The Complete Book on Gums and Stabilizers for Food Industry
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Gums are plant flours (like starch or arrowroot) that make foods & other products thick. Gums are used in foods for many reasons besides being used as a thickener. Gums are important ingredient in producing food emulsifier, food additive, food thickener & other gum products. The main reason for adding a gum or hydrocolloid to a food product is to improve its overall quality. India is the largest producer of gums specially guar gum products. Similarly stabilizers are an indispensable substance in food items when added to the food items, they smoothen uniform nature and hold the flavouring compounds in dispersion. Gum technology stabilizers are carefully controlled blends of various food ingredients. Most processed foods need some sort of stabilization at some point during production, transportation, storage and serving. The science and technology of hydrocolloids used in food and related systems has seen many new developments and advances over recent years. The breadth and depth of knowledge of gums and stabilizers has increased tremendously over the last two decades, with researchers in industry and academia collaborating to accelerate the growth. Gums as food constituents or as food additives can influence processing conditions in the following ways; retention of water, reduction of evaporation rates, alteration of freezing rates, modification of ice crystal formation and participation in chemical reactions. Some of the fundamentals of the book are functions of gum, typical food applications, gums in food suspensions, rheology and characters of gums, natural product exudates, flavor fixation, ice cream, ices and sherbets, gelation of low methoxyl pectin, seaweed extracts, microbial gums, transformation of collagen to gelatin, cellulose gums, dairy food applications, bakery product applications, analysis of hydrocolloids, gums in food products, general isolation of gums from foods, identification of gums in specific foods, group analysis and identification schemes, group identification methods, qualitative group analysis etc.

This book contains rheology of gums, plant sheet gums, microbial gums, cellulose gums and synthetic hydrocolloids different stabilizers used in food industry. The book will be very resourceful to all its readers, new entrepreneurs, scientist, food technologist, food industries etc.

Content:
Limitations of Spray-Dried Flavors
Slab Fixation
Microencapsulation (Coacervation)
Alginate Film Encapsulation
Protective Films
Description
Applications
Synergistic Effect
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Sample Chapter:
Functions of Gum

An army marches on its stomach is an old expression, widely attributed to Napoleon. It is unfortunate, but true, that many advances in technology have been greatly accelerated and expedited by the contingencies of war. The need for preserving foods for long periods of time during the Napoleonic campaigns led directly to the development of the canning process by Nicholas Appert in 1810. Considering the state of science and general lack of information at that time, this ranked as a considerable achievement.

A century later with the proliferation of little wars that eventually culminated in the First and Second World Wars, the logistics of supplying food for armies scattered over the world, led to many other advances in food science. Marked progress was made in the preservation of foods by quick freezing, irradiation, chemical additives, dehydration, and other methods.

Developments in dehydration technology were spurred by the need for transporting foods long distances by ship or plane. It is a rare soldier that does not recall with nostalgia perhaps, but not regret the powdered eggs and dehydrated potatoes that were part of the daily rations of the American soldier overseas during World War II. It is encouraging to report that these products were vastly improved during the years after the war, and today they can be considered to be quality products of the convenience food type.

Convenience Foods

The concept of convenience foods with the built-in maid ushered in a period of great innovation and technological advances in the food industry. This era, which also started during World War II, was primarily a result of the great changes, which took place in the American home at that time. Many women, employed in war industries, had limited time for the everyday kitchen tasks, and were ready for any time saving devices and foods that might be offered. After the war this feeling of emancipation from the kitchen remained and became a way of life, which exists today.

Pioneers in the food industry were quick to perceive this trend and took advantage of this beckoning market by plunging into the development of all types of convenience foods. For a period of time it might be said that the prevailing philosophy was that of the famous gastronome Brillat Savarin when he made the statement, which appears, at the beginning of this chapter.

Instant Coffee

One of the most successful post-war developments is that of instant coffee. Although soluble coffee was known before the war, it was not a widely accepted commodity it varied in quality, had poor stability, did not dissolve too well, and was expensive. In short, it did not enjoy popular consumer acceptance. War time needs, being the mother of inventions, led to technological improvements in the development of good quality soluble coffees to be included in military rations. These products had good performance, stability, and taste characteristics as a result of drying the coffee with fillers such as sugar or dextrose.

A major breakthrough was achieved subsequently with the development of a spray drying process for a 100% coffee product that had good flavor, performance, and stability. This 100% flavor bud product met with great success and paved the way for many similar products, resulting in continuous market growth over the past two decades. Today, instant coffee is so well entrenched in the American market, that it now outsells regular ground coffee. It has also been predicted that the current generation of teen agers who grew up on soluble coffee will become an adult market with a preference for soluble rather than regular coffee. This, of course, is conjecture and only time will tell.

Frozen Foods

The concept of quick freezing foods as a preferred method of preservation was originally developed by Clarence Birdseye in 1925. Applications of his methods led to a host of food products that could be
processed in season and preserved at the height of their flavor and textural development until ready to use. No longer does the housewife have to screen the sand from her spinach, or remove the discolored and damaged leaves, or even core the vegetable. It is not even necessary to cook it, watching carefully until the vegetable is soft and tender, but not too soft and crumbly. Now all she has to do is remove a frozen package of cleaned, cooked spinach from her freezer, put it in a pot of boiling water, and heat it until thawed.

The convenience and high quality of frozen vegetables, fruits, meats, etc., met with great consumer acceptance in the period after World War II and resulted in many new products, the outstanding example of which is frozen orange juice concentrate.

Freeze Dried Foods
The subsequent processing combination of quick freezing followed by low temperature vacuum dehydration was the logical outcome of a series of technological advances. Many new freeze dried food products have been developed, the most recent of which have been dry breakfast cereal combinations with freeze dried strawberries, bananas, and other fruits. Upon the addition of milk, the fruits hydrate to form truly fresh high quality fruits.

Gum Constituents
At this point, the reader might rightly ask, What does all this have to do with gums? The answer is, Everything. Gum constituents are present in almost every natural food and are largely responsible for the structure and textural properties of the plant. In prepared foods, gums are used as food additives to impart desirable textural and functional properties to the finished products. It is rare that a convenience food does not have one or more gums listed among the ingredients. Gums are so necessary in many foods covered that they are included in these standards and are not required to be listed on the label.

The use of gums to obtain superior quality in many products has become so accepted in certain foods that it is difficult to find a sample without it, even if one were to want it. This is best illustrated by ice cream. In the good old times, home made ice cream like mother used to make suffered from poor textural qualities such as presence of ice crystals, sandiness, and lack of smooth melt down. Today, commercially prepared ice creams contain various hydrocolloids as emulsifiers and stabilizers to eliminate such defects of quality. It is almost impossible to find a brand of ice cream that does not contain gums.

Effect on Processing
All food processes inherently involve the modification or denaturation of the characteristic food texture. The properties of the gum constituents present in many food materials have an important bearing on processing conditions and the resultant properties of the final food product.

In almost all food processing there is a change in the moisture content or the physical shape of water. The water is either completely or partially removed, as in dehydrated foods or it is physically changed to gas in cooking and blanching operations or it is converted to the solid form of ice in freezing operations. The change in the water content or its physical form is largely responsible for changes in texture of the processed food product, and is one of the most important factors to be considered in manufacturing high quality processed foods. Since both residual gum constituents and hydrocolloid additives greatly influence the type of physical transformation and rate of migration of the water component, these substances are important factors in food processing.

Pertinent Processing Parameters
Gums as food constituents or as food additives can influence processing conditions in the following ways: (1) retention of water (2) reduction of evaporation rates (3) alteration of freezing rates (4) modification of ice crystal formation (5) participation in chemical reactions. These functional effects are not isolated phenomena, which can be followed easily they are only evident in the textural qualities or rheological
behaviour of the final product. While the functional effects of a gum are its most important characteristics in determining its use in foods, these effects must be considered in context with many other factors, including price, availability, ease of handling, and legal restrictions related to their use.

Function in Food Applications

Gums are used in a wide range of specific food applications, ranging from adhesives to whipping agents. Typical specific functions and food applications are shown in Table 1, but the general function of gums can be limited to their two major properties gelling and thickening.

All gums, or hydrocolloids, by definition and usage have a thickening, or viscosity producing, effect when dispersed in a water medium. This property is the basis for their use as bodying, stabilizing, and emulsifying agents in many foods. A comparatively few of the important gums i.e., agar, algin, carrageenan, furcellaran, gelatin, pectin, and starch also have the ability to form gels under specific conditions of use. Gels, when referring to foods, are products that will retain their shape and will not flow unless pressure is applied. Probably the most common gelled food product is gelatin dessert gel, which has enjoyed enormous popularity in this country for many years. Other well known food gels are starch based milk puddings, gelatin aspics, and pectin gelled cranberry sauce. In Europe, milk puddings of the blanc mange type are very popular and are usually made with seaweed extracts of the carrageenan or alginate type.

There is an interplay between the viscosity and gelling characteristics of any specific gum and these factors must be taken into consideration when these gums are used for example, depending on the type of gelatin and on its concentration, gelatin can be used as a thickening agent rather than a gelling medium. In a related way, temperature also plays an effect as the temperature increases, the viscosity decreases, thus decreasing the effective thickening properties of the gum. This temperature increase is in most cases the same as an effective reduction in gum concentration.

Viscosity

Definition and Meaning

Viscosity is the resistance to flow of a liquid system. In colloidal suspensions it is increased by the thickening of the liquid phase as a result of liquid absorption and consequent swelling of the dispersed colloid. This thickening, or viscosity producing, effect of gums in food products is, in turn, responsible for other functional effects such as the suspension of solid particles, the emulsification of oil and water phases, the stabilization of liquid solid gas phases, the dispersion of solid and liquid phases, and related phenomena.

When hydrocolloids are used as viscosity producing agents for the purpose of suspending, emulsifying, or stabilizing a food system, shelf stability is extremely important and the selection of the proper hydrocolloid is critical. Degradation of the hydrocolloid and the resulting reduction in the viscosity of polymer solutions may impair the flow properties and appearance of the product sufficiently to reduce its consumer acceptability.

Since most gums are long chain polymers, they are subject to the type of molecular breakdown caused by cleavage of molecular bonds, resulting in lower viscosities. Determination of the exact causes of degradation or loss of viscosity is often difficult. Frequently, polymers are degraded by the use of high shearing equipment used to put them into solution, or by the high temperatures used in processing. In general, the low viscosity natural gums are more stable than the high viscosity types. Studies on the comparative stabilities of gums are more valid if comparisons are made between solutions of equal viscosity rather than of equal concentrations, which is so often the case.

Factors Effecting Hydrophilic Viscosities

The viscosities of hydrocolloid systems are effected by many factors and listed ten factors that cause
variations in the viscosities of hydrophilic systems: (1) concentration, (2) temperature, (3) degree of
dispersion, (4) solvation, (5) electrical charge, (6) previous thermal treatment, (7) previous mechanical
treatment, (8) presence or absence of other lyophilic colloids, (9) age of the lyophilic sol, (10) presence of
both electrolytes and nonelectrolytes. The importance of viscosity to the textural quality and consistency of
most foods is so great that above factors to be the ten commandments of food preparation. She illustrated
the importance of some of these in the preparation of a simple custard dessert: concentration of egg or
protein micelles temperature of cooking degree of dispersion of the micelles degree of hydration which is
influenced by the type of reaction and presence of salts beating of the egg use of milk or water aging of the
custard as well as the age of the eggs and milk presence of electrolytes in egg and milk and addition of salt
presence of nonelectrolyte, sugar. The viscosity of any food system is subject to the influence of many
complex parameters, and the hydrocolloids present or added are likewise subject to the same forces
encountered in the preparation of quality food products.

Typical Food Applications
The use of gums solely for thickening purposes is common in such products as pie fillings and beverage
dry mixes. In pie fillings, especially fruit type fillings, gums are used to thicken the fruit juice to prevent the
flow of the filling from the pie shell. In beverage mixes that are reconstituted with water, gums are used as
thickening agents to give the final product the necessary body. This is especially true for the sugar free,
dietetic products.

Soups and soup mixes are thickened with starches and gums to improve their body and consistency.
Likewise, sauces and sauce mixes contain gums to impart desirable texture and flow characteristics. For
low pH sauces, it is necessary to select thickening agents that are resistant to acid degradation. Gum
tragacanth and propylene glycol alginate are two of the preferred additives, since they are more acid stable
than the other common gums.

Thickening agents are incorporated into many breading mixes, so that they will not run off meats and fish.
Gums have also found a novel use in dog foods where they are added to dry meatlike pieces, which, upon
the addition of water, hydrate and thicken to form a thick gravy like sauce containing meatlike chunks.

Gelation
Hydrocolloid food gels are rigid, two phase systems that show resistance to flow under pressure and are
capable of retaining a firm, distinct structural form. They are liquid solid systems with a continuous network
of solid material forming the gel matrix and enmeshing or holding a continuous or finely dispersed liquid
phase. The solid, backbone phase is usually composed of long chain molecules in the form of a mass of
intertwined fibrils linked by primary or secondary bonds at widely separated sites along the molecule.
Although gels can be considered primarily to be solids, they exhibit properties of both solids and liquids.
They resemble solids in their structural rigidity and elastic response when distorting forces are applied, and
they resemble liquids in their vapor pressure, compressibility, and electrical conductivity.

Mechanism of Gel Formation
The beginning of gelation is shown initially by the gradual decrease in Brownian movement of the colloidal
particles concluded within the gel. This decrease is caused by the exertion of long range forces between
the molecules, which in turn results in the hydration and coherence of the particles. The viscosity then
begins to increase as gelation proceeds and the solvent (liquid) is absorbed by the swelling solute (solid)
and is gradually immobilized. As the process continues a three dimensional network containing enmeshed
portions of the liquid is gradually built up. The various fragments of the gelling polymer continue to react
and finally form one large continuous structure. At this stage the rigidity of the system becomes apparent.
Parts of the large molecular chains in the network can still react with other parts by cross linking to further
increase the rigidity of the whole structure.

**Gelation from Sol State**

Gelation can be induced in both sol or solid state systems. From the sol state, gelation can be achieved by increasing or establishing forces between solute molecules in one or more of the following ways: addition of a nonsolvent evaporation of the solvent present in the system addition of a cross linking agent reducing the solubility of the solute by chemical reaction changing the temperature adjusting the pH.

**Gelation from Solid State**

From the solid state, gels can be formed by allowing the solid phase to remain immersed in the solvent until sufficient liquid is imbibed to form a gel. Thus, a gel can be considered to be in an intermediate state of hydration between a sol and a solid.

**Types of Gel Linkages**

The formation of gels from solutions of long chain polymers can be explained as being due to the cross linking of adjacent molecules to form a continuous network possessing mechanical stability in the final gelled state. Entrapped within this network is a continuous liquid phase consisting of the solvent and solutes, some of which may include non cross linked polymeric materials.

The types of cross linking that may take place depend on the chemical properties of the constituent groupings on the polymers forming the gel matrix and the chemical conditions existing in the system.

**Rheology and Characters of Gums**

The main reason for adding a gum or hydrocolloid to a food product is to improve its overall quality. This improvement may relate to its appearance, convenience, stability, cost, texture, etc., all of which are eventually judged by the consumer. The consumer usually judges the product by simply eating it and seeing how it tastes. At this point he does not care if the added gum is a galactomannan or a sulfated galactan, nor does he worry about whether the vitamin A in the product is naturally derived from sharks liver or synthesized from b ionone. He is concerned with the taste and mouth feel of the product. If it tastes good, he is happy if it tastes bad, he is unhappy, and so eventually is the manufacturer of that specific food item.

Consumer acceptability the objective of every company selling food is directly related to food texture and flavor. At the risk of oversimplifying, it can be assumed that these two factors, texture and flavor, are the two most important properties of a food comestible, although it is conceded that other factors such as appearance, color, packaging, convenience, price, calorie content, etc., are also important and often supersede texture and flavor. But for mass market acceptance, good flavor and texture are essential. With products such as soluble coffee and frozen orange juice concentrates, the flavor characteristics alone have been sufficient to separate the products of good quality from the inferior brands. In the case of ice cream, the textural qualities predominate and serve to distinguish the good from the bad. Poor quality ice creams may have a gritty consistency due to ice crystal formation, while good quality ice creams are uniform and have a homogeneous texture leading to smooth melt down in the mouth. It is obvious that no one would buy a product that had a poor flavor or texture at least not the second time.

Oldfield makes the point that foods that cease to yield flavor before they have been sufficiently chewed for comfortable swallowing tend to produce an aversion towards further chewing together with an involuntary inhibition of the swallowing mechanism. He illustrates this with the impulse to spit out over cooked, tough steak. Another common example is that afforded by chewing gum. Most people will chew gum until the flavor is leached out and will then discard it even though the textural and chewing qualities have not been impaired.
While flavor is somewhat influenced by gums, in that gums play a part in flavor release and flavor retention in foods and are used to stabilize and fix flavor emulsions, the most important effect of gums is on texture. Texture is an abstract concept of a concrete property. All foods have texture if we think of texture as being the structural matrix of the food, but it is the perception of texture when the food is eaten that is important. This was most clearly stated by Szczesniak who defined texture as the composite of the structural elements of the food and the manner in which it registers with physiological senses. The importance of the physiological stimuli during eating is best described by Oldfield. Once biting and chewing start, an immensely complex pattern of stimulation is set up. With the help of the tongue the food is rolled across the gums and the hard and soft palates. The teeth themselves play a part in signalling the textural and rheological properties of the food and these properties are progressively changed by the process of mastication, while a changing pattern of stimuli results. As the food is broken up by the teeth, the increased surface area releases taste and smell stimulus substances in greater quantity. All these stimulus elements contribute to supply the brain with the material out of which it constructs the complex perception, and they also serve, some without entering consciousness, to maintain and modify the activity of the mouth. Eventually the food is swallowed.

