PHYSICAL

FUNCTIONS OF

HYDROCOLLOIDS

A collection of papers comprising the
Symposium on Physical Functions of Hydrocolloids,
presented before the Divisions of Agricultural
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Physical Functions of Hydrocolloids

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I N ALL times, ancient or present, men have jealously guarded trading advantages. These advantages might be in the physical possession of a commodity or position, or in some unique knowledge. A commodity or position can be acquired by chance or by force and maintained only by force. Knowledge acquired by chance or by diligent, intelligent search is a more peacefully maintained possession. Whether known as skill, trade secret, know-how, or working formula, its possessor cannot be deprived of that knowledge by force. He can, however, lose his trading position by a surfeit of his particular commodity or to a superior knowledge. Thus, traders in commodities based on skill or secret information tend to repress training and study in their fields. This is particularly true when the general advance of academic knowledge has not approached the area involved and where exercise of the skill or knowledge cannot be learned from observation or study of the product produced.

The use of hydrophylic colloids, vegetable gums, stabilizers—call them what you will—falls in this category. The achievement of a texture, a feel, an appearance, a unique physical system, are trade advantages worth holding.

These papers are presented, partly, because some of the outs would like to be in on the know-how, and some of the ins would like to be "in-er." That desire in itself could not produce a worthwhile report, unless those with the secret information realize that the gradual advance of systematic knowledge to their area can make these papers productive. The amount of information revealed will be governed by the extent of their awareness that the tide of general knowledge has reached a point where they benefit more from their contribution than they lose from their revelation. Through the agency of the food and drug laws requiring ingredient declarations on labels, the food-producing industry has perhaps been forced closest to this point. The heavy participation of food industry members is not without meaning.

The subject matter has been divided into 6 broad physical functions:

    Production of viscosity or body
    Gelation
    Stabilization of emulsions
    Stabilization of suspensions
    Stabilization of foams
    Control of crystal growth

Although there seem to be definite categories, there is an amazing degree of interrelation between these functions. Viscosity alters a gel structure. A

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gel structure, in turn, affects viscosity. The difference between an emulsion, a suspension, and a foam is that of a solid compared to a liquid as compared to a gas, but whichever way one looks or stands, the ramifications of flow and gelation are involved.
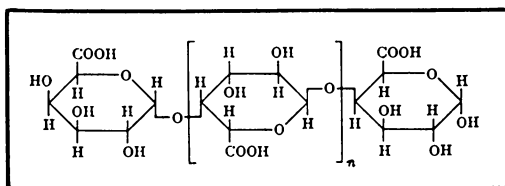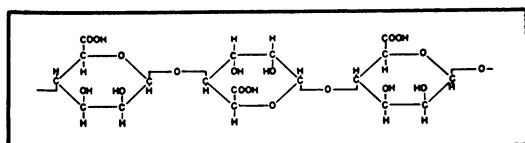
In all these papers certain names of hydrocolloids—gums, starches, mucilages—constantly recur.

A list of some of the more common, commercially available hydrocolloids, their names, and their structural formulas, as far as they are known, has been prepared for ready reference and is given below. Several of these formulas have been reproduced from the book, "Industrial Gums," through the courtesy of Academic Press.
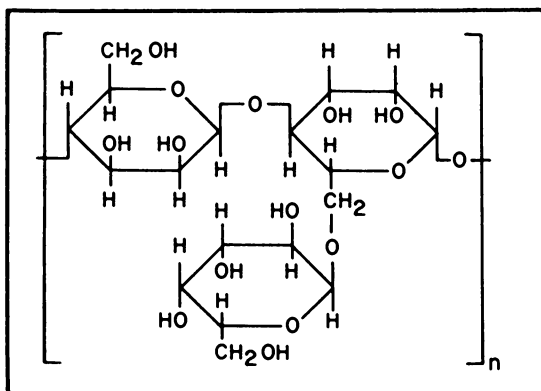
Guaran or Locust Bean Gum

Alginic Acid

Pectic Acid
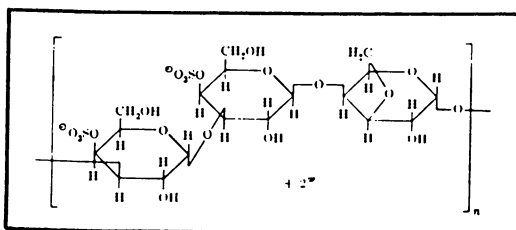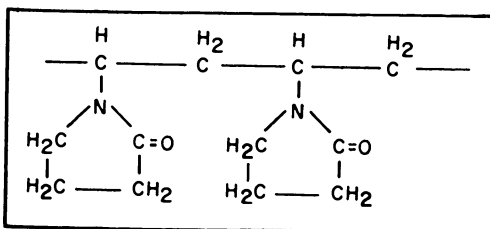

Gum Arabic

X = L-RHAMNOPYRANOSE OR L-ARABOFURANOSE
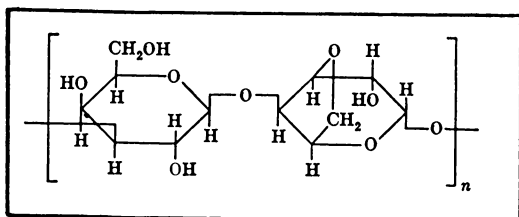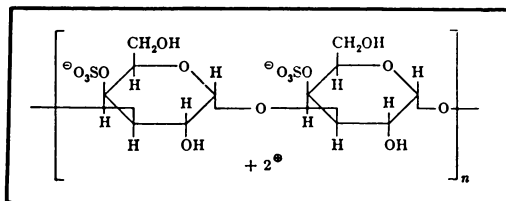GALP = GALACTOPYRANOSE
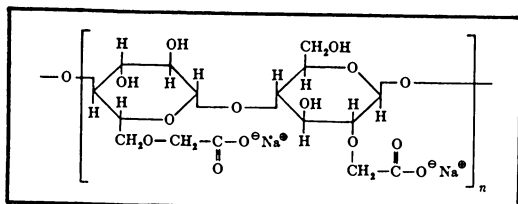GA = GLUCURONIC ACID
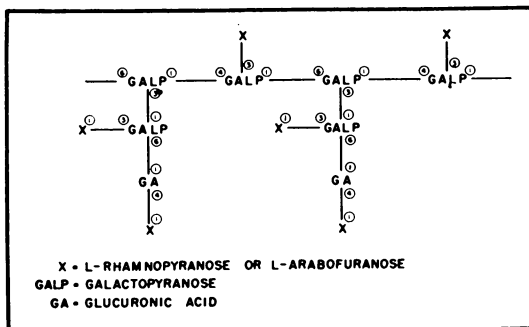
Poly-N-vinyl Pyrrolidone

Kappa Fraction
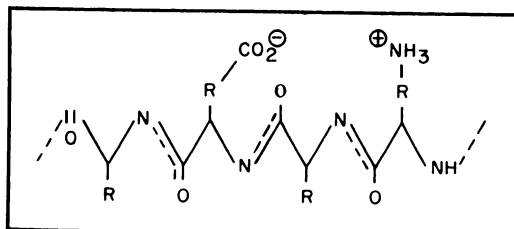
CARRAGEENAN

Lambda Fraction

Agar

Sodium Carboxymethylcellulose

Protein

The Practical Aspects of Viscosities of Natural Gums

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The viscosity of natural gums, such as cellulose gums, mannogalactans, seaweed, pectin, locust bean gum, guar gum, and tragacanth has important industrial applications in the food, pharmaceutical, cosmetic, textile, adhesives, and paint fields. The characteristics of viscosity are related to specific uses and to the economics of the process.

As distinct from the gelling properties of certain natural gums, usually exhibited by structural rigidity, viscosity is a thickening of the aqueous portion of a system by means of particle water absorption, and swelling of the colloid. From a practical angle, it manifests itself by the phenomena of thickening and reduced flow characteristics.

Some of the principal applications of this increased viscosity of the aqueous medium, due to the swelling of the natural gums, can be broadly classified as follows:

1. Restriction of flow, per se
2. Enhancement of the setting characteristics of other natural gums
3. Modification of the gelling characteristics of certain water-soluble colloids
4. Protection of emulsions
5. Suspension of a solid in an aqueous phase
6. Enhancement of the texture of a product

Because of greater familiarity with the incidence of these characteristics in the food industries, many of the illustrations of these phenomena will necessarily relate to that field.

Restriction of flow is one of the more important commercial functions of viscosity. For this purpose, which largely depends upon particle hydration, the mannogalactans and cellulose gums are usually found most economical. It is important, of course, to make a distinction here between restriction and stoppage of flow, the latter being accomplished to best advantage by the seaweeds, pectin, and gelatin. Locust bean gum, in concentrations from 0.4 to 2%, based upon the weight of the water in the system, competes with starch, because below the actual gelation points, it provides approximately five times the viscosity of most of the common starches. Guar gum and the cellulose gums, although somewhat more expensive, have the advantage of swelling at lower temperatures.

Considerable locust bean gum is used in pie filling preparations for thickening purposes. This is especially true of fruit-type fillings, because while preventing the flow of the filling from the shell, it also yields a clearer, more fruit-like filling, which is more palatable than the customary starch filling, in that it does not disguise flavor to as great a degree. Based upon the weight of the fruit juice and water of the filling, from 1 to 2% of locust bean gum suffices for this purpose. Recently, some of the larger pie bakers have also been experimenting with cellulose gums as pie filling stabilizers. In the custard-type pie fillings, where milk solids are an essential ingredient, the Irish moss extracts become very economical thickeners, because of the small quantity required, which varies from 0.03 to 0.1% of the filling.

Many cosmetic lotions of the type which are primarily solutions of an emollient, such as glycerol, are thickened by means of one of the vegetable gums. Tragacanth, arabic, and quince seed extract have been widely used, because they form somewhat smoother dispersions than the mannogalactans, and they exhibit, in dilute concentrations, less tendency toward striation. More recently, Irish moss extract, carboxymethylcellulose, and the various soluble alginates have been found to be applicable for this type of thickening. The product can still be dispensed from the container, with the use of the gums, in the range of 0.2 to 0.5%, the lotion attaining better appeal as far as consistency is concerned and being more easily kept at the desired point of contact with the skin.

The thickening effect of the gums can be put to good use in depilatory formulations. The viscosity imparted by the use of a hydrophillic colloid not only aids in retaining the ointment within the desired area of application, but also prevents it from being in too close contact with the skin. In this respect, part of the danger of skin irritation is avoided and the chemical action of the reducing agent, such as barium sulfide or stannous oxide, is consequently more easily controlled. For this purpose, a nonadhesive gum, such as locust bean gum, is to be preferred to one of the more sticky type, such as arabic. This field of utilization of a colloid, which entails control of the chemical action of a pharmaceutical or cosmetic paste by gum viscosity, has not been investigated very thoroughly, and offers distinct future possibilities.

Along the same lines, still in the cosmetic field, the gums are often used in waterless hand cleaners of the nonemulsion type, to provide the necessary viscosity for convenient application. These cleaners are essentially solutions of detergents and the most popular thickeners are the cellulose gums, which are stable in neutral or slightly alkaline media. The vegetable gums are also used in emulsion-type waterless hand cleaners, as emulsion stabilizers, rather than as simple viscosity agents.

In the printing and dyeing of textiles, the vegetable gums have a desirable thickening effect upon the dye solution, enhancing the evenness of application and enabling a sharper impression to be obtained when printing. Locust bean gum and gum karaya, as well as arabic, tragacanth, Irish moss extract, and sodium alginate have been used for this purpose. For the higher viscosity gums, solutions in the range of 0.5 to 2% are employed; in the case of gum arabic, from 20 to 40% solutions are required. As in all textile operations, the gums must compete with the starches and starch products, which are very economical thickeners. It is difficult to find, anywhere in the literature, a systematic study of the relative merits of the various common colloids, even though a great deal of empirical work has been done with them in this field.

Gum arabic, once widely used for adhesives of the aqueous type, has been replaced, in nearly all instances, by the less costly starch degradation products. Here, the arabic was not incorporated for viscosity purposes, but rather as a source of adhesive solids. However, with the advent of newer types of ad hesives, such as those of the proteinaceous, resinous, and latex varieties, there is, again, considerable interest in the application of the natural gums, this time for their thickening effect, because these types of adhesive materials, in them-selves, are not very viscous. The water-soluble gum, most applicable to any particular case, will depend to a large extent upon the type of adhesive being formulated. The mannogalactans are good general thickeners, the seaweed gums are desirable where proteins are used, while the cellulose gums are efficient in adhesives with high pH values.

In the food field, locust bean gum, the cellulose gums, and at times, one of the seaweed derivatives, are occasionally used to thicken soups. The usual range of gum concentration employed is from 0.2 to 0.6%. In the simple thickening of sauces, gum tragacanth or propylene glycol alginate is preferred because of their acid resistance, desirable texture, and flow characteristics. In dog foods, guar seed gum is preferred because it provides sufficient viscosity to retain the homogeneity of the product during processing, as well as prevent-ing fat separation or "leakage." Guar seed gum gelatinizes at lower tempera-tures than locust bean gum and, consequently, provides the necessary viscosity before sterilization of dog food, thus enabling the processor to obtain good distribution of ingredients while filling. Gums, as thickeners, are incorporated in many breading mixes, so that they do not "run" on fish or meat. Water absorption is also sufficiently improved so that the addition of water to the dry breading mix is not critical. Because a cold water swelling colloid is pre-ferred—this type of product being competitive costwise—the most common stabilizers are carboxymethylcellulose and guar seed gum, to the extent of about 0.25%.

For this purpose, as well as for many other food uses, the vegetable gums, as a group, are often preferred to the starches, especially those of the cereal variety, because they do not tend to retrograde at low temperatures, as do these starches. Consequently, with the increasing popularity of frozen food prod-ucts, the water-soluble gums are in greater demand.

The water-absorption characteristics of certain vegetable gums, as evi-denced by their viscosities, are often used to enhance the setting characteristics of certain gelling agents, such as agar, Irish moss extract, and pectin. Theoreti-cal studies indicate that this effect is more than additive, although experi-mental comparisons of this type are of a difficult nature, because they involve combinations of varying types of colloidal behavior. At any rate, from a practical angle, the phenomenon is of considerable interest and value. Locust bean gum, in particular, markedly increases the gel strength of pectin, agar, and especially of an Irish moss–potassium salt complex. Guar seed gum exhibits somewhat the same effect. This enhancement of gel structure by use of the simple viscosity, or water-absorption properties of another gum, is largely utilized in the food field. Meringue stabilizers, pie filling stabilizers, and ice cream stabilizers, are all based on such combinations. Not only is the gel structure improved by the addition of the viscosity-producing gum, but the eating qualities are enhanced as well. The latter factor has led to unsuc-cessful combinations in candy jellies, where, usually, the gelling agents alone are used. The difficulty probably lies in the high sugar content of these candies,

which tends to dehydrate the gum of the viscous type. However, with the advent of diabetic, or dietetic, types of low sugar content candies, interest in this problem has been revived.

The gums, which predominantly impart viscosity, not only enhance the setting properties of other of the water-soluble colloids, but at times, modify them distinctly. In the case of pectin gels, use of a cellulose gum or sodium alginate materially decreases the sharpness of gelation and imparts more smoothness and workability to the finished product. Gum arabic likewise has something of a softening effect upon agar gels, and proportions of the colloids must be carefully controlled. In marshmallow stabilization, where agar is often used, addition of gum arabic provides a tenderer and more edible confection.

The viscosity function of the natural gums is utilized in both oil in water and water in oil emulsions. Often the gums are referred to as emulsifying agents. They are considered not so much as emulsifiers, but rather as emulsion protectors or stabilizers. To a large extent, the function is to increase the viscosity of the aqueous phase so that it approaches, or slightly exceeds, that of the oil; hence, there is less tendency for the two phases, once emulsified, to separate by mechanical slippage.

In the pharmaceutical field, agar is commonly the base colloid for stabilizing mineral oil in water emulsions, used for laxative purposes. The concentration of agar is kept below the gel point, so that the emulsion will pour. Other gums, like tragacanth, Irish moss extract, or carboxymethylcellulose, may replace the agar, where desired. Usually, from 0.5 to 0.8% of the gum, based upon the weight of the aqueous phase, suffices to protect this type of emulsion, which is somewhat of a neutral variety.

Hand lotions, of the emulsion type, are also, in most cases, oil in water emulsions. A true emulsifying agent is usually used to form the emulsion and for cleansing properties. Vegetable gums, like tragacanth or Irish moss extract, are added, not only to stabilize the emulsion but to increase the emollient properties, because of the added viscosity effect.

Similarly, in the food industry, French dressings are typical examples of oil in water emulsions that are prepared by mechanical means, but are stabilized by the viscosity obtained through the use of a vegetable colloid. Initially, gum tragacanth was the basic gum used for this purpose. More recently, certain seaweed derivatives, particularly propylene glycol alginate, have been put to good use. The quantity of gum used is approximately 0.8% of the weight of the aqueous phase, or about 1 ounce to every gallon of water and vinegar in the French dressing. The gum is dissolved in the aqueous phase and the oil is mechanically emulsified by use of a colloid mill or homogenizer. It is important to gelatinize the colloid fully before final emulsification, or good stabilization will not be secured. In the cases of tragacanth and propylene glycol alginate, the usual procedure is first to inhibit lumping of the gum by wetting it out with a small portion of the oil, and then thoroughly dissolving it in the water, either by heating, with agitation, to 160° F. for 20 minutes, or by allowing the solution to stand overnight, with occasional stirring, before use.

Flavor emulsions are similarly stabilized by the viscosity produced upon addition of a vegetable gum, such as tragacanth, Irish moss extract, arabic, a cellulose gum, or one of the alginates, to the aqueous phase. Here the oil phase, in the form of the flavor, is in small proportion to the water. In the absence of the acetic acid, contained in the vinegar of the French dressing,

another preservative, such as sodium benzoate, is used to increase the shelf life of the product.

Salad dressings, on the other hand, are essentially stabilized by a starch, rather than a vegetable gum, for reasons of economy, production methods, and shelf life. Here, basically, the technology of the vegetable gums has, up to the present time, failed. However, in innumerable cases, a small percentage of locust bean gum is used in conjunction with the starch, acting as a reserve carbohydrate. If two identical salad dressings are prepared, one with and the other without the addition of the gum, very little difference in viscosity is noted, immediately after preparation. Then, upon storage, a slow syneresis, or thinning, of the starch dressing can be observed, and the loss of viscosity becomes noticeable. On the other hand, the salad dressing containing the locust bean gum retains its body, the vegetable gum seemingly gaining viscosity as the starch thins. Apparently, the gum, as a secondary colloid, inhibits breakdown and weepage by slow gelation. From 2 to 3% of locust bean gum, based upon the weight of the starch, is the usual quantity used in salad dressing, and the gum, admixed with the starch, is cooked with it, to form the starch paste.

The functional viscosity of the gums is also widely used to suspend solids in an aqueous medium. This can be considered as solid phase emulsification. As little as 0.03 to 0.05% of Irish moss extract will retain cocoa solids in suspension in chocolate sirup; this colloid is specific for the purpose, even in the absence of milk solids. Many chocolate-flavored fountain sirups are stabilized in this manner, which prevents the cocoa from settling and packing at the bottom of the container.

In similar concentrations, Irish moss extract, by virtue of its peculiar thickening properties in the presence of many proteins, has been advantageously used to suspend the milk solids in buttermilk and yogurt.

The utilization of the vegetable gums, especially those with good film-forming properties, to suspend the solids in paints of the casein and emulsion types, still offers a wide field for experimentation and application.

Huge quantities of the mannogalactans are used in the paper industry. One of the several functions of the gum is to suspend the paper pulp solids uniformly, partly because of the viscosity imparted by the colloid. Uniform sheet deposition is also enhanced.

Along the same lines, the cellulose gums find application in detergent compositions, because they are especially useful in alkaline media. While detergents are good wetting agents, their solutions are not as viscous as those of soaps and soil redeposition becomes very troublesome. Addition of a colloid to increase the viscosity of the wash water helps hold the dirt in suspension, preventing redeposition upon the material to be cleansed. Carboxymethylcellulose, the most popular of the gums for this purpose, is used to the extent of approximately 2% of the detergent. Here, the colloid must not only gelatinize over a fairly wide temperature range, but do so rapidly.

In a sense, the use of vegetable gums as toothpaste binders is due to their water absorption or viscous properties. Although in paste form, this is still essentially a matter of suspending the solids, in the form of finely divided abrasives like calcium phosphate, or chalk, in an aqueous medium of water and glycerol. The gum is gelatinized in the water and glycerol, and the solids are then incorporated. Formerly, gum tragacanth was the principal colloid used for this purpose, because it aided uniform flow of the paste from the

tube and onto the brush. Shelf life of pastes, prepared with gum tragacanth, was also good. Now the trend is toward the use of seaweed derivatives, like Irish moss extract and sodium alginate, as well as the cellulose gums. Tragacanth imparts a slightly stringy characteristic to the toothpaste which was once preferred for spreading purposes; the latter gums yield "shorter" pastes, which rinse more easily from the brush and mouth. Irish moss extract is particulary good in this respect.

The texture, or the eating qualities, of many foods are enhanced by the viscosity of a natural gum. Locust bean gum, guar gum, alginate, or carboxymethylcellulose from 0.07 to 0.12% in ice cream imparts a desirable "chewey" quality. Similarly, very few cheese spreads are prepared without the addition of some locust bean gum, usually about 0.6%. These spreads, essentially mixtures of a flavor cheese, nonfat milk solids, added flavoring, and water, would be thin, watery, and extremely unpalatable, without the viscosity provided by the colloid. The gum is pasteurized with the other ingredients, homogenized, and packaged. The processed cheese spread is then sterilized in the package, as far as practically possible.

Similarly, the use of Irish moss extract, as the suspending agent in chocolate milk, has, through the additional thickening of the drink, educated the public to expect and to enjoy a more viscous type of chocolate-flavored dairy drink. Consequently, should a method be devised to stabilize the drink properly without increasing its viscosity, it is probable that it would be considered insufficiently "rich" and deemed unpalatable.

One of the chief reasons for using a colloid, in all cases of thickening, is to prevent bleeding, weeping, or product separation. This is probably the reason for so often designating the water-soluble gums as stabilizers. The viscosity factor, of course, is only part of the stabilization process, the actual setting properties being the other.

Thus, while it is impossible to separate the viscosity and the gelling functions of the gums completely, because to a certain extent these functions depend upon "use" concentrations, viscosity alone plays an important role in the industrial field.

Some Aspects of Hydrocolloid Gelation

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The nature of gels has been the subject of much study with respect to imbibition, syneresis, elasticity, and fundamental gel structure. Multiplicity of sites on a long chain is necessary for gel formation, but other factors determine the nature of the gel. Flexibility of the chain imparts rubberiness and ability to imbibe solvent. Gelation is induced from a sol in many ways. The phenomena of gelation are best illustrated by representative systems. Borax-type gels exhibit peculiarities due to their state of dynamic equilibrium. Unusual gels, valuable for coatings, are formed with poly(vinyl alcohol) and certain types of phenols. The hydrocolloid with the strongest known gelling properties is extracted from the red alga *Hypnea musciformis*. The gelling and setting properties of this extract can be readily altered. Carrageenan, extracted from Irish moss, yields gels with potassium ion. Sodium alginate, an extract from any of the several types of brown algae, forms useful gels with calcium under controlled conditions. Pectin is unusual in that it is the basis for two different types of gelling systems: gels (with calcium ion) and jellies (with sugar).

Gels are dual-natured substances, because they exhibit properties that are typical of both liquids and solids. Thus, while they display vapor pressure, compressibility, and electrical conductivity typical of liquids, they may also show rigidity commonly associated with solids. This unusual combination of properties is caused by the physical structure of the gels: long-chain molecules linked by primary or secondary bonds at widely separated sites along the molecule (9).

It is convenient to classify gels into two categories: elastic and nonelastic. Elastic gels—e.g., gelatin—can be partially dehydrated to give typically elastic solids. Replacement of the lost water, sometimes with heating, readily regenerates the original gel. Hence, the gel system can be considered as reversible. On the other hand, nonelastic gels—e.g., silica gel—are nonreversible. Such

gels become glassy or crumble into a powder upon dehydration and cannot be regenerated by the simple addition of water.

The start of gelation is first manifested by the gradual decrease in Brownian movement. This may be caused by the hydration and coherence of the particles, as long-range forces between molecules begin to exert their actions. The viscosity begins to increase and the solvent is immobilized or absorbed by the swelling solute. As the action continues, a three-dimensional network is gradually built up containing "pores" of solvent. At the gel point, the rigidity is still small and most of the polymerizable material is still in monomeric, dimeric, and trimeric form. As the reaction proceeds, the smaller fragments continue to react with each other to form what is essentially one large molecule. The rigidity may become considerable at this point. Parts of the large molecule can still further react with other parts to form more cross links and thus increase the rigidity. If the molecular segments between linking points are relatively long and flexible, the gel tends to be rubbery and to have a greater tendency to imbibe solvent. It is apparent that in order to form a gel, the monomer units must possess a functionality of three or more, because difunctional molecules will lead to linear structures that cannot build up the necessary three-dimensional structure.

In general, gelling may be brought about by increasing or fostering the forces between solute molecules. This may be accomplished by:

Adding a nonsolvent
Allowing a "good" solvent to evaporate
Changing the temperature
Adding a cross-linking agent
Lowering the solubility of the solute by adding a substance that reacts with it
Changing the pH

These methods approach gelation from the sol state. A gel may also be obtained from the solid state. If solid gelatin is immersed in water, it will imbibe enough solvent to form a gel. Hence, it should be realized that a gel is an intermediate state of hydration between a sol and a solid.

Gels exhibit many unusual characteristics. One of the most interesting of these is the phenomenon of imbibition. A typical gel can imbibe many times its volume of water without loss of gel properties. The resulting swelling can produce considerable pressure. Imbibition is strongly affected by the presence of electrolytes, hydrogen bond formers, and hydrogen bond inhibitors. Anions such as sulfate, tartrate, citrate, and acetate are antagonistic to imbibition; while chloride, chlorate, nitrate, bromide, iodide, and thiocyanate enhance it, with increasing effectiveness. Thus, while the effect of the chloride ion is small, the addition of iodide or thiocyanate ions can cause a gel to disperse and to form a sol without heating the mixture.

Many organic compounds are known which are effective as imbibition agents. Typical of these are the hydroxybenzoic acids; the ortho has been found most useful. Even more efficacious is acetyl tryptophan (7). With all swelling agents, pH is an important factor and the least swelling occurs in the region of the isoelectric point. Syneresis, typical of many gel systems, is an exudation of liquid as the gel contracts. Both elastic and nonelastic gels may show this phenomenon. No rigid rule can be set up on gel concentration *vs.* syneresis. The total volume of the system, usually, does not change during syneresis; hence, syneresis is not to be considered the reverse of imbibition.

Katti (*18*) investigated, by a light-scattering technique, the gelling of agar,

gelatin, cellulose acetate, and other sols. He found that the gelation of lyophilic sols occurred in three steps:

The viscosity increases with no change in size or shape of the molecules.
The particles grow and become symmetrical, because the liquid enters the particles.
Particles continue to grow, but become unsymmetrical, because of aggregation.

Flory (8) states that gelled, insoluble products are formed by the intermolecular reaction of units which are trifunctional or higher. An infinite network structure is formed; however, it is limited only by the volume of the reaction mixture. The monomer size controls the rate of reaction.

The phenomenon of gelation is best understood by examining some typical gelling systems. Inasmuch as each gel presents peculiarities of its own, it is impossible to discuss every type available. The systems chosen for discussion show properties that illustrate important gel characteristics.

Borax Gels

Borax-type gels are of considerable interest, as they exhibit the phenomenon of dynamic equilibrium. Compounds which contain cis-hydroxy groups form complexes with boric acid and borates. When the compounds are of high molecular weight, the complex may form as a three-dimensional network (5). Many common hydrophilic gums such as locust bean gum (6), guar (39), poly(vinyl alcohol), algins, pectins, gum arabic, starch, hemicelluloses (consisting of sugars which contain cis-1,2-diols—rhamnose, mannose, galactose), and carbohydrate ethers (28) (the reaction product of galactomannans or glucomannans with glycerol monochlorohydrin), form gels with boric acid and borates (Figure 1). Borax gels form most readily in weakly alkaline solutions and are usually cleaved by acids or by strong alkali. The bonds forming the gels are in a state of dynamic equilibrium, which explains the rapid reformation of the gel when it has been mechanically broken. No syneresis occurs during this process.
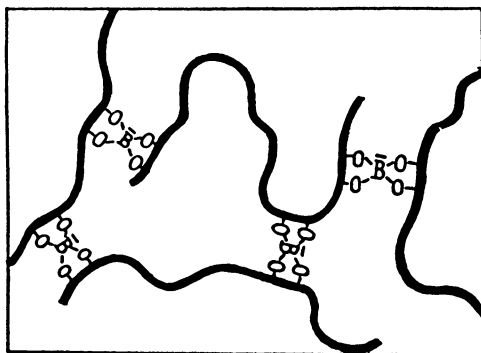

Figure 1. Cross linking of chain molecules of locust bean gum by borax (6)

The system has been used as an analytical tool (4), because the complex formed shows greater conductivity than the sum of the conductivities of the boric acid and the diol compound. Favorably situated diols have a pronounced effect in increasing the conductivity. cis-1,2-Diols fixed in position by molecular structure—e.g., o-dihydroxyphenols and cis-dicyclic polyols—are "favorable" structures. The reaction is depicted in Figure 2.
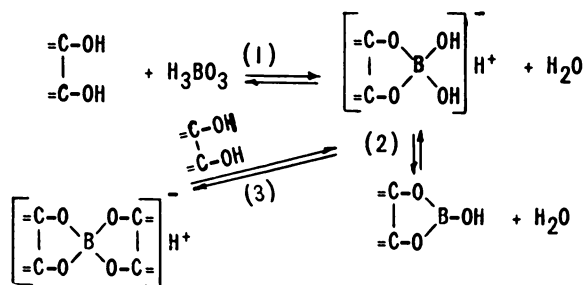
Figure 2. Mechanism of complex formation of diols by borates

1. Goes much to the right
2. Depends upon position of hydroxyls. The final product, a spirane, is a bis-diol boric acid, a fairly strong acid (4)

Alginate Gels

Algin is widely used as a viscosity promoter and gelling agent in many fields. It is generally used as sodium alginate, the sodium salt of the linear polymer of the anhydro-β-D-mannuronic acid. Each unit has a free carboxyl radical, two free hydroxyl groups, and a blocked aldehyde group (37). Gels are readily formed with acids and calcium salts. The ratio of calcium to sodium, pH, and the algin concentration are all important factors in the production of a good gel. The ester of propylene glycol (50 to 75% esterified) has been prepared; it is nonacid-precipitable, and forms soft calcium gels at high pH values (37).

