

- **Casein exists in milk in complex groups of molecules (micelles; consist of casein molecules, calcium, inorganic phosphate and citrate ions).**
- **As initial pH value of milk is decreased from 6.5, casein starts losing its colloidal dispersibility and stability and begins to precipitate at pH 5.3. Maximum precipitation takes place at pH 4.6 (isoelectric point of casein).**
- **Ion exchanges replace cations in deproteinated whey with hydrogen ions has been applied in reducing the pH to about 1.8 prior to using treated whey as the precipitant for acid casein.**
- **Ultrafiltration increase protein content of skim milk to 5-7% and to produce a permeate which is treated by cation exchange and then used to precipitate casein. These techniques avoid incorporating anions of HCl and H₂SO₄ in whey resulting from casein manufacture to increase value of whey for further processing.**

Processing Principle

Efficient separation of fat from milk is essential in production of edible casein. Fat needs to be reduced to the level less than 0.05%. Microbiological standards for edible casein requires pasteurization of either or both milk and curd.

Precipitation

**Drainage of
whey**

Washing

Pressing

**Milling and
drying**

**Tempering,
grinding, sieving
and bagging**

Yield



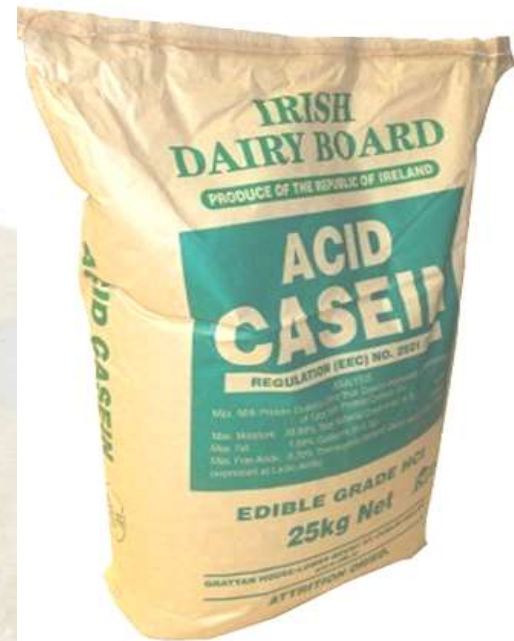
Basic principle of casein manufacture



Precipitation

- Casein exists in milk as calcium caseinate-calcium phosphate complex.
- When acid is added to milk, this complex is dissociated. As pH of milk is lowered, calcium is displaced from the casein molecules by hydronium ions, H_3O^+ and calcium phosphate associated with the complex is converted into soluble Ca^{2+} ions and H_2PO_4^- ions.
- At pH 5.3, casein begins to precipitate out of solution and at pH 4.6, maximum precipitation occurs.
- At this pH, all calcium is solubilized. **Calcium from caseinate molecule removed and calcium phosphate is liberated to the soluble form.** This makes it possible to wash these soluble salts from the curd and achieve low ash content in the final product.