Thus the act of eating (i.e., chewing and swallowing) can be visualized as a process of breaking down (or deforming) the food product in the mouth, with the type or character of the breakdown being dependent on the structure or texture of the food. In recent years this important area of investigation has been formalized into a branch of science known as rheology, the science of the deformation and flow of matter.

While it is not the purpose of this chapter to delve deeply into the subject of rheology, a subject, which is still regarded by some as a messy science, it is important to be able to understand the methods and instruments of rheology in order to measure and explain the effects of hydro colloids on food textures. Any tool that gives a meaningful number to a textural parameter, which in turn can be related to consumer acceptability, is useful to the food scientist. The phrase meaningful number must be carefully qualified, because many numbers are not meaningful and bear no relationship to the textural acceptance of the product in question. Thus the viscosity of beverages is not necessarily correlated with the mouthfeel or acceptability of the beverage. Beverages of identical viscosity can be either slimy and mouthcoating or smooth and pleasant. Likewise gel strength measurements on standard instruments such as the Bloom gelometer, will give satisfactory data on the overall strength and rigidity of the gels, but will completely fail to characterize the parameters of elasticity and brittleness which may be more important from the viewpoint of consumer acceptance.

Certain measurements, however, can be objectively correlated with mouthfeel and consumer approval. Recent work established a correlation between the organoleptic characteristics of hydrocolloid solutions and their rheological behavior. Measurements of solution viscosities at various rates of shear showed a relationship between the shape of the curve and degree of sliminess. This was subsequently confirmed in work on gum thickened sucrose solutions.

Studies of various hydrocolloid solutions showed that they could be grouped into three categories slimy, slightly slimy, and nonslimy-depending upon the shape of the curve (Fig. 1). This was a practical way of measuring rheological parameters of gums and using the physical data to select the ones preferred with respect to mouthfeel or texture.

The rheological behaviour of hydrocolloids is of special importance when they are used in artificially sweetened foods where large amounts of sugars are replaced by gums for bodying and textural effects. The organoleptic properties and acceptability of such foods are more critically related to their rheological parameters than sugarbased foods.

Thus, in general, the overall objective in studying the rheology of food products is to measure the various parameters of foods under stress and to define them mathematically so that they can be related to the consumer.
subjective, organoleptic textural properties of the food.

Background

Although the word rheology is only about 40 years old, the science and practice of rheology goes back many centuries. The first known rheologist, Amenemhet, an Egyptian who lived about 1540 B.C., studied the effects of temperature on the viscosity of water and then described his observations in hieroglyphics. This unlauded scientist invented a clock, which consisted of a conical vessel from which water could be made to flow steadily. Time was measured as the height of the water remaining in the funnel. The angle of the cone puzzled modern scientists because it was not corrected to provide a fall in height proportional to time. However, when a replica of the clock was built and operated through the great temperature differences which exist between Egyptian days and nights, the instrument constructed by Amenemhet was found to be correct. Cold water has a greater viscosity, or resistance to flow, than warm water the angle of the cone had thus been calculated and constructed to allow for this difference as the water was cooled by the cold Egyptian night.

In another part of the world, the Indians developed a crude system of rheology in about 100 A.D. which classified different substances into groups according to the sense responses of feel, temperature, sound, taste, and odor.

It wasn't until the sixteenth century, though, that any real progress in rheology was made. At this time, Leonardo da Vinci investigated the flow of water through orifices and channels, a series of experiments, which was followed in the next century by Galileo's studies on the cohesion of ropes. Hooke subsequently reported on the elastic properties of solids and stated that stress is proportional to strain in elastic solids. Newton, in the same era, made the first rotational viscometer in the course of his studies of the rotation of the planets in the solar system. He used a rotating cylinder in a pool of water and observed that resistance to flow is proportional to the rate of shear in liquids. This type of ideal relationship was later termed Newtonian flow in honor of its discoverer.

In the nineteenth century, Poiseuille studied the flow of water through glass capillary tubes and found that the quantity of water flowing through such tubes increased directly with the fourth power of the diameter of the tube and directly with the pressure of the water. In addition, the quantity of water decreased with increased viscosity and with the length of the tube. For his work, Poiseuille was honored by having the basic unit of viscosity, the poise, named after him.

The father of modern rheology is considered to be Eugene C. Bingham who coined the word rheology from the Greek rheos meaning flow. His classic book, Fluidity and Plasticity established a firm basis for this new science. Later, like so many other scientific endeavors, the study of the rheology of polymers was accelerated by the contingencies of war. For example, gasoline thickened by aluminum stearates used in flame throwers during the Second World War showed marked elasticity and peculiar flow properties. Rheological studies were made in an effort to understand and to improve the cohesiveness of the thickened ejected fuels. The flow peculiarities were attributed to normal stresses, which were pressures acting across or normal to the shear planes. After the war, the study of rheology led to the development of many useful products such as plastics, paints, foods, drugs, etc., and proved to be helpful in advancing the technologies of all of these industries.

Definitions

Rheology is the science of the deformation and flow of matter. It includes the study of elastic deformation and other phenomena not necessarily associated with flow. Matter is deformed, or starts to flow, only when it is acted upon by force. The force may be supplied deliberately, accidently, or may be all pervading as in the case of gravity. Rheology is concerned with forces, deformations, and time, and may also include temperature and other secondary parameters.
Food texture is a complex property comprising several interrelated physical parameters, of which viscosity in liquids and elasticity in solids are among the most important. Other related properties are tackiness, smoothness, plasticity, particle size, density, and temperature. Most foods do not have simple invariant rheological properties such as viscosities and elastic moduli, which are independent of stress and strain conditions and which can be defined by a single number. But the behaviour of these materials, even when they are variable, can be expressed according to defined rheological measurements and must be represented by flow curves (rheograms) rather than single numbers.

For a more complete description of the rheological behaviour of fluid foods, Charm believes that the parameter of tensile strength must also be considered along with shear strength and viscosity measurements. This property, although rarely measured, may play an important role in textural qualities and coating behavior of fluid foods. Charm measured the tensile strengths of catsup, tomato paste, and mayonnaise, and found them to be about twice the value of the shear strength. The overall significance of tensile strength has not yet been established, but it may be an important factor in defining the complete rheological picture of specific food products.

The prototype of the perfect, or ideal, (Newtonian) liquid is one that flows at a steady rate at constant pressure and at a rate strictly proportional to each pressure if a series of pressures is applied. Other liquids whose rates of flow are not proportional to the pressure applied are called non-Newtonian liquids. With respect to solids, elasticity and plasticity are two of the more important attributes of their structures. Bingham defined these properties quite clearly. When a shearing stress is applied to a perfectly elastic solid, a certain strain is developed which disappears completely when the stress is removed. The process is reversible and no work is done. Likewise, viscosity can play no part in the movement. This is a classic case of elastic deformation and not of flow.

The prototype of the ideal elastic solid is based on Hooke's Law and must meet the following criteria: (1) the deformation must be proportional to the applied force (2) it must be completely recovered when the force is removed (3) both the original deformation and its recovery must not be delayed by internal viscosities. If a shearing stress is applied to a body that is imperfectly elastic, it will be found that at least a part of the deformation will remain long after the stress is removed. In this situation, work has been done in overcoming some kind of internal friction. Plasticity can therefore be defined as a property of solids by virtue of which they hold their shape permanently under the action of small shearing stresses but are readily deformed, worked, or molded, under somewhat larger stresses.

The line of demarcation between a liquid and a solid is sometimes very thin and often difficult to define, let alone, measure but various situations will be reviewed in the discussions of the different types of flow behavior found in food products.

**Viscosity**

The most common way of characterizing a liquid or fluid material is by measurement of its viscosity, which is actually a measure of fluid friction. The force of friction can be considered as the energy required to move an object that rubs on another, i.e., viscosity is the measure of the internal friction resisting the movement of each layer of fluid as it moves past an adjacent layer of fluid. A highly viscous material is one possessing a great deal of internal friction it will not pour or spread as easily as a material of lesser viscosity.

In Newtonian systems, where the shearing stress is directly proportional to the rate of shear, the viscosity is constant and a single point viscosity measurement is sufficient to characterize the system. It is only necessary to plot the single point measurement and draw a straight line to the origin to indicate the true flow curve.

However most fluid foods are non-Newtonian systems where the viscosities are not constant but are
dependent on the rate of shear. In addition, yield values and the rate of change in resistance to flow with increased shear are also needed in order to define the flow picture of some systems accurately. The rate of change in resistance to flow is a measure of the magnitude of the systems non Newtonian behaviour and can be ascribed to various factors such as: (1) the ease of alignment of long chain molecules in solutions (2) the nature and uniformity of the particle size of the ingredients in dispersions or suspensions (3) the way the particles pack together in the dispersion (4) the amount of dispersion liquid and the extent of voids created when the system is disturbed. It is easily seen, therefore, that single point measurements with any type of viscometer are limited in meaning because they do not describe the flow behaviours at varying rates of shear and thus cannot adequately characterize the physical structure of the liquid. Therefore, depending upon their behaviour under imposed shearing forces, materials are categorized as Newtonian or non Newtonian. Only a few of these systems are present in food products, the more important ones being those where the flow is independent of time. These consist of Newtonian, Bingham plastic, pseudoplastic, and dilatant systems. Two other systems often encountered are thixotropic and rheopectic materials in which the flow is dependent on time.

Newtonian Flow

Newtonian flow can best be described by considering two parallel plates, A and B, of 1 cm\(^2\) area (A), with the intervening 1 cm space being filled with the liquid under consideration (Fig. 2). Viscosity is equal to the force (F) that is required to induce a unit rate of shear. The depth (d) of the substance in between is 1 cm. If a force (F) of 1 dyne is required to move plate A with constant speed of 1 cm per second, then the viscosity of this substance will be 1 poise. The innumerable parallel layers of the substance must move past each other once plate A is moved. If plate A is moved to the right, the layer next to the stationery plate B remains without moving. The layers above it travel, depending upon the distance from plate A, with an increasing speed to the right. Each single layer of the substance, therefore, passes the one below it and remains a little behind the one above it. Because the layers adhere to each other, a force is encountered that opposes this sidewise movement. This tenacity is called viscosity (h), or internal friction, of a system which, per unit area, is the same on each layer. Viscosity, then, is a measurement of the combined effect of adhesion and cohesion. The transmitted force (F) is therefore proportional to the coefficient of the inner friction as follows:

\[ \text{(dv/dr)}, \text{ or } D, \text{ is the rate of shear and is directly proportional to the applied force (F), and flow starts under the slightest pressure. The characteristic flow line of a Newtonian substance goes through the origin of a plot (or rheogram) of } D \text{ versus } F. \]

Newtonian fluids exhibit direct proportionality between shear stress (F) and shear rate (D). At any given temperature, these materials have a viscosity that is independent of the rate of shear. In simple terms, it will take twice as much force to move the liquid twice as fast. As shown in Fig. 3, the relationship between shear force and rate of shear is a straight line and the viscosity, in absolute units, is the inverse slope of the line. The viscosity of Newtonian liquids remains constant as the rate is changed. Newtonian behaviour has been found to be common to all gases and to all liquids or solutions of low molecular weights i.e., non polymeric materials and also to solutions of low concentrations of some high molecular weight polymers. The common denominator of these solutions is that the dissipation of viscous energy in them is due to the collision of fairly small molecular species. Newtonian foods include most simple solutions, such as sugar syrups, broths, bouillon soups, soft drinks, and milk. Most foods, however, fall into the non Newtonian categories.

Natural Product Exudates
Origin of Gums

A great many plants exude viscous, gummy liquids, which when exposed to air and allowed to dry, form clear, glassy masses. The shapes of these masses vary from spherical, teardrop balls typical of gum arabic producing Acacia trees to curved, ribbon like strands of tragacanth from Astragalus bushes. The colors of these exudates also vary widely from almost clear white to dark brown, depending on the species, climate, soil, and absorbed impurities.

The basis and reason for the formation and exudation of gums by plants, is still not understood, and many theories have been formulated to explain these phenomena. One theory suggests that gum formation is a protective mechanism resulting from a pathological condition. This hypothesis is supported by evidence concerning the production of gum arabic. Healthy Acacia trees, grown under favorable conditions of soil and climate, produce little or no gum, while trees grown under adverse conditions of high elevation, excessive heat, and scarcity of moisture produce sizeable quantities of gum arabic. And the yield of gum can be further increased by deliberately injuring the tree by stripping away the bark.

Other investigators believe that gum formation is part of the normal physiological metabolism of the plant as in the case of the gums in sugar beets and yeasts. Still others consider gums to be synthesized as a result of an infection of the plant by microorganisms in an effort to seal off the infected section of the plant and prevent further invasion of the tissue. This would probably be similar to the formation of a scab on a human wound. The formation of gum has also been attributed to fungi attacking the plant and releasing enzymes that penetrate the tissues and transform the constituent cellulose materials of the cell wall into gum. This has been suggested to be the mechanism of formation of the gum found in the gummosis disease of various deciduous trees. Yet another theory, particularly with respect to Acacia species, claims the formation of gums to be caused by bacterial action and suggests that specific bacteria are capable of producing different kinds of gum.

The most reasonable explanation however, seems to be the simplest one, namely that the plant produces the gum in order to seal off the injured part, primarily to prevent the loss of moisture and not necessarily to prevent infection. This concept is supported by the fact that gum arabic and gum tragacanth are both produced immediately by healthy trees that have been deliberately injured. But whatever the cause, it is fortuitous that many species of plant produce large quantities of gums that can be utilized in a constructive manner.

Physical Properties

The physical appearance and properties of the natural gums are of utmost importance in determining their commercial value and their end use. These vary considerably with gums of different botanical sources, and there are even substantial differences in gum from the same species when collected from plants growing under different climatic conditions or even collected from the same plant at different seasons of the year. The physical properties may also be affected by the age of the exudate, treatment of the gum after collection, such as washing, drying, sun bleaching, and storage temperatures.

Natural gums are exuded in a variety of shapes and forms, the best known being the teardrop or globular shape of various grades of gum arabic. Other characteristic shapes are flakes or thread like ribbons as with gum tragacanth. Still others resemble stalactites and after collection and fracturing yield irregular rod shaped fragments.

The surface of most gums is perfectly smooth when fresh but may become rough or covered with small cracks or striations upon weathering, resulting in an opaque appearance. These fissures or striations are often restricted to the surface, but may be deep in some gums, causing the tear drops to break up into smaller fragments during handling and shipping.

The color of gums in their natural exudate shape varies from almost water white (colorless) through shades
of yellow, amber, and orange, to dark brown. The best grades of gum arabic are almost colorless with slight traces of yellow. Some gums possess pink, red, or green lines and some black or brownish gums are also found.

Many gums when first secreted appear to be colorless, and it is believed that color is due mainly to the presence of various types of impurities. Color often appears as the gum ages upon the tree and may be due to extraneous substances that are washed onto the gum. Bush or grass fires can cause discoloration by scorching. Tannins from the sap or tissues of the parent tree are frequently the cause of discoloration and are believed to account for some of the very dark gums yielded by certain trees.

The water soluble plant gums are usually odorless and in this respect differ markedly from the oil soluble resinous exudates which have distinctive smells. The gums are usually tasteless and bland, except for some species which have a sweet, carbohydrate taste and some types that have been contaminated. Gums contaminated with tannins usually have a harsh, bitter flavor that is a serious disadvantage in food applications.

Gums vary in hardness, but since this is usually dependent upon the amount of moisture present (12-16%), it cannot be used as a means of classification as with minerals. Density is also variable and depends upon the amount of air entrapped when the gum was formed.

There are many plant gum exudates known all over the world, but only four are of real importance to the food industry. Many of the other gums are known and used in local areas where they are available, but only to a very limited extent. These gums have similar properties and can be used for similar applications where necessary. Some of the more common ones are damson, plum, cherry, peach, prune, lemon, almond, cashew, brea, chagual, mesquite, shiraz, cactus, neem, sapote, cholla, khaya, jeol, and many more too numerous to mention.

**Gum Arabic**

The oldest and best known of all natural gums is gum arabic, also known as gum acacia, Turkey gum, gum Senegal, and by many other descriptive and colorful local names. Gum arabic is the dried, gummy exudation obtained from various species of Acacia trees of the Leguminosae family. About 500 species of Acacia are distributed over tropical and subtropical areas of Africa, India, Australia, Central America and southwest North America, but only a comparatively few are commercially important. The important producing areas are the Republic of the Sudan, French West Africa, and several smaller neighboring African countries.