The principle behind the gelling of algin is one of "slow precipitation." In order to get a firm, elastic gel, the precipitating agent must be uniformly distributed throughout the system. The gelling tendency of algin is so strong that as little as 0.1% alginate can form a gel. Table jellies can be made from 0.5% of a mixture of calcium alginate and alginic acid (22).

It is believed that an alginate gel consists essentially of an insoluble alginate in a highly hydrated form. On the molecular scale, there is a randomly oriented network of alginate chains, probably held together at widely separated points by partly electrostatic and partly covalent forces originating from the incomplete ionization of the polyvalent salts, and from hydrogen bonding. These alginate chains, held together, are prevented from free motion. Water is entrapped in the relatively large spaces between the chains.

Thiele and Anderson (38) have studied the effect of variables—the nature of the ion and the degree of polymerization of the alginate—on the extent of orientation in the gel. Gels showing a highly oriented structure may be prepared by allowing the precipitating ions to diffuse slowly into a solution of sodium alginate.

The usual method of preparing alginate gels is to obtain an intimate mixture of the reactants before the formation of the insoluble alginate begins; hence practical gel formation depends on slowing down the precipitation reaction. This may be done by adding sparingly soluble salts, or by slowly releasing an acid—for example, by the combination of formaldehyde with ammonium ions, or the hydrolysis of glucono-δ-lactone (23).

Alginate gels, formed chemically, do not melt upon heating and are stable up to the boiling point of water. They can be liquefied by chemical reactions that will convert the alginate into a soluble salt.

The rigidity of a calcium alginate gel may be influenced by the species of seaweed from which the alginate was obtained. Alginates prepared from *Laminaria cloustonii* will give rigid gels that break sharply after a relatively small deformation. Alginates from *Ascophyllum nodosum* will produce less rigid gels which can be deformed to a greater extent without breaking.

Gelation of Poly(vinyl Alcohol)

The great chemical reactivity of poly(vinyl alcohol) has led to many methods of using it to obtain gels. They can be obtained at room temperature, by treating 10% aqueous solutions of poly(vinyl alcohol) with ferric chloride or Congo Red (*12*). Poly(vinyl alcohol) can be precipitated, by most salts, from water as a fine powder. Borax solution (1%) can also cause the gelling of aqueous solutions of poly(vinyl alcohol) (*14*). The following materials are known to be active gelling agents, at room temperature, for poly(vinyl alcohol) (*31*).

Borax	Congo Red
Gallic acid	Benzopurpurine
1-Naphthol	Pontamine Fast Red F
Resorcinol	Pontamine Bordeaux B
Sodium salt of salicylanilide	Pontamine Orange R

Many compounds can have a gelling action on poly(vinyl alcohol) solutions and in some cases the gels are thermally reversible. Gelling by means of polyhydroxy aromatic compounds has been of interest in photographic emulsions (*27*).

It has been established (*25*) that a firm, thermally reversible gel of poly(vinyl alcohol) can be formed by mixing it with polyhydric phenols, 1-naphthols, and dihydric naphthols. Monohydric phenols have no action. Compounds such as catechol, phloroglucinol, and 1-naphthol are typical gelling agents.

With a 5.6% concentration of poly(vinyl alcohol), the proportion of gelling agents should be approximately as given below, on the basis of the weight of the poly(vinyl alcohol): dihydric phenols 40%, trihydric phenols 30%, 1-naphthols 8%, and dihydroxynaphthalenes 3.5%.

White or colored gels are obtained with poly(vinyl alcohol) (*26*), by using the water-soluble salt of an aromatic amide where the hydroxy and carbonyl groups of the amide are attached to the same benzenoid ring. Several such compounds are illustrated in Figure 3.

Thermally reversible gels can be prepared from poly(vinyl alcohol) and alkali metal salts of *o*-hydroxybenzal derivatives having benzenoid groups at both ends (*24*). Colored gels can be obtained, depending on the type of ketone used (Figure 4).

The property of thermal, reversible gelation is obtained by the addition of water-soluble proteins and protein degradation products to an aqueous solution of poly(vinyl alcohol) (*2*). Protein products such as albumin, gelatin, glue, α-amino acids, and their condensation products—diketopiperazines—may be used. A typical formulation for the preparation of a thermally reversible gel is:

10 parts by weight of 10% aqueous poly(vinyl alcohol). 1 part of glycine

The mixture is heated to boiling for a few minutes and is spread out to dry at 20° to 60° C. The dried material is insoluble in cold water, but it swells to form a tough gel which is thermally reversible and transparent. Another

Salicylanilide

Disalicylbenzidine

2-Naphthyl salicylamide

Salicyl-o-hydroxyanilide
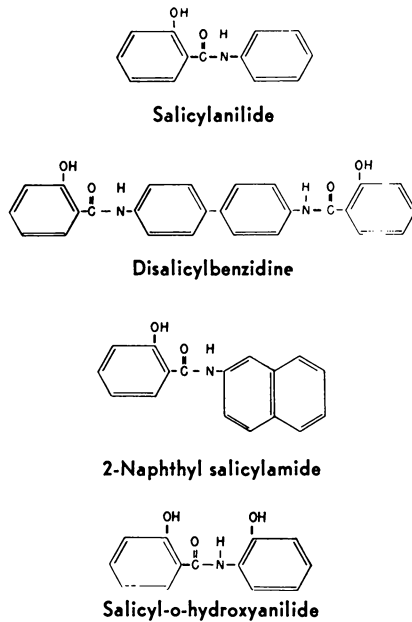
Figure 3.   "Phenolic amides" which gel
poly(vinyl alcohol)

combination includes 8.5 parts of poly(vinyl alcohol), 1.5 parts of gelatin, and 80 parts of hot water.

A layer of poly(vinyl alcohol) forms a gel when treated with aqueous alkaline solutions of acylacetamides of aromatic amines which have an unsubstituted methylene group between the two carbonyl groups (*29*). Several examples are illustrated in Figure 5.

Some gelling agents for poly(vinyl alcohol) find application in the production of gels for coating purposes. Poly(vinyl alcohol) coatings can be set to a rigid gel by adding a small proportion of a heavy metal nitrate—e.g., zirconium nitrate, ferric nitrate, or uranyl nitrate—and then applying the mixture in a thin layer. It is fumed with a volatile base such as ammonia, methylamine, or ethylamine (*21*), while still wet.

Some substituted hydroxy compounds give with poly(vinyl alcohol) firm, white gels which form clear coatings when dried in layer form. A few typical compounds are:

|	
Phloroglucinol	Gallic acid
2,4-Dihydroxybenzoic acid	5-Amino-1-naphthol hydrochloride
4-Chlororesorcinol	

Seaweed Gums

There are two general types of seaweed gums of commercial importance, the brown and the red algae (Figure 6) (*41*).

Sodium alginate is the principal brown algae gum, while the red algae are of two practical types:

Those that precipitate methylene blue and thicken milk—e.g., Gigartina and Chondrus.
Those with no effect on milk or methylene blue—e.g., Furcellaria, Hypnea, agar.
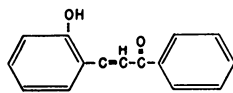
o-Hydroxybenzal acetophenone
(forms a red gel)
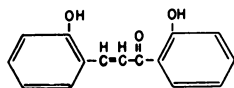
o-Hydroxybenzal-o-hydroxy ace-
tophenone (forms an orange
red gel)
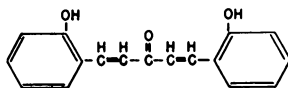
Disalicylal acetone (forms a
violet gel)

Figure 4. Some hydroxy
benzals which gel poly-
(vinyl alcohol)

ACETOACETANILIDE

ACETOACET-p-AMINOANILIDE

ACETOACET-p-ANISIDINE

DIBENZOYLACETBENZIDINE

BENZOYLACETNAPHTHALIDE

Figure 5. "Dimalonyl" poly(vinyl alcohol) gelling agents

Figure 6.   The principal commercial algae

Red Algae Gels

Hypnea musciformis extract (35% of the weed) does not gel without solutes, especially electrolytes. The most effective salts are those containing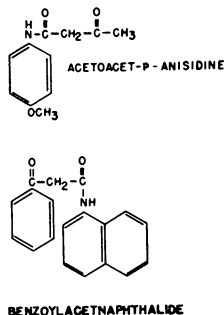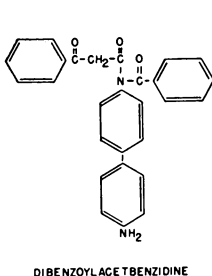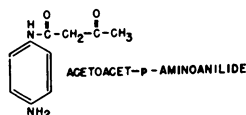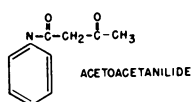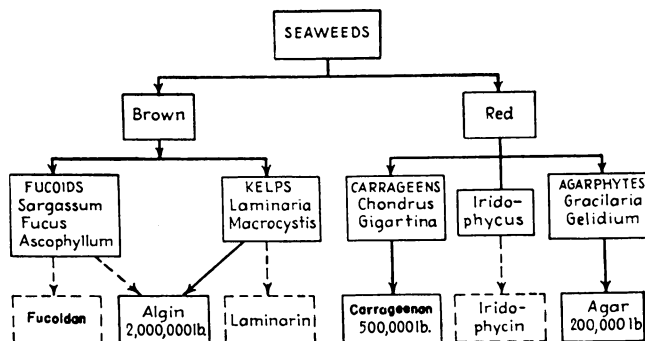 cesium, rubidium, potassium, and ammonium ions (in that order). Gel strengths were greater than for agar at the same concentrations.

The gelling properties are easily controllable. Thus, the gel strength increases almost linearly with an increase in the per cent concentration of the extractive and of potassium chloride (up to 1.5% of the salt). The hysteresis—i.e., the difference between the melting and the gelling points—is dependent upon the electrolyte. For potassium chloride, $\Delta t = 16°$ C.; for cesium or rubidum chloride, $\Delta t = 18°$ C.; and for dipotassium hydrogen phosphate, $\Delta t = 12°$ C. The chief advantages of *H. musciformis* are: highest gel strength of any known phycocolloid and controllable gel strength, and temperature of gelation (*16*).

Irish Moss

Carrageenan has long been considered to be a simple polymer of D-galacto-4-sulfate joined at carbons 1 and 3. While this unit is part of the main structural feature, recent work has disclosed additional fine points. Thus, carrageenan is known to be a mixture of components of varying viscosities and varying sensitivities to potassium.

Fractionation techniques have been carefully worked out (*33*). In one such technique, the potassium-sensitive component, κ-carrageenan, about 40% of the whole, was precipitated from dilute carrageenin solutions and removed by centrifugation. Lambda-carrageenan (60%) remained in solution and the rest (45% of the total) was precipitated by addition of ethyl alcohol. Low temperature (60° C.) extracts from the seaweeds gave higher ratios of κ- to λ-carrageenan than the 100° C. extractions. Treatment with potassium chloride and extraction at 30°, 60°, and 100° to 120° C. (*10*) yielded at least three different components, with the 60° C. fraction possessing the highest gel strength.

Branches at C-6 are long chains of D galactopyranose units joined as α-1,3-glycoside linkages. Each galactose residue carries a half sulfate ester at C-4. It has now (*30*) been shown that about 24% of κ-carrageenan is 3,6-anhydro-D-galactose. This amounts to about two of these units for each three sulfated D-galactose residues. The D-galactose represents 38.1%, the anhydro compound 20.1%, and the sodium sulfate portion 28% of the structure. These do

not add up to 100%, but as they are the only known components of κ-carrageenan, these proportions must be slightly revised. The molecular ratio of these components, as found, is 6:5:7.

O'Neill (30) has shown that carrageenan is a mixture of at least five different polysaccharides. The two main components are κ-carrageenan, which consists of sulfated D-galactose and 3,6-anhydro-D-galactose residues in a 1.2 (or 1.4) to 1 ratio, and λ-carrageenan, which is almost entirely made up of α-1,3-D-galactose, with the sulfate group at C-4. Chemical evidence gives a structure for carrageenan which consists of alternating D-galactose-4-sulfates and 3,6-anhydro-D-galactopyranoses. On each 10th unit, a D-galactopyranose-3,4-disulfate branch occurs. The structure is illustrated in Figure 7.
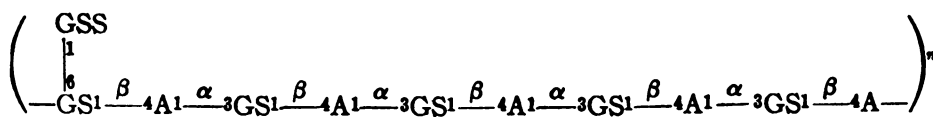
$$\left(\begin{array}{c} \text{GSS} \\ \overset{1}{\underset{6}{\mid}} \\ -\text{GS}^1 \overset{\beta}{\underline{\qquad}}_4\text{A}^1 \overset{\alpha}{\underline{\qquad}}_3\text{GS}^1 \overset{\beta}{\underline{\qquad}}_4\text{A}^1 \overset{\alpha}{\underline{\qquad}}_3\text{GS}^1 \overset{\beta}{\underline{\qquad}}_4\text{A}^1 \overset{\alpha}{\underline{\qquad}}_3\text{GS}^1 \overset{\beta}{\underline{\qquad}}_4\text{A}^1 \overset{\alpha}{\underline{\qquad}}_3\text{GS}^1 \overset{\beta}{\underline{\qquad}}_4\text{A}- \end{array} \right)_n$$

Figure 7. Proposed structure of κ-carrageenin (30)

A recent x-ray study (3) gave a slightly different picture of the structure. Kappa-carrageenan is, according to x-ray studies, a branched chain. Each unit contains two trisaccharides, each consisting of two sulfated α-1,3-galactoses, and a side chain containing a single sulfated D-galactose hooked onto the chain at the 6 position.

Apparently, λ-carrageenan is not a simple structure and must have some irregularity in the distribution of its sulfate groups. Also, an occasional side residue may be present. There are still unexplained points about the x-ray spectra of λ-carrageenan.

A possible explanation for the sensitivity of carrageenan to potassium, ammonium, rubidium, and cesium ions but insensitivity to lithium and sodium ions may be the ionic size of the hydrated cations. In the first group (potassium ion, etc.) the ions are all similar in size and in the range of 2.5 to 4.0 A. Sodium and lithium ions are twice as large. Bayley (3) proposes a link between chains in which each sulfate is surrounded by cations. Sodium and lithium would be too large to fit into this packing scheme. Excess potassium chloride is needed to precipitate potassium carrageenate, because all of the sulfate groups must be neutralized before the molecules can come close enough together to form gel. This is partially confirmed by the fact that the presence of sodium chloride lowers the potassium chloride requirement necessary for gelation.

Pectin

The term "pectin" denotes a series of water-soluble pectinic acids of varying methyl ester content and degree of neutralization. These substances possess different abilities to form gels with calcium ion and jellies with sugar and acid (19). Although pectin is one of the oldest hydrocolloids known, many features of its structures and properties remain enigmatic. Recently more definitive proposals for its structure have been offered and even these are doubtful. Figure 8 shows the similarities in the structures of pectic acid, cellulose, and alginic acid.

According to some, pectin appears to be a mixture of methyl esterified galacturonan, galactan, and araban in which some of the galacturonan molecules
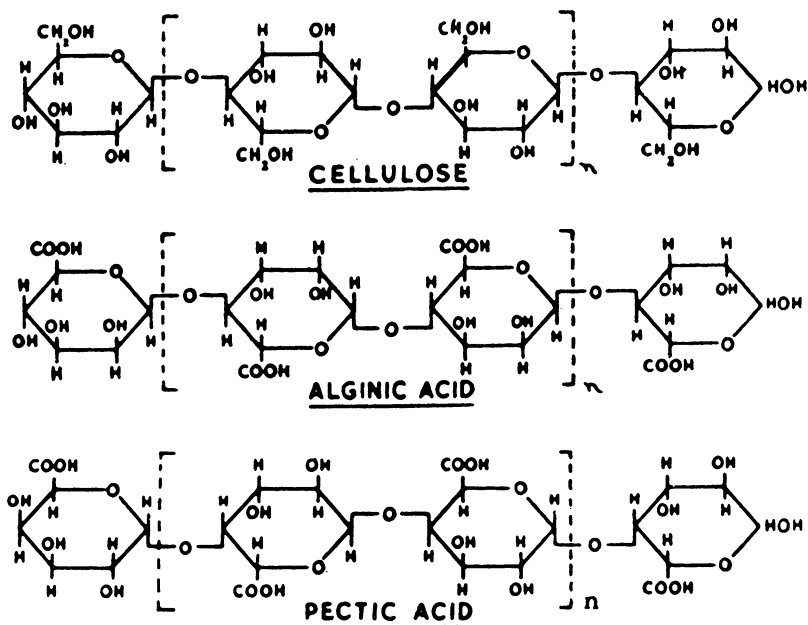
Figure 8.   Relationship of cellulose, alginic acid, and pectic acid

are linked to the galactans and arabans. The ratio of these components no doubt varies with the source of the pectin (40). Figure 9 depicts four units of a pectinic acid molecule with linkages through the oxygen atoms.
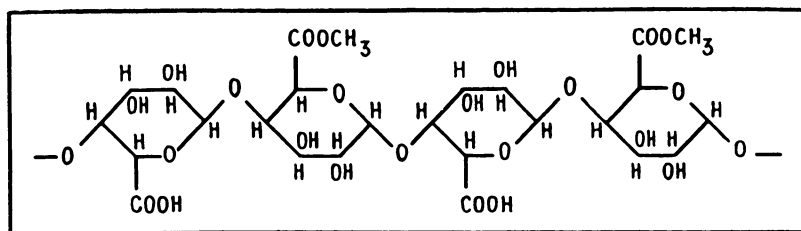
Figure 9.   Section of pectinic acid molecule

The jelly-forming power of pectin has been known since antiquity. The factors responsible for jelly formation have been combined in a mathematical formula (11):

$$r = Pl\ (l + Bm + a\ Bn) - f$$

where

$r =$ potential rigidity
$P =$ pectin concentration
$l =$ a factor depending upon the average molecular size
$B =$ degree of ionization
$a =$ degree of ionization
$m, n,$ and $f =$ constants

This equation reduces to the original Hinton equation (15), when one takes into account the importance of the concentration of the ionized and nonionized forms of pectin. In the Hinton equation, the concentration of pectin is the difference between the total and the ionized form.

The gel strength of hydrogen-bonded gels (65% sugar jellies) is largely dependent upon molecular weight and is not influenced by the degree of methylation or the method of de-esterification. Higher molecular weights give higher gel strengths. On the other hand, the gel strengths of ionic bonded gels (35% sugar–calcium pectinate gels) are less affected by molecular weight than hydrogen-bonded jellies, but they are strongly dependent upon the degree of esterification. Maximum gel strength is in the region of 30 to 50% degree of methylation. Enzyme-de-esterified pectins form weaker calcium gels than acid–de-esterified pectins (*34*). Gel strengths were measured on pectins which were increasingly de-esterified. When enzyme was used, the gel strength increased (more homogeneous), while with acid, the gel strength decreased, because of loss in molecular weight (*13*). Pectin gels can be regarded as a network of galacturonic acid chains cross-linked at the unesterified carboxyl groups with calcium ions (*1*).

Speiser *et al.* have studied the effect of molecular association and charge distribution on the gelation of pectin (*36*). Two basic types of gels are described:

Irreversible types stable to heat and additional solvent due to the presence of covalent bonds

Reversible gels which are dispersible on heating and are soluble in excess. These have secondary valence or ionic bonds

The solubility of pectin materials is an index to their gel-forming ability. Solubility, in general, decreases with an increase in the degree of esterification. Enzyme–de-esterified pectinic acids are more soluble than the acid–de-esterified acids. The solubility of pectinic compounds depends on the perfection of the spacial ordering, the molecular rigidity, and the magnitude of the intermolecular forces. The crystalline phase of a high polymer is usually less soluble than the amorphous phase. In the crystalline regions, the chains of polymers like pectinic acid are well aligned, and the maximum number of cross bonds (hydrogen bonds) per unit length of molecule is formed. When pectin goes into solution, nearly all of the hydrogen bonds between the chains must be ruptured simultaneously. For this reason pectic substances with low viscosity, and consequently a large concentration of strongly interacting carboxyl groups, tend to crystallize upon precipitation or drying, thus forming relatively insoluble aggregates. If there are bulky side groups, or if irregularities of a sufficiently pronounced nature are present in the polymer chains, a smaller amount of crystallization results and aggregates that admit solvent are formed.

In 65% sugar jellies the hydrogen bridges alone are active. Such gels are easily deformed and are elastic. In calcium pectinate gels, the most effective cross links are calcium ion bonds between the carboxyl groups. The bond distances are short; therefore an inelastic, rather brittle, gel results.

Pectin exhibits solubility and gel strength peculiarities. The more soluble the pectin, the greater its gel-forming ability, because the pectin that does not actually disperse but remains in a submicroscopic condition cannot contribute to jelly formation. Hence, any interference with the complete solubility of a pectin inhibits its gel-forming ability.

Work at the Eastern Regional Research Laboratory (*35*) was concerned with the de-esterification of pectin by two alternative schemes: acid and enzyme. It was found that whereas enzyme de-esterification of apple pomace pectin required several minutes, acid de-esterification took 1 to 2 days. Although 40° to 50° C. was optimum for both acid and enzyme de-esterification,

acid de-esterification required a pH of less than 1.0, whereas the enzymatic reaction pH was optimum at 6.0. It is believed that the acid de-esterification results in a random removal of methoxyl groups while enzyme de-esterification does not follow the same mechanism.

The comparison may be readily seen in Figure 10, which shows the effect of varying calcium content on the gel strength of 35% sugar jellies prepared from acid- and enzyme-demethylated pectinates of the same original methyl content (14). When enzyme- and acid-demethylated pectinates are compared near the calcium to pectinate ratio of 0.03, increasing the methoxyl content from about 4% to 7% caused a loss in jelly strength for the enzyme-demethylated pectin, but a gain in strength for the acid-demethylated pectin. Figure 11 shows that a higher methoxyl content decreases gel strength. Of interest also are the narrowness of the calcium sensitivity range and the fixed position of the peak. In Figure 12 is evidence that with acid-demethylated pectin there are greater strength and calcium sensitivity and a shift of the peaks with the calcium-pectinate ratio.
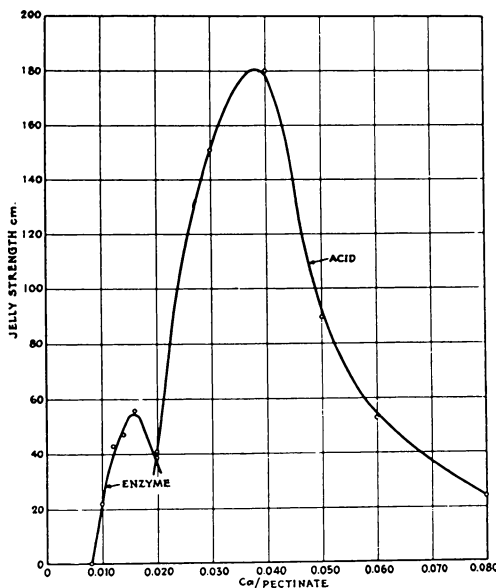
Figure 10. Comparison of acid- and enzyme-demethylated pectinates, both containing 5% of methanol

Studies at the Western Regional Research Laboratory (32) showed that enzyme partially de-esterified pectinic acid resembled pectic acid. This was attributed to the fact that the enzyme may have acted by regularly splitting off successive methoxyl groups, thus producing pectic acid-like segments. There is much that is still speculative about pectin. Heat-degraded pectin loses in gelling power and in viscosity, while its optical rotation remains unchanged (20). Acid- or enzyme-degraded pectin also loses in viscosity and in gelling power, but these effects are accompanied by a change in optical rotation.

Although gels may be formed by widely different mechanisms, they exhibit
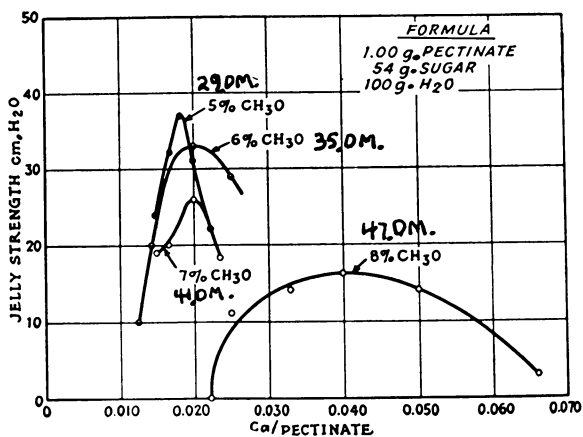
Figure 11. Effect of calcium on jelly strength of enzyme-demethylated pectinates
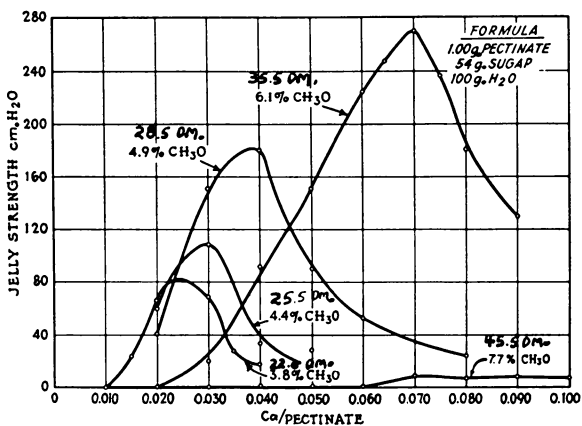
Figure 12. Effect of calcium on jelly strength of acid-demethylated pectinates

a distinctive set of physical properties, as previously described. Gel systems may be characterized by three fundamental concepts:

They are coherent, colloid, disperse systems of at least two components.
They exhibit mechanical properties characteristic of the solid state.
Both the dispersed component and the dispersion medium extend themselves continuously throughout the whole system.

This approach does not preclude gels having special, additional properties of their own due to peculiarities of their molecules. Such an example was in the thixotrophy of borax gels caused by the dynamic equilibrium of the bonds. Even gels that are formed by two apparently different mechanisms have the same fundamental gelling characteristics. For a timely and exhaustive review on gelling systems the reader should refer to the recent work of Whistler and BeMiller (41).

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Some Problems of the Gelation of Gelatin

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The gelation of gelatin is presented in the light of modern polymer chemistry. The sol-gel transition is considered from the number of cross links involved in the process. The kinetics of gelation are studied in terms of reversible and irreversible bimolecular reactions. Experimental data obtained by means of rigidity, osmometry, viscometry, swelling, optical rotation, and melting point are discussed and related to the theoretical mechanism of gelation.

Some problems of gelatin chemistry are reviewed, with the method and perspectives which physical chemists are using to solve them. One such problem is that of finding a relation between rigidity and some property of the gelatin related to its macromolecular nature. Because gel strength is destroyed by degradation, it has been assumed that gel strength is related to the chain length of the molecule, and hence to the molecular weight. Viscosity is related to molecular weight; hence gel strength and viscosity should be related. Industrial experience has shown, however, that they are not always related. Often, in fact, one property is maximized and the other is minimized purposely.

Ferry and Eldridge (7, 8), using a series of gelatins derived by progressively degrading a single ossein gelatin, determined the rigidity of the resulting gels and correlated it with the weight-average molecular weight of the gelatin sample. The weight-average molecular weight was calculated from the number-average molecular weight, which in turn was determined by osmotic pressure measurements. They plotted $G^{1/2}/C$ *vs.* the molecular weight at various temperatures of gelation. The resulting straight lines indicated that the final or equilibrium rigidity was proportional to the square of the concentration and to the molecular weight (Figure 1). [A method for determining the equilibrium rigidity, developed by Ferry (7), involves the rapid cooling of the gelatin solution to 0° C. from a temperature of over 35° C., maintaining this temperature for 24 hours, then slowly raising the temperature to the temperature of interest, and waiting until constant values are obtained for the rigidity.]