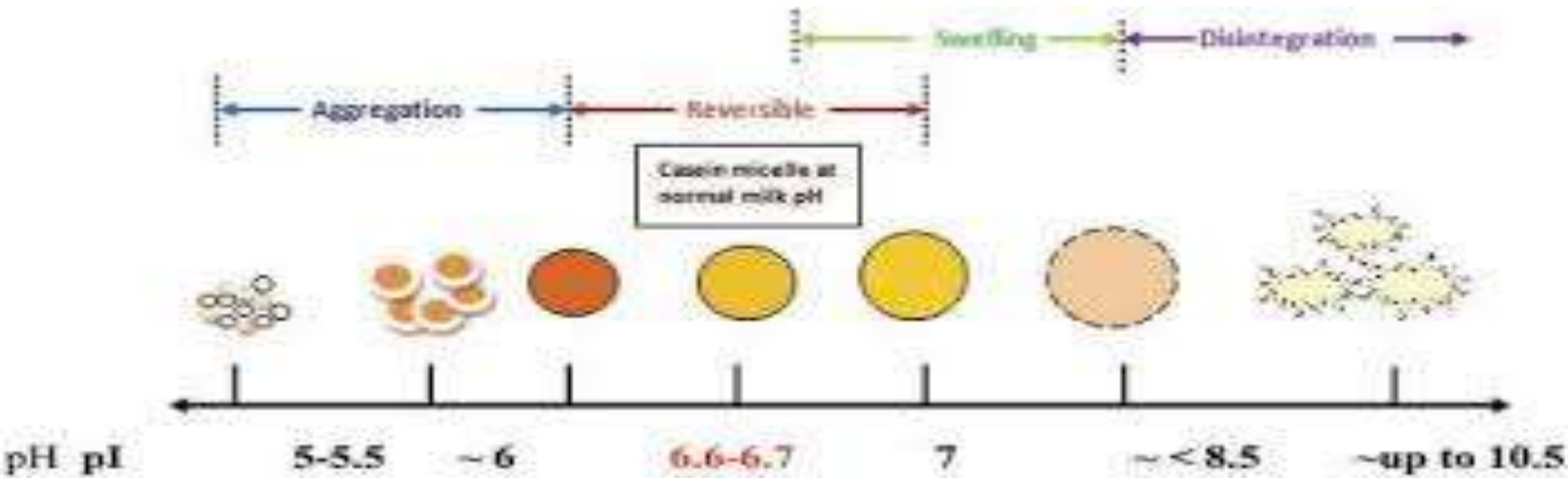
- Reaction of acid with caseinate complex is not instantaneous and pH will tend to rise slowly with time. Ample time to be allowed for achieving equilibrium conditions.
- When casein is precipitated from skim milk by direct addition of acid, temperature, pH of precipitation and mechanical handling of curd during its formation is important in determining subsequent properties of curd.
- Casein precipitated by acid is hydrochloric acid casein, lactic acid casein etc. but may simply be called acid casein.
- Acid precipitation processes (HCl casein, sulphuric acid casein or lactic casein) is used to produce edible quality casein.



a. Temperature and stirring during precipitation

- Kind of curd formed is quite sensitive to heat.
- Curd precipitated at $<35^{\circ}\text{C}$ is very soft and fine, and slow to settle and difficult to wash without loss.
- Precipitation between $35\text{-}38^{\circ}\text{C}$, curd is coarse provided stirring is not too fast.
- Stirring is necessary to distribute acid uniformly, but rapid stirring at $<38^{\circ}\text{C}$ produces curd so fine that it settles very slowly during drainage and washing and lost to some extent in washings.
- More rapid equilibrium, more complete precipitation and better yields.
- Curd can be made firm in either of two ways; by heating to a temperature above 38°C or lowering pH to 4.1.

- Curd precipitated at about 43°C has a texture resembling chewing gum, being stringy, lumpy and coarse, containing practically no fine particles, and separating cleanly from whey.
- High-grade casein, low in ash and readily soluble, is made by grain-curd process, provided pH value and temperature are closely controlled.
- Best product is made by use of hydrochloric acid.
- Temperature of precipitation of skim milk should be held close to 37°C for hydrochloric acid curd.



Drainage of whey

- After complete precipitation, curd has settled, whey should be removed from contact with the curd as soon as possible.
- Longer the curd stands in contact with whey, more difficult is to wash out acids, salts, whey protein and lactose, as the freshly broken curd tends to anneal itself, thereby, enclosing these constituents within protein film.



Washing

- **Quality casein is achieved through efficient washing.**
- **Improperly and insufficiently washed casein has high acidity, less soluble, has lower adhesive strength, develops yellowish colour on drying compared to properly washed casein.**
- **Significant amounts of lactose, minerals and acids are trapped within curd, which prevents their ready removal during curd washing.**
- **Calcium to be kept as low as possible in acid casein to maintain high solubility and low viscosity of casein.**
- **Sufficient holding time required during each washing stage to permit diffusion of these whey components from curd into wash water.**
- **Diffusion rate depends on size and permeability of curd particles, amount and rate of movement of wash water.**

- **Three separate washes of casein curd are required with contact times of 15-20 min each.**
- **When whey is removed from curd, wash water should be added equal in quantity to whey that has drained off.**
- **Curd should be well stirred in wash water by mechanical agitators, but breaking curd into fine particles is avoided. Firm and friable curd particles are required.**
- **Efficiency of washing can be achieved by removal whey at whey off stage.**
- **Whey contamination in wash water can cause sharp decrease in washing efficiency.**
- **Design and operation of casein washing system is minimization of fine casein particles in wash water.**