As mentioned earlier, the trees produce gum arabic only when they are in an unhealthy state from poor nutrition, lack of moisture, or hot weather. The gum is produced in breaks or wounds in the tree bark, and exuded in the form of spherical balls resembling teardrops. These exudates are collected by hand by the local natives and transported to central collecting stations where they are sorted by hand, and exported gum suppliers in all parts of the world. There the gum arabic is sorted again, ground, processed, and graded to meet various specifications.

**Standards**

Minimum standards for good quality gum arabic have been defined in the Indian Pharmacopeia as follows: 4% total ash (maximum), 0.5% acid insoluble ash (maximum), and 1% water insoluble residue (maximum).

In line with recent efforts to define standards for food grade additives, more rigid specifications have been established for arabic, karaya, and tragacanth, and published in the Food Chemicals Codex. Ghatti has not yet been included, probably because of its comparatively minor use in foods.

**Structure**

Gum arabic exists in nature as a neutral or slightly acidic (D glucuronic) salt of a complex polysaccharide containing calcium, magnesium, and potassium ions. It is a heterogeneous material and may be composed
of several slightly different molecular species. The most recent opinion is that the main structural feature of the molecule is a main chain of β galactopyranose units linked through positions 1®3, with side chains of 1,6 linked galactopyranose units terminating in glucuronic acid or 4 0 methylglucuronic acid residues. Additional groups are also attached to the C 3 positions on the galactose side chains. Complete hydrolysis of the molecule yields the four basic sugar constituents D galactose, L arabinose, L rhamnose, and D glucuronic acid. These sugars are found in gum arabic from all species of Acacia, but the proportions vary among the different species. A recent study by Anderson has reported the presence of methoxyl groups in certain Acacia gums and suggested that the methoxyl content has some structural significance that has yet to be defined.

The molecular weight is believed to vary from about 250,000 to 1,000,000, and also varies according to the method of measurement. The shape of the molecule is believed to be that of a short stiff spiral, or coil, with the length of the main molecule chain varying between 1050 Å and 2400 Å according to the amount of charge on the molecule.

Properties

Solubility

Gum arabic is unique among the natural hydrocolloids because of its extremely high solubility in water. Most common gums cannot be dissolved in water at concentrations higher than about 5% because of their very high viscosities. Gum arabic, however, can yield solutions of up to 50% concentration. At these high levels, it can actually form a highly viscous, gel like mass similar in character to a strong starch gel. In addition to forming high solids gels of this type, gum arabic can be used at much lower concentrations in combination with other gums as thickeners and binders. Comparative viscosities of the common natural plant exudates are shown in Fig. 1 and Table 1. Good grades of the gum give solutions that are essentially colorless and also impart no taste to the solution. Poor quality dark grades of arabic have an unpleasant astringent flavor and odor, probably due to the presence of tannins. These should never be used in food products. Gum arabic is insoluble in oils and in most organic solvents. It is soluble in aqueous ethanol up to a limit of about 60% ethanol. Limited solubility can also be obtained with glycerol and ethylene glycol.

Viscosity

Whereas most gums form highly viscous solutions at low concentrations of about 1 5%, gum arabic is unique in that it is extremely soluble and is not very viscous at low concentrations. High viscosities are not obtained with gum arabic until concentrations of about 40 50% are obtained. This ability to form highly concentrated solutions is responsible for the excellent stabilizing and emulsifying properties of gum arabic when incorporated with large amounts of insoluble materials. The viscosity of gum arabic solutions will depend upon the type and variety of arabic used. Measurements of the relationship of concentration to viscosity made by Taft showed slight, but not unreasonable inconsistencies, considering the differences in raw materials and methods of measurement. Their results are given in Table 2.

Rheological Behaviour

At concentrations up to 40%, gum arabic solutions exhibit typical Newtonian behavior. Above 40%, solutions take up pseudoplastic characteristics as denoted by a decrease in viscosity with increasing shearing stress.

Effect of pH

The effect of pH on gum arabic solutions has been reported by several investigators who tend to agree that
arabic acid is a strong monobasic acid. The viscosity of gum arabic rises sharply with increasing pH to a maximum at about pH 5.7, then falls slowly to about pH 10.14. The data reported by Thomas are shown in Figure 2. Normally, solutions of gum arabic are slightly acidic, having a pH of about 4.5-5.5 and hence are in the area of maximum viscosity.

**Effect of Electrolytes**
The addition of electrolytes to a gum arabic solution results in a lowering of the viscosity, even in a very dilute solution. This lowering is much more pronounced in more concentrated solutions. The decrease in viscosity is proportional to the increase in the valence of the cation or the increase in the concentration of electrolyte. The addition of more than one electrolyte gives an additive effect. This lowering of viscosity, which is accompanied by a lowering of the interfacial tension, produces favorable emulsifying conditions. Thus, while a good kerosene water emulsion can be obtained with a 10% gum arabic solution, equally good emulsions can be obtained with 0.5% gum arabic solutions in the presence of sodium sulfate or sodium bicarbonate.

**Effect of Aging**
Studies on solutions of gum arabic showed that all solutions underwent a decrease in viscosity with age. Unpreserved solutions showed the greatest drop in viscosity, while solutions preserved with benzoic acid (0.2%) exhibited the smallest loss of viscosity.

**Compatibility**
Gum arabic solutions will produce precipitates with many salts, particularly trivalent metallic salts. It is incompatible with some gums, such as gelatin and sodium alginate, but quite compatible with methylcellulose, carboxymethylcellulose, and larch gum. In many cases, compatibility is subject to the influence of pH and concentration, and compatibility of gum arabic with other components can be obtained by proper adjustment of these parameters.

**Emulsifying Properties**
Gum arabic is a very effective emulsifying agent because of its protective colloid functionality and has found widespread use in the preparation of varied oil in water food emulsions. It produces stable emulsions with most oils over a wide pH range and in the presence of electrolytes without the need for a secondary stabilizing agent. The gum arabic forms a visible film at the oil interface, but the mechanism of emulsification still is not understood. It is believed that arabic, as a film forming agent, prevents coalescence of the oil globules, thus permitting a high degree of dispersion by diminution of the diameters of the globules.

It has been found that the chemical nature of the oil used can cause marked changes in the properties of acacia stabilized emulsions. The relative viscosity of emulsions made with gum arabic changed in accordance with the oil used as the disperse phase. It has been suggested that the differences might be due to the presence of a stabilizing layer, the thickness of which varied with the oil used. This layer is presumably large enough to contribute noticeably to the volume fraction and thus the emulsion viscosity. A few other minor gum exudates from fruit trees also have been said to have excellent emulsifying properties. Solutions (10%) of apricot, prune, and sweet cherry gums have been reported to have protective properties similar to a comparable solution of gum arabic, but since these gums are only available in small quantities in certain geographic areas, they have not been used in any important food applications.

**Plant Seed Gums**
Almost all important food plants produce seeds containing starch as the carbohydrate reserve. This starch serves as the principal food stored for use by the embryonic plant in its initial growth stages. Many plant
seeds, however, contain polysaccharide food reserves that are not starch (glucose polymers), but are polymers of other sugar molecules such as galactose and mannose. These polymers also have constructive hydrocolloid properties, and when isolated, can be used like gums from other sources. While many of these seed gums are known and have been investigated, only a very few of them are important in the food industry, and at present only locust bean gum and guar gum enjoy a substantial degree of acceptance. Although psyllium seed gum and quince seed gum have also been utilized to some extent in the food industry, they still find their most extensive uses in the related pharmaceutical and cosmetic industries. The gums of flaxseed, tamarind seed, tara seed, flamboyant seed, and other seeds also have interesting hydrocolloid properties and may eventually prove to be economically and practically suitable in food applications.

As mentioned above, at present only locust bean gum and guar gum are of importance as food hydrocolloids with possible applications seen for psyllium seed and quince seed gums. This chapter will therefore be restricted to a discussion of these gums.

**Locust Bean Gum**

**Historical Background**

The locust bean, or carob bean, plant is an ancient leguminous plant (Ceratonia siliqua L.) which is indigenous to the near East and Mediterranean areas. That it has been known for thousands of years is shown by the fact that the ancient Egyptians used carob paste for binding their mummies. Arabs used the carob seeds or kernels as weight stones to weigh precious metals and gems such as gold and diamonds. As a matter of fact, the word carat is cognate with the botanical name ceratonia. Dioscorides, a Greek physician in the first century A.D., referred to the curative laxative and diuretic properties of the carob tree fruit.

In Biblical times, the pods of the tree were widely used for feeding cattle, horses, and pigs (hence the name swines bread). The pods were used for human consumption in times of scarcity, and perhaps regularly by the poorer people. The carob as food was immortalized in the Bible in the passage where the sojourn of St. John the Baptist in the wilderness is described. His meat was locusts and wild honey is believed to refer to wild carobs (Matthew 3:4) and one of the names for carob bean that has lasted through the centuries is St. John’s bread, or Johannisbrot. The Prodigal Son in the Bible also longed in vain to feast on the carob: and he would fain have filled his belly with the husks that the swine did eat and no man gave unto him (Luke 15:16).

Even today, the Biblical meaning of carob trees is commemorated in a traditional Jewish holiday. Jewish Arbor Day, TuBishvot, marks the tree planting season of ancient Israel and usually falls in February. It is the custom at this time to eat and display the fruits distinctive to Israel and one of the fruits honored on this occasion is the carob, or boksor as it is called in Hebrew.

The importance of carob as animal feed and human food slowly grew over the centuries as the tree was gradually introduced from the near East to other parts of the world. The Greeks were responsible for carrying it from Syria and neighboring areas to Greece and Italy while the Arabs, by virtue of their extensive Mediterranean trade routes, made the carob plant known in northern Africa and Spain. In more modern times, the carob was introduced to the Americas, Australia, and other parts of the world where climatic conditions were favorable to the cultivation of the plant.

The roasted beans have been used extensively as coffee substitutes, especially in Germany. In North Africa the poorer inhabitants of the carob growing areas still use the pulp as a preferred sweet for children because of its high (30 to 50%) sugar content. During the Spanish Civil War in 1936 to 1939, the inhabitants of the carob growing area ate the locust bean as food. In southern Greece during World War II, after the German army had stripped the country of livestock and most other foods, the rural inhabitants
lived largely on carob pods. For several years in the early 1920s there was considerable interest in California in various food products made from carob pods. Carob flour mixed with wheat flour was used to make an acceptable quality bread that was sold in the Los Angeles area for a short period. Another use was a sweet carob syrup with a unique flavor made by grinding the pods to a coarse powder, dissolving the sugars with water, and boiling the solution down to the thickness of honey. Breakfast foods made by beating the seedless pods into a powder were sold both as straight carob or mixed with wheat products according to the amount of fiber desired. Some very extravagant claims were made for the health and medicinal properties of some of these products until public interest waned. Today some carob products are still being sold but mostly as a chocolate substitute in health foods. Recipes have been developed by suppliers for the use of carob in cakes, cookies, candies, ice cream, malted milk, and other foods in which chocolate is normally used.

Botany
The locust, or carob, tree (Ceratonia siliqua L.) is a member of the legume family and is the only species in the genus. It is a large, handsome evergreen tree, 40-50 feet high, which has been used extensively for shade and avenue planting throughout southern California where the climate is similar to that of the Mediterranean countries where the carob tree thrives. It is very drought resistant and grows readily in areas where water is not abundant. However, it is a slow maturing tree and begins to bear fruit 5 years after budding and increases slowly to a maximum by the twenty fifth year when the tree is full grown. This feature of the carob tree is illustrated interestingly in an old Hebrew legend.

A famous sage, Honi ha Ma aggel, saw on his travels an old man planting a carob tree. When asked by the sage when he thought the tree would bear fruit, the old man replied, After seventy years. And dost thou expect to live seventy years and eat the fruit of thy labor? he was asked. The gentle reply was, I did not find the world desolate when I entered it, and as my fathers planted for me before I was born, so do I plant for those who will come after me.

Source
The locust, or carob, fruit itself has the shape of a long pod similar to a string bean and measures 4-12 inches in length, depending upon the variety. Within this brown pod are flinty, brown seeds approximately the size and shape of watermelon seeds. The weight of these seeds is 5-14% of the total weight of the pod. These seeds, or kernels, are the commercial source of locust bean gum, though only part of the seed is useful for that purpose. The seed is composed of a central, hard, yellow embryo germ portion (25-30%) that is surrounded by a large layer of white semi transparent endosperm (35-45%). This whole mass is in turn covered by a tenacious, dark brown husk, or outer coating (30-35%). The endosperm contains the gum and is therefore the desired part of the kernel. Successful production of a high quality locust bean gum involves the separation of the endosperm from the germ and from the seedcoat.

In commercial practice, the husk is first removed by mechanical abrasion or by chemical processes. The dehusked kernels are then split lengthwise and the endosperm is separated from the germ or embryo. The isolated endosperm is then finely ground, graded according to accepted standards of color, impurities, and viscosity, and sold as commercial locust bean (or carob) gum. It is obvious that the purity and quality of the gum depends on the efficiency of the separation of the endosperm from the other portions of the kernel.

The normal locust bean gum of commerce is usually a white powder with the following typical composition: galactomannan, 88% pentosan, 3-4% protein, 5-6% cellulose, 1-4% and ash, 1%.

In different parts of the world, locust, or carob, bean gum is marketed under other names, including: St. Johns bread, gum gatto, gum hevo, jandagum, lakoe gum, rubigum, lupogum, luposol, gum tragon, tragasol, tragarab, honey locust, and algaroba.
Structure
Locust bean gum is a galactomannan polysaccharide with a molecular weight of about 310,000. The structure is essentially a straight D mannose polymer linked C1 C4 with relatively regular branching on every fourth or fifth mannose group on C6 by single D galactose units (Fig. 1). The ratio of D galactose to D mannose seems to vary according to reports from various workers, but this is believed to be due to varying origins of the gums and possibly to the stage of growth or development of the plant at time of gum production. The structure of locust bean gum is similar to that of guar and differs only in having a smaller number of D galactose side chains.

Properties
Locust bean gum is only partly soluble in cold water and must be heated in order to achieve optimum viscosity. Leo claimed that locust bean gum could be made readily soluble in cold water by intimately mixing 4 parts locust bean gum with 6 parts corn sugar, then wetting, heating, steaming, drying, and finally grinding to an appropriate mesh size but maximum viscosity still required heating. Normally, in order to obtain the greatest efficiency as a thickener, it is best to disperse the gum in hot water and then cool the solution. The solution is extremely viscous and sticky, and 1% concentration of a good quality gum may have a viscosity of about 3500 cps (Fig 2). One of the earliest recorded uses of this property was the use of locust bean paste by the Egyptians in preparing the strips of cloth with which they bound their mummies.

Since locust bean gum contains small amounts of insoluble protein and cellulose impurities, solutions of the gum show a cloudy, whitish opacity, which is a serious drawback in food applications where clarity is desired.

Although locust bean dispersions or solutions in themselves do not gel, they have the unusual synergistic effect of imparting desirable elastic properties to carrageenan and agar gels. This effect is discussed in detail in the section on carrageenan.

Since locust bean gum is a neutral polymer, its viscosity or stability is very little affected by pH within the range of pH 3 11. The chemical reactions of this gum are also similar to those of the other neutral polysaccharides. Its esters and ethers have been made commercially, some of which, such as the carboxymethyl ethers, have found interesting industrial applications but are not permitted in foods.

Applications
Ice Cream Stabilization
Locust bean gum has found an important application as a primary stabilizer in ice cream mixes because of its unusual swelling and water imbibing qualities, as well as the smooth meltdown and excellent heat shock resistance it imparts to the final ice cream product.

Cheese Products
In the manufacture of soft cheese, locust bean gum speeds up coagulation, increases the yield of curd solids by as much as 10%, and makes separation and removal of the curd easier. The resulting curd has an excellent soft and compact texture, and the separated whey is limpid. The finished cheese has an excellent, smooth, resilient body and texture. It is also more homogeneous, and exudation of water from fresh cheese is reduced. These improved properties are believed to be due to the buffer function of the acidified locust bean gum solution, which acts as a protective colloid and maintains a constant pH in the finished cheese. Cheese spreads and melted cheese products can be prepared from very soft cheese having high water content. The incorporation of locust bean gum ties up the water and results in a firm, spreadable texture and a highly homogeneous product of fine quality. It is even possible to add water to the cheese products if desired. The gum, usually used in a concentration of about 0.6%, is mixed with other ingredients,
homogenized, pasteurized, and packaged in a stable form. Roundy found that locust bean gum improved the baking characteristics of spray dried bakery cheese products made with acidified milk cream combinations.

**Meat Products**
Locust bean gum has been used in the manufacture of processed meats such as salami, bologna, and sausages, where it acts as a binding and stabilizing agent and yields a more homogeneous product of improved texture and quality. It also has a lubricating effect on the meat mix, facilitating extrusion and stuffing. Due to its water retention properties, locust bean gum reduces loss of weight of these meat products in storage. Locust bean gum has also been used as a thickener for canned meat and fish products.

In the preparation of synthetic meat products, locust bean gum has been used as an important additive to contribute specific properties of meatlike texture. Protein food products simulating the nutritional and textural characteristics of meat were prepared from plant proteins extracted and isolated by several patented methods. The eating qualities of these chewy protein gels were beneficially modified by the incorporation of locust bean gum as an inner additive to impart the essential meatlike chewiness.