Saunders (16) found, however, that fractions of a given gelatin, while

differing in reduced viscosity, all had about the same equilibrium rigidity (Figure 2). Because the reduced viscosity is related to the weight-average molecular weight, this result clearly differs from that of Ferry. It can be seen from the figure that as the temperature is raised there results a slight dependence of rigidity on reduced viscosity. This dependence is more pronounced, the more dilute the gelatin. Stainsby, Saunders, and Ward (18) concluded that although there may be some relationship between chain length and rigidity, there is a much more important and subtle "structural feature," and that only if the chain length is reduced below a certain size will it lead to a decrease in rigidity.
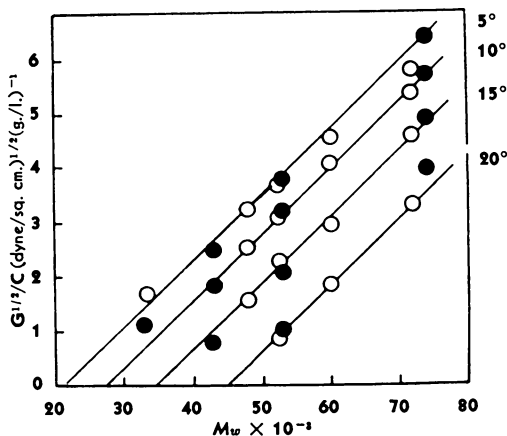

Figure 1. $G^{1/2}/C$ vs. weight average molecular weight at four different temperatures

G.   Rigidity
C.   Concentration
O.   Data from Ferry (7)
● Data from Ferry and Eldridge (8)
Figure from Ferry and Eldridge (8)

A number of workers (7, 11, 13, 15) have shown that the equilibrium rigidity of gelatin gels is approximately proportional to the square of the gelatin concentration. Ferry (6) pointed out that for a dimerization reaction, where only a small fraction of the total number of loci have joined, the concentration of cross links should be proportional to the square of the total concentration. Northrup and Kunitz (12) showed that as a gelatin gel was allowed to swell in water, the equilibrium rigidity decreased in proportion to the decrease in concentration of the gelatin in the swollen gel. From this one may assume that swelling does not break cross links, but merely reduces the number per unit volume.

These facts might then indicate that the rigidity is proportional to the concentration of cross links (7), and that the concentration of cross links formed is dependent on the square of the concentration of gelatin at the time of gelation. If the gel strength depends on the concentration of cross links, the strength of a gelatin gel at constant concentration will depend on the number of cross links formed per weight of gelatin, not per chain. The number of cross links formed per gram of gelatin is probably controlled by the nature of the gelatin, the temperature, the concentration of the gelatin, and the time elapsed during gelation. However, in order to form a gel there must be a minimum of

two reacted cross-linking sites per molecule. Actually, for network formation, there must be some chains present with more than two reacted sites per chain; otherwise only filaments would result. This means that there must be at least two cross links connecting each gelatin chain to the rest of the gel. Therefore an average of at least one cross link per chain is necessary to form a gel (because each molecule contributes 1/2 times 2 cross links).
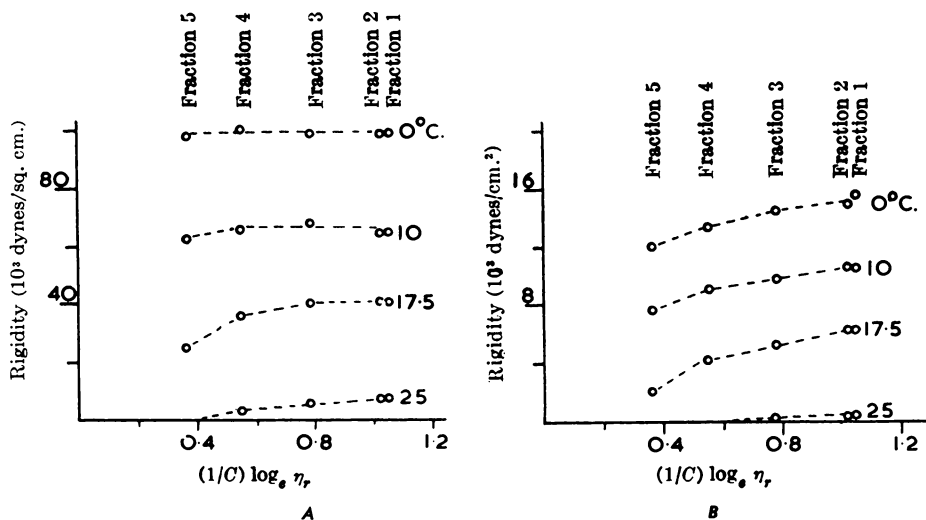

Figure 2. Rigidity of gels from gelatin fractions as function of reduced viscosity

Viscosities determined at temperatures from 0° to 25° C. in 1M sodium chloride at pH 7 (at C = 0.2%)
A. Gel concentration 5.5%
B. Gel concentration 2.2%
Figure from Saunders (16)

For a gelatin with a constant number of sites per weight, the number of sites per chain will be proportional to the molecular weight of that gelatin. Therefore for each gelatin there will be a minimum molecular weight, below which it will not gel. A gelatin sample, heterogeneous with respect to molecular weight, with a definite number of cross-linking sites per gram of gelatin, will also be heterogeneous with respect to the number of sites per chain. Fractions of this gelatin [prepared by fractional precipitation (18)] gelled at concentrations high enough and temperatures low enough to assure that every chain has at least two cross-linking sites reacted, will all have the same equilibrium rigidity. This occurs because all the fractions have the same number of cross-linking sites per gram of gelatin and every chain has taken part in gel formation. If the temperature is raised somewhat (or the concentration lowered) the number of cross links per gram are decreased, presumably by the same amount for all fractions. Under these conditions some of the smaller molecules of the lowest fraction will contain less than the minimum number of two reacted cross-linking sites per chain. Thus, in the lowest fraction there would be a small portion of nongel-forming gelatin. Therefore, although the same number of cross links are formed per gram of gelatin in the lowest fraction as in the highest fraction, the lowest fraction will have the lowest equilibrium rigidity. This is because chains with one cross-linking site per chain do not contribute to gel or network formation. Instead, they act as chain terminators or site

blockers. In other words, whenever a site on a chain reacts with a site on another chain containing only that one site, the network cannot grow in that direction any longer. Another factor of importance in reducing the equilibrium rigidity involves the fact that the gel-forming portion of the gelatin sample has now been diluted by nongel-forming material.

As the temperature is raised (or the concentration is decreased) the proportion of this nongelling portion is increased in all the fractions. The lowest fraction will contain most of this material. Finally, when the temperature is high enough (or the concentration low enough), even the highest fraction will contain some nongellable material. The result of raising the temperature (or lowering the concentration) is: At first all fractions will decrease in rigidity by the same amount; eventually, however, as a portion of the gelatin in the lowest fraction loses its ability to gel, its rigidity will decrease faster than that of the next highest fraction, and so on. Therefore, at any temperature (or concentration) where some nongelling material can form, the equilibrium rigidity of the fraction will more or less depend on the amount of nongellable gelatin present. This in turn depends on the molecular weight of the fraction, because the longer chains will be last to contain less than the minimum two reacted cross-linking sites per molecule.

From Figure 2,*A*, one can see that at 0° C. there is essentially nongel-forming gelatin present. There is a small amount in fraction 5 at 10° C. and a larger amount at 17.5° C. However, the equilibrium rigidities of the first four fractions are still independent of the reduced viscosity, and hence of the molecular weight. In fact, the temperature must be raised almost to the melting point of the lowest fraction (27.3° C.)—that is, to 25° C.—before significant quantities of the nongellable species are formed in the higher fractions. Figure 2,*B*, shows the same phenomena, but because the gelatin concentration is lower, there are less reacted sites per gram of gelatin and hence more chains with less than the required two cross links per chain. This results in larger quantities of the nongellable portion in each fraction, causing the molecular weight dependence of the rigidity even at 0° C. At the higher concentration essentially none of this material was present in any fraction at 0° C.

Ferry used nonfractionated, progressively degraded samples. Assuming that degradation does not progressively change the number of sites per weight (which might occur), it would increase the molecular heterogeneity while lowering the average molecular weight. This would increase rather rapidly the quantity of low molecular gelatin for a slight decrease in the average molecular weight. It is therefore possible that all of Ferry's samples contained considerable quantities of nongel-forming gelatin. It would be of interest to compare the reduced viscosity of Ferry's most degraded sample with that of the lowest fraction of Saunders. It is probable that the former would be lower than the latter. If even at the lowest temperature of measurement (5° C.) there were amounts of nongellable gelatin present in the samples, proportional to the degree of degradation and hence to the molecular weight, the observed relation between the equilibrium rigidity and molecular weight might easily be observed. This seems to explain the differences between the results of the two investigators. Finally, Ferry (7) mentions that the equilibrium rigidities of fractions of a calfskin gelatin were almost independent of molecular weight.

Pouradier and Venet (14) showed that the molecular weights (determined by osmometry) of fractions of a gelatin sample could be associated with their melting points. The relationship $T_f = A - B/M^a$ was found to hold for dif-

ferent gelatins (where T_f is the melting point and M the molecular weight), but with unique values of A, B, and a for each gelatin. Stainsby, Saunders, and Ward (19) found a unique relationship (for any one gelatin) between the melting point and the reduced viscosity and hence the molecular weight for a series of fractions obtained by fractionation with sodium dodecyl sulfate. Eldridge and Ferry (5) (Figure 3) also demonstrated a relation between molecular weight and melting point for a series of degraded ossein gelatins. Because it was shown previously that the rigidity at constant temperature is controlled by the molecular weight near the melting point (low concentration and high temperature), it would be reasonable to assume that the melting point at constant rigidity would be a function of the molecular weight. The melting point can be considered to be that temperature where the rigidity of the gel is zero.
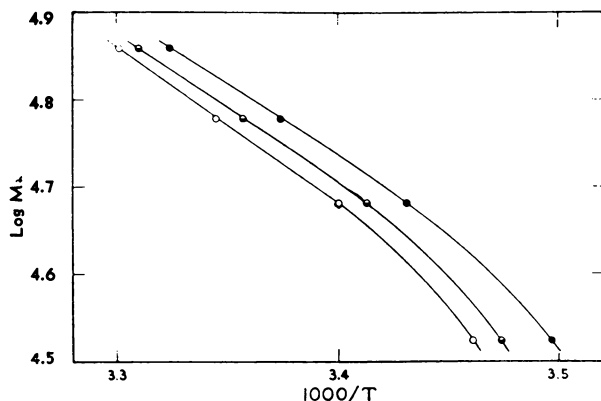

Figure 3. Relation between weight-average molecular weight and absolute temperature of melting

O, ◒, ●. Gelatin concentrations of 55, 40, and 25 grams per liter, respectively
All gels chilled at 0° C.
Figure from Eldridge and Ferry (5)

The reaction $2S \rightleftharpoons G$ was proposed by Smith (17). This equation represents the reaction of 2 moles of gelatin in the sol state to form 1 mole of gelatin in the gel state. It might also represent the joining of two cross-link sites to form one cross link. Ferry (6) pointed out that for this type of reaction, where only a small fraction of the total number of loci have joined, the equilibrium concentration of cross links should be proportional to the square of the total concentration. Therefore, if the rigidity is proportional to the cross-link concentration, the equilibrium rigidity should be proportional to the square of the concentration. In general, this is true (7, 11, 13, 15). The above mechanism, with the stipulation that the equilibrium goes only slightly to the right, therefore seems to be consistent with the facts. A study of the rate of gelation is more revealing. Equation 1 applies to a second-order reaction opposed by a first-order reaction (9).

$$t = \frac{X_e}{k(A^2 - X_e^2)} \ln \frac{X_e(A^2 - XX_e)}{A^2(X_e - X)} \tag{1}$$

where A is the concentration of the reactant, X is the concentration of the product (or the rigidity) formed in time t, X_e is the concentration of the product

formed at equilibrium (or the equilibrium rigidity), and k is the second-order rate constant. When only a small fraction of A reacts (or $X_e^2 << A^2$ and $XX_e << A^2$), the equation is reducible to:

$$t = \frac{C}{k} \ln \frac{1}{1 - D} \tag{2}$$

where $C = X_e/A^2$ and $D = X/X_e$.

Some preliminary studies of the rate of gelation are shown in Figure 4. The gelatin solutions were heated to 50° C. and then rapidly cooled (in about 2 minutes) to 10° C. (All gelatins used were calfskin in origin and were made up in a solution of pH 6.0 and containing $0.1M$ sodium chloride. The gelatin used for the rigidity studies had a standard rigidity of 250 Bloom.) The rigidity was measured by a standard Bloom gelometer, in units of Bloom. There are reasons why this is not the best method for measuring rigidity. However, for exploratory studies it is adequate and very convenient. Upon plotting $\ln 1/(1 - D)$ vs. time, a straight line does not result (Figure 5). A plot of $1/(1 - D)$ vs. time also did not yield a straight line (not shown), indicating that the reaction is not of the second-order, nonreversible type either. This indicates that the above-mentioned mechanism does not explain the results, although the equilibrium rigidity varies with the square of the gelatin concentration.
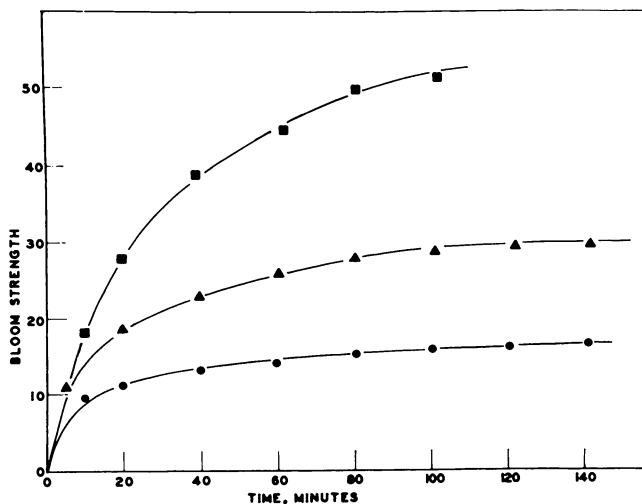
Figure 4. Rigidity vs. time for a high standard rigidity (250 Bloom) calfskin gelatin at 10° C., pH 6.0, 0.1M sodium chloride

■, ▲, ●. Gelatin concentrations of 3, 2.25, and 1.5%, respectively

It has been known for many years that the gelation of gelatin is accompanied by a large increase of the optical rotation in the levo direction. Smith (17) determined the final or equilibrium values of the specific rotation by setting the gel at a temperature several degrees below the temperature of interest. After a time, the temperature was raised to the temperature of interest and when the optical rotation became constant, it was recorded. This equilibrium value of the specific rotation was almost independent of the concentration above 30° C. and below 17° C. and increased as the temperature was decreased

to a constant value of $-313°$ at temperatures below $15°$ C.   Between $30°$ and $17°$ C. there is some concentration dependence of the equilibrium values. Kraemer and Fanselow (10), and later Ferry and Eldridge (8), showed in disagreement with Smith that $-[\alpha]_d$ was independent of concentration and increased continuously as the temperature was decreased as far as was experimentally feasible (to almost $0°$ C.).   This evidence prompted Ferry and Eldridge (8) to rule out Smith's suggested bimolecular reaction.
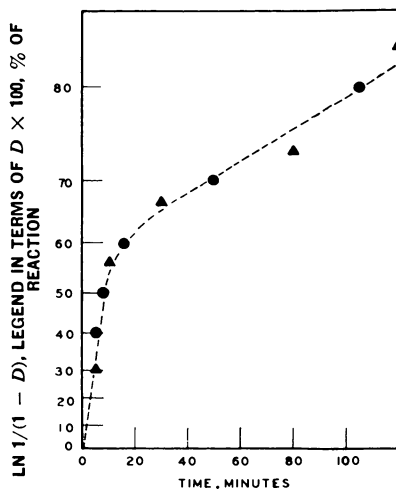

Figure 5.   Per cent of final reaction vs. time, 1.5% calfskin gelatin, at 10° C., pH 6.0, 0.1M sodium chloride

D   Fraction of reaction, plotted as ln 1/(1 — D)
●   Change in rigidity
▲   Change in specific rotation, $[\alpha]_D$
Gelatin solution, 1.5%, set at 10° C.

Smith measured the change of optical rotation with time, at several concentrations and temperatures by heating the gelatin solution to above $50°$ C. and then cooling it rapidly to the temperature of interest.   At high temperatures ($35°$ C. and above), the initial specific rotation is the same as the equilibrium value, and hence does not change with time.   One might conclude that these low constant values at high temperatures correspond to the sol state.   However, at lower temperatures there were large changes from the initial specific rotation (at $15°$ C. see Figure 6).   Smith found that the time needed for the specific rotation to change to one half of its final value was proportional to the concentration.   This is what would be expected from a second-order reaction.   A more curious finding by Smith was that the optical rotation (not the specific optical rotation) must increase approximately $0.85°$ per decimeter for a gel to form. He interpreted this to mean that a fixed concentration of gelatin must be converted into a more oriented state before the gelatin can gel.

Experiments conducted by the authors have confirmed and extended many aspects of the work of Smith.   The data involving the change of optical rotation (between $25°$ and $15°$ C.) fit straight lines when plotted as $1/(1 — D)$ vs. time (Figure 7), but not when plotted as $\ln 1/(1 — D)$ vs. time.   At the latter temperature only the data of 1% gelatin concentrations and below formed straight lines when plotted in this manner.

A nonreversible second-order reaction—e.g., $2S \rightarrow G$—would obey the equation:

$$t = \frac{1}{k(A - X)} - \frac{1}{kA} \qquad (3)$$

where A is the concentration of the reactant, X is the concentration of the product at time t, and k is the second-order rate constant. Equation 3 can be transformed to:

$$t = \left(\frac{1}{kA}\right)\left(\frac{1}{1 - D}\right) - \frac{1}{kA} \qquad (4)$$

where $X/X_e = D$ and $X_e \simeq A$.

A plot of $1/(1 - D)$ or $1/(A - X)$ *vs.* t will therefore yield a straight line for this type of reaction.
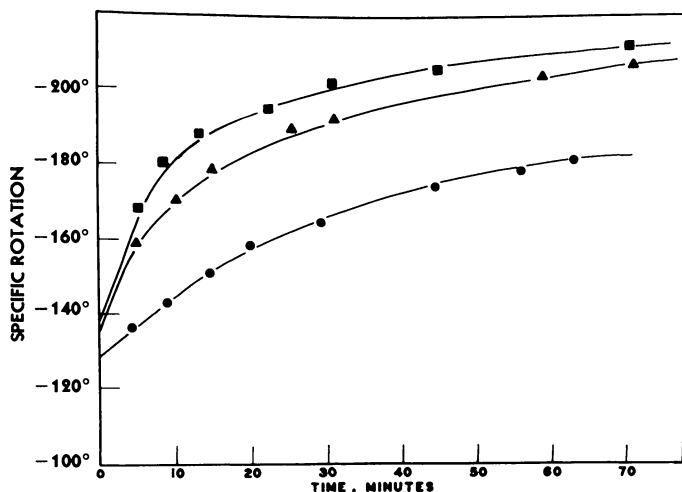
Figure 6. Specific rotation *vs.* time at 20° C.

■, ▲, ●. Gelatin concentrations of 5, 3, and 1%, respectively
Data from Smith *(17)*

This would indicate that the reaction tended to follow the scheme $2S \rightarrow G$ with the reverse reaction negligible. At temperatures below 15° C., the deviation from this straight line becomes significant, especially as the concentration is increased. However, the equilibrium specific rotations are practically identical at all concentrations at any temperature; therefore the equilibrium angular rotation is proportional to the gelatin concentration (X_e is proportional to A), which is to be expected for reactions obeying Equations 3 and 4. Though the equilibrium angular rotation is proportional to the gelatin concentration while the equilibrium rigidity is proportional to the square of the gelatin concentration, the rate of gelation as measured by these two properties is identical at 10° C. (Figure 5).

Summarizing: Although the relation between the equilibrium rigidity and the gelatin concentration points to a slightly reacted reversible second-order reaction, the kinetic study at 10° C. does not agree with this. Although the change in optical rotation seems to indicate a nonreversible second-order reac-

tion, at lower temperatures and higher concentrations, deviations occur, until finally at 10° C. the kinetics are identical to those of the rigidity; this occurs despite the fact that the equilibrium rigidity varies as the square of the gelatin concentration, while the equilibrium angular rotation varies directly.
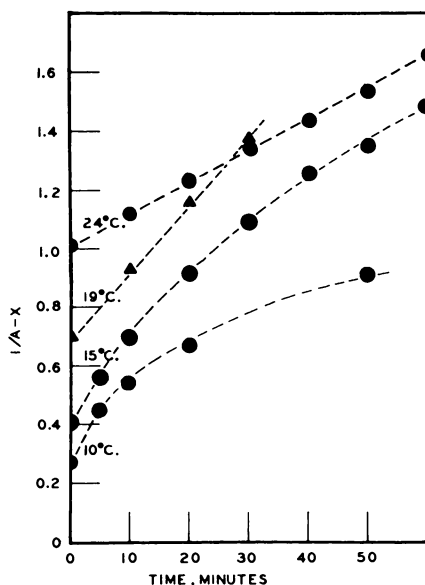

Figure 7.   Specific rotation *vs.* time

Specific rotation, plotted as 1/(A − X) [proportional to 1/(1 − D)]
Calfskin gelatin (250 Bloom), 1.5% solution at four temperatures at pH 6.0 in 0.1M sodium chloride

By measuring the optical rotation as it changes with time, after a gelatin solution is rapidly cooled to the temperature of interest, and extrapolating back to zero time, one can determine the initial specific rotation. It is approximately constant with the concentration, but varies with temperature. This initial specific rotation probably represents that of the sol molecule at that temperature before it is converted into the gel form.

The values of both the initial and the equilibrium specific rotations are plotted for two gelatin samples in Figure 8. The equilibrium values below 80° C. fall on steeply rising curves, while the initial specific rotations form a straight line of lesser slope. The two lines intersect at about 31° C. for one gelatin sample and at 27° C. for the other. The temperature at which the intersection occurs may be regarded as the highest temperature at which a gel san exist. At higher temperatures the initial and the equilibrium values become equal and form a continuation of the curve of the initial values. The two gelatins studied (calfskin) were chosen because of the large differences in their equilibrium rigidities. The higher grade gelatin had an equilibrium rigidity of 150 Bloom when a 6.67% sample was set for 18 hours at 10° C. A rigidity defined in this way is called the standard rigidity. The lower grade gelatin had & standard rigidity of only 115 Bloom.

Urea retards and prevents gel formation. It is thought that this occurs

because urea prevents the formation of hydrogen bonds and keeps the gelatin molecule in the sol form. The optical rotation of gelatin solutions containing 7M urea was measured and the results were compared with the initial specific rotations obtained by rapid cooling. The results coincided exactly with the initial specific rotation values obtained by rapid cooling. The hypothesis, that the initial specific rotation values correspond to the sol state molecule at the particular temperature, seems justified.
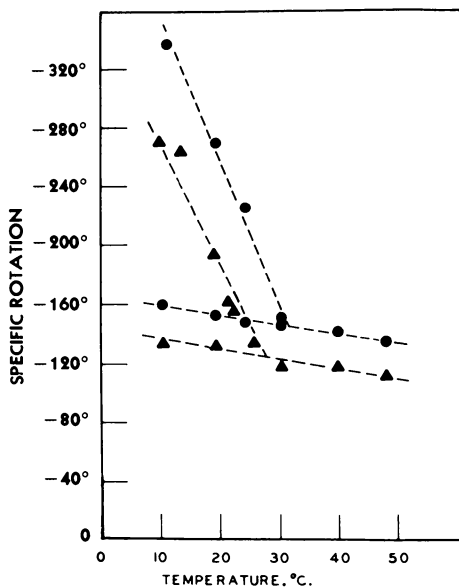
Figure 8. Specific rotation *vs.* temperature

Calfskin gelation at pH 6.0 in 0.1 M sodium chloride
● Standard rigidity of 250 Bloom
▲ Standard rigidity of 115 Bloom
Lower, more horizontal lines represent initial values
Sharply inclined lines denote equilibrium values at higher temperatures equilibrium and initial values are identical

Upon examining the portion of Figure 8 that applies to the less rigid gelatin sample, one can notice that the maximum gel temperature is lower than that of the high rigidity sample. Of greater interest, however, is that the ratio of the square of the change of the specific rotation of the weaker gel to that of the stronger gel at 10° C. is in the same ratio as the standard rigidities (also at 10° C.). This is reminiscent of the fact that with the same gelatin sample the equilibrium rigidity varies as the square of the gelatin concentration, whereas the equilibrium angular rotation and the change in angular rotation are proportional to the gelatin concentration. Therefore, the rigidity varies as the square of the change in specific rotation.

Cohen (4) has suggested that the high equilibrium specific rotation of gelatin at low temperature is due to a partial regaining of the helical structure of collagen. In order to regain such a structure, it would be necessary to impose severe restrictions on the molecule. As pointed out by Ferry and Eldridge (8),

these restrictions could be accomplished by intramolecular cross links. If the change in specific rotation is proportional to the degree to which the coiled structure is regained, it might be proportional to the number of intramolecular bonds which have formed per gram of gelatin. The change in angular rotation will then be proportional to the concentration (or the number per milliliter) of intramolecular cross links. The rigidity (as mentioned previously) may be proportional to the concentration of intermolecular bonds which are formed. It is assumed here that there is essentially no difference between intermolecular and intramolecular bonds or sites. Only the proximity of one site to another determines which will form. Because the number of intramolecular cross links formed per gram of gelatin probably does not depend on the molecular (or weight) concentration of the gelatin, it is evident that the equilibrium specific rotation should be independent of concentration, while the equilibrium angular rotation (and the change of angular rotation) is proportional to the concentration. However, the number of intermolecular bonds formed per gram of gelatin should depend on the molecular concentration. If only a small number of the available cross-linking sites react, it is reasonable to assume that the equilibrium rigidity is proportional to the square of the concentration of the gelatin, and hence to the concentration of the available sites.

At first glance, one might expect the intramolecular reaction to occur simultaneously with, and independently of, the intermolecular reaction. However, the intermolecular reaction may involve two consecutive reactions: first, an orientation step and second, the actual cross linking. This orientation may depend on the molecule's acquiring a certain shape, which would occur through the formation of intramolecular bonds exposing certain sites, thus making them available for intermolecular bonding. If this is the case, the intramolecular reaction and the intermolecular reaction may be considered to a certain (and peculiar) extent to be consecutive. Evidence has been obtained by Bourgoin and Joly (3), by means of flow birefringence measurements, that there are two steps involved in the gelation of gelatin. The first involves some "orientation" effect, and the second the actual gelation.

There are many questions yet to be considered and studied experimentally. For instance, gelation is affected by the pH and the types of salts present. A good start in explaining the factors involved here was made by Boedtker and Doty (2), who made light-scattering studies of the aggregation of gelatin. Bello, Riese, and Vinograd (1) studied the influence of certain electrolytes on the melting points of gels and gelatin. Finally, very little is known about the nature of the bonding sites, or how they arise. Perhaps the study of the binding of various amino acids and short-chain peptides by means of dialysis equilibrium experiments would cast light on the type, the origin, and the strength of the cross links that form upon the gelation of gelatin.

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Some Structural Aspects of the Gel Formation of Pectins and Related Polysaccharides

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The gelation process is considered a very specific process. This specificity is interpreted on a structural basis. Therefore some relationships between the chemical constitution and gelation properties of pectins and some related polysaccharides are outlined.

A gel is a system with small proportions of a substance dispersed in relatively large proportions of liquid, which behaves in certain respects as a rigid solid and yet retains many properties characteristic of fluids (*7, 9, 11, 14, 19*). Polysaccharide gels contain in general a few or even less than 1% of polysaccharide and 99% of water and low molecular weight solids. The gel nature can be based on the existence of a cross-linked polysaccharide network; the gelation takes place by cross linking of the dissolved polysaccharide macromolecules to a three-dimensional network. This process is considered very specific, because only a few polysaccharides can form true thermoreversible gels. In this presentation relationships between the chemical constitution and gelation properties of pectin and some related polysaccharides are discussed. The physicochemical aspects of the gel state are not outlined.

General Molecular Structure and Gelation

The high molecular weight of the polysaccharide molecules is the most important and limiting factor for any cross-linking reaction, such as the gelation process. The importance of a high molecular weight has been proved for practically every polysaccharide gel mixture and is therefore not discussed in detail (*7, 9, 11, 14, 19*).

The shape of the polysaccharide molecules, also not fully investigated, might have another important influence on the gelation properties. Linear chain molecules show in general much better gelation properties than branched ones. Heavily coiled molecules will obviously react preferentially with different segments of the same molecule; uncoiled molecules will react preferentially with each other. The coiling of the molecules is influenced by charged groups and side groups on the chain molecules, restricted free rotation of the glycosidic

bonds, etc. Side groups or some kind of molecular branching of chain molecules may hinder the contact of two molecules for steric reasons and therefore hinder a cross linking.

The main functional reactive groups of polysaccharides are hydroxyl, carboxyl, methyl ester, and sulfonic acid groups. They can participate in reactions with bifunctional reagents—e.g., formaldehyde—and will produce covalent bridges of highest stability between the polysaccharide molecules, forming a covalent three-dimensional gel network. Furthermore, they can participate in reactions with bifunctional complex-forming reagents—e.g., borate, phenols, and heavy metal ions—and will form a complex linked gel network. All these reactions need addition of bifunctional reagents to the gel mixture as bridging reagents and do not show direct chain-to-chain contacts. The cross links are merely points of attachment. The reaction is governed by the concentration of the added reagents; it depends in general on the presence of some single functional groups on the chain molecule, is in general not thermoreversible, and is not very specific.

