body condition scoring will be done according to Nicholson and Butter Worth and classify in to three categories as poor, medium and good [10].

### **Experimental**

#### **Sample preparation**

Fresh cattle blood (about 100g (100ml)) will be mixed with 10%, 17ml EDTA to prevent coagulation [2].

#### **Preparation of the adhesive glue**

This sample will then preserve up on addition of 2ml of 1% sodium azide ( $\text{NaN}_3$ ). By adding 5g of lime water (Lime:  $\text{H}_2\text{O}$  (1:3.5g, w/w)) and 4g of 30% w/w NaOH PH of the above solution will also adjusted. Curing agent Sodium Silicate ( $\text{NaSiO}_3$ , 37% w/w): 4g Aluminum dihydrogen ( $(\text{Al}_5(\text{P}_3\text{O}_{10})_3$ , 100:5)), will then be added to obtain the final adhesive after addition of 3g Ammonia ( $\text{NH}_3\text{H}_2\text{O}$ ) [10, 12].

### **Experimental tests of the adhesive glue**

#### **Viscosity test**

Sufficient of the glue sample will be taken (calculated from the apparent moisture content) to give 13.2 grams of dry glue and placed in a standard wide-mouthed bottle of 150 cubic centimeters capacity with an inside diameter of 59 mm., an outside diameter of 66 mm., and a height over all of 85 mm., and fitted with a No. 9 rubber stopper. Enough amount of distilled water will then added to the glue to make a total of 106.8 grams of water, including that naturally contained in the glue. This will give an 11% solution based on approximately anhydrous glue. The glue and water will be thoroughly mixed with a stirring rod and then allowed to stand at a temperature of 10° to 15° C. for at least 4 hours. The glue will then be melted by bringing the samples to a temperature of 62°C. In water bath in which the temperature of the water is below 70°C and the sample will be brought to 62°C in just 15 minutes.

The viscosity will be determined in a standard jacketed pipette viscometer or other suitable viscometer capable of expressing viscosity in the absolute unit of "poise." The instrument is equipped to hold the glue solution at approximately constant temperature. The temperature of the glue solution will be 60°C and the determination will be made as soon as the solution has uniformly reached the required temperature [13, 14].

#### **Test for Jelly Strength**

The samples from the viscosity test will be placed in the standard containers and used for jelly strength determinations. The glue solution should be free of air, or foam. The samples shall be allowed to cool to approximately 45° C and water will be mixed thoroughly with the solution. The samples shall then be placed in a chamber or bath at  $10 \pm 0.1^\circ \text{C}$  for a period of 16 to 18 hours. The determination of jelly strength will be made on a Bloom gelometer adjusted to give 4 mla. depression and to deliver a load of 40 grams per second to the surface of the jelly. The test will be completed within 2 minutes from the removal of the sample from the cooling chamber [13, 14].

#### **Apparent Moisture Content**

The loss in weight of a 10-gram sample, previously reduced to a size that will pass a No. 4 mesh screen, placed in a well-ventilated oven and heated at  $105^\circ \pm 3^\circ \text{C}$ . for 16 hours, shall be not less than 9 or more than 15 percent of the original weight of the glue [15, 16].

#### **Neutrality**

Portions of the solutions upon which the viscosity and jelly strength tests are made or other samples of equal concentration will be used to determine the acidity or alkalinity of the glue. The acidity or alkalinity will be determined in terms of pH and must be within the range of 5.5 to 7.5 [16].

#### **Foam**

Portions of the samples used in the viscosity and jelly strength tests or other samples of equal concentration will be used for a determination of the tendency to foam. Seventy-five cubic centimeters of the solution at 60° C will be placed in the standard container and agitated with a stirrer or propeller. The stirrer will be placed in the lower one-half of the solution and the speed of the stirrer during test will be between 13,000 and 15,000 r.p.m. The solution will be agitated for 1 minute and then allowed to stand at room temperature for 10 minutes, at the end of which there shall be not more than 2.5 cm. foam [15, 16]

#### **Odor and Keeping Qualities**

A 50 cubic centimeters portion of the glue solution used in previous tests will be placed in an uncovered container and held in an incubator at 37° to 38° C. for 48 hours. At the end of this time it shall be free from any odor of decomposition [14].