**Bakery Products**
Locust bean gum, used to supplement flour in the manufacture of bread and other leavened bakery products, produces doughs with constant functional properties and good water holding characteristics. Higher yields are obtained and the baked products have better textures, are much softer, and have a longer shelf life.

Addition of the gum to cake and biscuit doughs also gives higher yields and a considerable saving of eggs. Further, the cakes and biscuits are softer and have a longer shelf life. The cakes have a firmer texture, are easily removed from the cake pans, and are cut or sliced without difficulty.

Neukom investigated the effect of periodic acidoxidized locust bean gum on the dough and baking characteristics of wheat flour. It was assumed that the introduction of reactive groups (aldehydes) into the polysaccharide molecule would result in further reaction with flour proteins, leading to an increase in the toughness and rigidity of the dough. Locust bean gum, with, degrees of oxidation varying from 10 to 100% of theoretical, were incorporated into wheat flour at levels of 0.1 0.5% of flour weight. Dough properties were measured on the Brabender Extensograph, and bread baking tests were also made. At a certain concentration level, the oxidized locust bean gum distinctly improved the dough properties. The extensibility and resistance of the doughs could be manipulated to give values which from experience, are considered to be brought about by flour improvers. Neukom and Deuel concluded that these modified polysaccharides react with the flour constituents, and that the improving effect is enhanced as the degree of oxidation is increased (i.e., as the number of aldehyde groups introduced into the polysaccharide is increased).

In pies, locust bean gum has been found to be a very satisfactory stabilizer for canned berry and berry apple pie fillings. In frozen pie fillings, it has also performed satisfactorily in conjunction with certain starches. Carlin also suggested its use in stabilizing meringue toppings for pies in order to increase shelf life.

**Miscellaneous**
In special purpose dietetic foods, locust bean gum has often been used for various purposes. Arobon, a locust bean gum preparation, has been added to infant diets for the treatment of diarrhea. Martins suggested using locust bean gum (Nestargel) as an additive at 0.25 0.50% levels in fresh or dried milk in order to increase the product viscosity, thus giving the consumer a higher degree of satiety without increasing caloric content.
El Sokkary found locust bean flour to be an effective antioxidant for butterfat when added to ghee (processed butter) at levels of about 0.5%. It was believed that the gum exerted a synergistic effect upon the natural antioxidants in the butter.

Stevens used locust bean gum to stabilize citrus juice products, i.e., to maintain the natural cloudiness of the citrus fruit beverages, or at least to make it last longer. Recommended use levels for this application in citrus beverage concentrates were about 1 30 ppm locust bean gum, preferably in combination with 20 400 ppm sodium hexametaphosphate.

Katz used locust bean gum in preparing a base material for frozen desserts and confections. The base material, which was capable of floating on water, was a mixture of a bland tasting edible oil, sugar, locust bean gum, and propyl 3,4,5 trihydroxybenzoate, in the form of a solid, aerated slab. Another aerated dessert, developed by Mancuso, was based on gelatin, with locust bean gum or guar as an additive. A mixture of gelatin, locust bean gum, partially degraded soy protein, sugar, and an organic acid forms an aerated, flavored, chiffon type of gel dessert when dissolved and whipped in hot water, and then allowed to set.

Locust bean gum continues to be used as an effective thickening agent in salad dressings and various types of sauces.

Gaur Gum

**Historical Background**

Guar gum is derived from the seed of the guar plant, Cyamopsis tetragonolobus, of the Leguminosae family. This plant has been grown for thousands of years in India and Pakistan where it is a most important crop that has been long used as food for humans and animals. Some guar seeds have even been found in a recently excavated tomb of an ancient Egyptian pharaoh.

Although guar was well known in Asia, it was not introduced into the United States until 1903 when it was evaluated as a possible cover crop in the Texas, Arizona, and California areas by the United States Department of Agriculture. However, little interest was shown at the time, and until the advent of the Second World War, very little headway was made in the cultivation of the plant in this country. At that time supplies of locust bean gum, which was widely used in the paper and textile industries and usually imported from Europe and North Africa, became more and more limited and difficult to get. Therefore, interested groups, made a concerted effort to find a domestic plant that could provide a substitute for locust bean gum. This search led to the reexamination of guar gum, and guar was found to be the best answer to the problem.

In 1945, because of its extensive milling experience, General Mills undertook a study of guar, with respect to: (1) agricultural production of the plant in the southwest, (2) milling, and (3) adaptation of the product to industrial requirements. It was not until 1953, however, that the gum was produced in commercial quantities. Stein, Hall & Co., as well as General Mills, built plants in the United States for domestic production of guar gum, and some time later, the European producers of locust bean gum also began to process guar gum.

**Source**

The guar plant is a pod bearing, nitrogen fixing legume. The seeds of the plant are composed of the hull (14-17%), germ (43-47%), and endosperm (35-42%). In the manufacture of guar gum, the endosperm must be separated as cleanly as possible from the hull and germ. In practice, there are several methods for accomplishing this. The hull can be removed by treatment with sulfuric acid to loosen it, by heating and charring the hull by flame treatment, or by mechanical grinding and sifting. After the hull is removed, differential grinding is used to separate the germ. The endosperm and germ can be separated in this
manner because of the difference in hardness of each constituent. After the endosperm is separated from the hull and germ, it is ground to a fine particle size and sold as guar gum. Various trade names are often used for guar, such as Jaguar, Supercol, and Guar Tec.

**Structure**

Guar gum, like locust bean gum, is a galactomannan. But there are significant differences in their chemical structures and properties. Guar is structurally composed of a straight backbone chain of D-mannopyranose units with a side branching unit of D-galactopyranose on every other unit. Locust bean gum differs in this branching structure by having an average of one D-galactopyranose unit branch on every fourth D-mannopyranose unit (Fig. 1). The greater branching of guar is believed to be responsible for its easier hydration properties as well as its greater hydrogen bonding activity. Guar gum has an average molecular weight in the range of 200,000–300,000.

**Pectins**

The word pectin is derived from the Greek phctoV meaning to congeal or solidify. The actual chemical compound was discovered by Vauquelin in 1790, but it was not truly characterized until Braconnot first described it as the principal gelling agent of fruit and gave it the name pectin. Braconnot understood that pectin was the substance that gave fruits the ability to form jellies when boiled with sugar. He also recognized that sugar and the proper pH were necessary for the reaction, and he mentioned that he had to add a small amount of acid (hydrochloric or sulfuric acid) to break up the pectates when making his jellies. After Braconnot’s work on pectin, a great deal of scientific research was done during the next century from both the chemical and biological points of view.

**Nomenclature**

As a result of the vast amount of confusion that had been created over the years by various investigators in the field, the American Chemical Society finally adopted a standard nomenclature for these materials in 1927. The standard was later revised and broadened in 1944. Pectin was then defined functionally as those pectinic acids capable of forming the standard type of fruit jellies when sugar and acid were present in the correct proportions.

The uniform definitions adopted at that time and still in use today are as follows:

Pectic substances are those complex colloidal carbohydrate derivatives that occur in, or are prepared from, plants and contain a large proportion of anhydrogalacturonic acid units, which are thought to exist in a chainlike combination. The carboxyl groups of polygalacturonic acids may be partly esterified by methyl groups and partly or completely neutralized by one or more bases.

Protopectin is the water insoluble parent pectic substance that occurs in plants and which on restricted hydrolysis, yields pectin or pectinic acids.

Pectinic acids are the colloidal polygalacturonic acids containing more than a negligible proportion of methyl ester groups. Pectinic acids, under suitable conditions, are capable of forming gels in water with sugar and acid, or, if suitably low in methoxyl content, with certain ions. The salts of pectinic acids are either normal or acid pectinates.

Pectin (or pectins) are those water soluble pectinic acids of varying methyl ester content and degree of neutralization and are capable of forming gels with sugar and acid under suitable conditions.

Pectic acid is a term applied to pectic substances composed mostly of colloidal polygalacturonic acids and essentially free from methyl ester groups. The salts of pectic acids are either normal or acid pectates.

Protopectinase is the enzyme that converts protopectin into a soluble product. It has also been called pectosinase and propectinase.

Pectinesterase (PE), or pectinmethylesterase, is the enzyme that catalyzes the hydrolysis of the ester bonds in pectic substances.
bonds of pectic substances to yield methanol and pectic acid. The name pectase does not indicate the nature of the enzyme action and has given way to these more specific names.

Polygalacturonase (PC), or pectin polygalacturonase, is the enzyme that catalyzes the hydrolysis of glycosidic bonds between de esterified galacturonide residues in pectic substances. Pectinase is frequently used to designate the glycosidase as well as pectic enzyme mixtures.

The pectic substances, which are all modifications of galacturonic acid polymers, can be differentiated by the degree of methoxyl substitution this is the current accepted industry practice. Thus, Bender groups commercial pectins into five distinct categories according to their degree of methylation (DM): (1) 30 DM pectin for low sugar gels (2) 45 DM pectin for rapid setting, calcium precipitatable pectin suitable for high sugar gels and emulsions (3) 60 DM or slow set pectin for high sugar gels and confectionery jellies (4) 74 DM for typical rapid set pectin for jams and jellies (5) higher DMs for special purpose applications.

McCready, however, prefer a simpler, though arbitrary, classification of gelling pectins into three groups: (1) rapidset, (2) slow set and (3) low methoxyl. The boundary lines are not sharp, and the distinction between the three groups seems to be related to their solubility and degree of esterification (DE): (1) rapid set pectin 70% DE or higher (2) slow set pectin 50 70% DE (3) low methoxyl pectin -50 % DE or lower.

An even simpler classification, which is preferred and used herewith by the author, is to consider just two types of pectin: (1) regular pectins which require sugar and acid for gelling, and (2) low methoxyl pectins which have methoxyl contents below 7% and require calcium for gelation.

Function in Plants

The pectic substances, in combination with cellulose and starches, are structural components of all green land plants. Although they are found mainly in fruits and vegetables, traces have also been discovered in cereals where their contribution to structure is of minor importance.

Pectic substances are integral components of the cell structures and function as cementing substances in the middle lamellae. They are present in the various stages of molecular development and transformations, which are dependent on the specific morphology, and taxonomy of the plant as well as the stage of growth and maturity. The chemistry and interrelationship of these materials (pectins, pectinic acids, pectic acids) are still not completely elucidated and therefore continues to be the subject of continuing research by many scientific groups in all parts of the world.

The function of pectins in fruits and vegetables is primarily concerned with the retention of form and firmness of the plant. Pectins also seem to play a role in the control of the movement of water and plant fluids through the rapidly growing plant. The action of pectins as intercellular substance in plants is similar to the action of intercellular substance of animals, e.g., collagen, the precursor of gelatin. Protopectin, the water insoluble precursor of pectin, is abundant in immature fruit tissues. The normal process of ripening and maturing involves hydrolytic changes of protopectin to form pectin, followed after maturity by enzymatic demethylation and depolymerization of pectin to form pectates and eventually soluble sugars and acids.

In a similar manner, nature has provided not only enzymatic means for pectin breakdown in plants but has also provided the human digestive system with a somewhat similar enzymatic mechanism to digest the pectins normally ingested as a part of natural fruitstuffs. This ease of digestibility of pectic substances is quite different from that observed for the hydrocolloids derived from natural land and sea plants. Most of the gum exudates from trees or bushes have an aldobionic acid nucleus for the gum structure that is very difficult to break down. The seaweed extracts also consist of gel forming polyuronides with complex nuclei that are very resistant to hydrolytic breakdown. The pectic substances, on the other hand, can be broken down quite easily by digestion.

In general, the pectins of fruits at very early stages of growth are almost completely methylated and have a very high molecular weight. As growth proceeds and the fruit matures, pectic enzymes are believed to
attack the pectin and hydrolyze it into smaller polymers with lower methoxyl contents, higher carboxyl contents, and lower molecular weights. As the fruit continues to mature this catabolic process continues. Commercial pectin is usually extracted when the pectin still has a relatively high methoxyl content and molecular weight.

Structure
Pectin, a fairly complex heterogenous structure, is composed chiefly of polygalacturonide chains having a wide variety of molecular weights. Some of the carboxyl groups are esterified with methyl alcohol, some are neutralized with cations, and some are free acids. In addition to variations in its molecular weight and methoxyl content, pectin may also vary with respect to the distribution of ester groups along the chains. Small amounts of acetate and other groups are also sometimes attached to the molecule.

The pectic acid molecule consists of D galacturonic acid units in pyranose configuration linked together by a 1, 4 glycosidic linkages. In nature, the carboxyl groups are partially methylated to form the ester known as pectin. In addition, the secondary hydroxyl groups may be partially esterified by acetic acid. Thus the degree of esterification in natural products may vary within a wide range.

The pectin macromolecules may be changed by saponification or esterification. The configuration and relationship of the basic pectic acid molecule to cellulose and alginic acid is shown in Fig. 1.

Properties
The properties of the pectic substances depend greatly on their molecular weight and their degree of substitution. Properties such as water solubility, viscosity, coagulability, gelling tendency, and stability toward enzymes change directly with increasing degree of esterification. These changes can be explained by the alteration of the electric charge and the form of the pectin macromolecules. Solubility of pectin decreases with an increase in chain length and with a decrease in methoxyl groups.

Viscosity
The viscosity of pectin solutions depends on several factors, namely, the DM of the pectin, concentration, temperature, pH, and presence of salts and their concentration. Decreasing the concentration or the grade of pectin increases the viscosity, as would be expected. Temperature changes decrease the viscosity in a similar manner. However, if alkaline earth salts are present in pectins of 60 DM or lower, the decrease might be larger than expected.

Effect of pH
Even when sufficient pectin and sugar are present in the system, no gel will form until the pH is reduced below the critical value of about 3.6 known as the limiting pH value. Most slow setting pectins give optimum performance at pHs between 2.8 and 3.2, while rapid setting pectins perform best in a range of 3.0 3.4. The effect of pH is not entirely predictable, since it depends upon the DM and any salts that may be present. The tendency of a 30 45 DM type of pectin to gel would be decreased by a change in pH and prevented by lowered pHs. Solutions or dispersions of pectinic acids free of alkaline earth salts will increase in viscosity and finally gel at very low pHs.

The effect of added alkali metal salts such as sodium chloride is also not very predictable. The salt effect depends on the amount of salt, the type of pectin, and the pH of the solution. Small amounts of sodium chloride (as low as 0.6%) will produce a great increase in viscosity or gelation of a 0.8%, 40DM pectin solution when the pH is 2.9. But the viscosity will be decreased at a pH of 4.4. At still higher pHs (about 6) salt effects are minimized if phosphates are also added. It is believed that viscosity is solely dependent on the length and shape of the chains.

Effect of Calcium Salts
The effects of calcium salts on pectin viscosity are very important. These effects show up as an increased viscosity even for pectins of 75 DM or higher, and show a maximum viscosity at pHs of 8.55. The viscosity increasing effect of added calcium ions increases sharply as the degree of methylation decreases, thus freeing more carboxyls for cross linking of the chains by calcium ions. The increased viscosity is very evident at 60 DM and becomes greater as the DM increases until it reaches a maximum of 80.

In general, it can be stated that pectins of the same type can be compared with respect to viscosity when they are in solutions of the same grade, pH, temperature, and salt content. Viscosities of different pectin types can also be compared, but even small variations in pH or salt content of the media can noticeably change the final viscosities.

Low Methoxyl Pectins
Low methoxyl pectins, as opposed to regular pectins, do not require sugar for gel formation and are also not as sensitive to pH. On the other hand, they are sensitive to divalent metallic cations such as calcium.

Effect of Cations
Divalent metal ions can react with carboxyl groups from adjacent pectinate chains to form a gel network. This ionic cross linking by normal valence forces of divalent ions can be slowed down temporarily by such monovalent ions as sodium which can also react with the free carboxyl groups. Usually, the effect of such ions is to curtail the cross linking reaction of calcium and to improve the solubility of low methoxyl pectin in the presence of calcium. Sometimes a better gel results when salts such as sodium citrate are present in low concentrations.

Sugar
Low methoxyl pectins can form gels without the need for sugar, but the presence of small amounts (10–20%) of sugar tend to impart desirable textural properties to these gels. High concentrations of sugar (60% or higher) interfere with gel formation because the dehydrating effect of the sugar favors hydrogen bonding and decreases cross linking by ordinary valence forces. It is therefore important to determine the optimum sugar level for any specific gel application.

pH
Low methoxyl pectin gels can be prepared within a comparatively wide pH range. Good milk gels can be made at pHs up to 6.5, while fruit or vegetable gels can be made at pHs as low as 2.5. The practical and most desirable range for most salad and dessert gels is 3.2–4.0. Regular pectin gels have a limiting pH near 3.5 above this, gels cannot be formed.

Temperature
Temperature is an important factor in the formation of low methoxyl pectin gels. Low methoxyl pectin will form gels that are much more stable at much higher temperatures than can be made with other gelling systems such as gelatin. The temperature of gel formation and the stability of the gel will depend upon the initial gel composition. Gels made with high concentrations of pectin, such as tomato aspics, will form and be stable at temperatures of 120–150°F, while gels using low levels of pectin are not stable at temperatures above 100°F.