For thermoreversible gels other linkages between polysaccharides, probably with direct chain-to-chain contacts, have to occur. A variety of such reactions is known (24, 32)—coulombic interactions between ionic groups of different charge, which extend over relatively large distances and are relatively stable to heat; hydrogen bonds between hydroxyl and carboxyl groups, which extend over small distances, in the range of van der Waals radii and are very labile at elevated temperatures; and finally van der Waals forces, which are even weaker. A maximum interaction is obtained when the molecules or groups are in closest contact, in a distance closely related to the envelope of the van der Waals radii of the constituent atoms.

In spite of their sensitivity, secondary valence bonds may be of great importance. Polysaccharide molecules contain a great number of functional groups with restricted motion. If two chain molecules approach each other, they can therefore be held together by several linkages, which form large zones of attachment. The junction so formed, however, will have a relatively high stability only, when the functional groups are easily accessible and the chain molecules show a complementary surface in order to find a closest contact. For polysaccharides containing the sugar monomers in pyranose form, it might be supposed that functional groups in equatorial positions are more readily accessible than those in axial positions (16). Therefore the local positions of the functional groups are of great importance in gel reactions.

The gelation reaction itself involves changes of solvent-solute and solute-solute forces. These changes are brought about by (a) additions of sugar or salt to the gel mixture, causing dehydration of the macromolecules (salt also suppresses the dissociation of dissociated groups, decreasing the repelling action of the molecules) and (b) by dropping the temperature, causing a decrease of the kinetic energy of the particles. These changes cause the relative interactions of the functional groups of the macromolecules with the solvent to become weaker than those between the functional groups of two macromolecules—association (gelation) occurs.

According to their gelation properties, two main classes of polysaccharides can be distinguished, differing in the sensitivity of the gelation reaction and the stability of the gels. In searching for an explanation for these differences, it was considered possible that the different distribution of functional groups might produce this effect.

Polysaccharides of Class 1—e.g., pectin, regenerated celluloses, and eventually algin—are built up from only one type of monomer, linked with one type of linkage. They have the same regular structure along the whole macromolecule and are able to form zones of attachment at any place along the molecules, or theoretically even along whole molecules. Considering now a cross-linking reaction, the size of the zones of attachment between the macromolecules is therefore not governed by the constitution of the molecules, but merely by the reaction conditions. If this reaction goes completely to the association side, we have no longer a stable gel, but a complete coagulum. Therefore the gel is very unstable and the stability depends enormously on the pH, salt concentration, solids content, etc., of the gel mixture. Furthermore, if these gels are dried, the molecules are forced to complete association. All bonds have the same stability; the coagulum will not swell again in the original solvent—or it dissolves completely (Figure 1).
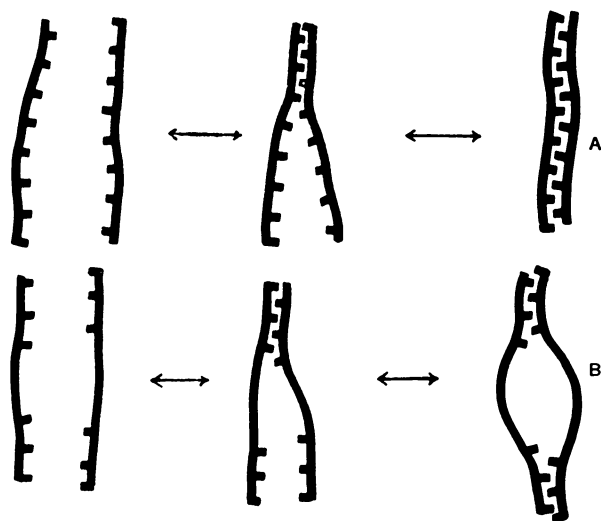

Figure 1. Association between chain molecules

A. Chain with one type of monomer
B. Chain with two types of monomers

Polysaccharides of Class 2—e.g., agar (composed of D-galactose, L-galactose, anhydro-L-galactose), tamarind seed mucilage (composed of D-glucose, D-xylose, D-galactose)—are built up from two or more different types of monomers, often linked with different types of linkages. They have therefore not the same regular structure along the macromolecules, but probably different sections with different affinities for each other. Considering now a cross-linking reaction, the formation of zones of attachment between the macromolecules is restricted by their constitution to discrete zones of mutual high affinity. Sections with a lower mutual affinity, however, may stay unaltered and stabilize the gel system. Therefore these gel systems have a relatively high stability, similar to covalent bonded gels. They are not easily affected by pH shifts, salt concentrations, etc. Furthermore they can be dried and will swell again proportionally to their original volume, because the energy of the new chain-to-chain contacts formed on drying remains below the energy of the initial zones

(Figure 1). These gels have "gel memory" (*11*). The protein gelatin shows analogous properties.

Even if the exact chemical composition of a polysaccharide is known, its fine structure is not defined. The fine structure is governed mainly by two variable factors, the conformation of the sugar monomers and the conformation of the chain. The conformation of the sugars describes the stereochemical position of every functional group on the sugar monomer and has been discussed in detail (*16, 27*). The conformation of the chain—i.e., the arrangement of the sugar monomers along the chain axis—has not yet been fully investigated. There is no doubt that the stereochemistry of the sugar monomers influences the conformation of the chain; on the other side, the position of the glycosidic bonds and the conformation of the chain may produce a tendency for the sugar monomers to adopt a shape different from the corresponding free sugars or their derivatives. Therefore different polysaccharides, or even one polysaccharide under different reaction conditions, can show different fine structures.

Amylose is an instructive example, showing the relationships between different conformations and chemical properties (*28*). In the discussion of gelation mechanisms, the evaluation of the fine structure of the polysaccharides is a very important point.

Some Special Gel Systems

Pectins, poly-D-galacturonic acid partially esterified with methanol (*6, 15, 17*), with a degree of methoxylation of 70% and higher, will form gels with additions of acid and sugar at a pH optimum of 3.0 to 3.4 at relatively high temperatures ("rapid set pectin"). Pectins with a degree of methoxylation of 50 to 70% will form gels with additions of sugar and more acid at a pH optimum of 2.8 to 3.2 and at lower temperatures ("slow set pectin"). The amount of acid required is approximately proportional to the amount of free carboxyl groups.

Completely methoxylated polygalacturonic acid forms gels with sugar alone (*4*). The added sugar seems to have a general dehydrating effect and can be replaced by similar hydrophilic compounds or even salts like ammonium sulfate (*19*). Pectins with a degree of methoxylation under 50% do not form gels with sugar and acid. They require such a low pH that flocculation occurs in the gel mixture. The smooth relationship among the degree of methoxylation, acid requirement, and gel stability (*12*) shows that a substitution of the carboxyl groups induces merely a change of the gel conditions, but probably not of the gel mechanism.

Very interesting is the influence of temperature, measured by mixing a pectin-sugar and a sugar-acid solution at different constant temperatures. After standing, the gelation occurs optimally at 25° C. At relatively high and low temperatures, no gel formation takes place (*3*). This sensitivity of the reaction indicates that the linkages must be of secondary valence order.

Pectins with a degree of methoxylation under 50% form gels in the presence of calcium ions and other polyvalent cations without sugar and acid. The amount of pectin required for the formation of calcium ion gels decreases with the degree of methoxylation. The amount of calcium ion required for the formation of gels shows an optimum for pectins with a methoxyl content from 5.5 to 6.5% and decreases with the degree of methoxylation in the range of 6.5 to 0% methoxyl (*2*). Ion selectivity experiments with pectins show that the selectivity for calcium ions decreases with the degree of methoxylation (*5, 13*).

Because a decrease in the degree of methoxylation causes a decrease in the amount of pectin required for gelation, the amount of calcium required for gelation, and the affinity of calcium for pectin, but an increase in gel stability, it can be assumed that the calcium ion bonding of pectin and its gelation have at least no direct connection as postulated in the calcium ion bridge theory. Furthermore according to the calcium ion bridge theory highly esterified pectins should gel with calcium ion too; and gels with Coulombic bonds should have a much higher stability than sugar-acid gels. Instead, both liquefy in the same manner, upon heating.

When the hydroxyl groups of high-methoxyl or low-methoxyl pectins are partially esterified with acetic acid, every type of gelation is completely inhibited (25, 30). A 2.5% acetylation inhibits the gelation of pectins completely. The sugar-acid and the calcium ion gelation are inhibited to the same extent; therefore their gelation mechanisms must be very similar. This sensitive and complete inhibition suggests that the hydroxyl groups are engaged in the gelation process and that the inhibition process must be a steric one. It can be accepted that hydroxyl groups participate in the formation of junction zones with hydrogen bonding between the secondary hydroxyl groups. This hypothesis is furthermore supported by the fact that if a pectin with acetyl groups, which shows inhibited gelation properties, is further acetylated to a very high degree, gelation is again possible (30). In this case a new regular surface with hydrophobic groups is formed on top of the old one. These gelation properties conform mostly to those outlined for one type of monomer polysaccharides.
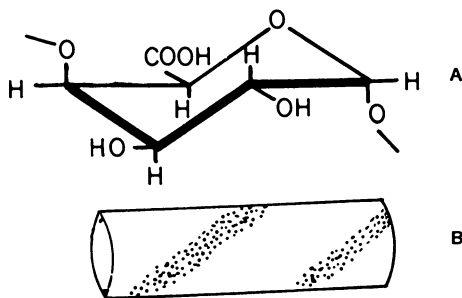

Figure 2.   Structure of pectin

A. Conformation of a D-galacturonic acid monomer
B. Conformation of chain with position of functional groups (schematic)

X-ray data suggest the following structure for pectin (21–23): The molecule is highly curled, so that even the free rotation of the glycosidic bonds is hindered. The conformation C 1 causes an angle of 90° of the carbon-glycosidic oxygen bond with the plane of the galacturonic acid ring. The screw symmetry of the chain is threefold. But all free hydroxyl groups and the carboxyl groups are in equatorial positions. In a very simplified picture the pectin molecules look like little flexible rods with all functional groups around this rod (Figure 2). There are two hydroxyl groups per monomer in readily accessible equatorial positions. Pectin can therefore not have a high crystallization tendency; it is soluble in water. But by reducing the charge of the molecules and by adding some dehydrating solids, pectin can form hydrogen bonds between the macromolecular chains. The regular rodlike and rigid structure is typical for pectin

and seems to favor a close, but reversible, approach of the chain molecules to each other. The equatorial position of all functional groups favors an optimal hydrogen bond formation.

Algin (*18, 31, 34*) is composed of poly-D-mannuronic acid; it differs from pectin in the positions of the hydroxyl groups (cis) and of the glycosidic bonds. The following discussion is based on this structure, although it has been questioned by the recent detection of D-glucuronic acid as a component of algin (*8*). Algin forms no sugar-acid gels, but only calcium ion gels. They have, however, not the same stability as pectin gels and are not in every case thermoreversible. Therefore algin gels are more like viscous coagulations than true gels. This is a very important point, because algin has the same arrangement of carboxyl groups as pectin. It shows, again, that carboxyl groups are not alone responsible for the formation of calcium gels. Algin does not form insoluble magnesium ion salts as pectic acid does.

The fine structure (*1, 16, 22, 33*) of algin seems to change between two conformations, C 1 and 1 C. If the chair form of the monomers is accepted as present in every case, in no conformation may all free functional groups occur in equatorial positions, especially not the free hydroxyl groups at C_2 and C_3. Therefore algin has only one hydroxyl group per monomer in an easily accessible position. This structural difference may explain the differences in the gelation properties between algin and pectins. Furthermore, it stresses the importance of the arrangement of the hydroxyl groups in the formation of the cross-linking zones.

Cellulose (*20*) gels are not of technical importance. Cellulose, however, is an interesting example of structural relationships. Cellulose is insoluble in water, because of its pronounced crystallinity, and the strong hydrogen bonding between the macromolecules. Therefore, cellulose gels can be obtained only by chemical decomposition of cellulose derivatives such as cuprammonium compounds or xanthates in aqueous solutions (*11*). These gels have a certain stability; but the pronounced tendency to coagulate shows that the solute-solute forces are much stronger than the solute-solvent forces. The fine structure of cellulose (*16, 20, 22*) is well known.

Glucose occurs in the chair form in the C 1 conformation; all functional groups and the glycosidic bonds have equatorial positions, a very stable conformation. The carbon–glycosidic oxygen bond makes an angle of approxi-
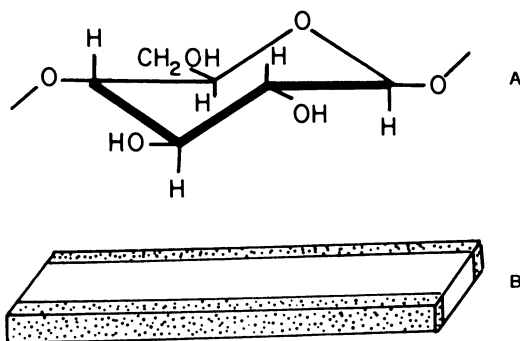

Figure 3.   Structure of pectin

A.   Conformation of a D-glucose monomer
B.   Conformation of chain with position of functional groups (schematic)

mately 20° with the plane of the glucose ring. The glycosidic bonds show free rotation. The cellulose chain has the form of a kinked band with twofold symmetry and with all hydroxyl groups on both sides in easily accessible positions (Figure 3). The very regular structure and this arrangement of the groups seem to favor the extraordinary properties of cellulose. In comparison to pectin cellulose has a very regular structure and cannot form labile gels.

Starch (*10, 26*) has a slightly different constitution than cellulose, but a very different fine structure and different physical characteristics. Starch can be dissolved in water, but does not form true thermoreversible gels. The gelatinization of starch (*26, 29*), although of great technical importance, can be regarded merely as a disintegration of the natural starch granules, a swelling or dissolution process. Therefore it cannot be compared with the gel reactions discussed. Because starches from different sources show a different composition and different properties, they cannot be discussed in detail in this paper.

Conclusions

A comparison of the structural differences and gelation behavior of the polysaccharides discussed leads to the following conclusions. Gelation seems to occur mainly through hydrogen bond formation. Several neighboring hydroxyl groups on different macromolecules together form zones of attachment. Because the hydroxyl groups are linked to a more or less rigid backbone chain, the fine structure of this chain is of great importance for arranging these groups in complementary positions, forming "functional surfaces."

Groups in equatorial positions seem to be more readily accessible for chain-to-chain reactions than groups in axial positions. Carboxyl groups seem not to share directly in the formation of the junction zones. They are important as regulators of the potential of the chain molecules.

A regular fine structure causing maximal hydrogen bonding between the molecules reduces the possibility of reversible processes and therefore reduces the gel-forming properties of the compound. Other polysaccharides with different types of monomers or with branched chain structures can be treated in a similar manner. However, much more study of their fine structure and the accessibility of their functional groups is necessary.

Although there is no direct evidence that molecular structure and gelation properties show such a close correlation, this hypothesis may help to show that the mechanism of gelation is a very specific reaction analogous to specific biochemical reactions, like antigen-antibody reactions, etc., in which polysaccharides are also involved.

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Functional Aspects of Hydrocolloids in Controlling Crystal Structure in Foods

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Food processors have become increasingly conscious of the factors that influence the popular acceptance of their products in line with changing consumer tastes and preferences. The methods of processing, distribution, storage, and merchandising of foods have changed considerably in the past two decades. The American housewife is ready to accept "easy to prepare" foods and factory-packaged processed foods, which she previously made at home. She has storage facilities available at home, which results in less frequent shopping tours. Many characteristics such as flavor, color, texture, density, separation properties, and shelf life exert a profound influence on consumer acceptance. Many carefully processed foods must travel a long path before reaching the consumer's table and must still retain their original goodness. Many foods are processed, then stored in warehouses, coolers, or freezers; shipped in trailers to distributing depots; again stored and then trucked to retailers. Here the product is stored in display cabinets under varying and changing conditions, and after purchase may be stored from several hours to several weeks in a home freezer or refrigerator until finally consumed. Original properties of body, texture, etc., must be maintained throughout these varying hazards.

Properties such as body, texture, smoothness, and chewiness in foods are related to the control of crystal structure. The most common and the most important crystalline materials encountered in foods are sugar and ice. It is necessary to control growth, or increase the size of these crystals, as in ice cream; and to prevent their disappearance or solution in the solvent, which is usually water, as in icings. In most instances, characteristic crystalline structure is controlled by formulation, type and ratio of ingredients, manufacturing techniques, and proper use of equipment.

Edible hydrocolloids are additives or adjuncts which expedite and modify production techniques in order to control crystal patterns. The mechanism of crystal equilibrium may be accomplished because these hydrocolloids have gelling characteristics, increase viscosity, affect solubility, suspend solids, bind and hold moisture, affect interfacial tension, or, as charged polymers react with other large molecules of opposite charge. Because of these properties these materials are not only added to control crystal structure, but also to prevent masking of flavors, prevent separation, induce smooth body and texture, improve whipping, thicken, gel, prevent sticking, improve gloss and luster, stabi-

lize emulsions, and speed setting and drying. It is often necessary to blend hydrocolloids in order to "stabilize" a specific food completely.

In many foods, it is essential to control either sugar or ice crystal patterns and in others there is a problem of controlling both. In Table I are listed the foods in which we encounter crystalline structure problems and the type of crystals with which we are concerned.

Table I. Hydrocolloids in Foods

A. For Ice Crystal Control	B. For Sugar Crystal Control
1. Ice cream	1. Ice cream
2. Ice milk	2. Ice milk
3. Mellorine	3. Mellorine
4. Sirups for variegated ice cream, tarts, and sundaes	4. Candy
	5. Icings for baked goods
5. Sherbets and water ices	6. Glazes for baked goods
6. Water ice stick confections	7. Doughnut glazes
7. Frozen fudge bars	8. Sirups for variegated ice cream, tarts, and sundaes
8. Fruits for ice cream	
9. Malt shake bases	9. Sherbets and water ices
10. Frozen fruit	10. Water ice stick confections
	11. Frozen fudge bars

The group of foods known as "frozen confections" present a problem of controlling or processing both sugar and ice crystals. This is easy to understand when we realize that water and sugar are present in a high percentage and that the product is consumed in a frozen state. It is also noteworthy that the majority of these goods fall into the category of "desserts" or "sweets."

Ice Cream, Ice Milk, and Mellorine

Ice cream is a frozen dessert prepared from dairy products and sugars with tremendous consumer acceptance. It is distributed and served in many forms and shapes. A typical formula for ice cream mix is:

Butterfat	10%
Milk solids nonfat	11%
Cane sugar	12%
Corn sirup solids	4%
Stabilizer	0.3%
Emulsifier	0.2%
Water	62.5%
	100.0%

The primary sources of fat are fresh cream, frozen cream, butter, butter oil, whole milk, and plastic cream. The milk solids nonfat (often called serum solids) are supplied by any one or a combination of condensed milk, superheated condensed milk, sweetened condensed milk, dry skim milk, skim milk, and sometimes fresh or dry whole milk. The sugars most often used are cane and beet sugar, corn sirup, corn sirup solids, and corn sugar or dextrose. The ice cream mix is blended in a steam-jacketed kettle with ample agitation, pasteurized, homogenized, and then cooled to 40° F. The mix may or may not be stored. Freezing is accomplished by incorporating air into it with beaters and applying refrigeration by direct expansion. During freezing (21) ice crystals and other crystals are formed and the process must be clearly understood and controlled. The semifrozen or plastic ice cream is then hardened or further frozen and stored in a hardening room at about —20° F. Ice milk is similar to ice cream and its consumption has grown in the last decade. It

differs from ice cream in that it contains lower levels of fat and slightly lower solids. Mellorine, which may contain low or high levels of fat, is a frozen product in which the butterfat has been replaced with edible refined and plasticized animal or vegetable fat. In Table II are shown representative ice cream and milk formulas.

Table II. Formulas for Ice Cream and Ice Milk

	Ice Cream, %	Ice Milk, %
Butterfat	10.0	5.0
Milk solids nonfat	11.0	12.0
Cane sugar	12.0	12.0
Corn sirup solids	4.0	5.0
Stabilizer	0.3	5.0
Emulsifier	0.2	0.1
Water	62.5	65.5
	100.0	100.0

Ice cream stabilizers are natural or synthetic hydrocolloids (3, 22) which have the characteristic property of imbibing or absorbing large amounts of water. They are effective in controlling mix viscosity, controlling the type of meltdown, and aiding in preventing coarseness due to ice crystal growth during storage. The amount and type of stabilizers permitted for use in frozen confections are limited by law in most states. When the Federal Standards of Identity for Ice Cream, etc., are issued, they will also be governed by national statute. In most areas 0.5% by weight of the mix is the maximum amount of stabilizing material permitted.

Emulsifiers assist the stabilizing hydrocolloids in controlling crystal structure. They accentuate the function of the homogenizer in reducing the size of the fat globules. They also reduce the interfacial tension between the fat and water phases of the mix. The result is smaller ice particles and air cells when the mix is frozen and a smoother and creamier finished product.

Part of the water in ice cream mix is bound by sugar solids and serum solids. The amount of water that is bound will depend on the types of sugars and the types and condition of milk proteins (27). Usually the sugar and serum solids are not present in sufficient quantity or are not strong enough to bind the "free water" present. A portion of this free water is frozen into small ice crystals in the freezer, the balance is frozen in the hardening room. If this water is not bound, it will freeze into large ice crystals, because freezing in the hardening room is substantially slower and without agitation. Further, during shipping and storage in dealer and store cabinets and in the home freezer, the fluctuating temperatures will result in melting and refreezing of these ice crystals. The slow refreezing of this melted ice will result in large crystals. This process is called "heat-shock." Resistance to it is greatly accentuated by the presence of water-absorbing or water-binding hydrocolloids.

Hydrocolloids for ice cream stabilization must fill the following requirements in addition to providing heat shock protection during temperature fluctuations (16).

1. Provide a smooth, creamy meltdown.
2. Produce uniform and normal viscosities.
3. Eliminate "wheying off" or separation in the mix.
4. Require no aging of mix for full development.
5. Produce desirable chewing qualities and good body.
6. Be insensitive to mix acidity variations

7. Dissolve and disperse readily in mix without premixing with sugar.
8. Give clean flavor release.
9. Help to prevent shrinkage.
10. Aid in overrun control.

The introduction of high temperature–short time pasteurization of mix has emphasized the need for hydrocolloids which are "quick-soluble" and do not require heat for complete activation.

Many hydrocolloids may fulfill one or several of the requirements of a fully balanced ice cream stabilizer and still present production problems. For this reason most stabilizers are blends of several hydrocolloids provided for the specific type of frozen confection being manufactured. Soft-served ice cream and ice milk present other production and distribution problems and require substantially different blends of gums. Many studies and comments have been made on the types and levels of hydrocolloids used for stabilizing ice cream, ice milk, and mellorine (3, 6, 8, 15, 16, 24–27).

Gelatin was probably the first material used for stabilizing ice cream. Although it is still accepted by many plant managers, its use has declined. Mix stabilized with gelatin requires aging prior to freezing. Ice cream stabilized with gelatin melts too rapidly and does not have good "heat shock" resistance. A gelatin of 200 to 250 Bloom strength should be used at a level of 0.3 to 0.5%.

Sodium alginate (algin) is one of the most widely used hydrocolloids for ice cream. It is supplied in several viscosity types. The lower viscosity material is recommended in order to prevent thick mixes. It is used at a level of 0.15 to 0.25%. It is added to mix at higher temperatures in order to minimize precipitation by calcium salts present in milk products. Sodium alginate is sensitive to high acidities often developed in some mixes and causes thickening.

Propylene glycol alginate is not sensitive to mix acidity or calcium ions and is replacing sodium alginate for stabilization of ice cream; 0.10 to 0.20% use is recommended.

Sodium carboxymethylcellulose (commonly known as CMC) was introduced in 1945 by Josephson and Dahle (10) for use in ice cream. It is cold water–soluble, will not react with acid, and has excellent water-binding properties. When properly processed, it is easily dispersible and quickly soluble in the mix. These properties make it well suited for high temperature–short time (HTST) mix. When used alone, it has a tendency to cause separation or "wheying off" in the mix. Irish moss extract is used with CMC to eliminate this condition. From 0.15 to 0.25% CMC is most often used in ice cream mix.

Locust bean gum also has excellent water-holding properties. It is cold water–dispersible, but complete hydration is accomplished only after pasteurization. This precludes its use in HTST systems. As with CMC, it causes mix separation which may be eliminated by its use with Irish moss extract.

Irish moss extract, or carrageenin, is a negatively charged polymer which reacts with positively charged protein molecules, imparting rapid increase in mix viscosity. There are many types used for ice cream, depending on the final use. It is generally used in conjunction with CMC or locust bean to prevent mix separation. Levels between 0.02 and 0.10% are recommended.

Guar gum is a galactomannan used like locust bean gum and at approximately the same levels. However, unlike locust bean gum, it swells in cold solution and requires no heat for complete hydration. It also induces mix separation which may be controlled with carrageenin. It is well suited for use in HTST systems.

Pectin, ground psyllium seed husks, karaya gum, tragacanth gum, and agar have also been used, but are not well accepted today. The use of many of these hydrocolloids in frozen confections singly and in combination, is covered by patents too numerous to list.

The growth of lactose crystals in ice cream results in a serious texture defect known as "sandiness." It is usually caused by temperature fluctuations, high serum solids in the mix, and high cabinet storage temperatures. The ratio of serum solids and moisture must be controlled. Hydrocolloids have some effect on controlling sandiness, but not as much as proper handling techniques and formulation.

Arbuckle has published some excellent work on microscopic studies of ice cream crystal structure and effects of hydrocolloids on this crystal structure. Some interesting examples of this work are shown in some of his papers (1, 18).

Sherbets and Water Ices

Water ices and sherbets are frozen confections which have become increasingly popular. Water ice is a semifrozen product (5) made of water, sugar, fruit, fruit juice with added flavor, color, acid, and stabilizer. Sherbet is made of the same ingredients as water ice, but also contains added milk solids. Most often they are produced like ice cream. Water ices may or may not be pasteurized. Sherbets are almost always pasteurized and in most areas are subject to the dairy products regulations. Listed in Table III are typical formulas for water ices and sherbet. Sugar is the most important solid in these products and a proper blend of the various types of sugars is essential in order to obtain good body and sweetness. Cane or beet sugar is mostly used and is blended with corn sugar (dextrose), corn sirup solids, and sometimes invert sugar. Milk solids nonfat are added to provide flavor and food value and to give characteristic body to sherbet. Fat helps lubricate the freezer and aids in controlling overrun. Excessive overrun may be obtained when gelatin or CMC is used as the stabilizer. The addition of as little as 0.5% butterfat generally relieves this situation.

Table III. Formulas for Water Ices and Sherbet

Water Ices	%	Sherbet	%
Cane sugar	24.0	Butterfat	1.0
Corn sirup solids	8.0	Milk solids nonfat	3.0
Stabilizer	0.5	Cane sugar	23.0
Water	67.5	Corn sirup solids	7.5
	100.0	Stabilizer	0.5
		Water	65.0
			100.0

Hydrocolloid stabilizers are vitally important in the manufacture of sherbet and ices. The absence of larger amounts of milk colloids and the presence of larger amounts of water emphasize the need for proper stabilization. Stabilizers help to maintain a firm body and smooth texture during manufacture, storage, and distribution. "Bleeding" and surface sugar crystallization are two problems related to crystal structure in sherbet and ices and are very closely associated with the use of the proper hydrocolloid stabilizer.

In "bleeding," unfrozen sirup migrates through the cellular structure of the ice to the bottom of the container. This occurs even at low temperatures, because high sugar solids prevent total freezing of the sirup. The proper use

of hydrocolloids thickens the sirup and retards or eliminates this migration. The reduction in overrun induced by proper use of hydrocolloids also helps in retarding bleeding. The resulting formation of small ice crystals also makes it more difficult for the sirup to pass through.

Surface crustation is caused by sucrose crystallization. It is characterized by hard white spots on the surface. It is remedied by the use of corn sirup solids and larger levels of hydrocolloids. During freezing in a continuous freezer there is ice separation caused by centrifugal separation of small ice crystals. Increase in mix viscosity by use of hydrocolloids inhibits this action.

In addition to the above, a good stabilizer should be unaffected by acid or calcium salts, be easily dispersed in water at low temperatures, control overrun, require no aging, impart good body, texture, and dipping qualities in long periods of storage, not result in a gummy, pasty, or crumbly product, and give clean flavor release.

Most of the hydrocolloids listed for ice cream may be used in ices and sherbets. Gelatin is used a great deal. However, it makes overrun difficult to control and consequently it is used in conjunction with other hydrocolloids. A 225 Bloom gelatin is used at 0.4 to 0.5%. Sodium alginate is affected by acid and calcium salts and is not often used. Propylene glycol alginate is more resistant in this respect and is used at levels of 0.15 to 0.25%. Carrageenin is used in many blends.

CMC, which is cold water–soluble and easily dispersed, is widely used. It is combined with other hydrocolloids because it makes overrun difficult to control. It is used at about 0.2%. Pectin is used in sherbet and ices at a level of 0.2%, locust bean gum at 0.25%, and karaya gum at 0.4%. Guar gum is being accepted for this application at levels similar to locust bean gum. Combinations are made in order to use the best qualities of the various hydrocolloids.

Variegated Sirups for Ice Cream

Variegated ice cream is a combination of ice cream and fruit or sirups. The flavors—usually strawberry, raspberry, chocolate, caramel, butterscotch, and marshmallow—are pumped or injected into the ice cream base to make contrasting streaks of color and flavor. They are also poured onto ice cream in cups to make frozen ice cream sundaes and on shaped ice cream pieces to form ice cream tarts. The sirup, or puree, must be properly distributed, in such a way that the flavor portion will not settle or become icy during storage. Large plants (7) run this sirup or puree through a freezer to whip in a small amount of air, as well as reduce the temperature to that approaching the temperature of ice cream. This results in a product that will exhibit less tendency to settle and become icy. Smaller plants resort to pumps which force the puree into the ice cream.