### Grease, Ashes and Other Miscellaneous Materials

If for any reason it seems desirable, tests may also be made for ash and grease content and the presence of materials that give a fictitious value to glue. The presence of more than 4 % ash in clear glues and 10 % in opaque (white) glues, or 3 percent of grease (determined by the Kissling or other satisfactory extraction method that shows total grease), or the presence of materials which increase the viscosity or jelly strength may be cause for rejection [15].

### Wood-Joint Tests

Selected pieces of wood, usually sugar maple, will be stored in an atmosphere at 30% relative humidity until they have reached equilibrium moisture content with this condition. Matched pieces, approximately 3/4" x 2.5" x 12") will be carefully surfaced to insure smooth, plane, and parallel surfaces. The pieces are then glued under controlled conditions of temperature, amount of glue spread, duration of assembly period, and amount of pressure applied. They will then allowed to remain under pressure. Overnight and then returned to 30% relative humidity for seasoning. A seasoning period of at least a week is allowed between gluing and testing. The glued pieces are then cut into specimens and tested in shear. The unit pressure required to break the joint and the amount of wood fiber torn in breaking are measures of the quality of the joint. [20-23].

### Preparation of glue from cow's milk

Casein is the principal protein found in cow's milk from which it has been extracted commercially for most of the 20<sup>th</sup> century. It is responsible for the white, opaque appearance of milk in which it is combined with calcium and phosphorus as clusters of casein molecules, called .micelles. The major uses of casein until the 1960s were in technical, non-food applications such as adhesives for wood, in paper coating, leather finishing and in synthetic fibres, as well as plastics for buttons, buckles *etc.* During the past 30 years, however, the principal use of casein products has been as an ingredient in foods to enhance their physical (so-called .functional.) properties, such as whipping and foaming, water binding and thickening, emulsification and texture, and to improve their nutrition. [35]

The amount of casein in cow.s whole milk varies according to the breed of cow and stage of lactation, but is generally in the range 24-29 g L-1. Casein contains 0.7-0.9% phosphorus, covalently bound to the protein by a serine ester linkage. Casein is consequently known as a phospho-protein. All the amino acids that are essential to man are present in casein in high proportions, with the possible exception of cysteine. Thus, casein may be considered as a highly nutritious protein. [34]

Casein exists in milk in complex groups of molecules (sometimes referred to as calcium phospho-caseinate) that are called .micelles.. The micelles consist of casein molecules, calcium, inorganic phosphate and citrate ions, and have a typical molecular weight of several hundred million. In terms of physical chemistry, the casein micelles may be considered to exist in milk as a very stable colloidal dispersion. The caseins, as proteins, are made up of many hundreds of individual amino acids, each of which may have a positive or a negative charge, depending on the pH of the [milk] system. At some pH value, all the positive charges and all the negative charges on the [casein] protein will be in balance, so that the net charge on the protein will be zero. That pH value is known as the isoelectric point (IEP) of the protein and is generally the pH at which the protein is least soluble. For casein, the IEP is approximately 4.6 and it is the pH value at which acid casein is precipitated. In milk, which has a pH of about 6.6, the casein micelles have a net negative charge and are quite stable.

Although casein has been shown to consist of several individual casein components, referred to as  $\alpha$ 1-,  $\alpha$ 2-,  $\beta$ - and  $\kappa$ -casein, each having slightly different properties (which are caused by small variations in their amino acid content), only the commercial product, which contains all of these components, is considered in this article.[35]

### EXTRACTION OF CASEIN FROM MILK

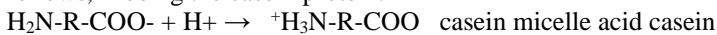
#### Separation

Casein is extracted from milk using the processes outlined in **Figures 1 and 2**. Whole cow.s milk (with a typical fat content of 4.65% - see Figure 1 in the introductory article) is first separated by means of centrifuges that produce cream (for the manufacture of butter or other milk fat products - see the article on milkfat products) and skim milk. Skim milk can thus be considered as the raw material from which casein products are made.[35]