Gel Formation

Theoretical Discussion
Commercial grade pectin has the unique property of dispersing in water to form a viscous colloidal sol, which will gel in the presence of appropriate concentrations of sugar and acid. The structure of these pectin sugar acid gels is entirely different from that of gelatin, and indeed, the mechanism involved in pectin gel formation is also quite different.
Seaweed Extracts

Botany

Algae, which belong to a major division of the plant kingdom, are composed of those nonseed bearing plants that contain photosynthetic pigments. The plants, which may vary in size from single cells to giant conglomerates, all share a common anatomical feature in the absence of a vascular or food conveying system. Since the plants must be submerged in the medium from which they acquire their food, they are found in ponds, lakes, and streams and in the salt seas and oceans where they attain maximum size. The larger forms of these plants are known as seaweeds, although they are not really weeds, but flowers of the sea as the poets have described them.

During the millenia of evolution, several parallel evolutionary branches of these marine algae developed, each branch using different pigment systems for photosynthesis. The largest and most numerous forms are the two major groups comprising the red and brown algae, while the smaller groups consist of the green and blue green algae, which are confined, in general, to fresh water regions.

All plants contain structural substances that hold the various cells together and that form a large proportion of the plant weight. These substances are usually hydrocolloid polymers composed of sugar units. In land plants, neutral polymers such as cellulose and hemicellulose are the major components, while in sea plants, the structural polymers are the more flexible, negatively charged polyelectrolytes.

The red algae, or Rhodophyceae, contain predominantly red pigments and are the source of several important hydrocolloids, namely agar, carrageenan, and furcellaran, all of which are polymers of galactose. The second important group is the Phyophyceae, or brown algae, which contain predominantly brown pigments. The largest and most numerous of the brown algae are commonly referred to by the inclusive term kelp, a term generally reserved for those forms growing in large masses such as the floating giants of the Pacific coast.

The major hydrocolloids of the brown seaweeds are the salts of polyuronic acids (mannuronic and guluronic acids). The soluble salts of this polymer, such as sodium salts, are generally referred to as algins. Any salt of the polymer is an alginate, while the organic salts or esters are called algin derivatives.

The important seaweed species that are used for the production of commercial seaweed extracts are shown in Table 1. These are not all inclusive, and undoubtedly other botanical species are often used, but in general, these specific types of red and brown algae form the basis of the industry today.

Historical Background

The utilization of seaweeds for food and medicine can be traced as far back as 3000 B.C. when Shen Nung, a famous oriental physician used the plants for their medicinal value. Later, in the time of Confucius the food uses of seaweed were lauded in the Chinese Book of Poetry, which extolled a housewife who cooked seaweed.

There is little doubt that agar was the first seaweed hydrocolloid isolated as an extract from the parent plant. It had been known in oriental countries for ages and was used in the form of a sweetened, and sometimes flavored, gel. The use of agar for foods and the extraction of similar gel forming seaweed extracts, were probably spread through the Orient and the western Pacific areas by the various migrations of the Chinese and Japanese. In areas such as Indonesia and the Philippines, the native weeds were exploited in a similar manner by the inhabitants, and a great deal of intercultural applications of the extracts were developed as evidenced by the host of colloquial names still in use for similar seaweed extracts.

In the western world, the seaweeds utilized were those found off the coasts of Europe, Africa, and North America and were mainly the carrageenan bearing red seaweeds and the algin bearing brown seaplants. Carrageenan, in many respects, was to the Occidentals what agar was to the Orientals. It was known for
many years in the seacoast areas of Ireland, Great Britain, France, Norway, and other European countries. And its vernacular name, Irish moss is quite indicative of its origins in the coastal Irish town of Carragheen whence its current name carrageenan is derived.

The importance of the carrageenan seaweeds to these various geographic communities is difficult to assess. Although they have been used locally for centuries, it was not until the nineteenth century that they became an article of commerce. And it has only been in modern times that they have been extracted as a pure hydrocolloid. Prior to this carrageenan was eaten as a whole plant or extracted indirectly by the housewife who wanted to make a pudding of the blanc mange type. During the Irish potato famine in the middle of the nineteenth century, these Chondrus crispus seaweeds were used to make a not very nourishing St. Patricks soup.

Algin or sodium alginate first became a commercial product due to the perspicacity of an English chemist, who observed that the viscous fluid found in the blisters or sacks on the surface of kelp plants was a unique substance of remarkable properties. Although his initial commercial venture was not successful, Stanford had sown the seed of a new industry. Today alginate products are manufactured in various parts of the world and are standard commodities of trade.

Furcellaran, the most recent seaweed hydrocolloid to achieve commercial importance in the food industry, was a result of the search for agar substitutes during World War II. As the story goes, a barber in Denmark was investigating various kinds of seaweeds in an effort to make a permanent wave liquid product. He found that the seaweed Furcellaria fastigiata, which is found off the coast of Denmark, gave a shiny, gummy material with good thickening properties. This discovery was commercialized. The extracts sold as Danish agar are now used in sizeable quantities in the food industry.

Today, with the ever growing realization that the sea is the last remaining great food resource on earth, a great deal of research is being done to find new seaweed extracts of commercial use. Many plants and extracts are being studied, and undoubtedly many new hydrocolloids will become available in the future for food applications.

Structure

Red Algae

The red algae are quite different from higher plant forms because large amounts of sulfated polysaccharides are accumulated in the cell walls or intercellular regions. The nature of the polysaccharide sulfate from each alga is distinctive and characteristic of each plant type and is useful for the classification and differentiation of the algae. For example, the polysaccharides of the Rhodophyceae usually contain galactose as the D or as the D and L enantiomorphs, often together with such derivatives of each enantiomorph as the 3,6 anhydride, the 6 0 methyl ether and/or various sulfate esters.

A major variation that has been consistently observed among red seaweed extracts is in ester sulfate content this may range from as low as 0% in the agarose fraction of agar to as high as 36% in carrageenan. The common red seaweed extracts have the following amounts of ester sulfate:

Anderson in their studies of the red algae structure have come to the conclusion that a close relationship exists between many of these polysaccharides, and that the same basic structure is common throughout many of these polymers. This structure is, namely, a chain of galactose units linked alternately a 1,3 and b 1,4. This basic structure is modified by different algae to produce many variations on the same structural theme. They differ from each other in having either the D or L configuration, the 3,6 anhydro group, the ester sulfate group, or by being methylated. These variations alone can yield thousands of possible compounds.

As the basic structures of these various seaweed gums become more accurately defined, it begins to appear that all of the seaweed gums may be composed of a common group of basic building blocks that

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form different types of polymers according to the type of plant and its stage of growth or development. This least common denominator theory is being investigated by studies of enzymes which might have exact specificities for the various building blocks in the molecules.

In summary, it would appear that the sulfated galactans of the red seaweeds are a family of related polymers, each with properties appropriate for a particular species growing in a particular environment.

Brown Algae

Alginic acid is the only important extract of brown algae at this time. It was considered to be primarily a polymer of anhydro 1,4-b D mannuronic acid until Fischer established the presence of L guluronic acid in the hydrolysis products of alginic acid. Based on this and other confirmatory work, alginic acid is currently regarded as a polyuronide comprising D mannuronic and L guluronic acids, the relative proportions of which vary in different species of brown algae.

The building blocks or molecular entities that have been isolated and identified in the four commercially important seaweed extracts are shown in Table 2.

Agar

Historical Background

In spite of its Malayan name, agar agar is of Japanese origin and was first fully exploited in Japan. According to Tseng, Chinese settlers in the East Indies introduced the use of Japanese agar as a food to the natives. To avoid a Chinese or Japanese name, they called it agaragar, a name used by the Malayans to indicate certain seaweeds and the jellies made from them.

In Japan itself, agar is called kanten, meaning cold sky. This name refers to the fact that the material used to be prepared on cold winter days or high up in the mountains where it was always cold. In other areas it is also known as Japanese isinglass, Chinese isinglass, vegetable isinglass, seaweed isinglass, Japanese gelatin, bar kanten, square kanten, slender kanten, tungfen (frozen powder), and many other colloquial names common to specific geographic areas.

The Dutch and other Europeans living in Indonesia later learned to use this Japanese product for making fruit and vegetable jellies and seem to have introduced this art of jelly making to their friends and relatives in Europe.

But it was not until 1882 that the world wide fame of agar was truly established when Robert Koch introduced the product into bacteriology as a culture medium. Koch himself did not realize the importance of this discovery as a major technical improvement, for in his famous experiments on the isolation of the tuberculosis bacillus, he disposes of this new culture medium in a single, insignificant sentence, So wachsen sie beispielsweise auf einer mit agar agar bereiteten, bei Blutwaren hart bleibenden Gallarte, welche einen Zusatz van Fleischinfus und Pepton erhalten hat.

The credit for first using agar as a culture medium rightly belongs to a housewife, Frau Fanny Hesse, who had been using agar for years in her kitchen for the preparation of jellies. She had received the recipe from Dutch friends living in Indonesia. When her husband, Dr. Walther Hesse, complained about the difficulty of using gelatin in cultivating microbes, she suggested agar instead. His successful application was communicated to the famous Dr. Koch, who in turn, introduced it to the world. The rest is history. Today, almost a century later, agar is still the best culture medium available. The gelling and colloidal properties that make agar the excellent bacteriological medium are the ones that have been utilized in various food applications, as will be discussed later.

Collection of Agar Weed

In Japan, the agar bearing seaweeds are gathered from rocks between mid and low tide marks, or else divers collect them from the sublittoral regions. In certain areas of Japan, the collection of seaweed by
diving has developed into a unique industry largely carried out by female divers. These diving, girls, known as amas, inhabit the Chiba prefecture (province) along the seacoast. They are trained from early childhood to dive for various seaweeds. The word ama originally meant the sea and was used for calling the divers when the boats were full. These women operate from rafts, boats, or even large wooden tubs, which are paddled to the collecting areas. There, they dive for the weeds and store them in the tubs or rafts. When sufficient material has been collected, the tubs are towed to shore by the women who swim with them. These bare breasted women develop an abnormally large chest expansion and lung capacity and would probably do well in Hollywood if a seaweed shortage should occur. They use no equipment except goggles and operate in water depths down to 30 feet. In deeper waters, below 60 feet, male divers equipped with diving apparatus gather the harvest. After the weed has been collected, it is dried on the shore and partly bleached. It is then sold to manufacturers for final processing. The deep water weed is considered to yield the best gelling extracts, and the optimum harvesting time is from April to September.

**Processing**

**Background**

For centuries, agar was produced by simply boiling seaweeds to obtain a jelly mass. The modern method of purification and preparation was discovered by accident.

According to legend, it was in the year 1658 or thereabouts that the Emperor of Japan and his royal party were caught in a sudden snowstorm and took refuge in a nearby inn. The innkeeper Tarozaemon Minoya by name prepared a dish of seaweed jelly for his royal guests. The left over jelly was thrown outdoors, and it froze solid during the night. The next day, when the sun came out, the frozen jelly thawed and the watery part drained off, leaving a dry, papery, translucent substance. The acute innkeeper found that this residue could be remade into a jelly by boiling it up with more water. The new jelly was clearer and of better quality than the original product.

This discovery was subsequently adopted by producers of agar. The process of purifying agar seaweed extracts by consecutive freezing and thawing operations became a standard procedure that is still used in commercial practice today in Japan.

**Current Process**

All commercial agar is manufactured essentially by hot water extraction followed by freeze thawing for purification. Agar weeds appropriate to give a final product of desired properties are blended in carefully predetermined proportions. The batch of weeds is soaked and washed with fresh water and then extracted by boiling in water in open iron kettles or by pressure autoclaving in modern plants.

At some point, calcium hypochlorite or sodium bisulfate is introduced in order to bleach, or decolorize, the agar so as to obtain the lightest possible product. The extract is filtered hot and the residue is re extracted one or two times. The extract is allowed to cool, and when gelled, the solid mass is allowed to freeze naturally or is frozen by refrigeration. The frozen gel is allowed to thaw, and the impurities are drained off with the excess water. The gel is then dried, ground, and packed for shipment.

**Structure**

The structure of agar has been studied for many decades, primarily by Japanese scientists, some of whom have spent their entire professional lives in this area of research.

Araki was the first to isolate agarose, and subsequent work by other workers led to the currently fairly well established opinion that agar is a mixture of at least two polysaccharides-agarose, a neutral polymer, and agaropectin, a sulfated polymer. The ratios of these two polymers vary widely and the percentage of agarose in agar bearing weeds can range from 50% to 90%. The two polymer components can be fractionated either by acetylation in chloroform to give a soluble agarose acetate and an insoluble
agaropectin acetate or by selective precipitation of the agaropectin with quaternary ammonium salts.

**Microbial Gums**

Anthropologists know of no society in which fermentation has not been employed to make life more pleasant. The cave man discovered that meat allowed to age a few days after the kill was more pleasing to the taste than meat eaten immediately. He also learned that intoxicating drinks could be made from rotting grains and fruits. These two unconscious uses of the fermentation process, the aging of meat and the manufacture of alcohol were the first applications of what today is a vast science. To primitive man, fermentation was a type of magic. He was not aware that he was using the natural activity of tiny living organisms, such as molds and yeast, to improve the taste and texture of his foods. But without knowing that these creatures existed, ancient man learned how to put them to work. For thousands of years, the soy sauces of China, Japan and other oriental countries were made from fermented beans. For centuries, the Balkan peoples of Europe enjoyed fermented milk or yogurt, while in Central Asia, the nomadic tribesmen enjoyed an alcoholic beverage called kumiss, made from fermented mares or camels milk. The preparation of one of man’s oldest foods, bread, which has been used in some form virtually everywhere on earth, involves controlled yeast fermentation.

The discovery of fruit fermentation by which wine is made, was made so long ago that the ancient Greeks believed that wine had been invented by the god Dionysus. Beer was also an ancient discovery, and a Mesopotamian clay tablet written about 500 years B.C. tells that brewing had been a well established profession for several thousand years. Beer was also a commodity that the Babylonian Noah, Utanpishtim, took on board his ark to make his trip more pleasant. Egyptian documents dating back to the Fourth Dynasty (about 2600 B.C.) describe the malting of barley and the fermentation of beer, and it is well known that the Pharaohs enjoyed a cloudy, unreliable beer made in this fashion. A Chinese rice beer, kiu, has been traced back to 2300 B.C. More recently, when Columbus landed in Central America, he found that the Indians drank a beer made from corn.

During the middle Ages, experimenters learned how to improve the taste of wine, bread, beer, and cheese, but they had no idea that they were dealing with a form of life too small to be seen by the naked eye. The true cause of fermentation was not understood until the latter part of the nineteenth century when Louis Pasteur arrived on the scene.

The change from art to science, which was initiated by Pasteur’s discovery that fermentation is brought about by living yeast cells, signaled the beginning of a new era, which in the last 100 years has wrought such miracles as the discovery of penicillin, streptomycin, and other antibiotics, as well as the food additives that help make our foods more nutritious and appetizing.

In the area of hydrocolloids, fermentation technology has also played an important part in the development of polysaccharide gums having unique functional properties that are capable of making important contributions to the food industry.

**Dextran**

**Background**

Microbial polysaccharides can be roughly divided into two groups homopolysaccharides and heteropolysaccharides. The homopolysaccharides include those polymers produced from sucrose by a variety of bacteria, of which the best known members are the dextrans.

The term dextran was first used to describe the slimy material formed in the juices of sugar beets, wine, and other sugar based food products. It was a well known nuisance in the sugar industry because it sometimes clogged up the pipes through which sucrose containing juices and solutions were transferred. Pasteur showed that these slimes were caused by microbial action. Shortly thereafter, Scheibler found that...
dextran is a carbohydrate with the empirical formula \((C_6H_{10}O_5)_x\). Since the material was closely related to starch and dextrin, he coined the name dextran for it. Later investigations showed that dextran can be formed by many microorganisms and is not a well defined substance with specific properties. It is more accurate to refer to dextrans when no clear definition of the bacterial origin and chemical properties of the substance are given. Much work on these microorganisms was erratic due to the study of impure preparations, but comparatively recently Hucker classified the microorganisms responsible for producing dextran from sucrose. The main dextran synthesizing bacteria belong to the Leuconostoc genus, species mesenteroides and dextranicum, tribe Streptococceae, and family Lactobacteriaceae. Subsequent work isolated other strains of bacteria that are capable of producing various dextran materials. All of the species, however, have one common characteristic, in that sucrose is the only suitable carbohydrate source for the manufacture of the polysaccharide. The organisms can grow on any medium containing sucrose, together with a few inorganic salts and a suitable source of nitrogen.

From the large number of microorganisms capable of synthesizing dextran, it was seen that one of the factors determining the properties of the polysaccharide obtained was the strain of the particular bacteria used. Likewise, the final structure of dextran obtained was closely related to the particular strain that produced it and it appeared that individual strains of bacteria have the ability to mutate over the years to the extent that the branches on the resultant polysaccharides eventually become attached at points on the main chain different than those found originally. Most of the work with dextran has been conducted on material produced by various strains of Leuconostoc mesenteroides, which was also given the designation B 512. Among the different types of bacteria that can produce dextrans, the Leuconostoc mesenteroides strain has been most thoroughly studied, and most scientific investigations are based on dextrans of this origin.