The high sugar content of these sirups depresses the freezing point and slows up freezing in the hardening room. The result is large ice crystals. The product should be stabilized to prevent ice crystal growth and to give meltdown characteristics similar to ice cream (23). Proper balance of sugar in the formula is necessary to obtain desirable qualities. The stabilizer should provide sufficient viscosity so that the sirup will not flow too rapidly and at the same time permit it to be readily pumped. Dahle and Aull (7) have studied this problem and have come to these conclusions. When 2% is used, 150 grade pectin is satisfactory for chocolate variegated material. Slightly over 1% is

needed to provide perfect stabilization with strawberry puree. Irish moss (0.3%), locust bean gum (0.5%), cellulose gum (0.75%), and gelatin (0.1%) are effective in strawberry and chocolate variegated products.

Frozen Fruits for Ice Cream

High on the list of accepted ice cream flavors are strawberry and peach. These two fruit flavored frozen desserts present several problems during manufacture and storage. The strawberries and peaches are received in a frozen state and then defrosted before being incorporated into the ice cream at the freezer. Improper freezing of the fruit results in large ice crystals and ruptured berries or pieces of fruit. They have poor texture, appearance, color, and flavor, due to juice drainage. The finished frozen ice cream is icy and coarse because of the large ice crystals formed in and around the fruit during storage. This condition reduces acceptability to the consumer. This undesirable condition is overcome by the addition of hydrocolloids or stabilizers.

The best method (2) is to mix the stabilizer with sugar and add it to the fruit prior to freezing during normal packing process. The inclusion of the hydrocolloid at this point is most convenient and economical for the ice cream manufacturer and prevents appreciable damage to the tender fruit tissue by arresting ice crystal formation in its initial stage. There is no loss due to drainage of sirup during defrosting prior to use in the ice cream plant. More uniform, smaller, and smoother ice crystals are produced in the finished ice cream. The hydrocolloids must not mask the fruit's delicate flavor, change its natural color, or contribute a heavy or pasty body to the fruit.

Cellulose gum, Irish moss extract, and propylene glycol alginate are the hydrocolloids most often used in this application at levels of between 0.25 and 1%, depending on the fruit-sugar ratio and the type of fruit.

Arbuckle (2) has done some excellent work in this field.

Water Ice Bar Novelties

The water ice bar is very well accepted by both children and adults and in many states is defined and standardized by law. The mix consists of sugars, flavor, color, stabilizer, fruit acid, and water and is quiescently frozen in molds submerged in cold brine. Sugar is the only source of solids in the mix and the content is considerably lower than in water ices. Sugar solids range from 16 to 19%. Low sugar solids will result in a brittle, icy pop; high sugar solids in excessive sweetness, bleeding, and crystallization if stored for any length of time.

Hydrocolloids are very necessary for water ice bars, to make a chewy and smooth product and to form small ice crystals. The stabilizer will also prevent drainage or "sucking" out of flavor and color. It will bind the water and prevent sugar from dissolving in free water and cause bleeding and sticking to the wrapper. It may also prevent or retard crystallization due to poor sugar balance and resulting "white spots." It may prevent settling of cocoa matter in chocolate water ice bar mix and in the confection and lengthen the melt-down time.

In most plants, ice pop mixes are prepared cold and the hydrocolloid should be readily dispersible and soluble in cold mix. The hydrocolloid must be compatible with acid. Karaya gum (0.4%), locust bean gum (0.25%), and pectin (0.2%) were originally the stabilizers used. More recently CMC (0.25%),

propylene glycol alginate (0.2%), and carrageenin (0.1% to 0.2%) have been used with satisfactory results.

A side effect of some hydrocolloids is prevention of color migration in frozen water ice bars containing food-grade aniline dyes. Stoloff (23) explains this effect with Irish moss extract by the fact that carrageenin is a negatively charged polymer which is attracted to the positively charged aniline dyes. The type of Irish moss extract used is a water gel former and forms a gel matrix which is uniformly distributed throughout the pop.

Figures 1 to 8 demonstrate the "drainage or meltdown test" developed in our laboratories (17). Ice pop I contains no stabilizer; II, 0.2% Irish moss extract; III, 0.15% karaya gum combined with 0.15% locust bean gum; IV, 0.2% CMC. The mixes were prepared cold, poured into the same mold, using one fourth of the mold for each mix. They were then frozen in the brine tank, defrosted, packed, and stored in the hardening box.

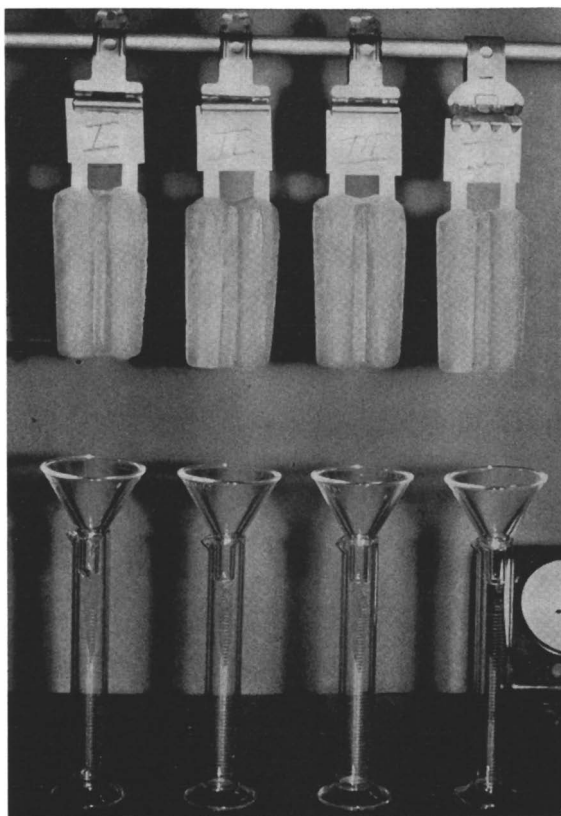Figure 1. Four ice bars after 30 minutes of melting
at room temperature (76° F.)

Frozen Fudge Bars

The frozen fudge bar-on-a-stick is a quiescently frozen mix, high in serum solids and sugar. Because this product is most often frozen without agitation, it is necessary to incorporate protective water-binding hydrocolloids to induce the formation of small ice crystals and a well-bodied, smooth, chewy confec-

tion.   Chocolate is the most popular flavor.   The hydrocolloids used will prevent setting of cocoa matter both in the mix and in the confection during freezing. Stabilizing materials are usually the same as those used in ice cream, and are used at about the same levels.
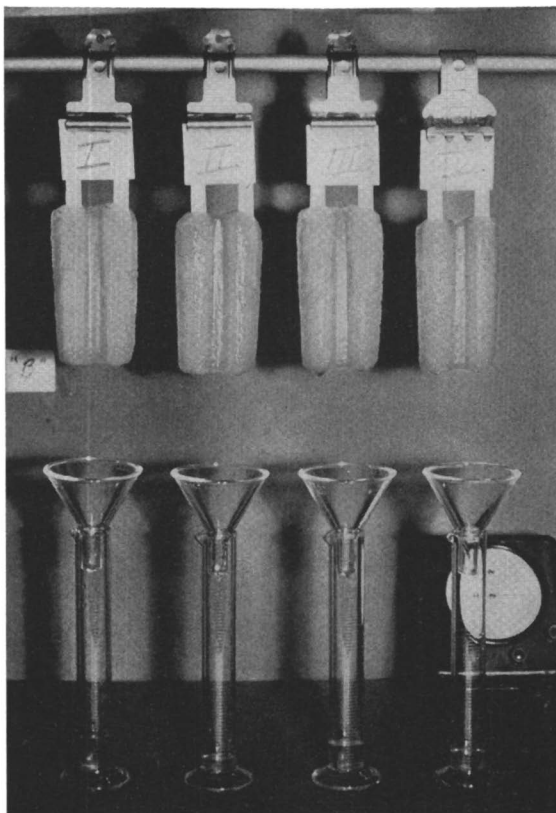

Figure 2.   Ice bars after 35 minutes at room temperature.   Note difference of level of melted liquid and juicy appearance of II and IV and formation of clear ice on upper portion of I and III

Icings for Baked Goods

Icings are significant factors in determining the acceptance of sweet goods and cakes offered through retail and wholesale channels.   They are also significant factors in packaging and distribution problems of these bakery products.   Eye appeal means sales in supermarket methods of merchandising. Icings are coatings or toppings composed basically of sugar and water.   The addition of other ingredients, such as shortening, milk solids, stabilizer, aerating agents, salt, and flavor, changes the character of the icing.   There are flat icings (generally applied to sweet goods), fudge-type cake icings which contain low levels of fat and are partially aerated, cream icings which contain higher levels of fat and are highly aerated by beating or whipping, and coating-type icings which contain very high levels of hard fat and have the appearance of candy coatings.   The flat or sweet roll type of icing presents difficult stabilizing

problems. It is applied to sweet rolls, packaged in cellophane by wholesale bakers, and sold through large food chains.

There are many difficulties encountered in the manufacture and distribution of these iced sweet rolls, which are hermetically sealed in cellophane. During hot and humid weather the icing melts and disappears and may stick to the wrapper. The icing may also crack and peel and develop a dull appearance.
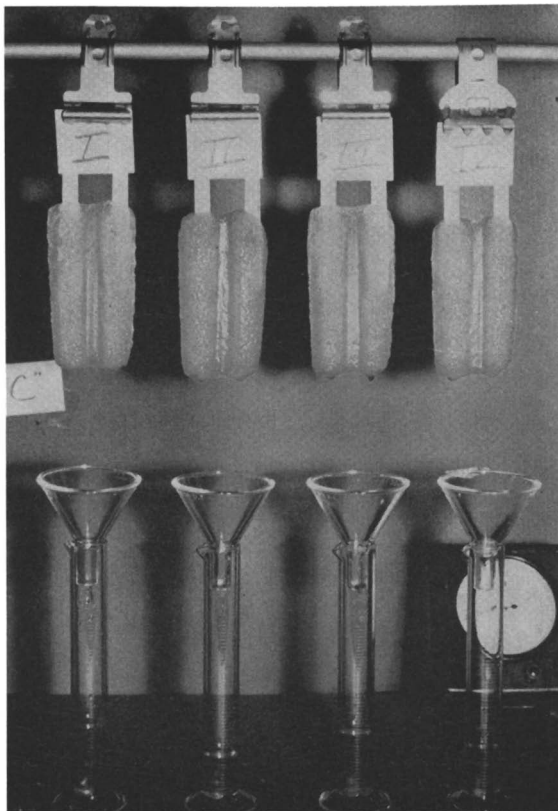
Figure 3.   Ice bars after 40 minutes.   Observations noted in 2 are accentuated by further passage of time

Problems in stability of flat icings (*12*, *14*) center around solubility of sugar and the movement of moisture in the sweet roll which is sealed in cellophane. Mickevic (*14*) points out that at 90° F. a saturated sugar solution will hold 69.5% sugar. In an icing with 85 parts of sugar to 15 parts of water, 34 parts of sugar are in solution; 51 parts are crystallized or never go into solution if the water is not heated above 90° F. As icing temperature increases—for example, on a hot summer day—more sugar goes into solution and the icing melts and may stick to the wrapper. Hydrocolloids which have affinity for water take up this water when the temperature increases and the sugar has a tendency to go from crystal to solution stage. Lipman (*12*) described this movement of moisture in the packaged iced sweet goods. Moisture is released by the baked product and is condensed on the icing surface because of its inability to escape through the moisture-sealed cellophane. The undissolved or crys-

talline sugar dissolves in this free moisture and the process is accelerated by heat. The icing disappears and the resulting sirup causes the cellophane to stick to the baked product. This condition may be remedied by using the minimum amount of water in the icing, by using cooled, well-baked sweet rolls, and by adding hydrocolloids to bind the free water. The hot flat icing was developed (12) to minimize the use of water. The hydrocolloids or a blend of hydrocolloids (usually sold as plastic or powdered stabilizers or icing bases) are mixed with about 20 parts of granulated sugar and 20 parts of water and brought to a boil. This sirup is added to 100 parts of icing sugar and mixed. The icing is applied hot (120° to 140° F.) to the sweet rolls. A hot sweet roll icing will contain considerably less water than a cold sweet roll icing and still have proper consistency. When the icing is applied hot, water rapidly evaporates from the surface and the iced baked product may be wrapped in less than 60 seconds.

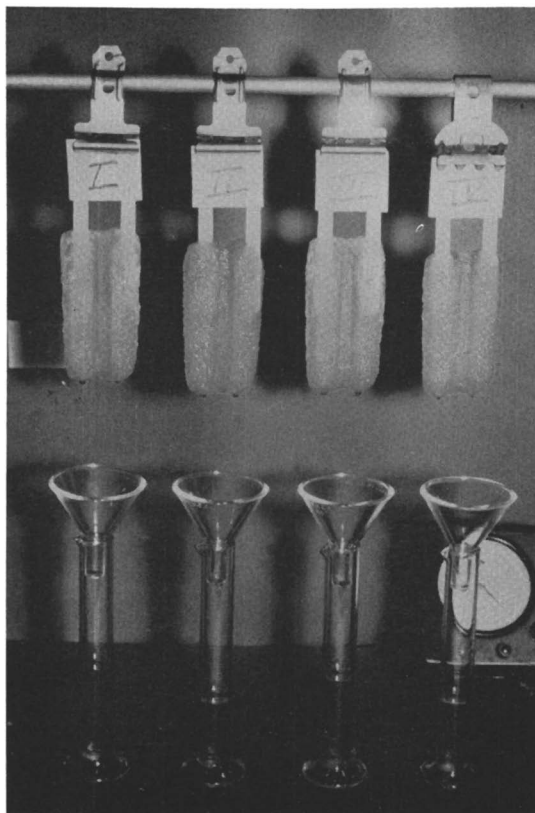Figure 4. Ice bars after 45 minutes. Note difference of appearance and drainage in I and III

The hydrocolloids used stabilize this type of icing by their ability to form a gel or a highly viscous solution. Agar-agar, locust bean gum, sodium alginate (combined with a buffer and calcium salt), Irish moss extract, pectin, and karaya gum are hydrocolloids used. The finished icing may contain from 0.1 to 0.5% hydrocolloids.
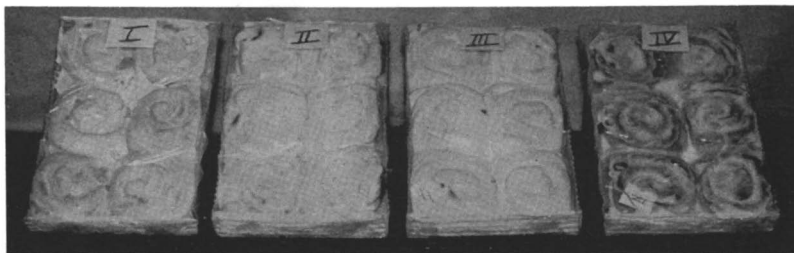
Figure 5.   Iced sweet rolls stored after 24 hours at room temperature.
Icing IV has melted, II and III are whiter
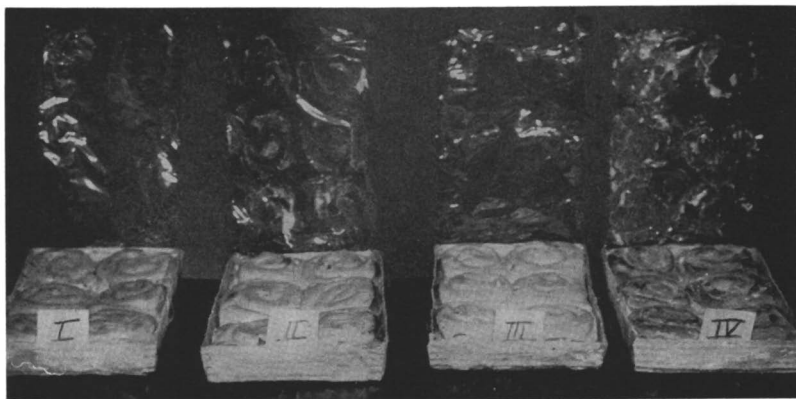
Figure 6.   Same set as in Figure 5 with cellophane wrapper peeled back.
II sticks slightly and IV sticks considerably

Figure 7.   Set stored in cabinet at 100° F., 85% R.H.   I melted; II
shows signs of melting; IV is badly melted; III is normal

Figures 5 to 8 demonstrate the previous discussion.   Four sets of iced sweet
rolls were prepared.   The icing was applied by an icing machine uniformly on
each package (3 ounces of icing on each).   Icings I and II and III are hot
sweet roll icings and icing IV is a cold flat icing.   Icing I is unstabilized, icing
II contains 2% cornstarch, icing III contains 0.2% agar-agar, and icing IV is
unstabilized.   One set was stored at room temperature (76° F.) and another
set in a cabinet at 100° F. and 85% relative humidity.

Doughnut Glaze

Problems of the preparation of a good doughnut glaze are similar to those
encountered in icings.   Doughnut glaze has a tendency to chip or crack and

sweat. This system is also one of sugar and water solubility and crystalliza-
tion conditions. The difficulties are minimized by making a glaze that has as
little water as possible and using the "boiling" or hot glaze method. The stab-
ilizer is boiled with part of the sugar and water, added to the icing sugar, and
mixed.
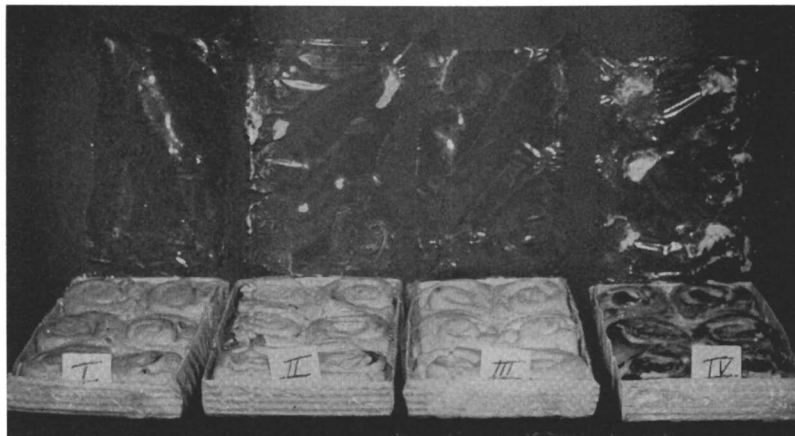
**Figure 8. Set shown in Figure 7 with wrapper peeled back. Note
sticking in II and IV. III, stabilized and made by hot or boiled process,
holds up best**

The reverse effect of solution is crystallization caused by excessive loss of
water in relation to the sugar solids present (4) and the cause of chipping and
cracking. Glucose, invert sugar, and a stabilizer are added to change the
crystallization properties of the sugar. The hydrocolloids used (4) are gener-
ally of the gelling types, such as agar-agar, pectin, Irish moss extract, gelatin,
and sodium alginate. The stabilizer, therefore, increases viscosity of the glaze
so that more adheres to the doughnut, produces quick setting to enable proper
handling, provides flexibility to prevent chipping, and prevents melting and
adhering of doughnuts. The quantity used (4) is between 0.5 and 1% based on
the sugar.

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Theoretical Aspects of Hydrocolloids in Controlling Crystal Structure in Foods

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Variations in the shape habit of crystals are possibly due to variations in the rate of growth in different directions within the crystal. This is illustrated by sodium chloride. Sodium chloride is an ionic bond type of crystal. Crystals of other foods vary from this to the predominantly hydrogen bond type, as in ice and sugar, and the predominantly van der Waals bond type, as in glycerides. Depending upon the type of crystal and other conditions, hydrocolloids can affect crystal growth in foods in at least three ways: They can have direct effect on the crystalline solid as it forms—for example, by adsorption; they can affect the solvent—for example, by changing its physical properties; and they can combine with or otherwise affect impurities present which might otherwise influence crystallization.

We know of many examples of the effect of impurities of crystallization. In many cases impurities will completely inhibit (*2–4*) nucleus formation. Reading the literature on this subject impresses one with the frequent occurrence of hydrocolloids as crystal modifiers, particularly where sugar or water is the material being crystallized. The use of gelatin, locust bean gum, or sodium alginate in ice cream is just one example of many practical applications of hydrocolloids in crystal modification.

Mechanism of Action

Unfortunately, we do not know enough to explain the mechanism of action of these crystal modifiers in each case. Instead, let us look at what we know about crystal growth mechanism and propose some ideas regarding the action of hydrocolloids.

Crystallization might be defined as the process of orientation of ions, atoms,

molecules, or other building blocks into a fixed, repeating arrangement called the crystal. The fixed, repeating arrangement or lattice results in layers of the building blocks within the crystal and plane surfaces called faces in a geometric pattern on the outside of the crystal. The combination of faces or geometric pattern is called habit. Repeating arrangement is an important part of the definition, because some solids have particles in a fixed but not repeating arrangement. They are called glasses.
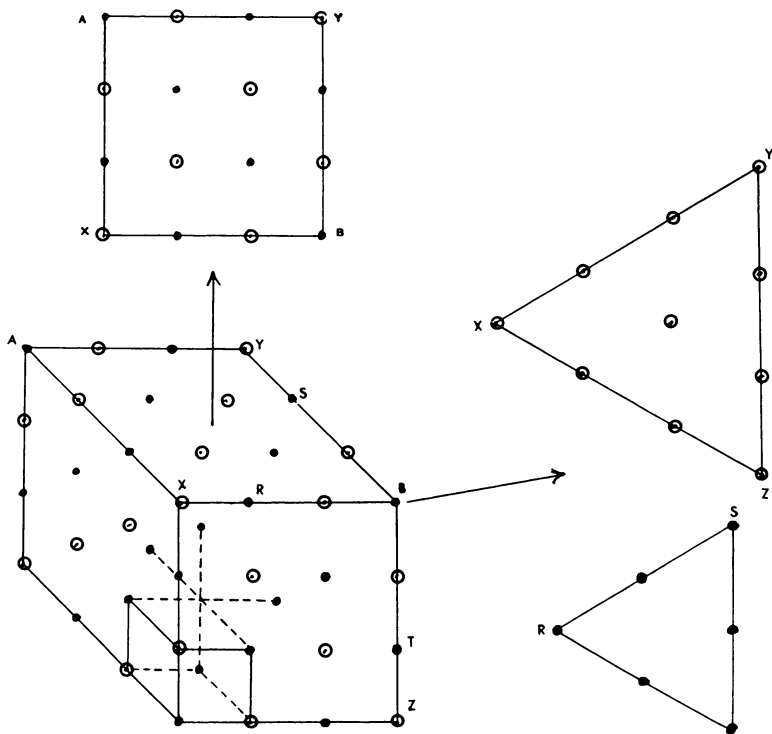
Figure 1. A crystal of sodium chloride (lower left) showing arrangement of atoms within the crystal and two principal directions of growth. Growth perpendicular to cube face encounters layers of atoms shown at upper left. Growth along diagonal of cube encounters alternating layers shown at right

Time is an essential part of the crystallization process. A large crystal cannot form spontaneously. It must start with a nucleus which grows by addition. As the solution immediately adjacent to the growing crystal face is depleted of building blocks, more must be supplied by diffusion through the liquid.

Crystallization takes place normally when the temperature is lowered to the point where thermal motion is no longer great enough to overcome the forces of attraction between blocks or when the solvent is removed to the point where it can no longer supply the attractive forces necessary to keep the blocks apart.

In crystallization from the melt, as in the freezing of water or the solidification of molten sugar, the liquid phase is one component and temperature alone is the determining factor in whether or not crystallization will take place.

In crystallization from solution, as in the manufacture of salt from brine, the liquid phase is multicomponent, having one or more solvents and one or more solutes. Here both temperature and concentration are determining factors.
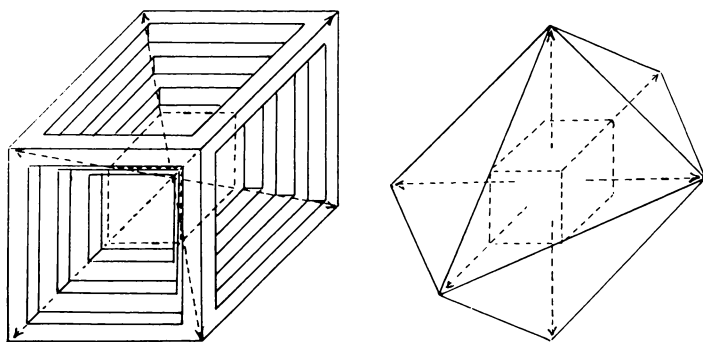

Figure 2. An octahedron resulting from rapid growth perpendicular to faces of cube and a skeleton crystal resulting from rapid growth along diagonals of cube

Differences in Crystal Habit

Why do we get differences in crystal shape or habit? This may be a matter of directional rates of growth. Factors affecting directional rates will then affect the habit. Directional rates of growth can be illustrated with a relatively simple crystal structure, that of sodium chloride.

In crystalline sodium chloride, sodium and chlorine atoms are arranged at the corners of cubes in such a manner that each chlorine atom is immediately adjacent to only sodium atoms and each sodium atom is immediately adjacent to only chlorine atoms. This arrangement gives a high degree of stability because of the large number of bonds between unlike or oppositely charged atoms. The common habit is the cube.

Such a lattice has two principal directions in which crystal growth can take place. One is perpendicular to the face of the cube. Growth in this direction proceeds by laying down layers of atoms, each composed of both sodium and chlorine atoms. Another direction is a diagonal of the cube. Growth in this direction proceeds by laying down alternate layers of all sodium atoms and all chlorine atoms.

When growth in the direction perpendicular to the face of the cube is rapid, the cube face disappears and an octahedron results. Salt octahedron shape can be obtained under certain conditions—for example, when grown in the presence of urea. When growth in the direction of the diagonal of the cube is rapid, the edges and corners of the cube grow in preference to the center of the cube face and a skeleton crystal results. One common table salt is composed largely of crystals of this type.

Therefore we have two extremes in crystal habit in sodium chloride, the octahedron and the skeleton, the prevailing shape depending upon the relative rates of growth in different directions in the crystal lattice. The common cube shape is formed when a balance in the two rates of growth prevails.

Crystal Bonds

What are the types of bonds holding crystals together? It is important to

consider these in connection with the action of hydrocolloids. The strongest, the ionic bond, is almost twenty times stronger than the next strongest. It is the force of attraction between a particle with a negative charge and a particle with a positive charge. It is the bond in crystals of sodium chloride.

The next strongest bond is perhaps the most prevalent in food materials. It is the hydrogen bond, the bond which hydrogen forms between two electronegative atoms. For example, the hydrogen of a hydroxyl group in one molecule will bond with an oxygen or nitrogen atom in another molecule. It is a predominant bond in crystals of sucrose and in ice.

The third bond, and perhaps the weakest of the three, is that due to van der Waals forces. These forces pull together particles of all material regardless of composition or electric charge. They vary with the size of the particle and would be greater for a hydrocolloid than for a smaller particle. They are the predominating bonds in crystals of fats and waxes.

Effect of Hydrocolloids on Crystal Growth

Hydrocolloids affect crystal growth in three ways:

1. If the hydrocolloid is compatible, it can attach itself to a growing crystal surface, thus altering the normal growth of the crystal.

To be compatible, the possible points of bond formation in the hydrocolloid must have spacings which will fit the spacings of the possible points of bond formation in the crystal. This is similar to the orientated overgrowth of one crystal on another, called epitaxy (1, 5). In the case of ionic bonds the possible points of bond formation in the hydrocolloid would be groups such as carboxyls. These, being negative in charge, would have to fit points of positive charge in the crystal.

In the case of hydrogen bonds, groups such as hydroxyls in the hydrocolloid would have to match locations of oxygen or other suitable atoms in the crystals.

Because of the probable lack of compatibility in most combinations of crystals and hydrocolloids, this effect is probably not as common as others.

2. A second method of modification is competition between hydrocolloid and crystal for the blocks which go into making the crystal. The very term "hydrocolloid" indicates the tendency for these materials to bind water. Growing ice crystals would compete with any hydrocolloid in solution for water molecules to continue growth. Gelatin in solution can blind in this way 2500 molecules of water for each molecule of gelatin.

Competition acts in crystallization from solution as well as from a melt. Thus, in crystallization of sugar from solution the hydrocolloid could bind sugar molecules and thereby hinder growth of sugar crystals.

An increase in viscosity usually accompanies competition. Water molecules bound by the hydrocolloid are no longer effective as solvent molecules and the concentration of the solution is thereby increased. Increase in viscosity itself has a retarding effect on crystal growth.

3. A third action of hydrocolloids is combination of them with impurities which would otherwise affect crystal growth. For example, a hydrocolloid which combines with calcium would eliminate its well-known effect on the crystallization of sugar.

Thus, we have the three C's in the effect of hydrocolloids on crystallization: compatibility, competition, and combination. The rules under which they act are not simple. They depend on many yet unstudied variables, such as con-

figuration of the hydrocolloid and its relationship to the spacings of the crystal, the type of bonds involved in combinations of hydrocolloid and solvent or solute, and interactions of hydrocolloid and the many compounds normally present in food materials.