Processing conditions must be chosen to give firm casein curd particles at precipitation and to avoid shattering during washing

a. pH of wash water

- **pH of wash water should be about 4.6 for first two washings to avoid formation of gelatinous layer over curd particles in excessively acid water and softening and re-dispersion of curd in alkaline waters.**
- **Gelatinous layer if formed over curd particles inhibits drainage of salts and lactose from particles.**
- **Adjustment of same pH of wash water as that of casein facilitates in maintaining equilibrium.**
- **For pH adjustment, H_2SO_4 is preferred as casein is much less soluble in this acid than in hydrochloric acid.**
- **Third wash should be given with neutral water.**



b. Temperature of wash water

- **Casein curd has usual property of acting somewhat like sponge in water, contracting to expel water when heat is applied (syneresis) and relaxing when water temperature is lowered.**
- **Application of heat makes curd becomes hard and rubbery, while cold water softens it and causes curd to be quite fragile and readily broken.**
- **Temperature of first wash should be about the same as the precipitation temperature to give good curd shrinkage.**
- **Temperature of last wash water to 32-40°C for better expulsion of water during subsequent pressing.**

Pressing

- Pressing the curd reduce its moisture content thus, minimizing energy required for removal of remaining water by drying.
- If pressing has not been adequate, subsequent grinding will give lumps of curd that will dry on the outside to give hard, impervious surface that prevents escape of moisture from inside, condition known as **case hardening**.
- Pressing of curd should not be for less than 12-15 h with 34 kg/cm² pressure.
- Precipitation of curd at pH of 4.1-4.3, and curd well-washed in waters, of proper pH and at temperatures of 41°C would give a firm, friable curd which would drain well and press well.
- Final moisture content is usually 55-60%.


Milling and drying

- **Pressed curd is liable to deterioration by action of molds and bacteria and therefore, should be shredded and dried.**
- **Pressed curd is milled to produce particles of uniform size and surface for drying. Otherwise, uneven drying occurs.**
- **Large particles or lumps may dry on the outside forming a hard, impervious outer surface that prevents diffusion of remaining moisture from interior of particle.**
- **For internationally recognized compositional standards for edible grade product, casein curd is dried to <12% moisture in any drier.**
- **Dried casein is relatively hot as it emerges from drier and the moisture content of individual particles varies. So, tempering and blending dried product done to achieve cooled final product of uniform moisture content.**

- **Proper control of temperature and humidity of air coming in contact with the curd are essentials for efficient drying of casein.**
- **52-57°C for air entering a tunnel drier is suitable for any type of curd.**
- **Higher temperatures can lead to discolouration and defects in sensory attributes of dried casein and impairing its solubility.**
- **Temperature in drier does not rise above 57°C towards end of drying when comparatively small amounts of water are being evaporated.**
- **Drying should not be interrupted, but should continue until percentage of moisture is approx. 8%.**
- **Properly dried casein has same fine, granular characteristics as the properly ground curd from which it is made.**

Tempering, grinding, sieving and bagging

- Tempering (holding casein for period (24 h) to allow efficient cooling, hardening of casein and evenness of moisture throughout the batch).
- Casein shows variation in moisture content during day's run as it comes from drier.
- Agitation is necessary for efficient tempering.
- Efficient tempering consists of re-circulating the dried casein by pneumatic conveyance. **Advantage:** Air used for transport of casein assists in cooling curd. Cool, tempered casein is ground. Casein must be cooled before grinding because warm casein is plastic and causes "burn on" of rollers.
- Grinding and sieving operation leads to produce highest proportion of product in size range desired by buyer.



**Yield of edible acid casein is about 3
kg/100 kg skim milk**

Industrial Uses of Caseins



CHEESE MAKING

Coagulation of Casein Present in Milk
Results in Formation of Cheese.



PROTEIN SUPPLEMENTS

Casein is used to make protein supplement as it is considered very good and efficient supplier of nutrients.

DENTAL USES

Casein is used in making products for tooth remineralization.



MAKING PAINTS

Casein paints are water soluble and dry up fast. They have been used since ancient Egyptian times.



FIBER AND PLASTICS

Fibers and plastic are also made from casein or extruded casein.



GLUE MAKING

Casein based glues are used for bottle labelling and lamination of fireproof doors.