#### Precipitation

The operations involved in the precipitation of casein in New Zealand. Precipitation by means of acidification can be considered in terms of simple chemistry as

follows, R being the casein protein:



(pH = 6.6) (pH = 4.6)

Colloidal dispersion Insoluble particles in the case of enzyme coagulation of casein, there is no change in the pH of the milk. Instead, the addition of a specific enzyme, *chymosin*, which is found in the stomach of newborn calves, specifically cleaves a highly charged portion from the  $\kappa$ -casein, called glycomacropeptide. That action causes the remainder of the  $\kappa$ -casein (now called *para- $\kappa$ -* casein) to lose its considerable power in stabilizing the micelles in milk, and the result is the formation of a three-dimensional gel network or clot of the casein in the presence of calcium ions. This reaction is essential in the manufacture of virtually all cheese types and in the production of rennet casein.[34]

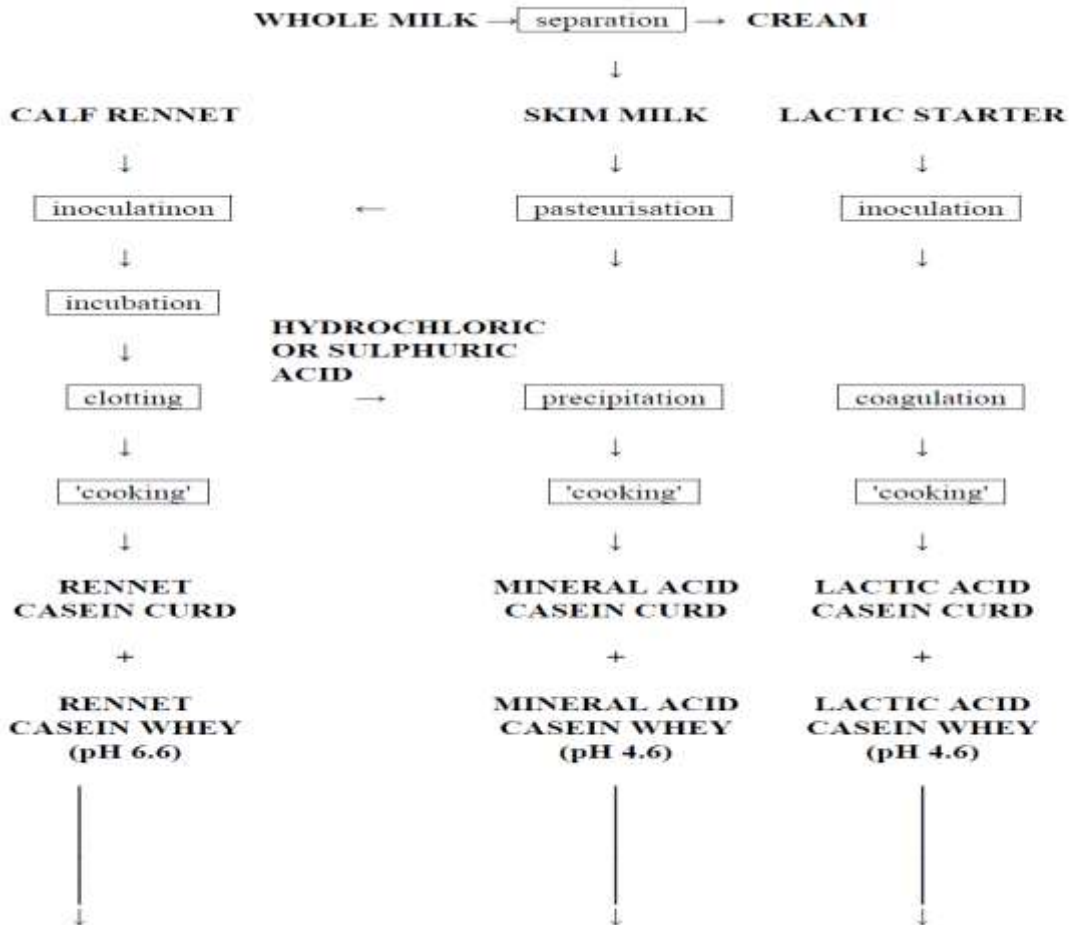
#### Wet-processing operations

When the casein has been precipitated, the mixture is heated (a process known in the dairy industry as .cooking.). Heating of the precipitated casein causes the particles to shrink and expel moisture (whey) (rather like a sponge), and also to agglomerate together to form clumps of curd. The curd is then separated from the whey and washed several times with water in vats prior to mechanical dewatering by pressing or centrifuging.

