

Hydrocolloids — Competent Ice Cream Stabilizers

History of ice cream

Our love affair with ice cream is centuries old. The ancient Greeks, Romans and Jews were known to chill wines and juices. This practice evolved into fruit ices and, eventually, frozen milk and cream mixtures. In the first century, Emperor Nero reportedly sent messengers to the mountains to collect snow so that his kitchen staff could make mixtures flavored with fruit and honey. Twelve centuries later, Marco Polo introduced Europe to a frozen milk dessert similar to the modern sherbet that he had enjoyed in the Far East. The Italians were especially fond of the frozen confection, which, by the sixteenth century, was being called ice cream. In 1533, the young Italian princess, Catherine de Medici went to France as the bride of the future King Henry II. She was having recipes for frozen desserts included in her gifts.

Over time, recipes for ices, sherbets and milk ices evolved and served in the fashionable Italian and French royal courts. The first public sale of ice cream occurred in Paris at the Café Procope in 1670(1).

Composition of ice cream

Ice cream and related products are generally classified as frozen desserts, which include ice cream, frozen custard, frozen confectionaries, ice milk, ice lollies, sherbets etc., which are popular among all age group of people. Ice cream is a frozen dairy product made by freezing a mix with agitation to incorporate air and ensure uniformity of consistency(2, 3).

Ice cream is often described in terms of two phases: continuous and dispersed. The continuous phase is

a combination of an unfrozen solution, an emulsion and a suspension of solids in liquid. Water, sugar, hydrocolloids, milk proteins and other solubles make up the unfrozen solution. Suspended in the aqueous phase are insoluble solids, including ice crystals, lactose crystals and milk solids. The aqueous phase also forms an emulsion with dispersed milk fat globules.

The complex physical structure of ice cream presents a challenge for food technologists. Simply stated, overall goal of designing the ice cream is to incorporate several different insolubles (air bubbles, ice crystals and fat globules) into an aqueous phase in the smallest sizes and in the greatest numbers possible.

Ice cream has the following composition(4):

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- Greater than 10% milk fat by legal definition, and usually between 10% and as high as 16% fat in some premium ice creams.
- 9-12% milk solids-not-fat: this component, also known as the serum solids, contains the proteins (caseins and whey proteins) and carbohydrates (lactose) found in milk.
- 12-16% sweeteners: sucrose or usually a combination of sucrose and glucose-based corn syrup sweeteners.

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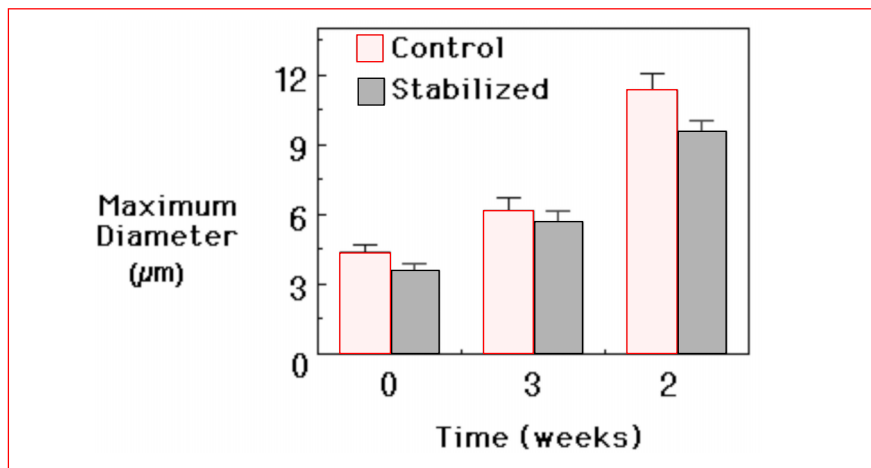


Figure 1: Effect of stabilizers on size of ice crystals in ice cream

- 0.2-0.5% stabilizers and emulsifiers.
- 55-64% water, which comes from the milk or other ingredients.

These percentages are by weight, either in the mix or in the frozen ice cream. When frozen, about one half of the volume of ice cream is air (over-run), so by volume in ice cream, these numbers can be reduced by approximately one-half, depending on the actual air content. However, since air does not contribute weight, we usually talk about the composition of ice cream on a weight basis, bearing in mind this important distinction.

Today, ice cream is made from a blend of dairy products, viz. cream, condensed milk, butter fat, sugar, flavorings and approved additives. The additives, which act as emulsifiers and stabilizers, are used to prevent heat shock and the formation of ice crystals during the production process.

Role of stabilizers

Stabilizers primarily work by controlling water in an ice cream mix, thereby affecting mix viscosity, texture, slowing ice crystal growth, improving air incorporation, melting properties and preventing mix separation. Stabilizers are often used to impart structure and firmness to ice cream, which

assists in packaging. Stabilizers also help to suppress the effects of altitude abuse, which reduces the occurrence of shrinkage, control the rate of melt and provide protection against whey separation in resale mix or production facilities that have slow hardening operations.

Additionally, stabilizers help to reduce crystal size (Fig.1)(4). The smaller crystal size makes the final product smoother and creamier. Also, since freeze/thaw causes the ice crystals to grow, it is beneficial to start with the smallest crystal possible. Stabilizers also help to prevent syneresis, which also leads to large crystals forming, creating a graininess which is not organoleptically satisfying.