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Some Lesser Known Aspects of Stability in Commercial Emulsions

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The stability of emulsions has manifold applications in the food industry, the manufacture of agricultural pesticides, and the processing of synthetic rubber. Mayonnaise and oleomargarine are two widely used emulsions. The behavior of mayonnaise at room temperature and at temperatures below it is considered. The factors which influence the "breaking temperature" are discussed. Under frying conditions, oleomargarine emulsions break down; however, the addition of surface active agents has a stabilizing effect. Agricultural pesticide emulsions are affected by pH and by the inorganic cations of the water when the "concentrate" is mixed with it on the farm. Synthetic latices of the GR-S type elastomer obtained by "cold" polymerization process have to be stabilized. The emulsifying agent also has to have good solubility at the lower reaction temperature.

More accurately worded, the title of this paper should read: "Some Poorly Understood Aspects of Stability in Certain Commercial Emulsions." Its objective is to present some empirical data relative to certain commercial emulsions. It is assumed that the specialist in any given field is already familiar with most, if not all, of the data herein reported pertaining to the emulsion in his particular field. The data are presented for consideration by the specialist in a given field who is insufficiently familiar with the problems in another, apparently unrelated, specialized field with the hope that such "cross breeding" may be provocative of fresh thinking and new approaches. Moreover, no attempt is made herein to generalize or to construct hypotheses.

The behavior of mayonnaise emulsions when thawed after some exposure to temperatures below room temperature, is considered first. The mayonnaise emulsions are of such a stability that on standing at room temperature for one year or even longer, they show no perceptible oil separation. Such mayonnaise emulsions fall into two categories when thawed back to room temperature after exposure at a given temperature below room temperature: those that show no oil separation and those that do show oil separation. Another way to

express the behavior of otherwise stable mayonnaise emulsions is in terms of a maximum temperature, somewhere below room temperature, to which, after being exposed for a given time—24 hours—and then thawed, the mayonnaise shows separation of oil. This temperature is designated as the "breaking temperature."

The mayonnaise behavior here discussed is of considerable practical importance, because of the potential spoilage hazard incurred when mayonnaise is placed in transit or in storage in cold climates or at winter temperatures in temperate climates.

The principal factors which affect the breaking temperature are: type of salad oil (cottonseed, corn, soybean, or other), proportion of oil, proportion of total moisture, and proportion of yolk. To a much lesser degree, the breaking temperature is also influenced by the mean particle size of the dispersed oil and the concentration of crystalloids in the water.

There is here a question of something much more complex than simply the crystallization of the liquid constituents of the system, consisting, usually, of salad oil, vinegar, water, egg yolk, salt, sugar, and spices. It is not uncommon for the breaking temperature to fall in the range $+15°$ to $0°$ F. and there have been mayonnaise brands on the market with breaking temperatures as low as $-20°$ F. This range of temperatures is clearly below the freezing points of the liquid constituents of the system.

A phenomenon far more intricate than just conventional freezing points is demonstrable, by a consideration of two mayonnaise formulations, identical as to crystalloid content and with the following composition:

	Mayonnaise, %	
	No. 1	No. 2
Corn oil	72	69
Hen egg yolk	12	12
Total moisture	18	23

Total moisture designates the sum total of the moisture content of the yolk, vinegar, and water added as such.

Notwithstanding the fact that the crystalloids present are dissolved in the case of mayonnaise 2 in some 28% more water than for mayonnaise 1, the breaking temperature of mayonnaise 2 is some $12°$ F. lower than that of mayonnaise 1. Obviously, were it simply a matter of freezing point lowering, the difference would have to be in the reverse direction.

Let the conclusion not be drawn from these examples that increasing the total moisture content lowers the breaking temperature in all cases. This is by no means invariably the case. The rule that appears to be valid is that for a given proportion of yolk and oil (all other factors being constant), there is an optimum moisture content which gives the lowest breaking temperature for that system. Moisture contents on the higher or lower side of the optimum cause a higher breaking temperature.

Moisture content is but one aspect, albeit an important one, of mayonnaise stability with respect to breaking temperature.

Oleomargarine, another commercially important emulsion, presents problems with its behavior during frying.

A conventional margarine would have the following percentage composition:

Blend of partially hydrogenated oils	80.0
Ripened ("cultured") skim milk	17.1

|	
Sodium chloride	2.5
Mono- and diglycerides of fat-forming fatty acids	0.3
Sodium benzoate	0.1

When such a margarine is exposed to the usual frying conditions, a most disagreeable course of events ensues: The moisture escapes with a noisy, almost explosive violence, much of the fat spurts out of the frying pan, and the milk solids bake onto the bottom of the frying pan in the form of a tenaciously adhering, charred mass. The disadvantages encountered are: The operator's hands are scalded by spurts of hot fat, the top of the kitchen stove is greased by the escaping fat, and removal of the adhering, charred milk curd from the bottom of the frying pan is a major operation. So highly objectionable are these defects that it is impossible to fry with such a margarine. It can serve as a spread for bread or as an ingredient of cake, but it is utterly unfit for frying.

It appears that as the margarine is heated to temperatures approaching frying, the emulsion breaks down, and the aqueous phase drops, by gravity, to the bottom of the frying pan, superheats, and finally breaks out with almost explosive violence through the supernatant fat layer. Moreover, the milk solids bake at the bottom of the frying pan in the form of a tightly adhering, charred mass.

It was discovered sometime ago that a variety of "balanced" surface active agents, when incorporated in the margarine—in the case of the more effective ones, in proportions as low as 0.1%—obviate the objectionable frying behavior. The margarine fries quietly, there is no spurting or spattering of fat, the milk curd browns to a pleasing color, and it remains in a loose, finely divided state. The introduction of 1 part of a surface active compound to 1000 parts of margarine has brought about a dramatic change in the frying behavior.

Representative types of "antispattering" agents are:

Monopalmitin sulfate (sodium salt)

$$C_{15}H_{31}C\overset{\overset{O}{\|}}{-}O-CH_2-\overset{\overset{OH}{|}}{CH}-CH_2-O-SO_3Na$$
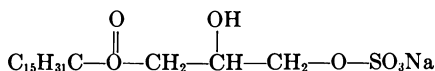
Dodecyl phosphate (sodium salt)

$$C_{12}H_{25}-O-\overset{\overset{O}{\|}}{P}\underset{ONa}{\overset{ONa}{<}}$$
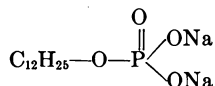
Monostearin sulfoacetate (sodium salt)

$$C_{17}H_{35}\overset{\overset{O}{\|}}{C}-O-CH_2-\overset{\overset{OH}{|}}{CH}-CH_2-O-\overset{\overset{O}{\|}}{C}-CH_2-SO_3Na$$

Cetyl betaine chloride

$$\left[C_{16}H_{33}-O-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{CH_3}{|}}{\underset{CH_3}{N}}-CH_3\right]^{+}Cl^{-}$$
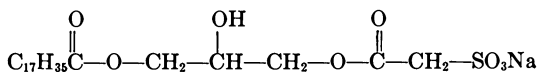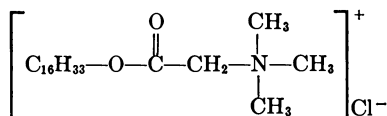
Lecithin
Monomyristin diacetyl tartrate

$$C_{14}H_{29}\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH-\overset{\overset{\displaystyle O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}{|}}{CH}-COOH$$
$$\underset{\underset{\displaystyle O}{\|}}{O-C-CH_3}$$
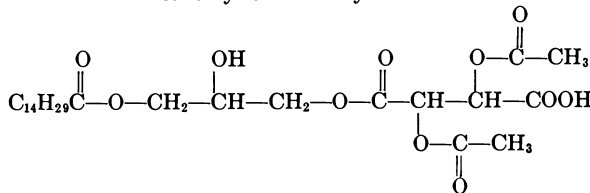
When one compares the frying behaviors of two margarines, designated for convenience as A and B, identical in all respects except that A contains an antispattering agent and B does not, one observes a number of differences during frying, in addition to those already indicated. In the case of A the molten fat is frothy and turbid, almost opaque, whereas in the case of B the fat is clear and transparent. It appears that in the case of A, the emulsion remains relatively stable, bubbles of water vapor containing finely divided casein at the interphase find their way to the surface in a quiet, orderly fashion, while in B, the emulsion breaks, the aqueous phase drops to the bottom of the frying pan, and all the adverse consequences described, appear.

While antispatters exert this remarkable influence on the frying behavior of margarines comprising milk as an ingredient, they are ineffective in margarines in which milk is absent. Margarines churned with salt solution in place of milk are occasionally available on the American market, but much more commonly in Europe. There is something to be thought out by those concerned with the theory of emulsion stability, as to the role played by the finely divided milk solids in the presence of the antispattering agents.

Role of Inorganic Cations

One aspect of the stability of agricultural pesticide emulsions—insecticidal, herbicidal, fungicidal—is concerned with the role played by the inorganic cations present in the natural waters encountered. An important form, if not the most important, in which the pesticides are sold, is the "concentrate," which is a solution of the toxicant and a blend of emulsifying agents in an appropriate hydrocarbon solvent, with, at times, other minor constituents. The pesticide concentrate composition is designed to give the desired emulsion spontaneity and stability when the concentrate comes in contact with a large proportion of water on the farm, the point of consumption.

While the concentrate formulator has sufficient control over most of the variables involved such as proportions and kinds of toxicants, emulsifying agents, and solvents, he is helpless as far as the chemical composition of the "water" at the point of consumption is concerned. This presents a grave problem. The gamut ranges from extremely soft, river and ground waters through moderately hard waters, to hard waters containing a crystalloid content equivalent to several hundred parts per million of calcium carbonate. At the very extreme of these factors the formulator has to contend with the preparation of a concentrate which gives emulsion spontaneity and stability in liquid fertilizers which are aqueous solutions with an extremely high crystalloid content, often as high as 65%. Emulsifying agents have lately become available which operate satisfactorily in these highly concentrated solutions, and also at extremely low pH.

A toxicant concentrate, emulsifying agent which leaves little to be desired
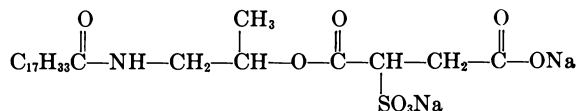
in waters of moderate or slight harness can be a complete failure in an extremely soft river or ground water. However, in such a case, the introduction into the soft water of an ionizing material, sodium bicarbonate, in proportions as low as 1 p.p.m. corrects the situation and the effectiveness of the emulsifying agent is fully restored.

A striking aspect of this situation is that one cannot assume that an emulsifying agent which operates successfully in distilled water will also be satisfactory in naturally soft waters. This assumption could involve one in serious problems. It appears that soft river, lake, and ground water can contain soil and plant extractives, probably of an organic character in extremely low concentrations, which radically differentiate these waters from distilled water. Hence, the use of a given emulsifying agent in distilled water cannot be taken as a criterion of effectiveness in natural, soft waters.

These and related data add up to an impressive demonstration of the extraordinary significance of ions relative to emulsion stability.

Stabilization of Synthetic Latices

Finally brief reference should be made to the stabilization of synthetic latices, particularly "high solids" latices of the GR-S type and the improvement of the "cold" GR-S polymerization by a synthetic emulsifying agent known as EMCOL K-8300, which is a sulfosuccinic acid ester (sodium salt) of the isopropanolamide of oleic acid:

$$C_{17}H_{33}\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-O-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle SO_3Na}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-ONa$$

In the case of synthetic rubber, the change from the conventional emulsion polymerization to emulsion polymerization at much lower temperatures—cold polymerization—resulted in distinct improvements in the final product, but also serious process problems. Some of these were associated with the low solubility or gelling of the conventional soaps at the low temperatures of the cold polymerization. These difficulties have been ameliorated to a great extent, by modifying the emulsifier combination, with the introduction of a proportion of EMCOL K-8300. Preflocculation, an extremely annoying and troublesome defect of the conventional emulsifying systems, is eliminated, so that one need not be concerned with precipitation and sedimentation. "Stripping" of the residual monomer is also facilitated. The polymerization rate is accelerated coniderably as is reflected in a reduction in the polymerization time from 70 hours to approximately 35 hours and, apart from everything else, that latex stability is substantially enhanced.

Emulsions and Foams

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The basic problems involved in emulsion and foam chemistry are discussed with emphasis on how to solve them and how to correlate the information thus obtained for future use and interpretation. A blending of theoretical and practical knowledge has to be used, and examples are given to illustrate the methods of solving the industrial problems involved.

The industrial importance of emulsions and foams today cannot be overestimated. There is every indication that this field will be of even greater utility and importance in the near future.

In the operations of a consulting laboratory, one is constantly confronted with a variety of problems which involve the technology of emulsions and foams. These problems cover a diversity of interests such as foods, cosmetics, adhesives, polymers, and others.

This presentation is based on a brief summary of some of the problems which confront a consultant and doubtless face many a technical man. Some possible approaches, to obtain the data necessary for solving these problems in a simplified manner, are indicated.

In emulsion and foam technology much is known concerning the properties and behavior of systems which involve only two or three components. Given a particular system and data concerning concentration, temperature, and manner of mixing, we can today predict fairly well the properties of the comparatively simple emulsion or foam. However, most emulsions and foams of importance are multicomponent systems and in these systems the predictability of the action or the properties of the emulsion or foam on a theoretical basis often becomes small.

The "Edisonian" approach must be used with most of the problems with which we are concerned. By Edisonian approach the following is meant: From past experience it has been determined that a certain mixture of materials will produce a satisfactory emulsion or foam. To solve a particular problem then one would ordinarily start with an emulsion which is known to be satisfactory for a similar purpose. By altering the components one by one, using different amounts, adding to or subtracting from the original formula, after a greater or lesser expenditure of time and effort, a stable, suitable, satisfactory, new formu-

lation is obtained. A standard procedure for the preparation is then set up and the experimental work is finished. What has been done to make the solution of the next emulsion problem any easier? Practically nothing; the next problem which comes along will be solved by approximately the same technique.

Theory and Technology

The impression that little or nothing is known about emulsion theory and technology, however, is far from the truth. Indeed, a great deal is known—much has been learned from theoretical studies and the Edisonian techniques have made their contributions. In terms of the stability of an emulsion one can predict to a certain extent the effects of radical changes in the types of emulsifier used, changes in pH, addition of certain salts, etc. Qualitatively the effects of changes in viscosity or particle size can also be predicted.

What basic facts are available now, what is still to be learned, and what can be done in addition to what is known now, which will allow us to go into the laboratory, run a few basic experiments, and on the basis of the data thus obtained formulate a group of emulsions or foams meeting certain specific requirements?

Thus, in the relatively simple case of oil in water emulsions, where a surface active agent such as a soap is used as the emulsifying agent, it is known that the soap adsorbed on the surface of the oil particles decreases the interfacial tension, thus stabilizing the emulsion. The adsorbed soap ions also give a net electrostatic charge to the dispersed oil droplets, serving to repel other oil droplets, with the net effect that flocculation is hindered (and stability is increased). It is even possible to measure the amount of adsorbed soap ions and to calculate the values of the surface potential.

When foreign electrolytes which do not react with the soap are present, the ions responsible for bringing about coagulation are the ones with charges opposite in sign to those on the dispersed particle. The effect of the valence of the ion follows the Schulze-Hardy rule for the precipitation of sols by electrolytes wherein the coagulating power of an ion increases considerably with the increasing valence of the ion.

The most stable emulsions are those with the greatest viscosity; this refers primarily to the continuous phase. The reason is obvious; the viscosity of the medium is responsible for hindering the movement of the dispersed droplets. These are some of the known basic facts about systems involving a few components.

However, in the case of multicomponent emulsions there are far more complex problems. They involve not only the expansion of these basic concepts from simple systems to complex systems, but there arises the additional problem of how to present the accrued data in an orderly fashion. With the multitude of reagents and experimental conditions that can be used, the permutations and combinations lead to thousands of possible formulations. As a means of correlating this tremendous amount of available data one might suggest the setting up of a series of diagrams similar to two-dimensional phase diagrams for systems which could be classified according to their components and other variables for future reference.

Because the main point of interest is the stability of an emulsion, a series of phase-type diagrams could be plotted. A hypothetical diagram could have as its ordinate the temperature of mixing and as its abscissa the rate of mixing. A line could be drawn on this diagram indicating that above any given

temperature, at a given rate of mixing, there would be one phase and below that temperature, two phases. The direction and shape of the curve would have to be determined experimentally for a given set of components, keeping everything else constant, except temperature and rate of mixing. In this particular series, another diagram for the given emulsion formula might be one in which the units on the abscissa represented the ratio of one major component to another—i.e., oil to water—and the ordinate represented the percentage of the emulsifying agent. A line would be drawn, indicating the critical ratios of the components and the concentration of the emulsifying agents which would determine whether a one- or a two-phase system is present. It is assumed, again, that all other variables such as temperature, pH, rate of mixing, electrolyte concentration, and emulsifying agent are held constant.

Other diagrams could be devised indicating the influence of pH, electrolyte concentration, etc., on the appearance of one or two phases. Three-dimensional diagrams might also be of great aid.

Although this is tedious work involving much measuring and weighing, once the data have been obtained they can be summarized on charts which can be filed in a usable punch card system, which in turn can be used to indicate clearly what to expect when emulsions of a similar type are to be prepared. A great deal of this type of information is already available in published reports and in the files of various laboratories.

It is hardly possible to predict that a general theory will ever be evolved which will cover all possible types of industrial emulsions and foams. However, it seems that if the information described were gathered in a systematic fashion, the data could be classified in a logical order for different types of emulsions. Hence, cosmetic-type emulsions, salad dressing, and mayonnaise-type emulsions would each fall into its own individual category. The suggestion therefore is made that a repository of such information be made available to all who are interested.

Considerable effort would be necessary to maintain such a library of emulsion information. Nevertheless, the time and attention already devoted to emulsion experimentation represent an investment from which the science deserves no little dividend. Communication to, through, and from a proposed information center may be the only means of avoiding much expensive and unnecessary duplication of work. It would definitely expedite the interpretation and significance of all accessible emulsion data.

Foams

Closely akin to the subject of emulsions is the field of foams, mentioned only in passing. The two fields are similar, in that their properties both depend on surface effects, changes in interfacial tension, electrolyte composition, and manner of preparation.

However, the fundamental theory of simple foams is not as well formulated as the theory for simple emulsions. Because foams consist of gases dispersed in a semisolid film, the properties and behavior immediately become more dramatically subject to external variables, such as temperature and external air pressure. Minute changes in surface tension of the film can make or break the foam. However, a similar approach might be suggested in the foam field. In this case, the variable with which we are most concerned is whether or not a stable foam is produced and the diagrams would be drawn accordingly.

The problem of de-emulsification and defoaming is not to be ignored. The

problems here are just as difficult and often more troublesome than the converse questions. The same approach is suggested as previously discussed.

Analogies are dangerous, but one point may be emphasized, and possibly overemphasized. Is not the art of emulsion at a point similar to that where Kekulé found the "art" of organic chemistry some 100 years ago? His contribution of the benzene structure began the tremendous advances in this field with which all are familiar. It is unlikely that on the basis of present knowledge any simple formula will suffice; however, any correlative efforts must be of help.

Practical Aspects of Foam Stabilization

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In confectionery manufacture aerated products such as frappé, mazetta, or ice cream are based on the use of foams. Foams are affected by vapor pressure, surface tension, crystallization, denaturation, and gelation. The production of foams in aerated icings and in whipped cream products is analyzed.

It is ironical, but true, that the average food production worker, who is dealing with reactions where foam or compounds involving foam is a factor, is not familiar with the simplest, practical aspects of the problem.

Often a worker producing a frappé or a mazetta for confections has very little knowledge of concentration or temperature effects, the degree of dispersion or solvation of the protein compound he is using, the thermal or mechanical treatment of the foam-producing agent, the presence or absence of other lyophilic colloids, the age of the solution he is using, or the presence of electrolytes or nonelectrolytes. He is able to produce a frappé, mazetta, or marshmallow which according to the *art* is nearly perfect. Housewives are able to make a variety of aerated products, such as meringues, confections, and ice cream, without considering the shelf life or the stability of foam products beyond a very short period of time.

Likewise, the practical food foreman knows that by following certain manufacturer's recommendations and certain processing conditions in his plant, he is able to produce stabilized foam products to the satisfaction of his superiors and the public, most of the time; yet when problems of instability and poor shelf life of the finished product are brought to his attention and all simple adjustments fail to produce a satisfactory result, he must turn to the food or colloid chemist for the theory and industrial application of foams.

Definitions

Foams are agglomerations of gas bubbles separated from each other by thin films (5). Mainly, the problem is concerned with one class of colloidal systems —gas dispersed in liquid—but liquid dispersed in gas, solids dispersed in liquid (suspensions), and liquids dispersed in liquids (emulsions) cannot be ignored. The dispersion of a gas into a liquid must be studied and observed by the food technologist to improve the contact between the liquid and gas phases, the agitation of the liquid phase, and most important, the production of foam (10).

Gas or air may be dispersed into a liquid by mechanical means (beaters) or by introducing bubbles of desired size directly by disintegrating massive streams or bubbles of gas. Bubbles are introduced either by sprayers (simple bubbling) or by porous dispensers (diffusers).

With foams, one is dealing with a gaseous state or phase of matter in a highly dispersed condition. There is a definite relationship between the practical application of foams and colloidal chemistry. Bancroft (4) states that "adopting the very flexible definition that a phase is colloidal when it is sufficiently finely divided, colloid chemistry is the chemistry of bubbles, drops, grains, filaments, and films, because in each of these cases at least one dimension of the phase is very small. This is not a truly scientific classification because a bubble has a film round it, and a film may be considered as made up of coalescing drops or grains."

Stability Factors. The food technologist versed in the art of foam stabilization considers the following factors important: vapor pressure, surface tension, formation of rigid systems through crystallization, denaturation, and gelation. In a foam the surface of a liquid has been enormously extended; thus, the surface tension of the liquid must be small. Otherwise, it would tend to reduce the surface. To produce a stable foam, the vapor pressure should be small for substances with high vapor pressure, thus increasing the gaseous phase. The substance at the surface must have a tendency to gel or solidify to give the rigidity and permanence necessary for a stable foam.

Another important factor is that the surface film must not coalesce readily. Adams (1) states that more important than low surface tension for the stability of a foam is that the solution have a surface tension which is easily and quickly variable. Animal and vegetable proteins added to a solution in the proper amounts, aided by stabilizers, fulfill these needs in the food field.

Denaturation is a change in which the natural protein becomes insoluble in solutions in which it was previously soluble. It is brought about by physical means such as heat, pressure, and surface force, or by chemical means, although very few chemical agents are used in this connection in the food field. Gel-type solutions are usually beaten before they become too thick or firmly set. As air is incorporated, the volume increases and the firmness of the gel stabilizer sets the foam.

Industrial Applications. Practically, in the formation of foams there is a dispersed gaseous phase in a liquid medium. Some practical applications are in the use of egg whites, vegetable protein whipping agents, gelatins, and proteins from milk, primarily in the baking and confectionery fields. The consumer is interested in the whipping properties of these protein food materials which are capable of forming an aerated mass when whipped on a conventional, horizontal, or vertical-type mechanical beater. The protein is in a sugar-type solution and is whipped until a maximum amount of air bubbles is produced to form a stiff mass, which usually has a certain amount of stability. The amount of stability depends on whether the product is to be used immediately or later.

In the stiffness test (6), the food producer is interested in the appearance of the foam, the rate of flow, the stability of the foam, and the permanence of the peaks, and a very practical person has to know whether it is "dry." Many of these factors are controlled by the use of continuous beaters or whippers. Some of these are glorified beaters in which a fixed amount of air is incorporated along with a fixed amount of liquid, and by varying the revolutions per minute of the mechanism the large bubbles are continually reduced in size until a prod-

uct emerges in which the air is wholly incorporated in the liquid medium. Actually, the air bubbles are surrounded by thin films of liquid. In this type of mechanical whipping, where time and temperature are definitely factors, a certain amount of fatigue is experienced by the whipping protein. The operator knows that if he beats a marshmallow premix stock until it reaches the maximum, continued beating will break down the bubble structure and the specific gravity will rise until there is very little foam stability left. There is always the danger of overwhipping or "protein fatigue" in the use of mechanical beaters.

According to a recently patented process (2, 3), it is possible to produce foams of very uniform bubble structure without the ordinary mechanical whipping or beating. In this method the liquid protein material is premixed by jetting with target dispersing a fixed volume of air to liquid, and the product passes through a diffusion chamber and emerges in a whipped state. This diffusion chamber can be of a rigid ceramic porous material, such as a laboratory filtering stone, or it can be a packed tube of aluminum oxide spheres. This causes the material, both air and liquid, to pass through a tortuous path in which the liquid surrounds the very small air bubbles that are formed as it passes through the diffusion chamber. The stability of the foam in this type of unit depends on the type of whipping agent involved, the concentration of the whipping agent, and the viscosity of the solution. The protein must preferably be in solution, in order to obtain the best stability. The pressure at which the material is forced through the diffusion chamber also affects the specific gravity of the aerated material. The longer the path and the smaller the cross section of the tortuous path, the better the incorporation of the air and the finer the bubble structure. In preparing aerated food confections, the smaller and more uniform the bubble structure, the better the shelf life of the product.

Actually, vegetable proteins can be whipped by the diffusion method to produce frappés which weigh less than $1/3$ pound per gallon, whereas this same material, if whipped on a conventional, vertical, or horizontal beater, could not produce this specific gravity, because of the heat involved due to shearing and the denaturation of the protein material due to constant beating.

In diffusing aerated confections under heating conditions, if the material can be processed at a high temperature, the bubble structure, after emerging from the diffusion chamber, will contract the air cell upon cooling, and thus become even smaller.

When there is a high percentage of proteins, such as in gelatin—which will form an elastic film in conjunction with corn sirup and other sugar products—stability is not too much of a problem. In freshly whipped egg or vegetable protein foams, frappés, or mazettas, in which the foam product is incorporated as part of a complete food batch, the foam is assimilated before its stability becomes a factor; and further processing tends to stabilize the foam.

On the other hand, in preparing whipped products which are to stand for a long period of time, it is often necessary to add various gums, such as Irish moss, algin, and locust bean gum, to have a product that will react in some way with the protein being whipped, to make a firm film and stable foam.

In the production of aerated confections it is very important to add various hydrocolloids, in order to obtain a foam which will withstand the specific stability requirements of the specialty food product involved.

In the confectionery field, a classical example of stabilizing a foam system is the production of nougat. In this case a cooked mixture of sucrose, sorbitol,

and corn sirup is added—in which the sugar content is high enough to crystallize out upon cooling. Thus the resulting mass forms a grain structure which holds the foam material or frappé made of either egg whites or vegetable proteins in a very finely divided state. This system will not break down on being subjected to heat or excessive humidities (8).

Aerated icings are of two types (7). First, there are those which aerate through the extension of a protein film which may be egg albumin, soybean albumin, gelatin, gliadin, or milk protein. Secondly, there are those which aerate through the extension of a fat film which is usually a vegetable or animal shortening containing 3 to 10% of mono- or diglycerides. Without this added emulsifier, which reduces the surface tension of the fat, a shortening would not aerate.

There are three essentials for a stable icing foam. The first is a low vapor pressure. When a bubble rising in a liquid comes near the surface, it lifts a dome above the bubble. If the vapor pressure within the bubble is low enough (as in the case of very cold soda water), the bubble is retained in the liquid.

Secondly, a stable icing foam requires a low surface tension. Consider the case of egg whites in a beater. With slight whipping, entrapped air bubbles are large and the whites appear foamy, yet transparent and runny. With longer whipping the whites become less transparent, white, and more solid. Thus, because of the low surface tension inherent in the egg protein in solution, more and more air may be incorporated and held in place by the colloidal protein which forms a film around each air cell.

Thirdly, a stable icing foam requires a tendency for the surface of the extended protein film to solidify, thereby giving structure and permanence to the foam. Egg albumen is a hydrophilic (water-loving) colloid, for it is readily soluble in water. However, when subjected to heat, egg albumen becomes insoluble in water or is said to be hydrophobic (water-hating). Through this phenomenon of changing solubility, egg whites make very stable foams if used at sufficient concentration.

The presence of certain solids also affects foam stability. Lactose will greatly aid in the stability and plasticity (desirable in freezing) of soybean protein icing foams. Such a system is said to be a three-phase foam: a liquid (protein in solution), a gas (air), and a solid (sugar, starch). The use of starches in meringues similarly presents a three-phase system. A solid particle will tend to prevent coalescence or merging of two bubbles in a foam if it is in simultaneous contact with both bubbles. The thinner the protein film in a foam, the smaller probably will be the effect of particles on its stability. Egg albumen films are thinner than soybean albumen films; hence stability is greater with solids in soybean foams than in egg foams. Some degree of wettability is also desirable with solid particles in an aerated icing. If too wettable, the solid will be sucked into the bubble and, conversely, if insufficiently wettable, too much extension between bubbles will take place and the structure stability will be lessened.

Stabilizers are rarely required in aerated fat icings, for sufficient structure is provided by the fat to keep the icing stable.

In the case of aerated protein icings, however, stabilizers are essential. Where hot water is used, gelling-type stabilizers work best (agar, gelatin, Irish moss extract). In cold foams, prepared with cold water, cellulose-type gums are used to contain water in the foams; colloidal precipitates, such as are formed through the reaction of carrageenin and protein, are very helpful.

Dry, butter cream icing mixes, which are in demand both by restaurants and for home use, generally consist of a dry blend of icing sugar and a flaked, emulsified fat. When water is added and this mixture whipped, aeration takes place. For an extra smooth icing, dry invert sugar may replace all or a portion of the icing sugar contained in the mix. The percentage and type of food emulsifier are important in stabilizing the foam or air structure. Surfactants, such as mono- and diglycerides, polyethylene derivatives, lecithin, alginates, pectins, gums, agar-agar, Irish moss extractives, or gelatin, are added to assist in the stabilization.