#### Drying and dry processing of casein

The dewatered curd, with a moisture content of about 55%, is dried by means of hot air using either fluidised bed driers with multiple decks or pneumatic-conveying ring driers to produce dry casein having a moisture content of 10-12%. The warm, unmilled casein is then subjected to several dry processing steps (Figure 2), including cooling (usually by air conveying), tempering, or conditioning to ensure that moisture is distributed evenly between large and small particles, milling, sifting (to produce coarse, medium and fine mesh particles), blending (to ensure uniformity) and bagging. The 25 kg bags of casein are placed on pallets and stored ready for shipping. [35]

Figure 1 - Processing steps involved in the precipitation of acid and rennet caseins from milk.



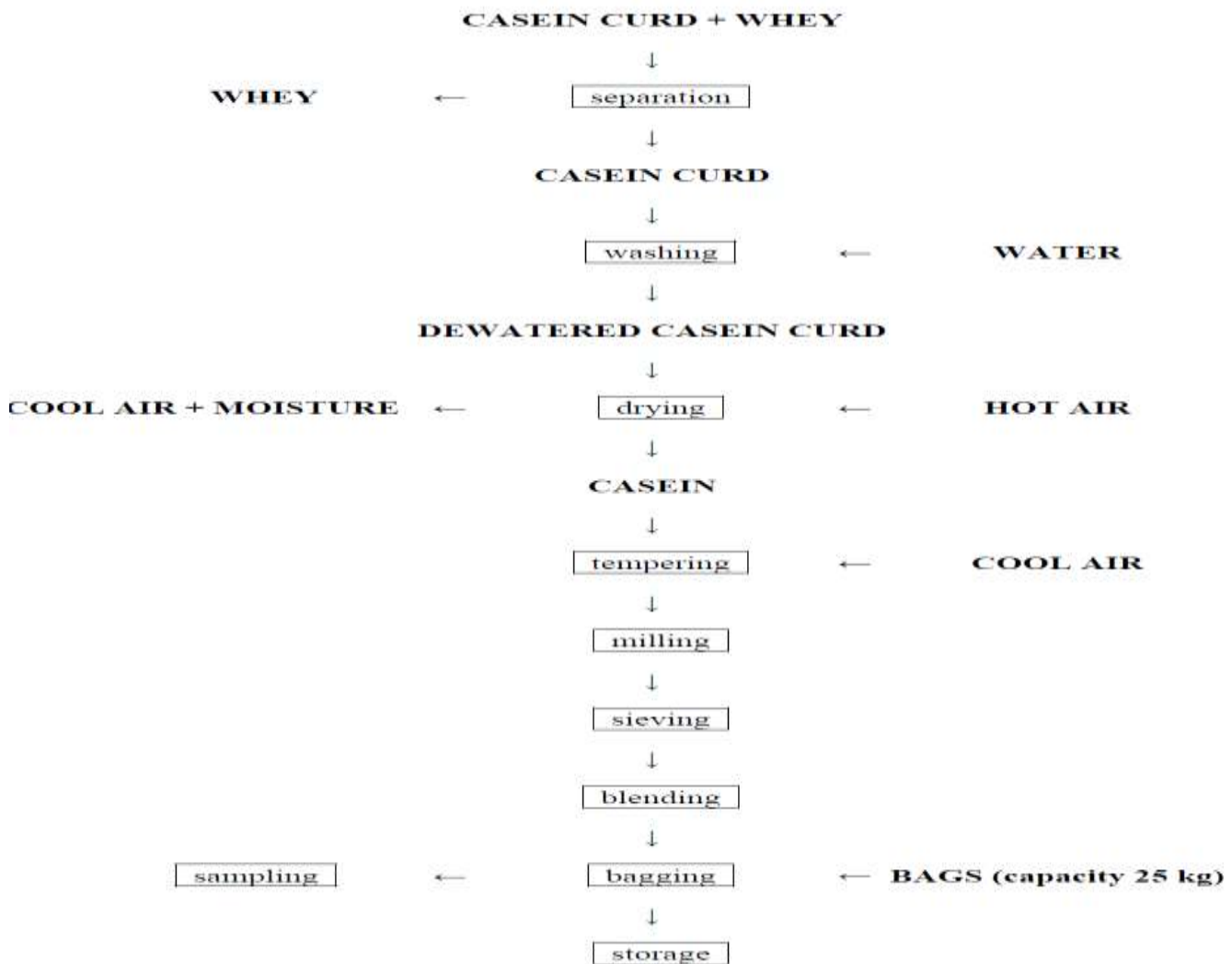


Figure 2 - Processing operations in the washing and drying of caseins.

#### Methodological Procedure how to prepare glue from cow's milk [33]

##### Materials Needed:

milk, regular, low fat, or skim vinegar, 5% acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$  baking soda, sodium bicarbonate,  $\text{NaHCO}_3$  beakers, 1000-mL and 250 or 400-mL strainer cheese cloth (available from hardware stores or natural food stores) stirrer, hot plate

##### SAFETY PRECAUTIONS:

Wear safety goggles or glasses. Vinegar is a dilute solution of acetic acid. It should not cause any injuries to the skin, but it should be washed off with water in case of contact. If vinegar gets in the eyes, rinse well with water. Other materials used in this experiment do not pose any safety hazards.