1. Casein is unique, used in **foods and non-food industrial/technical applications.**
2. Food and pharmaceutical grade casein is an excellent protein nutritionally and functionally.
3. **Due to their high amount of polar groups**, caseinate shows good adhesion to wood, glass or paper and this hydrophilicity makes caseinate films excellent barriers to non-polar substances (oxygen, carbon dioxide and aromas).
4. Caseinate -based polymers used in protective coating and foams, paper coating, adhesives or injection moulding disposables.
5. Excess fat present in casein may make casein unsuitable such as in paper coating, may result in faulty imprints, in plastics it would prevent binding of individual components and in glues it would decrease their adhesive strength.

Application of Casein in Glues



- Although animal glues had been commercially important for wood gluing long before casein was used, it was difficult to make them water-resistant and poor durability than that of casein.

Casein glues

Prepared glues

- Sold in form of dry powders which contained all necessary ingredients except water. Proportion of powder to water is usually about 1:2 by weight and large batches could be prepared with a mechanical mixer in <30 min. Once mixed, the glues generally had to be used within a working day

Wet-mix glues

- Prepared by mixing together ground casein, water and additional chemicals according to the formula

Principle technical applications of casein

Product	Property	Applications	Remarks/importance
Coating	Film forming ability Adhesion Technical properties	Paints Ink Paper Packaging Leather finishing Textile coating	Still used in some paints Still used Still used To be developed Historical Historical
Adhesive	Good processability Bond strength Water resistance obtained by cross linking	Water based glue	Historical Still used in some few applications
Plastic	Strength Good mechanical properties Water resistance obtained by cross linking	Rigid plastic Disposable Fibre Coating, Film/foil in packaging application	Historical Historical Historical To be developed Laboratory scale
Surfactant	Surface tension Stability of interface	Emulsifier, detergent	Enhancement by chemical modification

- ❖ Besides casein and water, an alkali must be used to dissolve the casein. eg., sodium hydroxide
- ❖ Lime may be added if the glue is to be water resistant. Lime promotes cross-linking of casein and will cause casein glue to form an irreversible jelly which is insoluble in water.
- ❖ Various additives change the properties of casein glues, e.g., sodium silicate prolongs working life of glue and copper chloride increases water resistance of glue after it has dried.
- ❖ Preservation of solutions of casein glue against putrefaction and mold growth may be accomplished by using chlorophenol derivatives and viscosity of solutions of casein glues may be reduced by addition of viscosity-modifying agent (urea or ammonium thiocyanate).

- ❖ Casein glue is used for gluing timber in internal woodwork such as laminated beams and arches and in interior doors, plywood, wood particle board.
- ❖ Casein adhesives may also be used for bonding paper, in packaging, in foil laminating, in holding seam of cigarette together, in seaming of paper bags and in securing abrasive strip on the covers of match boxes.



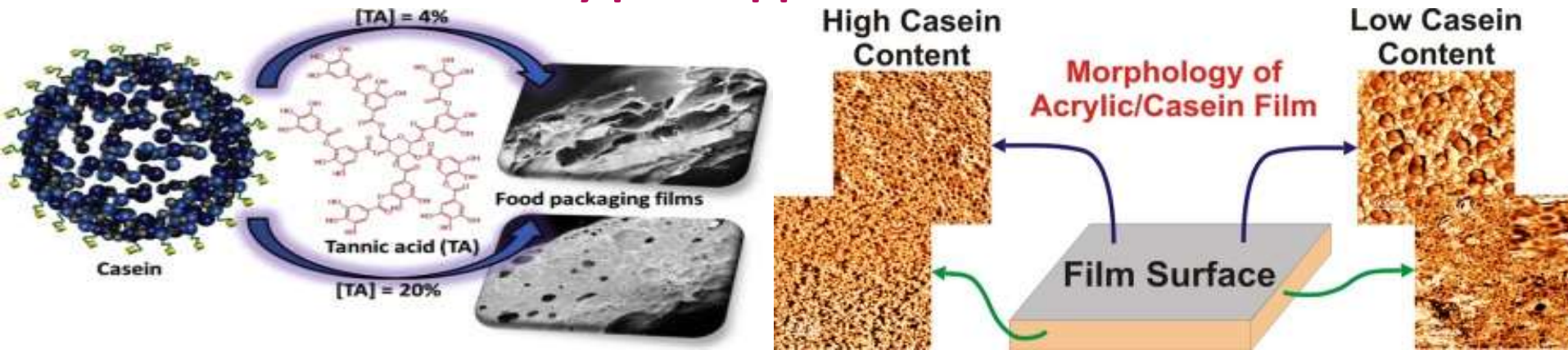
Casein as an Adhesive in Coating Paper and Cardboard