Whipped toppings, either gas dispenser or mechanical, present many problems in foam stabilization. Usually less fat is used in gas-dispensed types. All-vegetable protein whips are now on the market. The percentage of fat, emulsifiers, and gum stabilizers varies with the type of whipping and personal preference.

One of the greatest foam stabilization problems confronting dairy technologists has been the stabilization of whipped cream products. This problem has been accelerated by the use of pressurized natural and imitation whipped cream products. Regular whipping cream containing over 18% of butterfat has fair stability, but when used in large quantities there is a need for a stabilizer to hold the body of these products. To stabilize whipped cream, various emulsifiers and gum stabilizers have been used, such as monoglycerides and polyoxyethylene derivatives of the monoglycerides and sorbitan monostearate. Gums, such as locust bean, karaya, and Irish moss, have been used effectively for these products.

Recently much research and development have been done in stabilizing dairy products, to produce an imitation whipping cream using canned evaporated milk, half and half breakfast creams, and in some cases whole milk. In some of these cases a fat other than dairy butter is added to produce a more stable product. In all these imitation products an emulsifier is used with the fat; this is homogenized with the dairy product and the stabilizer is then added to this product, which can be one of the above-mentioned gums. The product is then whipped through a mechanical beater or under pressure with carbon dioxide and nitrous oxide. In all-vegetable protein whips, the amount of ingredients varies with the types of whipping and with personal preference.

Stable beer foam that leaves "lace curtains" (9) on the wall of the glass as the drink is consumed has always been considered highly desirable, but the reason for it and a method of evaluating it have not been available. The proteins in beer are actually degradation products formed from the original proteins in the raw materials, during the brewing process. They are known to have a profound effect on the stability of beer, but little is known of their nature. The substance that is responsible for foam adhesiveness is derived from hops, and is probably isohumulone. This adhesiveness increases with hop boiling time and with the hopping rate when the boiling time is constant. Therefore, foam stability of beer or "foam life" will be left with the brewmasters, whose problems have been handed down from generation to generation.

In practically all our food products we have depended on the practical application of foam stability to solve our problems. The answer to many of our problems lies in the theoretical aspects of the stability and formation of foams. As yet, little time has been spent on the chemical and physical properties of foam.

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Formation and Stability of Foams

Theoretical Comments

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The structure and the formation of foams are discussed from a theoretical point of view. The conditions for foam stability are stressed and a novel hypothesis is presented on the action of hydrocolloids as plasticizers of the walls of foams.

In a theoretical approach to the problem of foams the first question to be formulated was of a very practical kind—why do food manufacturers make foam? Is it the ease of digestion which is aimed at—or the large bulk to impress the buyer and little substance to lower costs? If physical chemists knew the answer, it would have been easier for them to conclude what kind of foam is wanted and how it should be best made.

Structure

Foams consist of bubbles separated from each other by thin—liquid or solid—membranes. The bubbles must have no connection with their neighbors; if such a connection exists—i.e., both phases (the gaseous and the condensed) are continuous—the system is a sponge rather than a foam. Bread is the most important kind of food that is chiefly sponge and a little foam.

Formation

Foams can be produced either by condensation or by dispersion. In the first group of methods, the gas which finally will fill the bubbles is first present as single molecules in another medium. Thus, carbon dioxide is liberated, molecule after molecule, by the yeast in the dough and gradually gathers to form bubbles. However, the confectionery products mentioned by Alikonis (1) are made by dispersion. This means that the gas filling the bubbles was originally present as a continuous phase and the work of forming the foam consisted in separating small volumes of the gas from its bulk and coating these volumes with a film to prevent coalescence.

This cutting off of small gas volumes can be accomplished in many ways, but there are again two main groups to be considered: whipping and bubbling. The fundamental laws behind these processes are more or less understood; how-

ever, science still cannot give great help to the designer of a new beater.

In the whipping process air is mixed with the liquid and, by rotating wires or blades, is extended into long "sausages" or filaments. As long as the force which produced these filaments continues to act on them, they are stable, but instability ensues as soon as they drift into a quieter zone. Surface tension is the prime cause of this instability. When the filament is long enough, its surface area is greater than the combined surface area of two or more spheres produced by breaking the filament; thus, the free surface energy decreases, when spherical bubbles form from the filament, and the process occurs spontaneously. The number of bubbles formed from a given filament depends on the viscosity of the surrounding medium; greater viscosity tends to give rise to smaller bubbles.

In bubbling, the control of the bubble diameter is a little easier. In these methods bubbles are made at an orifice or a multitude of orifices. If there is only one orifice, of radius r, and if bubble formation is slow and undisturbed, the greatest possible bubble volume is $2\pi r\gamma/g\rho$; γ is the surface tension of the liquid, ρ the difference between the densities of liquid and gas (practically equal to the density of the liquid), and g is acceleration due to gravity. Every type of agitation lowers the real bubble size. On the other hand, if there are many orifices near enough to each other, the actual bubble may be much larger than predicted by the above expression.

Formation and Stability

If, by one of the above procedures, a few or even many bubbles have been introduced into a liquid, there is still no foam. In a foam, films between the bubbles are thin; otherwise, the system is a "gas emulsion." How, then, can a true foam be achieved? If it is assumed that, because of some kind of stirring, two bubbles move to meet each other and the liquid layer between them gets thinner and thinner and if this process continues for a sufficient time, the two bubbles will touch and, eventually, coalesce. Many such encounters would destroy the foam. It is clear, therefore, that bubbles should be free to approach each other closely, but should be unable to cross the last short fraction of the initial distance.

This stipulation, which at the first glance appears self-contradictory, can be fulfilled in more than one way. The one which is, perhaps, the easiest to understand gives rise to foams on boiling or gas-evolving hot liquids such as molten metallurgical slags or, presumably, molten fats. The bulk of the liquid is hot, and its viscosity is small; hence the bubbles rise rapidly in it, but the surface layer is chilled by the cold air above. The viscosity of this layer is greater; hence the bubbles ascend slowly in it and the foam is relatively stable. Often the "domes" of the bubbles are cooled below the melting point of the film material; thus, a solid foam forms which, of course, is stable for an indefinite time.

Surface films much more viscous than the bulk of the material occur also at a constant temperature. Thus, proteins denature at interfaces and produce interfacial films. Evaporation of the solvent into the atmosphere leaves a layer of higher concentration on the surface of the solution. As, usually, higher concentration means higher viscosity, a viscous surface film results. Again, the loss of solvent may be so great that the films solidify and a solid foam of an indefinite persistence is obtained. As a first approximation, the foam on milk consists of evaporated milk.

The persistence of soap lather or of the froth on such liquids as aqueous *n*-butyl alcohol has a completely different mechanism (*2*), but this seems not to be important in the confectionery industry and is not discussed here.

Hydrocolloids

In a symposium on hydrocolloids it is natural to ask what is the function of agar and similar products in the compounding of edible foams. In the absence of experimental results no convincing answer can be given. However, it seems probable that hydrocolloids act as plasticizers of the walls of the above foams. This suggestion can easily be tested. Using the methods long standardized in the plastics industry, one should study the effect of the addition of hydrocolloids on mechanical properties (such as brittleness and total elongation) of films having the composition of marshmallow, for example. If the relation between these properties and the concentration of the hydrocolloids in the mix is similar to that between these properties and the concentration of a plasticizer in a polymer, the above hypothesis would be confirmed and some progress would be achieved in the understanding of a common industrial process.

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Practical Aspects of Dispersions

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Some considerations involved in the development of stable dispersions are the dispersion phase, the liquid phase, and the interphases. Careful consideration should be given to the specific properties contributed by the protective colloids and surfactants to the finished product: appearance, feel, application, compatibility, stability, viscosity, odor, taste, etc. Systems such as liquid suspensions consisting of inorganic pigments, organic medicaments, and waxes as the dispersion phases have been investigated and the stabilizing effects of protective colloids and wetting agents upon the individual products have been reported.

Dispersion is the minute uniform distribution of one substance throughout a dissimilar substance. Considerations involved in the development of stable dispersions which are discussed here are: the dispersion phase, the liquid phase, the interphases, and stabilization.

The Dispersion Phase

In any discussion of the dispersion phase, the physical state of the aggregates, whether they are inorganic pigments or organic medicaments, must be considered. The following physical states may occur:

1. Crystals, which may range in size from 0.005 to 1 micron in length in a wide variety of forms.
2. Particles, which are built up from crystals at the time of precipitation and usually range from 0.1 to 5 microns.
3. Aggregates, composed of several particles which owe their cohesiveness to surface forces or a matrix derived from the manufacturing process. These range in size up to 44 microns.
4. Dry agglomerates formed by dry handling. These are loosely held particles and aggregates cushioned from one another with absorbed air. They may range in size up to $1/4$ inch (11).

As a result of the forces inherent in agglomerates, such as surface charges or mechanical interlocking of particles, the following problems are encountered in dispersion formulations.

1. Reduction of the agglomerates to the desired size.
2. Wetting of the particle surfaces.

3. Removal of adsorbed or occluded films.
4. Stabilization of the system.

Most particles of the dispersion phase occur in a wide distribution of sizes consisting of aggregates of the primary particles. To ensure maximum stability, these aggregates must be reduced to an acceptable minimum size. When particles larger than the accepted minimum size are present in a dispersion, the physical properties of the dispersion are influenced by the size of the larger aggregates.

The American Society for Testing Materials proposes as a practical working unit the term "ultimate working unit" as a primary or individual particle or a group of primary particles that retains its structure throughout a dispersion process and subsequent applications.

Particle size data are usually represented by a histogram, where the dimensions of the particles are plotted against their frequencies of occurrence.

Figure 1 represents a particle size distribution histogram. Where a preponderance of smaller particles occurs, the curve is right skewed; and where a preponderance of larger particles occurs, the curve is left skewed. The symmetrical histogram is rarely found in practical applications.
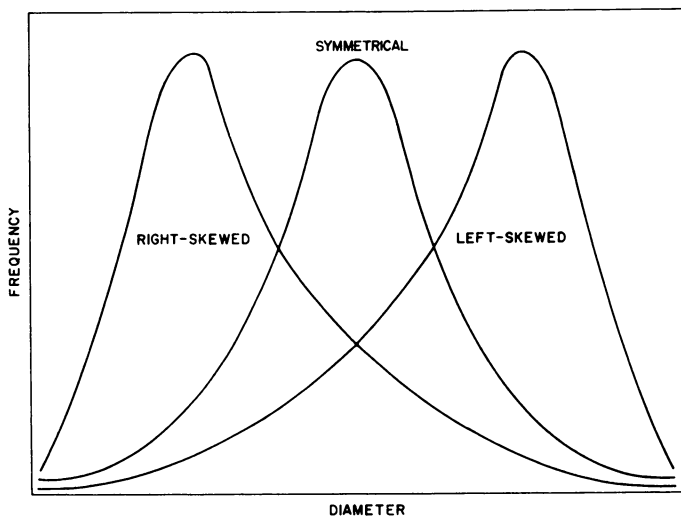

Figure 1. Particle size distribution histogram

It is apparent that the arithmetic average is not a true index of particle size for practical considerations. For example, in a powdered material where particles are classified as 95% at 2 microns and 5% at 0.1 micron, the computed arithmetic average would be on the order of 0.4 micron (5).

The Liquid Phase

To effect a dispersion of a solid in a liquid, mechanical work must be performed, and the forces and stresses imposed on the aggregates, through the liquid, cause them to break up into the smaller units. Once dispersed, the particles in their new environment are free to move about and form new associations, differing, however, in important respects from the original aggregations.

When wetting occurs, the air and moisture, usually adsorbed on the sur-

face of powdered solids, are displaced by the liquid. When wetting does not occur, the solid floats on the surface of the liquid, or if the specific gravity is sufficiently high, the mass settles, trapping air in the immersed mass. The moisture and/or gases adsorbed on the surface of the powder play an important role in the dispersion characteristics of the solid.

The Interphases

One of the most important aspects of dispersion technology is the solid-liquid interphase. Interfacial phenomena determine to a large degree the physical characteristics of the final dispersion.

For wetting to occur, the adhesive forces of the liquid for the solid must exceed the cohesive forces of the liquid for itself.

One of the measurements to express wetting is based on the contact angle. A contact angle of 0° indicates complete wetting, while a finite contact angle indicates incomplete wetting. The contact angle is measured through the liquid phase and values from 0° to 180° are theoretically possible, although a contact angle of 180° denoting complete "nonwetting" is considered impossible, since there is always some attraction between liquid and solid (Figures 2 and 3).

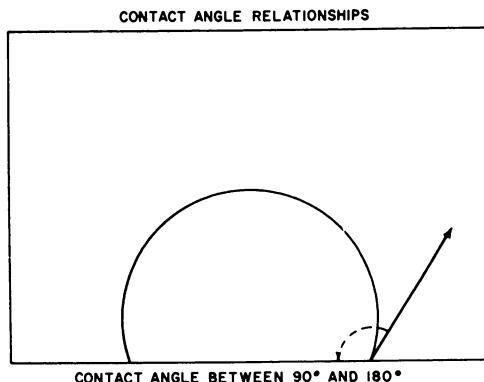CONTACT ANGLE RELATIONSHIPS

CONTACT ANGLE BETWEEN 90° AND 180°

Figure 2. Example of incomplete wetting

When wetting occurs, adsorbed liquids and gases are displaced or dissolved in the wetting medium. A solid displays its own surface phenomena only in the absence of adsorbed substances; when adsorbed materials are present on the surface, the solid assumes the surface properties of the adsorbed materials; when the liquid displaces or dissolves the adsorbed films, the solid again assumes its own surface properties.

Stabilization of Suspensions

To prepare a stable suspension the liquid must wet and spread over the surface of the solid, displacing adsorbed materials. The wetted aggregates must then be stabilized so they do not agglomerate when the system comes to equilibrium.

When aggregates are reduced to their component parts, the particle cannot

usually be reconstituted to form aggregates with properties identical to the original. Some factors preventing the particles from agglomerating and assuming the original properties of the aggregates are: displacement of originally adsorbed materials, influence of liquid medium, and charge influences. A flocculated mass, however, may be broken by stirring, only to form again when the stirring stops.
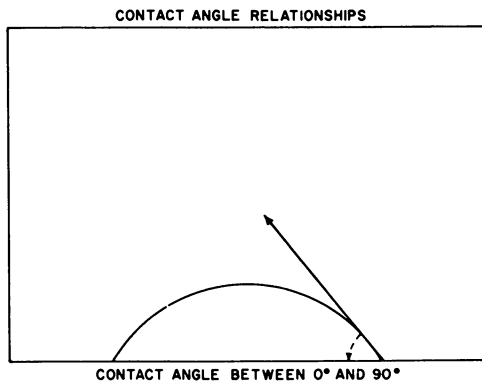

CONTACT ANGLE RELATIONSHIPS

CONTACT ANGLE BETWEEN 0° AND 90°

Figure 3. Example of complete wetting

Deflocculation is a state of the dispersion of a solid in a liquid in which each solid particle remains geometrically independent and unassociated with adjacent particles.

The nature and intensity of the attractive or repulsive forces among particles in a state of suspension in a liquid medium depend primarily on the electrostatic charges of the particle. Other factors contributing to these forces are particle size and surface area of the solid, the physical properties of the suspending medium, the presence of adsorbed gases or liquids, the proximity of the particles, and Brownian movement (5).

The deposition of similar charges on the particles of a colloidal suspension is important in achieving stability of the suspension. The similarly charged particles repel each other, minimizing aggregation.

If a hydrophobic solid is suspended in water and a small amount of oil is added to the system, the oil will preferentially wet out the solid. If a sufficient amount of oil is added, the oil films are brought together and coalescence (a first-order reaction) and agglomeration (a second-order reaction) take place.

Work is necessary in order to separate these agglomerates and is proportional to that required to enlarge the liquid-liquid interphase formed between the continuous phase and the immiscible liquid.

By introducing surfactants, which lower the interfacial tension, it is possible to reduce the work necessary to deflocculate agglomerates. In liquid suspensions the introduction of an interfacial tension depressant facilitates wetting of the solid by the liquid and the displacement of adsorbed gases from the solid surface. Certain solids have adsorbed films whose adhesional forces are so great that they resist all mechanical efforts to displace them. Upon the addition of a surfactant, the films are displaced and a solid-liquid interface is achieved (1).

A separate class of materials, known as protective colloids, exerts a stabilizing influence by acting as a bridge between the continuous phase and the particles which they envelop. In many instances the optimum stabilizing effect is achieved when the protective colloids are used in conjunction with a compatible interfacial tension depressant. The protective colloid must have an affinity for the continuous phase. When stabilization occurs through protective colloidal action, the particles lose their surface property identities in respect to charge, agglomeration, etc., and assume the properties of the protective colloid.

When protective colloids are used as stabilizing agents, the following properties contributed by these stabilizing materials should be considered:

1. Appearance of finished product
    A. Body
    B. Pour characteristics
    C. Smoothness
    D. Stringiness
    E. Sheen
2. The feel
    A. Tackiness
    B. Slip
    C. Lack of grit
3. The application
    A. Spreading qualities
    B. Drying time
    C. Penetration
    D. Adhesion
4. Compatibility
    A. With active components of the system
    B. With diluents, excipients, and inert materials in the system
    C. With other protective colloids and surfactants
5. Stability
    A. Effect on maintaining particles in maximum state of suspension for the projected shelf life
    B. Sedimentation
        1. Hard packing
        2. Soft packing
        3. Reconstitution
6. Viscosity
    A. Consistency desired
    B. Thixotropy
    C. Dilatancy
7. Optical properties
    A. Degree of opacity or translucency desired
8. Emulsifying properties
    A. Primary emulsifier
    B. Secondary emulsifier
9. Preservation
    A. Subject to bacterial attack
10. Toxicity
    A. Internal consumption
    B. External application
11. Cost
12. Odor
13. Taste
14. Use of combinations of protective colloids
    A. Synergistic effects
    B. Antagonistic effects
15. Special properties
    A. Film former
    B. Astringency
    C. Therapeutic uses
    D. Foam stability

The practical aspects of stabilizing agents for suspensions are of great importance to the cosmetic and pharmaceutical industries. The following

figures represent various products utilizing protective colloids as stabilizing agents. Figure 4 represents a sunburn remedy suspension and compares the stability characteristics of a system with and without protective colloids. Sample 1 consists of a dispersion of zinc oxide and ethyl aminobenzoate in water. Dioctyl sodium sulfosuccinate was used to lower the interfacial tension so that the insoluble medicaments are completely wetted, displacing adsorbed gases and resulting in an air-free product. Poly(vinyl alcohol) and magnesium aluminum silicate are used as the protective colloids. Other medicaments such as phenol and camphor are solubilized with polyoxyethylene sorbitan monolaurate and alcohol. The solubilized lipophylic phase serves as a plasticizer for the protective colloids, allowing the deposition of a smooth, continuous, medicated film after application and evaporation. Sample 2 consists of a zinc oxide dispersion with no protective colloids. Figure 4 shows the initial exposure; sample 1 shows no separation. while sample 2 shows a 5% separation.
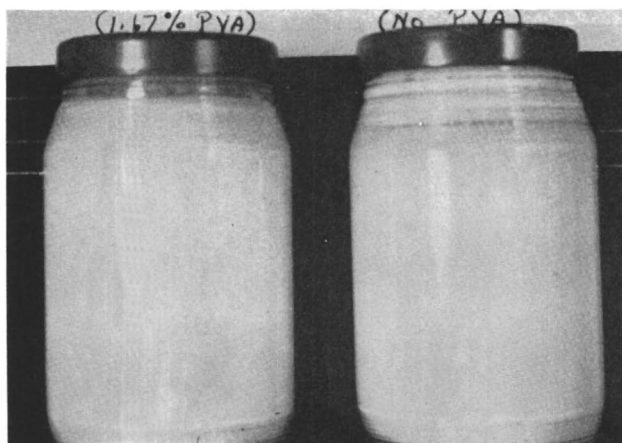
Figure 4.   Stability of sunburn remedy suspension with
and without protective colloids

Initial exposure.   *Left*, Sample 1.   *Right*, Sample 2

After 24 hours at room temperature sample 1 showed no separation, while sample 2 showed more than 75% separation. Figure 5, representing the exposure for 6 months at room temperature, displays the same stability pattern as the 24-hour samples, except that sample 2 after 6 months is more difficult to reconstitute.

A study was made of the comparative stabilities at various exposures of an upset stomach remedy suspension. This product consisted of a dispersion of bismuth subsalicylate and phenylsalicylate in an aqueous system. Methylcellulose and magnesium aluminum silicate were selected as the suspending agents, because the presence of polyvalent metallic ions precluded the use of hydrocolloids affected by these ions. In addition, it was found that methylcellulose contributed a demulcent effect. The viscosity, as well as the suspension characteristics of the combination of protective colloids used, was of a synergistic nature. These colloids formed a thixotropic system. The thixotropy undoubtedly aids in stabilizing this system. In order to make this product palatable and impart elegance, color and flavor were added. Sample 1 (with protective colloids) showed no separation, while sample 2 (without

protective colloids) showed more than 80% separation after 24 hours. Apparently the two systems reached equilibrium after 24 hours, showing little or no additional change with time.

The stability characteristics of two different antiperspirant lotion systems were compared. Sample 1 represented an aqueous emulsion containing an aluminum salt. The internal phase consisted of stearyl alcohol and ethylene oxide reaction products, polyoxyethylene sorbitan monostearate and polyoxyethylene sorbitan tristearate. Methylcellulose was used as a stabilizer and bodying agent. Sample 2 represented a dispersion of magnesium aluminum silicate in an aqueous system containing aluminum ions. Because of its com-

Sample 1   Sample 2

Figure 5. Sunburn remedy suspensions after exposure for 6 months at room temperature

patibility with aluminum ions methylcellulose was used to impart body. The magnesium aluminum silicate was used as the opacifying agent and was, itself, the dispersion phase. The perfume was solubilized with polyoxyethylene sorbitan monolaurate, which served as a plasticizer for the protective colloids, allowing the application to be smooth and nonballing. Alcohol in this product permitted rapid evaporation and quick drying, requisites for this type of product. After 6 months at room temperature, sample 2 (the dispersion) showed no separation, while sample 1 (the emulsion) showed approximately 10% separation.

The stabilizing effects of methylcellulose and hydrated magnesium silicate were applied to calamine lotion. Sample 1 was the U.S.P. XV calamine lotion, and sample 2 the U.S.P. XV calamine lotion with 0.5% of methylcellulose. Sample 1 showed 50% separation, while sample 2 showed 12% separation after 24 hours at room temperature.

Generally, cellulosic protective colloids exhibit greater synergistic stabilizing effects with magnesium aluminum silicate than with hydrated magnesium silicate or bentonite. The potentiating effects of magnesium aluminum silicate and cellulosic hydrocolloids on the stability of suspensions can be demonstrated (Figure 6). This system represents a suspension of zinc oxide, ethyl aminobenzoate, and color pigments in an aqueous system containing antihistamine stabilized with carboxymethylcellulose and magnesium aluminum silicate. Glycerol is included as a humectant and plasticizer for the protective

colloids. Dioctylsodium sulfosuccinate is the wetting agent used to wet and displace the adsorbed films from the insoluble powder. Experience has shown that when the adsorbed and occluded materials are not displaced when the system is still mobile, and before stabilizing influences are introduced, the finished product may contain considerable amounts of gases liberated from the suspended powder. If the bulk is packaged in this condition, the gases will gradually rise to the surface, resulting in slack fill. Figure 6 shows that there is no visible separation in the product initially and after 6 months at room temperature. However, particle distribution analysis would probably reveal some gravitation of the larger particles.

Initial exposure

After 6 months
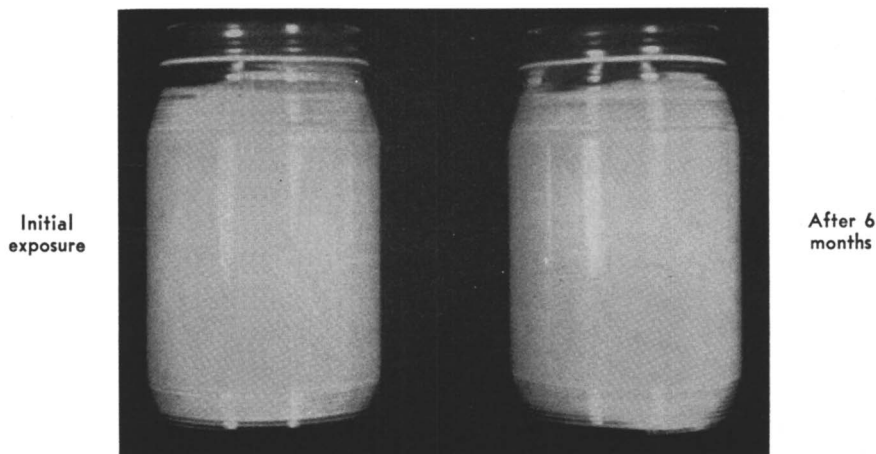
Figure 6. Effect of magnesium aluminum silicate and cellulosic hydrocolloids on stability of suspensions

Another example of the synergistic stabilizing effects of magnesium aluminum silicate with carboxymethylcellulose is represented by a medicated liquid cream for cosmetic purposes. The suspended material consists of zinc oxide, titanium dioxide, ethyl aminobenzoate, and color pigments. Dioctylsodium sulfosuccinate is used as the wetting agent. Glycerol is included as a humectant and plasticizer for the protective colloids. As can be seen, the stability is excellent. Figure 7 shows the viscosity characteristics of this product. The broken line represents the viscosities of the unstirred product, and the unbroken line, the viscosities after stirring. This product is thixotropic, the viscosity limits being in a practical range for this type of product. The phenomenon of thixotropy undoubtedly plays an important role in maintaining the particles in a suspended state.

Carboxypolymethylene exhibits a stabilizing effect against separation and viscosity change of a cetyl alcohol–stearic acid–sodium lauryl sulfate system. Samples 1 and 2 are identical, except that the former contains carboxypolymethylene (adjusted to pH 7). Sample 1 shows no separation, while sample 2 shows 13% separation after 6 months. Figure 8 shows the viscosity characteristics of the above samples. The broken line represents the viscosities of sample 1 at different time intervals, and the unbroken line, the viscosities at the same time intervals for sample 2. Apparently the carboxypolymethylene prevents the agglomeration and precipitation of stearic acid, which would result in separation and loss of viscosity.
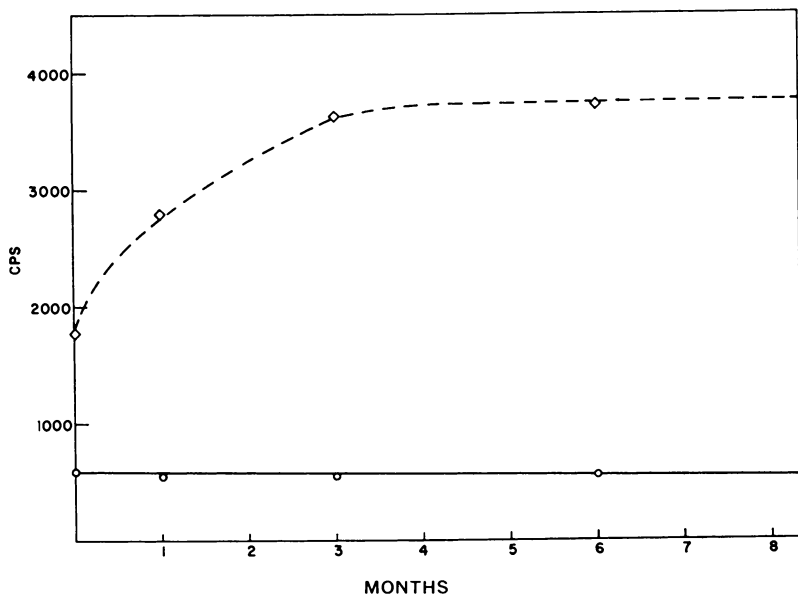
Figure 7. Synergistic stabilizing effect of magnesium aluminum silicate with carboxymethylcellulose on medicated liquid cream

– – – Unstirred viscosity
——— Viscosity after stirring

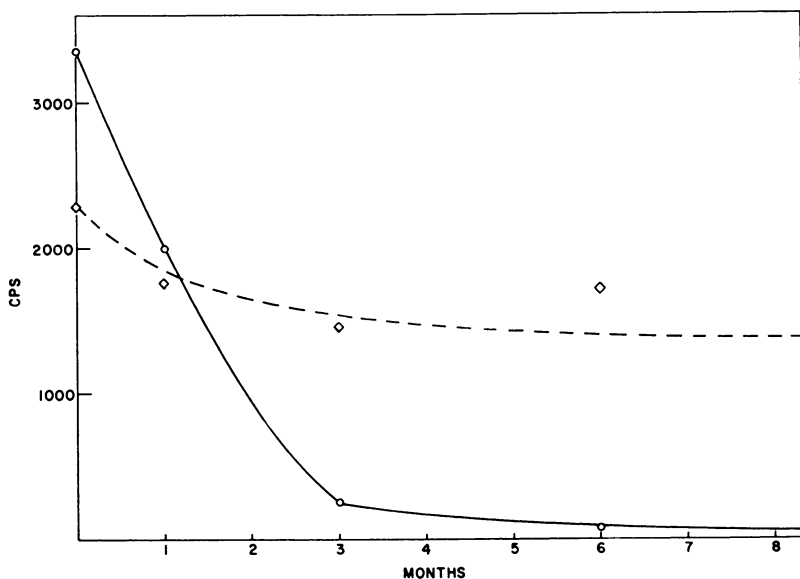Brookfield viscosity, No. 3 spindle, 20 r.p.m. at 25° C. *vs.* time

Figure 8. Stabilizing effect of carboxypolymethylene against separation and viscosity change of a cetyl alcohol–stearic acid–sodium lauryl sulfate system

– – – Sample 1 (carboxypolymethylene)
——— Sample 2 (no carboxypolymethylene)

Brookfield viscosity, No. 3 spindle, 20 r.p.m. at 25° C. *vs.* time

Carboxypolymethylene also exerts a stabilizing effect on a cetyl alcohol–sodium lauryl sulfate emulsion containing 15% of talc. The differential in the distribution of particles at all levels of those stabilized systems discussed above can be considered negligible for all practical purposes.
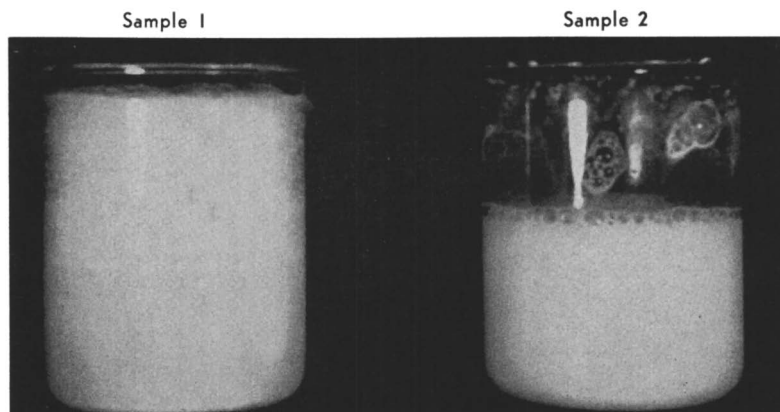
Figure 9. Stabilizing effect of methylcellulose on foams generated by a suspension of effervescent antacid granules containing magnesium trisilicate and aluminum hydroxide

Figure 9 illustrates the stabilizing effect of methylcellulose on the foams generated by a suspension of effervescent antacid granules containing magnesium trisilicate and ammonium hydroxide. Samples 1 and 2 are identical, except for 0.01% of methylcellulose contained in sample 1. The foam in sample 1 (methylcellulose) is stable even after 5 minutes, while the sample without methylcellulose has virtually no foam after 30 seconds.