##### DISPOSAL:

Solid materials can be disposed of in the trash. Liquids can be poured down the drain with running water.

##### EXPERIMENTAL PROCEDURE:

Measure 500 mL of milk into a 1000-mL beaker. Add 100 mL of vinegar to the milk and stir well. Warm the mixture on a hot plate, stirring occasionally.

When the mixture gets warm, the milk will curdle, forming lumps. Remove from the heat and stir until curdling stops. You have formed the famous curds and whey of *Little Miss Muffet* fame.

Place a piece of cheese cloth in a strainer and strain the mixture to separate the curds from the whey. Gently squeeze excess liquid from the curds.

Place the curds in a beaker and add about 50 mL of water and 5 grams (about one teaspoon) of baking soda (sodium bicarbonate) to neutralize any remaining vinegar and stir well. You now have white glue or casein glue. Test the glue by pasting together two pieces of paper. Let the glue dry and try to separate the paper.

#### IV. CONCLUSION

Preparation of adhesive from natural products is essential and efficient in our day to day activities. From the above study it can be concluded that preparation of glue from animal blood is very stronger than glue prepared from milk and from plant extract. Preparation of glue from plants is using starch extracted from the plants. In the above clearly explained the method how to



prepare the adhesive as well as how to confirm the strength of adhesive for attaching the required materials such as paper, wood, leather etc.