- ❑ Coating is prepared by mixing mineral material with a solution of an adhesive and applying this mixture in a thin, even layer to surface of paper sheet.
- ❑ Function of adhesive is to bind coating material so firmly that it will not be removed or 'picked' off during printing.
- ❑ Coating material which covers individual fibres on paper surface, forms a surface which is receptive to printing ink.
- ❑ After polishing, surface of coated paper is smooth, even and continuous which is needed for high quality reproduction of illustrations.
- ❑ Casein is preferred binder for cast-coating and in enamel grades of coating. Used in coating stock and bleached kraft board for food cartons.



Casein in Sizing

- ❖ Casein acts as binder for coating material, generally a mixture of mineral materials, which is applied as thin layer on surface of material.
- ❖ Casein glue has been used as sizing material for sealing of absorbent surfaces.
- ❖ Film-forming ability of casein is retained even when deposited from very dilute solution. Casein sizings is used on shoe heels, varnishes, paper making, leather finishing and textiles.
- ❖ Casein has been applied to wool to reduce its felting properties and nylon in order to ensure successful wearing or knitting.
- ❖ Casein film can be water resistant by inclusion of 'hardeners', either in solution or by post-application to the film.



Paper Industry

- ❖ **Hydrophobic/hydrophilic balance of casein increases its affinity for pigments, ink-binding properties and its adhesion to various substrates.**
- ❖ **Casein is used as size for high quality glazed papers.**
- ❖ **Water resistance can be achieved by exposure to formaldehyde vapours or by dipping in concentrated solutions of formaldehyde.**
- ❖ **Formaldehyde are cross linking agents which bind free amino groups to protein to give three dimensional network. eg., wallpaper becomes water washable by adding coating of casein solution brushed over with a solution of formaldehyde.**
- ❖ **With high solid contents (china clay, chalk) coating solutions become too viscous, so in some applications, flow modifiers are added to enhance the casting process.**

**Casein is
of high
cost**



- ❖ **Viscosity can be lowered by reducing mol wt of caseins and by denaturing protein. Achieved by addition of urea, by alkaline or enzymatic hydrolysis, or by disulphide bond reducing agents (mercaptoacetic acid or 2 –mercaptoethanol).**
- ❖ **Pigments can be directly mixed with the formula to obtain coloured size and coatings.**
- ❖ **High quality paper finishing and enamel grades of paper.**

Casein Fibre

An Innovative Milk Fibre

Textile Industry

- ❖ For producing casein fibre, acid casein is dissolved in NaOH (200 g/litre), and solution is then forced through spinneret into a coagulating bath.
- ❖ Bath usually contains acid, inorganic salts and often heavy metal salts.
- ❖ Fibres formed resemble wool, except they have lower tensile strength and do not 'felt' (shrink on washing) like wool.
- ❖ Dissolved salt produces large osmotic pressure and causes considerable shrinkage in diameter of freshly extruded filaments. Also reduces tendency of filaments to stick together.
- ❖ Aluminium sulphate is used in coagulating baths and also employed with formaldehyde for stretching and hardening fibres. Hardening of fibres (acetylation) is important as strength of wet casein fibres is less than half that of dry fibres.



**Milk Fiber Extracted
from Casein**



Making Tows



Dyed Milk Tows



Milk Yarn



The Yarn Is Used in Art

Principal proprietary casein fibre (1936-1945)

Aralac	National Dairy Products Corp., USA
Casolana	Co-op Condensfabriek Friesland, Netherlands
Fibrolane	Courtaulds Ltd., UK
Lanital and Merinova	Snia Viscosa, Italy



- ❖ Casein fibres were used in combination with wool and other fibres (cotton, viscose, rayon) for woolen spun cloth, filling materials (artificial horsehair), carpets and rugs.
- ❖ Bristles also produced from casein fibres for use in brushes.
- ❖ Caseins also combined with acrylates become a protective coating against greying of cotton.
- ❖ Chemically-modified caseins, either grafted with acrylate esters or crosslinked, are used as anti-static finishing of natural (wool, cotton and silk) and synthetic (polyester) textile fibres.
- ❖ Co-polymer fibres containing casein is prepared in Japan as a substitute for silk.