**Production**

The formation of dextran depends upon dextran sucrase, an enzyme of the dextran producing microorganism. This enzyme is active outside the bacteria cells and passes into the culture medium either through secretion or autolysis of the cells. Dextran can therefore be produced either by the cultivation of these organisms or by synthesis using the cell free enzyme extract. Only the first method has been used in large scale industrial production.

The production of dextran by cultivation of Leuconostoc mesenteroides is carried out at suitable temperatures and pH in a fluid medium containing sucrose, nutritional substances necessary for the growth of the bacteria, and the buffer material, which limits the pH displacement during fermentation.

The process takes place in two phases. First, the bacterial cells divide, releasing the dextransucrase into the medium. Second, the enzymatic polymerization of glucose units to dextran takes place. Gradually, as the dextran is formed, the medium thickens into a tough, viscous mass. When the viscosity is greatest, the maximum yield is obtained, and the dextran is precipitated by the addition of methanol, ethanol, or acetone. The white, rubberlike precipitate is then dried and pulverized to give a white to slightly yellowish dextran hydrocolloid.

Parameters that influence the type of dextran obtained are the following: (1) strain of the organism, (2) optimum pH of the synthesis, (3) incubation time, (4) manner of inoculation, (5) composition of the culture medium.

**Structure**

Structural studies by Sloan have shown the dextran produced by B 512 to contain 95% of \((1\rightarrow6)\) linked units of a D anhydroglucopyranose, and 5% of \((1\rightarrow3)\) linked units. Van Cleve subsequently demonstrated that the B 512 dextran contained a repeating segment of approximately 23 anhydro D glucopyranosyl units. Of these, 21 units are \((1\rightarrow6)\) linked, 1 unit is a branch \((1\rightarrow3)\) linked, and 1 unit is an end group. About 80% of
the external branches are only one D glucose unit long. A typical structural segment is shown in Fig. 1.
The molecular weight of the polymer is dependent upon the fermentation medium. If no primer or acceptor
is present, the dextran formed has a molecular weight of more than 100,000,000. If a primer such as
maltose is used, the dextran molecules will be predominantly below 50,000 molecular weight. If a dextran
primer of 15,000 40,000 is employed, the majority of the resultant dextran will have a molecular weight of
75,000±25,000, the preferred type for use as a blood extender.

Properties
Dextran is a neutral polysaccharide, readily soluble in hot or cold water to give clear, viscous solutions. It is
tasteless, chemically inert, and compatible with most ingredients normally used in foods.
It has typical hydrocolloidal characteristics such as emulsifying and stabilizing properties in oil water
systems. It is also known for its humectant and water holding qualities, and it imparts effective bodying
attributes to liquid foods.
The chemical structure, due to its low degree of branching, affords a high degree of stability to hydrolytic
depolymerization, which makes it useful as a synthetic blood plasma extender.
Physiologically, dextran, when ingested, is hydrolyzed slowly to form absorbable carbohydrates, which are
utilized. This was shown by feeding tests on animals and humans. Dextran, given by mouth, produced a
modest but sustained increase in blood reducing substances and liver glycogen. The evidence suggested
that the intestinal breakdown of dextran is not ascribable only to bacterial action, but more likely to an
enzyme or enzymes present in the intestinal mucosa.
More recently, Baker reported that biological tests demonstrated that when dextran containing a high
proportion of a (1®6) linkages is included in a normal diet on a regular regimen, gain in body weight is
inhibited. Even though dextran is edible and assimilated without unfavorable effect on the human system, it
appears that the a (1®6) linkages are resistant to attack by bacteria and enzymes present in the
gastrointestinal tract. This may suggest its use in low calorie foods or reducing diets.

Applications
Medical
Dextrans have been proposed for use in a large number of industrial and medical applications, but the
 greatest use has been in medicine where partially hydrolyzed dextrans have successfully been used as
blood plasma extenders in the treatment of shock. For this application, a dextran possessing a molecular
weight in the range of 50,000 100,000 is required, and a great deal of experimental work has been done to
produce dextrans in this range.

Baked Goods
Bohn found that the incorporation of small quantities of dextran in yeast raised bread doughs containing
both yeast and gluten produced breads that were softer and had a greater volume and longer shelf life than
ordinary breads made from doughs without dextran. The dextrans preferred were derived from Leuconostoc
mesenteroides and had molecular weights of about 20,000,000 40,000,000. The amount of dextran used
ranged from about 0.01 10% by weight of the flour contained in the dough. The addition of dextran to the
doughs increased the water absorptive properties of the resultant dough and also made the dough more
extensible by softening the gluten.
Toulmin prepared edible containers, such as ice cream cones, from dextran. The dextran was mixed with
sugar, milk, and water or oily plasticizer to give a mash that could be molded and baked in the usual
manner after forming.

Beverages
Hamburg used dextran to replace 10-20% of the malt in the production of pilsener beer. The dextran beers were reported to have good flavor and foam stability and had the same color as pure malt beer. The carboxymethyl dextran derivative is an effective foam stabilizer when added to beer or other fermented malt beverages at about 0.5% concentrations.

Dextran has been used as a stabilizer for chocolate milk beverages. Mahoney also found it effective in the stabilization of the soft drinks and flavor extracts. Likewise, Wadsworth found it to be useful in the production of noncrystallizing sugar syrups where stability and viscosity were important qualities. Dextran has also been suggested for use as a bodying agent in low calorie, sugar free beverages.

**Confectionery**

Mahoney described dextran as a desirable constituent for use in all foodstuffs in which there is a sugar component. Its value was in its capacity to prevent crystallization, improve moisture retention, improve body, and maintain flavor and appearance. It was effectively used in candies, fondants, jellies, and canned fruits.

Wadsworth subsequently combined the entire sterile culture liquor of dextran with sucrose syrup to prepare a noncrystallizing sugar syrup of exceptionally high viscosity.

Corman used purified dextran sucrase to convert a sucrose solution enzymatically to a higher viscosity, fruit additive, dextran syrup, containing all the D fructose originally present in the sucrose molecule. The product had enhanced sweetness and superior odor and flavor over that from the whole culture process. Viscosity could be controlled by reaction conditions and by the addition of the dextran sucrase.

**Preservative Coatings**

Dextran has been employed for preserving a large variety of foods by preventing the food from drying out during storage and by protecting it against the deleterious effects of exposure to air.

Toulmin used an aqueous solution for dispersion of native or hydrolyzed dextran to preserve shrimp and other products. Similarly, other foods, such as meats, dried fruits, and cheese, could be coated with a film of dextran, which protected the food against drying in storage, and yet permitted the product to vent the gases.

Novak used aqueous dextran dispersions containing antibiotics as a preservative coating for quick frozen foods, such as fish or spinach. The dextran film lengthened the storage life and retarded decay during thawing by absorbing and moisture. In a similar manner, Woodmansee and Abbott coated sub scalded chicken broiler parts with dextran to protect them against dehydration and skin darkening in fresh storage. In work with the carboxymethyl dextran derivative, Novak found it to be effective as a flavor fixative. Citrus oils emulsified in gelatin to prevent deterioration are protected against insolubilization of the gelatin by incorporation of less than 1% of carboxymethyl dextran. In a related fashion, coating monosodium glutamate crystals with carboxymethyl dextran offers protection against potency loss and agglomeration of the granular material.

**Miscellaneous**

Owen suggested the use of dextran as a conditioner in chewing gums as well as a stabilizer in ice cream products. It could also be used in the manufacture of frostings and synthetic creams. In general, dextran could replace, in whole or in part, such gums as gum arabic, karaya, locust bean gum, tragacanth, or alginates.

Polysaccharide B 1459 (Xanthan Gum)

**Background**

The successful work on the fermentation of sucrose to produce dextran (B 512) led to concerted efforts by the Northern Utilization Research and Development Division to find other microbial polysaccharides that
might be industrially useful. They were particularly interested in using glucose (corn sugar) as a fermentation medium, since one of the functions of the Northern Regional Laboratory at Peoria, Illinois, was to find new uses for the agricultural crops in that area, of which corn was a major one. The laboratories were quite successful in achieving their objective. One new gum, Polysaccharide B 1459, had such interesting properties that several industrial companies investigated the possibility of commercializing it. The Kelco Co. started producing it commercially under the trade names Kelzan (industrial grade) and Keltrol (food grade), while Archer Daniels Midland Co. carried it through advanced development stages as Product 7097 and patented an improved biochemical process for synthesizing it. Two other large companies, Eli Lilly & Co. and Commercial Solvents Corp., also explored the commercial potential of this material for food, drug, and cosmetic applications, but apparently the product did not go into production. The Jersey Production Research Company found the gum to be a very effective water and brine thickening agent for oil well drilling operations and developed a new and novel process for making it.

Gelatin

The above epigraph aptly describes one of the most popular and widely eaten American foods, gelatin desserts. The shimmering, tender texture and brilliant clarity of a quality gelatin dessert have widespread esthetic as well as organoleptic appeal to a broad majority of consumers. And the properties of gelatin that lend themselves to the preparation of such gelled food products are unique and cannot be exactly duplicated by any other hydrocolloid. This has given gelatin a tremendous advantage in the area of packaged dessert mixes, so that today the majority of gelatin produced in this country is used in dessert foods.

Gelatin is defined in the Pharmacopeia as a product obtained by the partial hydrolysis of collagen derived from the skin, white connective tissue and bones of animals. The fact that gelatin is obtained with ease and in relative purity from an abundant starting material probably has much to do with the fact that it has become the classic protein of colloid chemistry, and has been the subject of an enormous amount of experimental work.

Of all the common natural hydrocolloids, gelatin is the only protein of importance, largely because of its novel gelling and thickening properties. Recently, with advances in technology, other protein gums are becoming subjects of interest for the hydrocolloid chemist. The most important of these are the soy proteins, which, like gelatin, also have interesting and exploitable gelling, thickening, and other colloidal properties. Egg albumin, a relatively old protein, is being given new functional properties, which permit its use in a much wider variety of foods. In addition, the milk protein caseinates have been found to have very effective emulsifying and stabilizing properties, while cereal proteins make excellent whipping agents.

However, since gelatin is by far the most important protein hydrocolloid, this chapter will be limited to gelatin.

Background

Gelatin, derived from the Latin verb gelare meaning to congeal, has been known for thousands of years. The extraction of glue by cooking hides dates back at least to the time of the ancient Pharaohs of Egypt. Bogue cites a 3000 year old stone carving, found in the ancient city of Thebes and belonging to the period of Thotines III, which describes the gluing of a thin piece of rare red wood veneer to a yellow plank of sycamore.

Later, in the Roman era, Pliny, Lucretius, and others referred to the manufacture of glue. Pliny wrote, Glue is cooked from the hides of bulls. Elsewhere in his writings he referred to glue, which had been mixed with gums, milk, eggs, and wax as a vehicle for paints, used by the ancient Egyptians. Much later, in the
Elizabethan period, Shakespeare and Bacon made frequent references to glue in their writings. Indeed, a commercial glue industry appears to have been established in England about 1700. A similar industry developed in the United States within the following century.

During the early years of the Napoleonic era, gelatin was manufactured on a large scale in an attempt to alleviate the food shortages resulting from the English Naval blockade of Europe. The first manufacture of edible gelatin is credited to Arney, who was granted a patent in 1846 for the preparation of a powdered gelatin for forming compositions from which may be prepared jellies and blanc manges also, when mixed with falina, or starch, or starchy vegetable flour, for thickening soups, gravies, etc. At present, gelatin is manufactured in the United States by at least eleven companies in the amount of about 60 70 million lb annually.

Collagen

Collagen, which means glue producing material, is the principal protein component of the connective tissues, which serve as the major stress bearing elements for all mammals and fishes. Although much of the collagen is located in major tissues such as skin, tendon, and bone, collagen fibers pervade almost every organ and tissue. Collagen is unique among proteins because of its unusual amino acid composition. It owes its distinctive structure to its high content of the cyclic amino acids, proline and hydroxyproline. In addition to these compounds, collagen also contains large quantities of glycine and alanine, the more common nonpolar amino acids with short side chains.

It is now believed that proteins consist of long chains of amino acids connected through their a amino and a carboxyl groups to form peptide linkages. These chains can be either stretched out or folded. Additional bonds, between adjacent chains or between adjacent parts of the same chain after folding, become a necessary part of the structure and stabilize the functional protein configuration.

The basic collagen polymer unit, sometimes called tropocollagen, is thought to consist of three helical polypeptide chains wound around each other to form a coiled coil, which behaves as a firm, rigid rod. Recent work indicates that irrespective of source, collagen has a molecular weight of about 350,000, a length of 3000Å, and a diameter of about 14Å. As shown in Fig. 1, it has now been established that two types of bonds contribute to the secondary and tertiary structure of collagen: (1) intramolecular cross links existing between the individual chains of the collagen molecules, and (2) intermolecular cross links.

The gross collagen fibers are capable of undergoing considerable mechanical and physical changes, which may vary from reversible swelling and partial, melting to irreversible disorganization of the entire structure. But all these changes occur without solubilization of the fiber.

Transformation of Collagen to Gelatin

Gelatin is the water soluble product of the dissolution or degradation of water insoluble collagen fibers. The transformation or transition of collagen to gelatin is the process whereby the highly organized, quasi crystalline, water insoluble collagen fiber is transformed from an infinite assymetric network of linked tropocollagen units to a system of water soluble, independent molecules with a much lower degree of internal organization. Since the original collagen structures are not all the same, and since there are many paths by which the structure may be broken down, there are obviously a great many varieties of gelatin formed by the destruction of collagen.

The hydrogen bonded configuration of the collagen macromolecule can be broken down by heating collagen solutions in acid to about 40°C. The transition is sharp and complete within a few minutes over a small temperature interval, and the disordered molecule falls apart in one of three ways, as shown in Fig. 2.

1. If there are no additional restraining bonds between chains, three randomly coiled single strand peptide chains result (Path 1). The three chains, known as a chains, are not of identical composition and probably...
2. In those cases (Path 2) where two chains are joined by one or more covalent cross linkages, denaturation leads to the appearance of two particles, one an a chain and the other a two stranded molecule with approximately twice the molecular weight of the a chains. The two stranded b component may be composed of two similar or two dissimilar a chains. The weight distribution would be 67% b and 33% a.

3. In the final case, it can be assumed that at least two covalent cross linkages hold the three chains together. The disordering process (Path 3) melts out and removes all traces of secondary structure, but the three chains cannot separate and remain as a unit in solution. This three chain structure is called the g component.

It is obvious that there is no reason why every molecule of tropocollagen should have the same number of identically disposed intramolecular cross linkages, and thus, it is most reasonable to assume that any given preparation is heterogeneous with respect to the degree of intramolecular polymerization. The ideal conversion of the collagen monomer to gelatin is therefore the one via Path 1. The number average molecular weight of the gelatin system should be one third the molecular weight of the collagen monomer, and the weight average molecular weight should be slightly higher due to the nonidentity of the chains. The best values of the collagen monomer molecular weight are substantially above 300,000, and hence the minimum molecular weight of the parent gelatin must be greater than 100,000. Reports of lower molecular weights for gelatin probably indicate that peptide bond hydrolysis was a factor in those studies. Reports of the a gelatin having molecular weights of about 80,000 are not consistent with recent studies on acid soluble collagen.

Therefore, it can be assumed that native collagen fiber is an ordered array of parallel tropocollagen rods, staggered by approximately one fourth of their length. Each tropocollagen rod is composed of three chains of a character but probably of different chemical composition, and may contain intra tropocollagen cross linkages to produce the b sub unit of two chains or the g units with bonds joining each of the three chains. All g units may not be of the same degree of intramolecular polymerization and may in addition be bonded together with interunit cross linkages to form g polymers.

Manufacture of Gelatin

The bulk of gelatin manufactured is derived from three basic sources and consists of two types of finished gelatin product. Type A gelatin is derived from acid processed materials, primarily pork skin. Type B gelatin is derived from alkaline, or lime processed, materials, primarily cattle hides and bone (ossein). In Europe, a substantial quantity of type A gelatin is made from ossein.

Sources

a. Pig Skins. One of the major sources of gelatin in the United States is pig skins. They are frozen just after removal at the meatpacking plants and delivered to the gelatin plants in refrigerated cars. Since some of the fat remains on the skins, it is preferable to process these by acid pre treatment in order to avoid forming a soapy emulsion that would make extraction of the gelatin extremely difficult.

b. Cattle Hides (Tanners Stock). These are calf or cattle hide trimmings not usable for the manufacture of leather. The whole hides are shipped to tanners and the trimmings from the hides in various stages of the process, before actual tanning, are used by the gelatin manufacturer.

c. Ossein (Bone). Although this is one of the best known gelatin raw materials, it is the one least used in the United States. Ossein is the residue of dried cattle bones remaining after acid pre treatment to remove the calcium phosphate. Even though ossein is a very expensive raw material, if properly processed, it makes an excellent gelatin for photographic use and one that can command higher prices.