## V. REFERENCES

- [1] Browne, F. L. 1933. Water-resistant animal glue. Forest Products laboratory Report No. R40.
- [2] Gill, A. H. 1925. A comparison of various tests upon glue. *Indus. & Eng. Chem.*, 297-306.
- [3] Jennings, D. 1933. Quality of fish glues. *Chem. Trade Jour.* 221 105-107.
- [4] Bogue, R. H. 1922. The chemistry and technology of gelatin and glue McGraw-Hill Book Co., New York.
- [5] Duhamel, M. Monceau, D. 1989. The Art of Making Various Kinds of Glues
- [6] Alexander, J. 1923. Glue and gelatin. Chem. Catalog Co., New York.
- [7] Brouse, D. 1931. Age and strength of glue joints. *Woodworking Industries*, June, pp. 32, 33.
- [8] Nicholson, M., Buttrworth, M. 1986. A guide condition scoring of Zebu cattle international livestock center for Africa, Addis Ababa, Ethiopia.
- [9] FPL. June, 1955. Animal Glues: Their manufacture, Testing, and Preparation. FPL Rept. No. 492. 13 pp.
- [10] May, 1959. Blood Albumin Glues: Their Manufacture, Preparation, and Application. FPL Rept. No. 281-2. 5 pp.
- [11] Tressler, D. K. 1924. Examination of liquid glue. *Indus. & Eng. - Chem.* 16, 943-5.
- [12] National Association Of Glue Manufacturers 1930'. Standard methods ' (revised) for determining viscosity and jelly strength of glue. *Indus. & Eng. Chem., Anal. Ed., 2*, 348-51.
- [13] Peck, E. C. 1932, Moisture content of wood in dwellings. U. S. Dept. of Agr. Circ. 239.
- [14] John Packer version of the introductory lecture given by Owen Brett (Ados Chemical Company) at a symposium on adhesive technology organised by the Polymer Group of the NZIC, 1990, p1-10
- [15] National Association Of Glue Manufacturers 1930'. Standard methods ' (revised) for determining viscosity and jelly strength of glue. *Indus. & Eng. Chem., Anal. Ed., 2*, 348-51.
- [16] LiuY, LiKC. Chemical modification of soy protein for wood adhesives. *Macromol Rapid Commun* 2002;23:739-42.
- [17] ChengEZ, SunX. Effects of wood-surface roughness, adhesive viscosity and pressure on adhesion strength of protein adhesive. *J Adhes Sci Technol* 2006;20:997-1017.
- [18] <http://www.wooddigest.com/print/WoodDigest/CARB-Setting-Limits-on-Formaldehyde-Emissions/2905S>.
- [19] Hojilla Evangelista MP. Adhesive qualities of soybean protein based foamed plywood glues. *J Am Oil Chem Soc* 2002;79:1145-9.
- [20] ChengEZ, SunXZ, KarrGS. Adhesive properties of modified soybean flour in wheat straw particle board. *Compos Part A—Appl Sci Manuf* 2004;35:297-302.
- [21] YangI, KuoML, MyersDJ, PuAB. Comparison of protein-based adhesive resins for wood composites. *J Wood Sci* 2006;52:503-8.
- [22] Steele PH. Biocomposite material and method of making. US Patent 5635123; 1997.
- [23] KuoML, MyersDJ, HeemstraH, CurryDG. Soybean-based adhesive resins and products utilizing such adhesives. US Patent No. 6306997; 2001.
- [24] LiZ, SunXS. Adhesive performance of amino group of soybean glycinin proteins. *J Biobased Mater Bioenergy* 2007;1:64-70.
- [25] ConeCN. Glue and process of manufacture therefor. U.S. Patent no. 2400541; 1946.
- [26] GossettJM, EstepJrMH, PerrineMJ. Production of glue from soluble blood. US Patent no. 2874134; 1959.
- [27] BunningCK. Method for manufacturing glue for binding agent in manufacture of chipboard or other cellulose products. US Patent no. 4180412; 1979.
- [28] NassA. Method for the manufacture of an adhesive from animal blood. US Patent no. 4333767; 1982.
- [29] WangY, Wang D, SunXS. Thermal properties and adhesiveness of soy protein modified with cationic detergent. *J Am Oil Chem Soc* 2005;82:357-63.
- [30] Saito M, Ichikawa N, Taira H. Fractionation and emulsifying properties of plasma proteins. *Agric Biol Chem* 1988; 52:2831-6.
- [31] KumarR, ChoudharyV, MisshraS, VarmaIK, MattiasonB. Adhesives and plastics based on soy protein products. *Ind Crops Prod* 2002;16:155-72.
- [32] SellersT. Wood adhesive innovations and application in North America. *For Prod J* 2000;51:12-4.
- [33] LudescherRD. Physical and chemical properties of amino acids and proteins. In: NakaiS, MolderHW, editors. *Food proteins: properties and characterization*. New York: Wiley; 1996. p.23-70.
- [34] HowellNK. Chemical and enzymatic modification. In: NakaiS, MolderHW, editors. *Food proteins: properties and characterization*. New York: Wiley; 1996. P.235-80.
- [35] Southward C. R. (Consumer and Applications Science Section, New Zealand Dairy Research Institute). 1960, p1-13