Leather Industry

- Coating leather with certain preparations and then subjecting it to mechanical operations (glazing, plating, brushing and ironing).
- After finishing, leather is said to have been seasoned.
- Polyol plasticised casein is used in finishing operations combined with additional components (acrylates, phenol derivatives, pigments for coloured products or binders (gelatine/sulfonated castor oil)).
- For application to leather, casein is first dissolved in alkalis (ammonia, borax, sodium hydroxide/trisodium phosphate) or acids.
- Acid solution of casein (conc. 1-6% by weight) produces clear, bright finish for naturally-finished vegetable tanned leather (**russet leather**).





Film-forming
properties, adhesive
strength and
viscosity-enhancing
characteristics

- ❖ Casein is hard, but tends to be brittle, so oils and glycerol may be added to casein solution to increase its plasticity and reduce brittleness of film.
- ❖ Casein product treated with chlorocarbonate plasticizer can overcome natural brittleness of casein.
- ❖ Casein may also be incorporated with other binders (shellac, carnauba wax, blood albumin, gelatin and sulphonated castor oil).

Find the best casein solution for your leather.....

Rennet Casein



- Used exclusively for making casein plastics.
- High mineral content of rennet casein results to good adhesion and plastic characteristics.
- Casein plastic were first produced after First World War (10,000 tonnes of casein plastic is made throughout world).
- Dyed easily, giving colourful and lustrous products.

Good film forming and coating abilities

- Low frequency of secondary structures (α -helix and β -sheets).
- Caseins are random coil polypeptides with high degree of molecular flexibility
- Able to form typical intermolecular interactions (hydrogen, electrostatic and hydrophobic bonds).

Good emulsifying and stabilizing properties

- Strong amphipathic nature of caseins, arising from balance of polar and non-polar amino acids residues, causes them to concentrate at interfaces to form a protein film.

Rennet Casein Plastic

- Rennet casein plastic is superior to that of acid casein.
- First available in France and Germany under trade name “Galalith[®]” in 20th century.
- Casein plastics have been patented under trade names of Erinoid[®] (UK), Aladdinite[®] (USA), Casolith[®] (Netherlands), Lactoloid[®] (Japan) and Lactolithe[®] (France).
- In casein plastic, casein (if ungrounded) is milled, sieved through a screen with apertures (600 μm) and mixed thoroughly with water to final moisture content between 20-35%. At this stage, filler (titanium dioxide/zinc oxide) may be added to produce either white/opaque plastic, and dyes may also be included to produce coloured plastic. Wet casein is then stored for hours/overnight to allow water and casein to come to equilibrium and ensure uniform moisture content throughout whole mixture.
- Extrusion mixture is then placed in hopper feeding the extruder, which consists of screw rotating in water-cooled barrel.

Bio-plastic Revisited



- **Casein mixture is delivered by screw into heated nozzle section, where it undergoes several compression and expansion stages and consequently form casein plastic.**
- **Extrusion of plastic mass generally occurs at 60 -100°C to produce a smooth rod or strip sheet from nozzle section.**
- **Extruders can be equipped with up to three screws, which may feed casein with different dyes into single nozzle section.**
- **By manipulation of feed rates of casein in each barrel and alteration of design of mixing head, various streams of casein plastic merge and produce beautiful designs.**



- **Warm plastic, which emerges from nozzle of extruder is initially soft and pliable.**
- **This is immediately immersed in cold water, which has effect of hardening plastic and preventing/reducing development of internal stresses.**
- **Rods of casein plastic are subjected to 'dowelling' after they have cooled.**
- **This process trims surface irregularities to produce smooth rods of uniform diameter. These are sliced into discs (or 'button blanks') which are subsequently placed into dilute solution of formaldehyde for several weeks in order to 'cure' or harden plastic.**
- **Cured blanks are later dried, machined into buttons and finally polished by mechanical tumbling in presence of wood chips and oil seeds.**