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The Physical Stability of Dispersions

Basic Considerations

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Stability may be inherent or induced. In the latter case, the original system is in a condition of meta-stable or neutral equilibrium. External influences which induce instability in a dispersion on standing are changes in temperature, volume, concentration, chemical composition, and sediment volume. Applied external influences consist of shear, introduction of a third component, and compaction of the sediment. Interfacial energy between solid and liquid must be minimized, if a dispersion is to be truly stable. Two complementary stabilizing techniques are ionic and steric protection of the dispersed phase. The most fruitful approach to the prediction of physical stability is by electrical methods. Sediment volumes bear a close relation to repulsion of particles for each other.

For decades the problem of stability has plagued colloid chemists and others engaged in the manufacture and use of dispersions. Only a determined practical approach to the solution of this problem has been responsible for the modest accumulation of theoretical knowledge in existence today. In the field of dispersions, for example, problems of physical instability have been solved for paints, pharmaceuticals, adhesives, asphalt, detergents, and commodities used in the graphic arts, in addition to the numerous successful encounters with instability (or sometimes with undesired stability) in the food industry.

Stability implies a resistance to change, and may be defined qualitatively in those terms. In the specific case at hand, stability is defined as resistance to molecular or chemical disturbance. This requirement recognizes that *a flocculated dispersion may be more stable than a peptized dispersion* from the standpoint of its future behavior. A physically stable dispersion is one which will not undergo molecular replacements at the interface between the dispersed solid and the continuous phase.

For purposes of this survey an important distinction must be made between a commonly used criterion of instability and the sense in which the term is used here. A stable dispersion is not necessarily one which will not settle, because the only disturbance involved in settling is motion of translation of the parti-

cles, where solvent molecules are not displaced from their original environment at the particle surface. Only in the rare instance in which the particles and suspending medium have the same density will a dispersion be truly and thermodynamically nonsettling.

Stability Requirements

The basic requirement of stability is that the system under consideration be in its condition of minimum energy (except for potential energy due to height, as in the case of a settling, but stable, dispersion). All other conditions lead either to instability or to less clearly defined states such as metastability. Most articles of commerce owe their useful properties to the fact that in reality they are applied or consumed while they are in a metastable condition. They have no difficulty in existing in this condition so long as certain prescribed conditions of storage and treatment are met, but after they are transferred to the use environment they change over to an even more stable form. Food preparations are particularly fruitful in supplying examples of this generalization.

In terms of the two-phase system which comprises dispersions of solids in liquids, the minimum energy requirement is met if the total interfacial energy of the system has been minimized. If this requirement has been met, chemically, the fine state of subdivision is the most stable state, and the dispersion will thus avoid changing physically with time, except for the tendency to settle manifest by all dispersions whose phases have different densities. A suspension can be stable and yet undergo sedimentation, if a true equilibrium exists at the solid-liquid interface. If sedimentation were to be cited as evidence of instability, no dispersion would fit the requirements except by accident—e.g., if densities of the phases were identical, or if the dispersed particles were sufficiently small to be buoyed up by Brownian movement.

In a practical sense, stability of a dispersion ofttimes is accompanied by a retarded separation of the phases. Unfortunately, a quantitative definition cannot be based on this rate of separation because of the overwhelming influence of density, viscosity, and thermal effects. In short, a kinetic criterion, such as sedimentation rate, is not as likely to portray stability as one based on thermodynamic considerations. In this latter category are sediment volumes, turbidity, consistency, and electrical behavior.

During preparation most dispersions pass through an unstable condition. Individual particles must be separated from their neighbors, and air has to be displaced from the particle surface by the medium; both of these operations are difficult to perform. In addition, if the dispersion medium contains solute, the displacement may not find the particles wetted in the right molecular ratio for true stability. And yet no manifestations of instability may be visible at the time of preparation because the physicochemical measurements taken on the dispersion are not designed to uncover tendencies toward time-consuming molecular changes at the interface. One of the objectives of this survey is to show that practically all of the numerous stability criteria are designed to reveal how far a system has departed from a certain reference condition, rather than how it will behave in the future. But first, some mention must be made of the factors of importance to dispersion stability.

The causes of inherent instability in dispersions are found at the particle-liquid interface, and the chief parameter against which stability is measured

is time. Another type of instability results from external influences such as changes in composition or environment, fluctuations in temperature, and the application of shear; it is called "induced instability" in contrast to the designation "inherent instability," given to changes brought about by time alone.

A study of these two types of instability is based on the concept that equilibrium can be manifest in various ways, only one of which represents true stability in the thermodynamic sense. The major objectives are to interpret these types of instability in terms of three recognized stabilization mechanisms operating at the solid-liquid interface, and to indicate the limits within which a system can have all of the outward appearances of true stability without being at its minimum energy.

Types of Equilibrium

A mechanical system consisting of a block on a plane (4) is depicted in Figure 1. The block is capable of lying in momentary equilibrium with its surroundings in various ways. This equilibrium can be characterized as stable, metastable, neutral, or unstable, depending on whether the block is resting on its broad side, on a flat end, on a rounded end, or on a sharp edge, respectively. The potential energy of the block varies from minimum to maximum as its center of gravity is raised, with auxiliary minima for metastability and plateaus for neutral equilibria as shown in the figure.
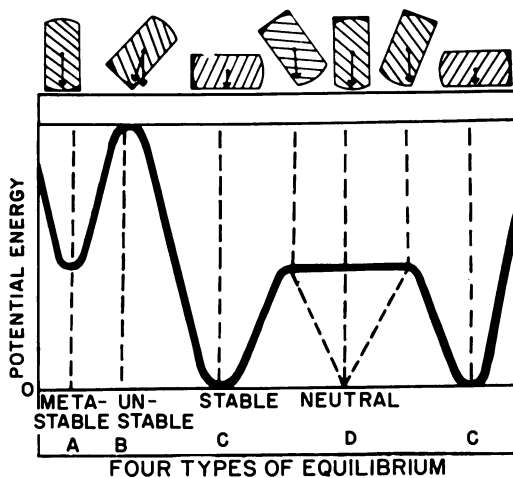

Figure 1. Mechanical system of indicating equilibrium

Position A represents many cases of practical "stability"; it does not represent the condition of minimum energy and is more accurately referred to as metastable, because it pertains to a condition of comparative rather than absolute stability.

The unstable position, B, does not remain in equilibrium long enough to represent the state of any dispersion except at the instant of its preparation or during the transition of a dispersion from a metastable to a stable condition. Of chief interest here are conditions A and D, for they are the mechanical

counterparts of the equilibria that cause dispersions to change physically with time.

Similar considerations apply to chemical or physicochemical equilibria such as encountered in phase transitions. A chilled salt solution may be stable (at or below saturation), metastable (supercooled to an extent not allowing nucleation), or unstable (cooled sufficiently to nucleate spontaneously). In the case of a solid, S, dispersed in a binary liquid, $L_1 + L_2$, instability at the instant of formation gives way to a neutral or metastable condition wherein three types of contacts are established:

$$\text{S–S, S–L}_1\text{, and S–L}_2$$
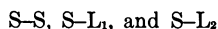
A quantitative calculation of the distribution among these three possibilities is not yet possible, although one can conclude that a combination of statistics and a knowledge of adsorption energies will be required for the task. Only when the distribution reaches that demanded by free energy considerations will the system be stable.

Inherent Instability

If a dispersion changes spontaneously in physical structure with time, it has been said to be inherently unstable. These changes may be brought about by a chemical reaction, by more subtle chemical changes (starch retrogradation), as a result of perfection of shape or size distribution of the dispersed solids (digestion of barium sulfate precipitates before filtration), from solubility of the solid in the liquid and the resulting cementation of the particles (salt cakes), as a result of solvent-particle incompatibility (lampblack in water), by the gradual displacement of an adsorbed ion by another species (ion exchange, especially in clays), or by a change in flocculation tendencies on settling.

If one is confronted with the problem of improving the stability of a particular dispersion, he does not necessarily have to consider all of these alternatives. Hydrocolloids, for example, undergo hydration and consequent swelling before appearing to be fully stable, prior to which they are not likely to display incompatibility toward water. Changes on storage of certain pharmaceutical dispersions usually are chemical, although cementation by solubility of the solid in the vehicle sometimes occurs. In the latter case, shelf life may be prolonged if the solid phase is finely dispersed, so that the discrete particles can be kept apart by Brownian motion. Many lyophobic colloids can be stabilized by proper selection of a dispersant which charges the particles with ions.

Examples of inherent metastability are numerous. The implication here is that the dispersion is characterized by a deep energy minimum by the time observations of its behavior are made. Sometimes the criterion of when this this state is reached can be based on simple measurements such as a one-point viscosity determination—for example, the leveling off of viscosity of a paint during milling. This behavior is shown in Figure 2, in which the dotted line represents the increase in viscosity which invariably accompanies the breaking up of ultimate particles. The high viscosity of the poorly milled dispersion results from the particles banding together in clusters to offer the smallest possible surface to the vehicle.

Dispersion instability can result from an order of addition which creates a

thermodynamically unfavorable set of interfaces. The introduction of a third component such as water to a lithographic ink can upset the equilibrium existing at the pigment-vehicle interface, especially if the pigment has a high energy surface.
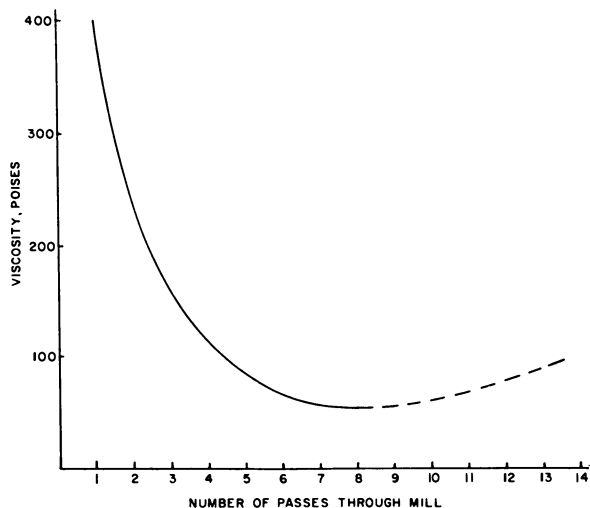
Figure 2. Viscosity as a criterion of degree of dispersion

Induced Instability

When an external influence is responsible for changes in the distribution of types of molecular contact (which for a dispersion in a binary medium were designated S–S, S–L$_1$, and S–L$_2$, referred to as linkages in the discussion), the resulting instability is said to be induced. The variation may be one of temperature (sintering of particles), of environment (pigment flooding), of shear (breakdown of greases), of volume concentration (evaporation), or of sediment volume (centrifugation).

Induced instability of a dispersion is the most important form of instability encountered in practice, for here the dispersion is unable to maintain a given structure during changes in storage conditions. Sometimes the structural breakdown is permanent (in which case the initial dispersion at rest is metastable); at other times the structure is rebuilt on removal of the external influence.

Examples of reversible breakdown of structure have been reported for procaine penicillin dispersions (7), for model systems of calcium carbonate in polybutene (6), and for numerous other systems. During shear the particles are forced into contact with each other with sufficient kinetic energy to overcome any natural barrier against their displacement of a lyosphere around each individual particle. A dispersion which is inherently stable can thus be forced by shear into a condition of instability.

Of all the forms of induced instability, temperature fluctuations are most widely experienced by an unattended dispersion once it has been stored or applied. The caking of pharmaceuticals so that they will not pass through a hypodermic needle has been mentioned (7); another example is the failure of

certain adhesives with time. Floor, roof, and wall coverings, or the cements used to bind them to the substrate, generally fail because of a combination of temperature fluctuations and moisture. The problem of deciding which factor is responsible for failure reduces to the basic principles of ascertaining the affinity of a solid for one or more of the components of a fluid vehicle versus water. Adsorption studies are useful here.

Introduction of a second solvent, incompatible with the continuous phase of a normally stable dispersion, produces an unstable condition if the new solvent wets the surface of the solid better than does the original vehicle. The instability induced by the introduction of a oily vehicle to an aqueous dispersion of an organic pigment is exploited commercially in the so-called flushing of pigments from an aqueous liquor into a vehicle.

Stabilization

Because stability depends on the ability of the particles to remain at discrete distances from each other, the well-known relation described by Morse (5) can be used as a starting point for stabilization mechanisms. As shown in Figure 3, two uncharged (and nonrepelling) bodies approach each other until they have attained an equilibrium distance corresponding to the position of minimum energy. The solid line actually represents a compromise between the repulsive forces operative between two atoms when their electron clouds overlap and the attraction which always exists between two bodies.
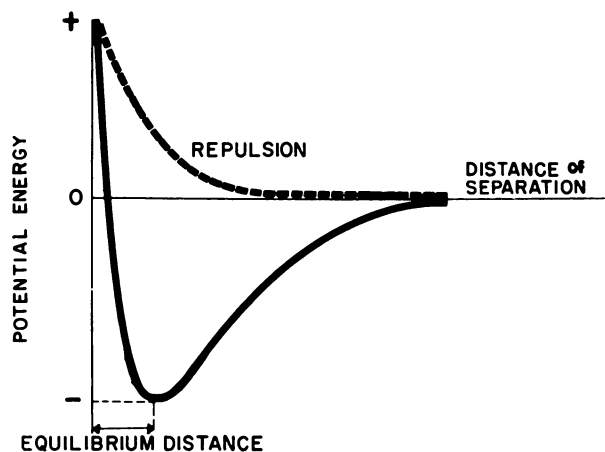

Figure 3. The Morse curve

Verwey and Hamaker (10) have modified the Morse curve to take into account the approach of two charged bodies, as shown in Figure 4. Here, as one moves outward toward increasing distance of separation, an electrostatic repulsion is encountered because the charges are similar. A secondary minimum is then encountered as a result of the concentration of counter ions around each charged particle. The shallowness of the secondary minimum shows that the deflocculated system is metastable. The importance of the Verwey and Hamaker concept lies in its ability to show graphically the correlation between the secondary minimum and the metastable position. A, Figure 1.
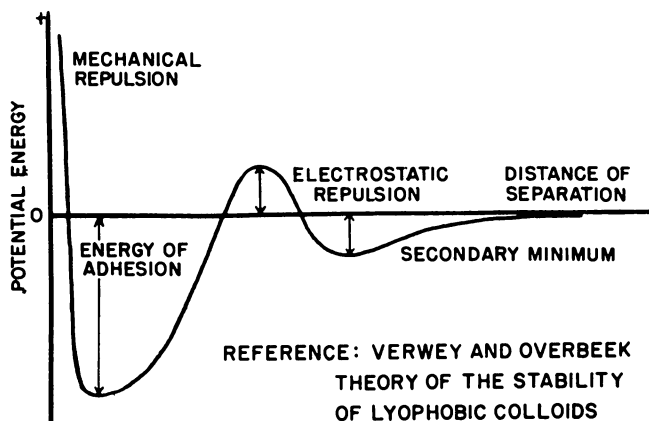
Figure 4. Potential energy curve for the interaction of two particles

The situation changes as a stabilized sediment begins to accumulate at the bottom of the container. A tendency toward compaction of the sediment by gravity occurs as the sediment height increases, and the particles are forced closer to each other than the distance corresponding to the peak in the Verwey and Hamaker energy curve. The external influence which induces settling, whether gravity or centrifugation, causes the particles to suffer an attraction which draws them to the equilibrium distance, where the energy is the lowest. Before crowding, the dispersion can exist indefinitely in a metastable condition; only after compaction does it attain a truly stable arrangement. After compaction the height of the electrostatic repulsion barrier works against redispersion of the solids.

The influence of gravity on a sediment can be shown schematically by the fine line of Figure 5, where it is shown to have the effect of tilting the entire
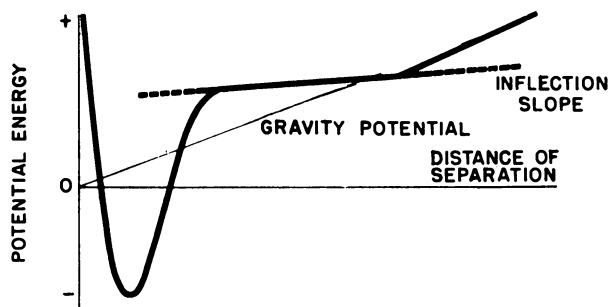

Figure 5. Potential energy under influence of gravity

potential energy curve in proportion to the mass of material bearing down on the particle under consideration. As soon as the inclination becomes great enough to impart a positive slope to the inflection between the repulsion peak, E_r, and the secondary minimum, the particles overcome E_r and flocculate. In passing to the bottom of the well at E_a they respond to the attractive forces that are present in all matter, regardless of the presence of stabilizing charges.

The choice of a means of stabilization depends on the external influence to be counteracted. To counteract settling, the viscosity of the medium is increased or the density differential reduced; to overcome flocculation during settling, the electrokinetic (zeta) potential is increased; to prevent caking after settling, zeta is reduced or sediment height is decreased by increasing its area; to improve thermal stability, a solute with a high adsorption energy is adsorbed on the surface of the particles; to resist shear, weak S–L molecular bonds are avoided.

Best approach toward a general solution of all problems of induced stability appears to be a two-pronged surface treatment involving electrostatic and steric protection. In order to increase repulsion energy, zeta should be increased; and to enable the particles to resist compression to a distance of separation less than that at E_r, a bulky molecule should be attached firmly to the surface. Some systems do not accept both steric and ionic protection; but for those that do, the combination shows most promise. E_r should not be increased without some assurance that the particles will not be subjected to drastic compressive forces.

Finally, in instances in which a bulky solute molecule with several functional groups can be added to the system, a fragile sort of structure can be built up by simultaneous attachment of these molecules to create a network with the characteristics of a gel. This system is then permanently metastable toward settling and caking, but may not withstand the ravages of shear or high temperature.

Criteria of Dispersion Stability

Rheology has provided several indexes of dispersion stability. The decrease in a single point viscosity with degree of dispersion (Figure 2) has, at best, only qualitative significance. The decrease in viscosity with rate of shear that characterizes flocculated systems is a much more valuable criterion of the degree of dispersion, as shown in Figure 6. But even this test has limitations, for it demonstrates only that a highly flocculated dispersion is more susceptible to shear than a stabilized system. More involved rheological methods are discussed by Reiner (8) and are not covered here.
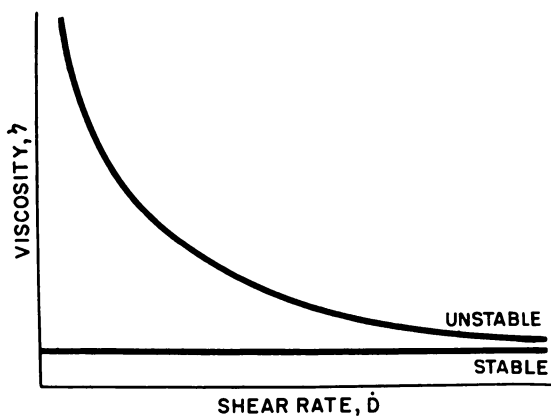

Figure 6. Viscosity as stability criterion

Rheological determinations are destructive of the structures they measure; for this reason they do not portray the actual structure of the dispersion at rest. Accordingly, various methods have been devised for extrapolating to zero the results of measurements at various shear rates. The most useful one has been the conversion of viscosities to fluidities at various shear rates and the extrapolation of the resulting nearly linear relationship to zero shear, as shown in Figure 7. Sometimes a power of the shear rate, D, provides a better distinction between a sol (essentially a liquid) and a gel (essentially a solid), as shown in the figure, but the difference between a finite intercept (sol) and zero fluidity (gel) is largely fictitious because of the dependence of the intercept on the exponent n.
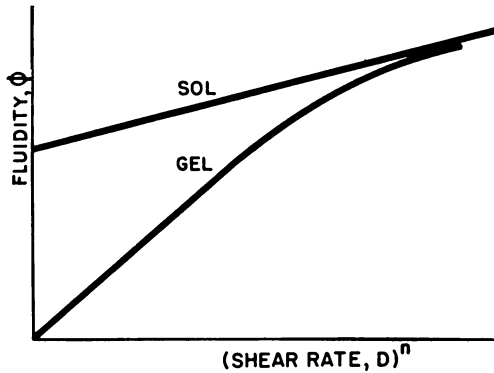
Figure 7. Detection of gelation by fluidity

Perhaps the best rheological stability criterion is the volume occupied by the sediment per unit volume of original dispersion. A flocculated dispersion settles rapidly to a high sediment volume, while a deflocculated one settles slowly to a low volume, as shown in Figure 8. Of course, the ultimate volume depends on the concentration of the dispersion; and in order to give a criterion of more fundamental interest the concept of relative sediment volume RSV may
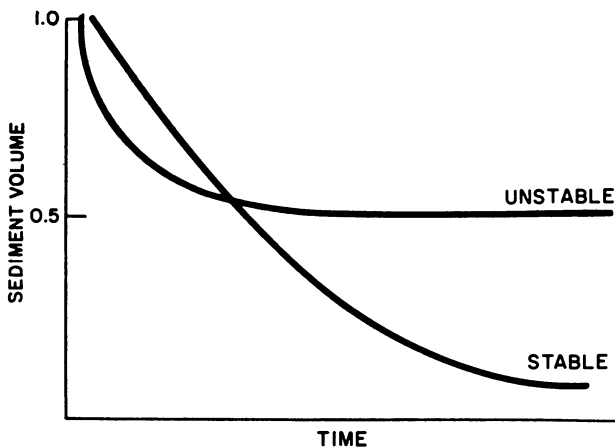
Figure 8. Sedimentation as stability criterion

be useful. Whereas SV is a fraction, RSV always exceeds unity. SV is related
to viscosity by the formula (9)

$$\eta = \eta_{solv}\left(1 + \frac{2.5V}{1-SV}\right) \tag{1}$$

where η_{solv} is the viscosity of the medium, 2.5 is the Einstein (3) constant for
the contribution of the rigid particles; V is the volume concentration, and SV,
the sediment volume, is expressed as the fraction of the total volume of the
dispersion. The equation states that sediments have infinite viscosity, which
is not rigorously true because of the assumptions involved.

SV can be linked to the E_r of Figure 4 by recognition of the fact that high E_r
increases stability and therefore permits the sediment to be compacted before
forming network links. From Figure 9 it may be seen that a 10% dispersion
of spheres may settle to a volume as low as 14%, but no lower, if the spheres
are of uniform size. On the other hand, a zero repulsion energy is likely to
result in, say, a fivefold increase in sediment volume, as shown schematically
in the figure. Schematic curves for 10, 20, and 30% dispersions show that
the optimum concentration for testing stability lies between 10 and 20% in the
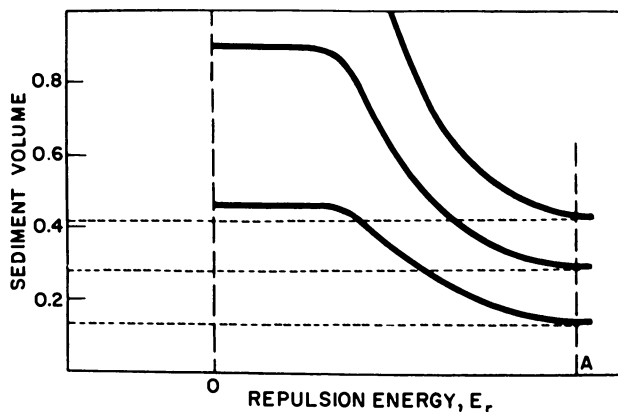case selected.

Figure 9.   Interparticle repulsion and sedimentation
volumes

By now it should be clear that most stability criteria, and sedimentation in
particular, in reality measure how unwillingly the dispersion renounces its
metastable condition. If the dispersion had achieved what has been recog-
nized in Figure 1 as true stability, it would no longer be a dispersion. The
ultimate state would contain exclusively either the completely solvated S–L
linkages, or else an irreducible minimum of them. Only if the secondary mini-
mum of Figure 4 lies deeper than the energy minimum at equilibrium is a
dispersion truly stable. Because this condition has not yet been demonstrated
to be readily attainable, existing stability criteria are properly directed toward
assessing the strength of the metastable condition. The time is not yet ripe to
insist on a literal interpretation of stability, because too few dispersed materials
meet the requirement.

Closely allied with sedimentation phenomena is the question of adherence
of a sediment to the substrate (1). The low energy of repulsion of a system

which flocculates during settling causes the particles to form loose aggregates before they have completed their fall, thereby reducing adherence by lessening the number of linkages to the substrate.

Electrical criteria useful in assessing the stability of dispersions have been pointed out by Bruggeman (2) and by Voet (11, 12). The conductivity of a deflocculated dispersion of conducting solids in a nonconducting medium increases steadily with shear (as shown in Figure 10) because of the increased frequency of particle contacts during which charges are transferred. On the other hand, a flocculated system initially will drop in conductivity with shear because the conducting network is broken by the shearing action; it will then behave like the deflocculated system and become a better conductor as shear is increased further.
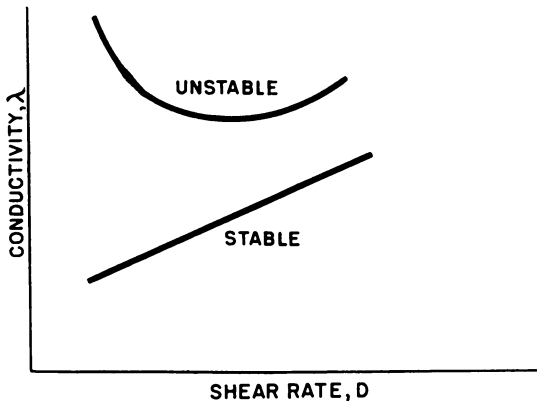

Figure 10. Conductivity as stability criterion

Another electrical measurement useful in detecting flocculation in anisometric particles is the response of dielectric constant to shear. The alignment along streamlines of flow which results from laminar shear in a viscometer decreases the dielectric constant of the system if the dipole moment lies along the long axis of the particle. Another way in which this phenomenon can be meas-
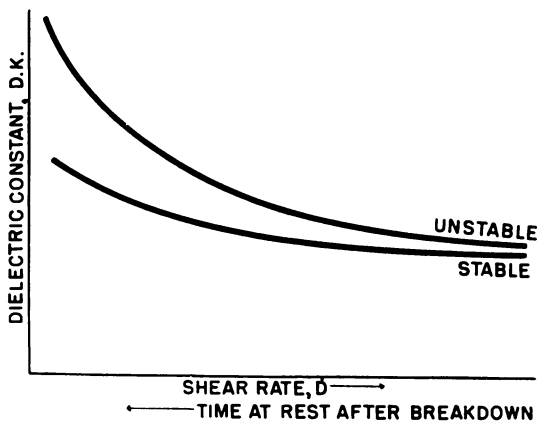

Figure 11. Dielectric constant as stability criterion

ured is to observe the increase in dielectric constant with time after cessation of shear. These two criteria are shown in Figure 11.

Because stabilization in the Verwey and Hamaker picture is electrical, the use of electrical methods for predicting the stability of a dispersion appears to be mandatory. Other than the work of Voet described above, little has been done in this direction. Beyond doubt, the important developments in the area of dispersion stability that will come forth will be based either on electrokinetics (for high dielectric media, especially hydrocolloids) or electrostatics.

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