Processing
The manufacture of gelatin is shown in the flow diagram in Fig. 3. In general, all gelatin is manufactured by one of the two following processes or modifications thereof.

**Acid Processing (Type A)**

Acid processing is usually based on the use of pig skins and ossein, and the most important commercial acid process in the United States is the preparation of edible gelatin from, frozen pig skins. The pig skins are thawed, washed in cold water, and soaked in approximately 5% solutions of inorganic acids. This plumping process hydrates and swells the skin without causing appreciable solubilization. Hydrochloric acid, sulfuric acid, phosphoric acid, and sulfurous acid are the most frequently used acids. The acid soak usually takes 10 30 hours, after which the supernatent acid is removed and cold water is used to wash away the excess acid and raise the pH of the soaked skins to about pH 4. Most of the noncollagenous proteins have isoelectric points in the pH 4 5 range and are thus most readily coagulated and removed. The acid conditioned skins are then subjected to a series of hot extractions where the two variables are time and temperature. The initial extraction (first run) is carried out for the longest time at the lowest (about 60°C) temperature. The temperature is raised about 5 10°C in each successive extraction and five to ten extractions may be made. In general, the gelatin made from the first extract excels subsequent extracts in gel strength, and each run is kept separate and blended later to match various requirements.

The dilute gelatin extract is pressure filtered and concentrated by vacuum evaporation. The warm concentrated solution is then cooled almost to its gelling point, poured onto a belt conveyor, and immediately conveyed into a refrigeration chamber where it is chilled rapidly until it gels. Upon emerging from a refrigerator chamber as a continuous sheet, it is cut into suitable lengths and placed on wire frames, which are then placed into a drying room or drying tunnel, where the temperature is carefully controlled. Continuous dryers are now in use where both temperature and humidity are controlled. The rate of drying is closely regulated to avoid melting or surface dehydration. When the moisture has been reduced to approximately 10%, the gelatin is removed and ground or pulverized to form the final product. Each batch of dried gelatin is graded and stored separately. Gel strengths and viscosities are the criteria for grading and the different grades of gelatin are blended to give a finished product with the desired specifications.

**Alkali Processing (Type B)**

Bones are initially demineralized with dilute acid to remove the calcium salts, particularly the phosphate, and then both the ossein and cowhides are treated in a similar manner. The raw collagen stock is washed and thoroughly hydrated in cold water in large tanks or pits. Excess water is drained and lime is added in sufficient amounts so that when fresh water is added a saturated solution of calcium hydroxide is formed. An excess of calcium hydroxide must be maintained to make up for the amount consumed in the conditioning reactions. The hides are left in the liming pits for periods of 3 12 weeks or longer, depending upon the nature of the stock, ambient temperature, type of operation, alkalinity of the lime liquors, etc. The lime treatment removes most of the extraneous albuminoids such as globulins, mucopolysaccharides, albumins, as well as carotenes and various other pigments. After liming is complete, the lime is washed from the surface of the stock with running water for a day or so. The residual base is then neutralized by washing with dilute hydrochloric acid until the collagen is deplumped, or until it becomes limp and flaccid. At this point, the collagen has a pH of 5 8 and is ready for conversion to gelatin.

The collagen stock is then loaded into extraction kettles and gelatin is extracted in a series of cooks at successively higher temperatures. The highest quality gelatins are obtained in the first few extractions and the liquors from each cook are filtered, concentrated, and dried separately as for the Type A gelatins. Again, the overall balance of viscosity and gel strength for any particular quality of gelatin is usually achieved by blending gelatins from several different extractions.
Final Products
While all gelatins have similar functional properties, there are differences between the Type A and Type B gelatins, which are important in the selection of the appropriate gelatin for any specific application. These differences in physical properties are shown in Table 1 and will be discussed in more detail in the following sections.

Chemical Composition

Amino Acids
Gelatin consists of 19 amino acids joined by peptide linkages to form long polymer chains. It gives a typical protein reaction and may be hydrolyzed by any of the proteolytic enzymes to yield its constituent amino acid or peptide components. Gelatin is not a nutritionally complete protein in that it is lacking in the essential amino acid, tryptophan. However, it contains a small amount of the rare amino acid hydroxylysine. Gelatins from different sources may exhibit small variations in amino acid composition, as shown in Table 2.

The variations in chemical structure between the Type A and Type B gelatins produce differences in the physical properties, including the isoelectric and isoionic point.

Gelatin is an amphoteric substance, i.e., one that has both acidic (carboxyl) and basic (amino, guanidino) groups. The overall charge of the molecule depends upon the pH of the solution and other ions present. The pH at which the ionization of both the acidic and basic groups are equal is called the isoionic point (pI). At this point, the net charge is zero. If electrolytes are added to the solution, this point may be shifted to a new pH. This new pH, known as the isoelectric point (IEP), is defined as the pH at which gelatin molecules do not migrate in an electrical field (because they are neutrally charged at that point). In some cases, the pI and the IEP are identical.

Ash
Ash yielded by gelatin varies with the type of raw material and the method of manufacture. Type A or pork skin gelatins contain small amounts of chloride, while ossein gelatin contains principally calcium phosphates. The J.P. limit on ash is 2%, but most commercial gelatins have lower ash contents.

Metal Content
The metal content of gelatin is rigidly controlled, and the presence of such materials in gelatins is unlikely unless impure acids or chemicals are used in the process of manufacture. The D.S.P. limit for arsenic is 1 ppm and for heavy metals 50 ppm. Most gelatins meet these requirements without difficulty.

Sulfur Dioxide Content
The addition of sulfur dioxide gives hard gelatin capsules an increased transparency, greater brilliancy, and improved stability all qualities that are desired in capsule manufacture. The J.P. permits not more than 0.004 % sulfur dioxide in most cases, but for gelatin used in capsules, as much as 0.15 % is permitted. However, these are special grade gelatins that are not used in normal food consumption.

Cellulose Gums
The history of hydrocolloids in foods has until very recently been the story of natural materials derived from seaweed extracts, tree and bush exudates, plant seed flours, and similar sources. Almost all these natural materials are polysaccharides or mixtures of polysaccharides. Today a new and growing category of gums, which is still in its infancy, is that of the chemically modified natural gums. Although these man modified polymers are currently only a small fraction of the total gum market (food and industrial) about 100 million lb of the total 3 billion lb of water soluble gums sold domestically they are steadily pressing at the position of the natural gums and enlarging their foothold in the field as newer and better modified hydrocolloids
Proponents of synthetic gums, pointing to the giant advances of organic chemistry, feel that as silk was replaced by nylon, rubber by neoprene, waxes by plastics, so the natural gum polymers are targets for the organic research chemist. Although exact duplications may not be possible, or even desirable, a sufficient number of the functional properties of the natural materials can be reproduced by chemical synthesis or modifications to create marketing opportunities for these new materials.

Modification of inexpensive natural materials such as cellulose and starch yields synthetic gums that have many of the properties of natural gums. They also have the advantages of low cost, steady and inexhaustible supply, constant uniform properties, tailor made functionality designed to meet specific applications, domestic availability, and sometimes new unique properties not available in natural gums. Moreover, pure synthetic gums, derived from the proverbial coal, air, and flame of the ancient alchemists, are also being created, some of which are already being used as food additives. These materials, usually much more expensive to make, offer the promise of completely novel hydrocolloids for new technological breakthroughs.

As starting materials, the organic chemist has available two of nature's cheapest and most abundant raw materials starch, at about $0.06–0.09 per pound, and a cellulose pulp, at about $0.09–0.14 per pound. Both of these readily available polysaccharides are excellent starting materials for the production of gums. They both can be chemically modified easily by heat, oxidation, or chemical treatment. Proper control of the modification makes possible a great variety of products. As Whistler pointed out, it is conceivable that as more is learned about the relationship of structure to the physical properties of polymers, specific gum properties will probably be custom tailored into starch and cellulose molecules so that the properties of the custom made products will more closely match the properties desired in special gum applications. Caution is urged, however. It must be remembered that although sophisticated chemical procedures may modify a polysaccharide to give the desired end product, the materials and processing costs may be so high that the new gums will not be competitive in price with the natural gums. This chemical modification of natural polysaccharides is both a stimulating challenge for industrial chemists and a substantial protective barrier for the lower cost natural gums. It is probable that in the foreseeable future, chemically modified starches and celluloses, as well as the purely synthetic gums, will continually compete with the natural gums for the expanding markets for these materials.

In 1961, as previously mentioned, the traditional market for water-soluble gums was estimated to have been 3 billion lb. Of this total, the largest percentage by far was held by the natural gums, including the starches, whereas only about 100 million lb were composed of the synthetic gums. However, this compilation is not complete, since it does not include data on such hydrocolloids as Gantrez An, Polyox, Carbopol, and other newer and less well known gums. In addition, estimates of the potential market for water-soluble films alone range up to 20 million lbs per year.

In the food industry, the chemically modified and synthetic gums at present occupy a minor role. Of the total market of 100 million lb in 1961, only an estimated 12 million lb was consumed by the food industry. The modified or synthetic gums used in foods were chiefly well established gums such as carboxymethyl cellulose and methylcellulose. The newer chemically synthesized polymers will have a difficult, uphill, and expensive battle to develop markets in the food industry because the stringent Food and Drug Administration regulations require extensive animal feeding tests and experimental assurance of nontoxicity before allowing their use as food additives. As a result, most companies developing water-soluble gums tend to look for industrial applications and strive to develop profitable markets in these nonfood industries before attempting to penetrate the food industry. The ease of penetration or acceptance is, of course, dictated by the novel and unique functional properties offered by the new gum that cannot be matched by the current available ones, or by the simple advantage of a cost reduction or product quality improvement.
In general, the chemically derived hydrocolloids tend to offer some of the following advantages over the natural gums: (1) uniform properties and specifications, (2) stable prices, (3) unlimited availability (not affected by crop failures, labor shortages, etc.), (4) low biological oxygen demand (B.O.D.) (5) domestic products not subject to import fluctuations.

Cellulose Derivatives

Cellulose is the major constituent of most land plants and is the most abundant natural material in the world. Together with the hemicelluloses and lignins, it forms the cell walls and intercellular layers, which are the primary structural support for the plant.

The purest natural cellulose is cotton fibers or linters, which on a dry basis consist of about 98% a cellulose. Wood contains about 40 50%, and together with cotton linters, it is the most important commercial source for raw material cellulose. Agricultural residues, such as corn stalks, corncobs, and wheat straw, contain about 30% cellulose and are available as a vast reservoir of potentially available raw material.

The cellulose molecule is composed of a chain of repeating cellobiose units, each of which consists of two anhydroglucose units it can be more briefly described as a linear polymer of b D glucopyranose (Fig. 1 with R = H).

Physicochemical studies have shown the degree of polymerization of cellulose to be greater than 3000 so that, with the spatial arrangement of the glucose residues, the molecules are long and threadlike. X ray measurements, however, show that in native cellulose, the molecules are aligned to form fibers, some regions of which are highly ordered and have a crystalline structure due to lateral association by hydrogen bonding. The crystalline regions vary in size and represent areas of great mechanical strength and high resistance to attack by chemical reagents and hydrolytic enzymes. The physical and chemical properties of cellulose are largely dependent on the relative amount and arrangement of the crystalline regions. The cellulose molecules tend to remain extended but may normally undergo a degree of turning and twisting. Because of its size and strong associative forces, it can only be brought into solution under certain conditions, usually by chemically modifying the polymer and forming cellulose derivatives. In this way, many diverse and useful functional properties can be imparted to the cellulose molecule.

As with many other notable discoveries, the first chemically modified cellulose polymer was made by accident. Christian Schonbein, a professor of chemistry at the University of Basel in 1846, was conducting some experiments in his kitchen. The flask in which he had been distilling nitric and sulfuric acids, accidentally broke and the corrosive liquid spilled all over the floor. As the story goes, Schonbein, unable to find a mop, wiped up the mess with his wifes cotton apron, which he then washed and hung up over the hot stove to dry. Instead of drying, however, the apron flared up suddenly and disappeared. Schonbein had invented guncotton (cellulose nitrate). This accidental discovery was a major factor in the advances of polymer chemistry and stimulated the development of many other synthetic cellulose derivatives.

The cellulose derivatives commonly encountered in the food industry are ethers in which alkyl or hydroxyalkyl groups have been substituted upon one or more of the three available hydroxy groups in each anhydroglucose unit of the cellulose chain. The effect of the substituent groups is to disorder and spread apart the cellulose chains so that water or other solvents may enter to solvate the chain. By controlling the type and amount (degree) of substitution, it is possible to produce products that have a wide range of functional properties.

In addition to derivatives of cellulose made by chemical substitution, a modified cellulose made by acid hydrolysis has recently been developed that has functional gum properties. This hydrolyzed cellulose, called microcrystalline cellulose or Avicel, has found novel uses in the food industry, primarily in low calorie foods. Although not soluble in water, Avicel has a great water absorptive capacity. Thus it functions as an effective thickening and bodying agent similar to many hydrocolloids.
Properties

Avicel

Cellulose and starch are both condensation polymers of glucose. The differences in linkages between the glucose units however are sufficiently great to cause great differences in properties. Pure cellulose is substantially insoluble in water, while starch can be readily dissolved in hot water. However, recent developments in cellulose technology have led to the preparation of pure a cellulose products, which have hydrophilic properties and which can function as hydrocolloids in various food applications. One of the most important of these products is a microcrystalline a cellulose sold under the trade name of Avicel. The normal a cellulose found in natural plants is a fibrous material, which does not absorb water and is comparatively inert under most conditions, while Avicel, a specially hydrolyzed a cellulose, is nonfibrous and has water absorptive properties.

Avicel is prepared by the acid treatment of a cellulose under special processing conditions, as disclosed by the patent of Battista. By controlled hydrolysis with hydrochloric acid, a cellulose is converted to two components an acid soluble fraction and an acid insoluble fraction. The acid insoluble crystalline residue is washed and separated. It is called cellulose crystallite material or microcrystalline cellulose. Essentially, the amorphous regions of the polymer are hydrolyzed completely, leaving the crystallite regions as isolated microcrystallites, which are defined as the level off degree of polymerization cellulose, or DP cellulose. In other words, if the hydrolysis reaction were continued, the degree of polymerization would not change, indicating that the level off period or limit of reactivity, has been reached. The reported level off DP consists of 15 375 anhydroglucose units, the constituent chains of each aggregate being separate from those of neighboring aggregates. These aggregates are characterized by sharp X ray defraction patterns indicative of a substantially crystalline structure.

The commercially available microcrystalline cellulose comes as a white, fine flour which is low in ash, metals, and soluble organic materials. It is insoluble in water, dilute acid, common organic solvents, and oils. It is partially soluble, with some swelling, in dilute alkali. Table 2 summarizes the chemical and physical properties of this material.

Avicel RC

A major drawback of this Avicel product has been the fact that it requires a great deal of energy to completely disperse and hydrate the dry material. In addition, in many food applications, the incorporation of large amounts of Avicel gives a chalky, drying mouth feel to the food that makes it organoleptically unacceptable.

These drawbacks have been recently overcome by the addition of carboxymethylcellulose to the a cellulose prior to drying the final product. The addition of carboxymethylcellulose improves the functional properties so that the material can hydrate and disperse with comparatively little mechanical effort. It also reduces or eliminates the chalky taste in many food formulations. This new product, whose trade name is Avicel RC, has substantially different properties from the original Avicel. Specifications and properties of Avicel RC are given in Table 3. A great deal of the previous literature describing Avicel applications is not valid for Avicel RC. Therefore a clear cut distinction should be made between these two products in food applications and evaluations.

Food Applications

The main food applications for the original microcrystalline cellulose were described by Trauberman: (1) Avicel in dry form or as a gel can be incorporated as a bulking agent in many food products to effect significant calorie reduction without impairing the palatability or appearance of the food. (2) Avicel dispersed in water produces stable gels containing up to 20% or more of solids. These gels are spreadable, and at
lower concentrations creamy colloidal suspensions can be obtained. (3) In dry form, Avicel is an effective absorbent and can convert oil base foods, such as cheese and peanut butter, and also syrups, such as molasses and honey, to free flowing, granular powders for use in dry package mixes and similar convenience foods.

The primary application proposed for Avicel was as a new ingredient for the control of calories in a wide range of food products. The promotional literature by the manufacturer, Food Machinery Corp., proclaimed Avicel to be a noncaloric ingredient and stated that it contributes functional properties, such as stability, body bulk, opacity, texture, and palatability. These applications were disclosed and illustrated by Battista in a broad spectrum of diversified food uses. They were all basically reduced calorie food compositions. The examples covered are methods and formulations for making a wide variety of low calorie products, such as honey flavored doughnuts, peanut butter cookie dry mix, bran muffins, layer cake, fibrous breakfast food, chocolate pudding, chocolate dessert topping or sauce, soft pudding, peanut butter streusel type crumb topping, low calorie cream salad dressing, imitation butter or margarine, mayonnaise type salad dressing, cheddar cheese spreads, dry mix ice cream, malted milk shake, catsup, caramel candy, and milk chocolate. Avicel RC has novel rheological properties, which makes it useful in the preparation of stable emulsions and suspensions such as pourable salad dressings and chocolate drinks. When properly dispersed, the particles of microcrystalline cellulose and carboxymethyl cellulose form a gel network of weakly bound particles. This gel structure stabilizes and prevents the coalescence of liquid droplets of emulsions as well as the settling out of solid particles in suspensions. If a shear force (such as shaking) is applied to this thixotropic system, some of the bonds break when the yield value is exceeded and the system flows. Upon standing, the gel structure gradually reforms to give the original stable emulsion or suspension. This property can be quite useful in the formulation of many food products.