- **If sheet plastic from casein is required, rods of casein plastic are placed side by side in heated hydraulic press and then subjected to high pressure.**
- **Casein plastic sheet so produced must be cured in formaldehyde for periods varying from 1 week-6 months, depending on thickness of plastic.**
- **Once cured, plastic sheets may be dried carefully to avoid rupturing material within it during expulsion of excess moisture and formaldehyde.**
- **Sheets of casein plastic tend to warp during this process and must be straightened in low pressure hydraulic presses.**
- **Even when hardened, casein plastic can absorb moisture and its moisture content can vary according to changes in humidity (limitation).**

Articles fashioned from casein plastic

Knife handles
(imitation
ivory)

Combs

Imitation
tortoise shell

Pens

Shoehorns

Present range of casein plastic articles (buttons, buckles, novelties and knitting needles) is somewhat more limited

Casein in Paints

- In paint technology, synthetic resin emulsions were produced in which ratio of casein to drying oil was much lower than oil-phase reinforced casein paints.
- After World War II, styrene-butadiene latex paints were developed in which casein was used as thickener and stabilizer (1-2% by wt) of the finished paint.
- **Casein is used in paints for its ability to disperse both white and coloured pigments and its power to thicken the binder.**
- Used as protective colloid, as film former and improve flow and leveling properties of paint.
- Paints marketed in both powder and paste form.



Casein in Rubber Products

- Casein is used as reinforcing agent and stabilizer for rubber used in motor vehicle tyres.
- Casein hardened by formaldehyde was used to replace part of carbon black used in vulcanizing of rubber.
- **Properties: resistance to breaking, extensibility, resistance to tearing, hardness and abrasion** of rubber which contained, for instance, 18% carbon black and 10% casein were either similar to or better than rubber containing 28% carbon black and no casein.
- Dunlop Rubber Company Ltd. used casein with paraformaldehyde as a protective colloid to improve stability of dispersion of a resin-latex composition.

Casein-Based Packaging Films and Biomaterials

- **Transparency, biodegradability and good technical properties (barrier properties for polar gas such as O₂ and CO₂) make casein films innovative materials for packaging.**
- **Casein-based materials have two major drawbacks in common with other protein-based biomaterials: limited mechanical properties and water sensitivity.**
- **To overcome weakness and brittleness, plasticizers are added to enhance work ability, elasticity and flexibility.**
- **Plasticizers reduce intermolecular hydrogen bonding while increasing intermolecular spacing.**
- **By decreasing intermolecular forces, plasticizers cause an increase in material flexibility but also a decrease in barrier properties due to increasing free volume.**

- **For casein-based materials, common plasticizers are polyols, sugars or starches owing to their miscibility with protein and their ability to enhance elasticity and flexibility.**
- **Incorporation of polyol -type plasticizers (glycerol and sorbitol) in protein -based films causes decrease in tensile strength and increase in ultimate elongation.**
- **Difference between protein (casein or whey protein) based films and synthetic films (LDPE, HDPE and PVC wrap film) concerns elongation at break.**
- **Maximum elongation is rather low in plasticized protein based samples (<85%) compared with synthetic films (from 150% for plasticized PVC to 500% for LDPE) which limit application domains for protein based films.**
- **Milk protein-based films exhibit better mechanical properties.**
- **Another drawback of caseinate films deals with their water sensitivity and water vapour permeability.**

- **Mixing protein with oils, waxes or acetylated monoglycerides is easy route to drastically reduce water sensitivity.**
- **Casein based films and biomaterials obtained from caseinates is used in packaging in edible films, coatings for fruits and vegetables or in mulching films.**



Technical Applications of Casein (Non-food)

**Cleaners and dish
washing liquids**

**Hair setting products
and cosmetics (cold
wave lotions, hair
sprays and hand
cream)**

**Casein hydrolysates is
active substance for
skin hydration**

Presents good metal and ion binding properties, so suitable for absorbing and recovering chromate in wastes from manufacturing processes (electroplating and water purification)

Building and Civil Engineering

- Preparation of bitumen emulsions
- Light weight concrete
- Gypsum wallboards
- Preservation and restoration of old stone buildings
- Foaming agent for de-icing equipment

Insecticide spray (as a spreader)

Fungicides (as an adhesive)

Fertilizer and in coated seeds (as an adhesive)



Agriculture

PRINTING

Everything you need to know