Canned Shelf Stable Spreads and Salads
A fairly recent development has been the use of Avicel RC in the manufacture of canned salad and spread type products that are sterilized in the container. This application was made possible because of the ability of Avicel stabilized emulsions, such as salad dressings, to withstand sterilization conditions as severe as 240°F for 75 minutes even in the presence of food acids. Discoloration was not experienced except where other heat sensitive substances were present. These salad dressings could be blended at any desired ratios with pieces of chopped meats or vegetables. It is now possible to retort in the container such products as ham spread, chicken salad, tuna salad, salmon salad, potato salad, and macaroni salad. Durkee Famous Foods Co. has marketed a ready to serve canned tuna salad made with Avicel RC.

Salad Dressings
The use of Avicel with water at solids levels of 30 36% gives gel like materials varying in degrees of thixotropy, viscosity, and opacity. These gels make it possible to prepare colloidal spreads containing up to 20% solids or more. These colloidal gels are particularly useful in the formulation of smooth food products such as dressings, spreads, dips, sauces, and aerosol type toppings.

At higher solids contents, the gels have the physical characteristics of animal fats or hydrogenated vegetable oils. Vegetable oils and fats normally used in products similar to mayonnaise or salad dressing can be partially replaced with Avicel, thus reducing the caloric values by more than 50%. By combining the gels with edible oils or fats and using the proper dispersing agent, calorie control foods that taste like sour cream, hollandaise sauce, and cheese dips can easily be made.

One such product, a low calorie salad topping containing 82 % fewer calories, has been marketed by Otto Seidner, Inc., of Westerly, Rhode Island. This product, made with Avicel, contains only 3½ calories per teaspoon instead of the normal 20 per teaspoon.

Frozen Desserts
Frozen desserts with better eating quality, added heat shock stability and improved control of ice crystal formation have been claimed through the use of microcrystalline cellulose. The cellulose particles, a source of solids, are said to give body, bite resistance, and chewiness to frozen desserts. In addition, the added stiffness improves the extrudibility of the products. Avicel RC has been used in ice cream, sherbet, ice milk, soft serve ice cream, and artificially sweetened ice cream. Frozen whipped toppings, especially suited for frozen baked goods have been formulated with Avicel RC. These stable emulsified toppings can withstand several freeze thaw cycles.

**Aerosol Toppings**
Aerosol (foamable) preparations, such as toppings, possessing excellent body, spreadability, and stability, are easily prepared using Avicel RC. The value of Avicel in aerosol or foamed food toppings has been illustrated in a patent by Herald. In addition to reduced caloric content, toppings made with Avicel also have the desirable properties of foam retention (no sagging), smoothness in appearance and eating quality, and a rich mouth feel despite the lower content of fatty materials. In addition, it was claimed that the products after extrusion and foaming do not leak water, collapse, or develop a coarse texture on standing.

**Dairy Type Products**
Avicel RC has found application in the formulation of various synthetic or simulated dairy products. A synthetic product, Sour Kreme dressing, containing 40% less calories than sour cream has been proposed for special dietary needs. A nondairy synthetic cream has been prepared in the form of a stable, white emulsion resembling real cream, yet containing no dairy ingredients. In addition, coffee whiteners made with Avicel RC exhibit superior keeping qualities and an ability to withstand several freeze thaw cycles. A formulated nondairy product, Cheez Spread, which also maintains its texture and consistency through many freeze thaw cycles is made possible by the functional properties of Avicel RC.

**Free Flowing Spreads**
Microcrystalline cellulose, which has a vast surface area because of the many fissures and holes in the submicroscopic surface area, is extremely absorbent, particularly to fatty materials. This function or property makes it possible to convert oily or syrupy products into dry, free flowing powders. It has been suggested that butter flavored mixes can be formulated that will produce smooth, butter flavored, bread spreads upon the addition of water and stirring. By use of other flavors, such as cheese and spices, other flavored spreads may also be prepared.

**Meat Products**
The oil absorbent characteristics of Avicel offer advantages for use in various meat products. When used on the surface of bacon, it was claimed to curb curling and prevent sticking of the slice strip during storage. When used as a coating on each side of hamburger patties, it was claimed to prevent loss, of some of the juices and to reduce shrinkage. A suggested use for the material is in meat products, to be added by housewives or institutional operators to ground meat in preparing meat loaf dishes, sauces, etc. It could also be used as a vehicle for absorbing oily seasonings or flavor components and for incorporating these materials into processed meats.

**Color Fixative**
Natural dyes can be absorbed by the microcrystalline cellulose aggregates. The latter may then be used to carry edible dyes into fat based products, such as butter or margarine, without causing speckling or blooming in the product. Trauberman suggested that since many of the oil soluble dyes have been banned for food use, this application may be helpful for coloring fatty foods with water soluble nontoxic natural
Battista accomplished this by binding suitable colors, lakes, pigments, etc., onto the cellulose crystallite aggregates. These were then used to color various foods, particularly those that tolerate little or no water, such as hard candies, bakery icings, confectionery coatings, cake mixes, and beverage powders.

**Bakery and Pasta Products**

In dry form, Avicel powder, which resembles flour, can be easily incorporated into foods by blending or homogenization. In baked goods, it has been used for the production of low calorie cookies marketed by Weston Biscuit Company. The cookies, sold as Sweet 16 cookies, contain only 16 calories apiece and are fortified with vitamins.

A pasta of Avicel in water can be extruded into ribbons and other shapes. In this way low calorie spaghetti, macaroni, and other products can be made.

**Cloud Agent**

It has been suggested that Avicel can be used as a clouding or opacifying agent for beverages at concentrations of less than 0.5%. This was tried by the Nestle Company in its Keen soft drink powder in order to impart cloudiness to the reconstituted beverage.

**Protective Film**

Avicel also has effective film forming properties. It therefore has been suggested for use as a water soluble, edible protective coating for foods and has been claimed to be particularly suitable for frozen foods such as vegetables, meats, ice cream, confections, butter, and cheese.

**Synthetic Hydrocolloids**

Within the last two or three decades, various synthetic and chemically modified hydrocolloids have been created and investigated. Some of these polymers have replaced older traditional natural gums in various food applications, and increasing commercialization of improved synthetic gums will undoubtedly stimulate competition between these and the natural gums.

There are organic chemists who believe that the day will come when every natural product will be synthesized in the laboratory, and at the same time improved functionally in such a way as to overcome inherent undesirable properties. On the other hand, there are those who believe that synthetic gums will never economically replace the cheaper natural gums such as starch ($0.10 - 0.15 per pound), gum arabic ($0.35 per pound), and guar and locust bean gum ($0.45 per pound), and that at best the semisynthetics (chemically modified starches, cellulosics, etc.) will be the limit of practicality for the synthetic chemist. But in all cases, the economic incentive and specific quality will be the guiding force behind these decisions.

In the synthetic gum field at present, most research efforts seem to be directed toward two objectives: (1) synthesis and development of gums having properties identical to and superior to those of the well known natural gums, and (2) synthesis and development of gums having completely new and novel properties for entirely new and yet undefined applications.

Several completely synthetic gums have been developed which have already been used successfully in the food industry or which have the potential of finding food applications in the future. The main hurdle for employment in foods is the lack of Food and Drug Administration clearance, which is based on lengthy feeding studies, some of which are in progress. But in general, these hydrocolloids have been reported to be nontoxic and must eventually be considered for food applications.

**Polyvinylpyrrolidone (PVP)**

**Background**
Polyvinylpyrrolidone is a comparative newcomer to the field of industrial water soluble polymers. It was developed by W. Reppe in Germany in the late 1930s and was first used during the Second World War as a blood plasma expander. After the war, other uses, primarily in nonfood fields, were developed, and in 1956, the General Aniline and Film Corporation began full scale production of this material in the United States.

Polyvinylpyrrolidone is a polymeric N-vinyl lactam known chemically as poly 1-vinyl-2-pyrrolidone, but more generally as PVP. Its chemical structure is shown in structure I. It is produced commercially by a purely synthetic route involving acetylene, formaldehyde, ammonia, and hydrogen as shown in Eq. (1).

Domestically the General Aniline and Film Corp. produces four different viscosity grades, which are offered in both powder form and aqueous solutions. These differ primarily in molecular weight, as in the tabulation. In addition, special pharmaceutical grades of PVP are available under the trade name Plasdone, and food additive grades are supplied as Polyclar.

At present these materials range in price from a low of about $1.25 per pound to $3.20 per pound for the pharmaceutical injectable grade. It is felt that its physiological inertness and its protective colloid function remain to be exploited in the food field, and that only a fraction of the market potential for PVP has been realized to date. With the growth of markets and long range development of PVP, the price may eventually come down to the range of 60-70 cents per pound and offer severe competition to other water soluble gums in this price range.

Properties
Polyvinylpyrrolidone is very versatile and offers various functional properties for a multitude of applications. It has a wide solubility and compatibility range. It is an excellent protective colloid and suspending agent and has very good film forming properties. It is also a good binder and stabilizing agent and has desirable adhesive properties. It is a complexing agent and can be used for detoxification purposes. The commercial versatility of PVP, which has led to the increasing use of this polymer in a wide variety of fields, is due primarily to the following outstanding properties: (1) wide solubility and compatibility range, (2) complexing and detoxifying ability, (3) physiological acceptability, (4) protective colloid action, (5) film forming ability, (6) adhesive qualities.

Solubility
Polyvinylpyrrolidone is readily soluble in cold water and gives fairly viscous solutions (Fig. 1). With lower molecular weight material, concentrations as high as 60% can be dissolved in aqueous media. The viscosity of PVP is not affected by pH over the broad range of 0-10. Solutions of PVP also have a high tolerance for many inorganic salts, particularly the lower molecular weight types. PVP solutions are stable over long periods if they are protected from mold growth by antimycotics such as sorbic acid.

In comparison with other commercially available water soluble gums, PVP has unusual solubility in organic solvents. It is soluble in the lower alcohols, glycols, nitroparaffins, methylene dichloride, amines, and organic acids, and when it is anhydrous the solubility range is increased to include ketones, esters, and aromatic hydrocarbons.

The complexing action of PVP is demonstrated by its ability to form molecular adducts with other substances. In some cases, the result is a solubilizing action, as with iodine in other cases the result is a precipitating action, as with tannins in beverages.

Film Formation
One of the most unusual properties of PVP is in its film forming nature. PVP can be cast from a variety of solvents to give films that are clear, glossy, and hard at low humidities. They are very hygroscopic and exhibit excellent adhesion to a wide variety of surfaces, such as glass, metals, plastics, and human hair. As
with most water soluble resins, PVP films are hygroscopic and the degree of water absorption is a function of relative humidity. Because of its unique properties, PVP film has found widespread application in the cosmetic field, where it is used extensively in the formulation of various hair sprays and hair fixative preparations. In this field it has also been used in barrier creams, hand cleaners, hand lotions, dentifrices, and shaving preparations as well as in deodorant sprays and after shave lotions. Insoluble films having the same stability, physiological compatibility, and other properties of soluble PVP can be made by reacting PVP with polymeric carboxylic acid compounds.

**Toxicology**

The physiological background of PVP has been well explored because of its earlier uses as a blood plasma extender, and a long history of use has shown it to be essentially a physiologically inert material. PVP is essentially nontoxic when given by oral administration, skin absorption, inhalation, or intravenous or intraperitoneal injection. It is not a primary irritant, skin fatiguing material, or sensitizer and it is nonantigenic.

By definition the acute oral toxicity (LD0) is greater than 100 g per kilogram of body weight. Acute intravenous toxicity (LD50) is equal to 12.15 g per kilogram of body weight. Chronic oral toxicity was also investigated by feeding rats and dogs 1-10% PVP K 30 by weight of their total diet for up to 24 months. No toxic effects or significant pathological changes attributable to the PVP were observed.

**Food Applications**

In the food industry, PVP has found an important application in beverage manufacture as a clarifying agent. It is known that PVP forms insoluble complexes with certain tannins. This property is applied to clarification and chill proofing of vegetable and fruit beverages, such as beer, whiskey, wine, vinegar, and fruit juices. Usually, taste and clarity are improved and other desirable properties are enhanced. The trade name for PVP offered for beverage uses is Polyclar in the United States. PVP has been approved for use as a clarifying agent in beverages under prescribed conditions by Food and Drug Administration.

**Beer**

The use of PVP as a selected precipitant for tannins in beer was discovered. In efforts to find a method of getting rid of the tannins in beer in order to extend shelf life, McFarlane et al. conducted a long search for these selective precipitants. They found that PVP was the most effective and useful. Chill haze is generally regarded as being due to a proteintannin complex formed by a slow reaction between barley protein, b-globulin, and a tannin of unknown structure but probably of high molecular weight. Proteolytic enzymes such as papaïn, the active ingredient of most chill proofing agents, break down and solubilize the protein of the protein tannin complex. The chill stability imparted to the beer by this process may be of a temporary nature, since upon storage for long periods the components of the protein tannin complex may recombine and reform a haze. On the other hand, PVP is concerned with a tannin rather than a protein component, and since PVP removes all the tannins it would appear that selective precipitation will result in a more permanent chill proofing of the beer. McFarlane et al. found that under certain specified conditions PVP permanently removed the chill haze material from beer without harming palate fullness, flavor, or head retention. They found the optimum requirement to be about 1 lb of PVP per 100 barrels but this varied for beers brewed under different conditions. Insufficient PVP failed to give adequate protection, whereas an excess caused the appearance of haze during pasteurization. However, a method was described whereby the optimum amount of PVP for a given beer could be easily determined before proceeding to full scale brewing trials. In addition, the use of PVP to remove these tannins improved taste and taste stability, foam retention, chill haze stability, and filtration ease, and gave cleaner worts from the cooler, cleaner, better tasting storage beer, shorter storage time, a saving on hops, and lower enzymatic chill proof requirements.
The optimum amount of PVP used generally falls within the range of 120 200 parts per million, or about 3 5 lb of PVP per 100 barrels of beer but the optimum must be determined experimentally for a given brewery. The usual practice in breweries is to boil the malt cereals and hops with water for a specified period, after which the hot liquid, called hot wort, is strained free of hops. It is recommended that the PVP be added a few minutes before the end of the kettle boil. At this stage, the PVP content after filtration of the finished beer is properly zero (less than 1 ppm). A different mechanism for preventing chillhaze takes advantage of the observation that a large excess of PVP (an extra 100 200 ppm) forms a soluble complex with the critical materials.

The preferred PVPs for preventing chill hazes in beer are the ones with molecular weights of less than 30,000. They are used at a level of less than 2lb per 100 barrels. Stone, in a later patent, claimed that McFarlanes clarification procedure could be improved by using the low molecular weight PVP polymers ( K 15), or copolymers of PVP with olefinic compounds such as vinyl acetate or vinyl alcohol. These additives would stabilize the beer or ale without causing precipitation of the protein tannin complex.

Hoggan reported a unique advance in brewing technology involving the use of an insoluble form of PVP. This material (once known as AT 496, now called Polyclar AT), is reported to have the advantages of water soluble PVP, such as the high selectivity for tannins (anthocyanogens), without the disadvantages that may be associated with the presence of residual PVP in the finished beer. In addition, it appears to possess a particular affinity for the part of the anthocyanogens that combine specifically with protein to form chill haze materials. Other advantages stated are that Polyclar AT did not absorb bittering substances and that there is no effect on the foam properties of treated beer. In addition, copper content is reduced significantly and the flavor is not adversely affected. In fact, it was reported that beers treated with Polyclar AT possess less astringent after bitterness, which seems to help accentuate the bitterness associated with the isohumulones. The levels recommended are about 3 4 lb per 100 barrels.

Berntsson showed that the haze forming constituents in beverages are precipitated by the use of 0 8 g PVP per hectoliter of beverage, with the preferred PVP having a molecular weight of 7,500 40,000. General developments in this field led to the production and sale of a specialized PVP product, Polyclar H, for use in the fining and stabilizing of beer (General Aniline and Film Corp., 1958). Polyclar H, currently sold by the General Aniline and Film Corporation for specific use as a clarifying and stabilizing agent for the brewing industry, is claimed to contribute the following desirable attributes: (1) markedly increases the amount of trub removed as hot break (2) modifies the characteristics of trub, facilitating removal by decanting, filtering, or centrifuging (3) reduces potential haze materials in the beer (4) significantly reduces the amount of chill proof required (5) enhances the flavor and foam properties of finished beer (6) improves the clarity and stability of beer (7) exerts a hop sparing action (8) improves stability to taste.

More recent developments have led to the use of the insoluble, cross linked form of PVP (Polyclar AT) as a clarifying and stabilizing agent for beer and also wine, whiskey, fruit juices, and tea. Sucietto used a combination of cross linked PVP and activated charcoal to render aged distilled whiskeys haze resistant.
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