Due to the ability of small percentage of stabilizer to absorb and hold large amounts of water, stabilizers are also used to create various textures and reduce the amount of free water in the ice cream mix by binding it as water of hydration or by immobilizing it within a gel structure. This results in good body, smooth texture, slow melt down and heat shock in the resultant product (5, 6, 7).

Following are the important functions of stabilizers in ice cream(4)-

- In the mix: to stabilize the emulsion to prevent creaming of fat and in the case of carrageenan, to prevent serum separation due to incompatibility of the other polysaccharides with milk proteins; also to aid in suspension of liquid flavors.
- In the ice cream at draw from the scraped surface freezer: to stabilize the air bubbles and to hold the flavorings in dispersion.
- In the ice cream during storage: to prevent lactose crystal growth and retard or reduce ice crystal growth during storage. Also to prevent shrinkage from collapse of the air bubbles and to prevent moisture migration into the package.
- In the ice cream at the time of consumption: to provide some body and mouth-feel without being gummy and to promote good flavor release.

Hydrocolloids as stabilizers

The average consumer, seeing "natural" on food labels, perceives it as a positive factor, mainly because it is typically associated with food safety and significant health benefits. For this reason, natural hydrocolloids are widely used as stabilizers.

Natural hydrocolloids come from natural sources and are processed by natural means, such as mechanical or heat extraction, water extraction and not by chemically reactive processes. Such natural hydrocolloids include guar gum, locust bean gum, xanthan gum, carrageenan, starch, sodium alginate etc. Gelatin, a protein of animal origin, was used almost exclusively in the ice cream industry as a stabilizer, but has gradually been replaced with polysaccharides of plant origin due to their increased effectiveness and reduced cost.

Mingling of stabilizers

Hydrocolloid based stabilizers are a group of compounds, usually

polysaccharide food gums, which provide different functions in frozen deserts. When discussing ice cream stabilization, it's necessary to specify the product's composition, since its composition and ratios are critical to stabilizing the various physical phases. Each of the stabilizers has its own characteristics and often, two or more stabilizers are used in combination to lend synergistic properties to each other and improve their overall effectiveness.

Guar, for example, is more soluble than locust bean gum at cold temperatures, thus it finds broad application. Carrageenan is not used by itself, but rather as a secondary colloid to prevent the wheying-off of mix, which is usually promoted by one of the other stabilizers.

Blends containing locust bean gum, guar and carrageenan are excellent stabilizing systems for ice cream. The ratios of these gums in the blends will be adjusted as needed, depending on the type of desired effect. Using a system with emulsifier, guar and carrageenan in a full-fat ice cream is an economy product. For a higher-quality full-fat ice cream, using a blend of emulsifier, guar, locust bean gum and carrageenan gives excellent properties. A wide range of stabilizers work in light and low-fat ice creams. The same systems can be used as in full-fat products, but at higher levels(5).

In ice cream manufacturing, it is always difficult to get all the properties of ice cream using a single stabilizer. Today, food technologists have found a new technique of mingling or blending these stabilizers in different proportions to get excellent properties in ice cream.

Stabilizer selection begins with a clear understanding of the end product. For example, high-butterfat and high-solids formulations require less

physical stability than lower-fat or non-fat formulations with less total solids. Many times, lower quality and less-costly options can be used effectively in these higher-fat, higher-solid products. Reduced-fat products contain higher levels of water than their full-fat counterparts. In these products, higher levels of hydrocolloids can control the increased water and to replace some of the mouth-feel imparted by the milk fat.

Formulators must also consider how their product will be distributed and stored throughout the country. Poor freezer storage and/or altitude differentials from the point of production to the shelf often require more-specialized stabilization mechanisms to ensure quality.

Natural hydrocolloids

Though alike in many ways, hydrocolloids also have many differences with respect to their property and compatibility. Knowing the characteristics of each, allow product designers to incorporate the correct ingredient or ingredients blend in a particular application. The choices require consideration of the entire product spectrum from mixing and processing, through finished product attributes, storage and end use.

Guar gum [CAS No. 9000-30-0, E-412]

Guar gum is a nonionic hydrocolloid obtained from the ground endosperm of the legume *Cyamopsis tetragonolobus* (L.) Taub., an annual

plant, which grows mainly in arid and semi-arid regions. The carbohydrate part (> 82%) of guar gum consists of a high molecular weight polysaccharide (50,000-8,000,000) composed of galactopyranose and mannopyranose units combined through glycosidic linkages known as galactomannan. The mannose:galactose ratio is about 2:1(8).

Guar gum is one of the most highly efficient water-thickening agents in the food industry. It is a GRAS food substance under section 184.1339 in Title 21 set by the U.S. Code of Federal Regulations. It also has a high percentage soluble dietary fiber (80% to 85%). It is a low-cost thickening and stabilizing agent for different food applications. It is soluble in cold water and gives visually hazy, neutral pH solutions. Solutions are stable between pH 4 to 11; viscosity peaks between pH 6 to 8.

Guar gum is compatible with most nonionic and anionic gums, featuring useful synergism with some microbial gums. Solution of guar gum shows pseudoplastic or "shear thinning" behavior in solution. The degree of pseudoplasticity increases with concentration and molecular weight. Solutions of guar gum do not exhibit yield stress properties.

Today, guar gum is widely used as ice cream stabilizer. Guar is preferred for its relatively low cost and the body it contributes to the product. It hydrates well in cold water and, hence,

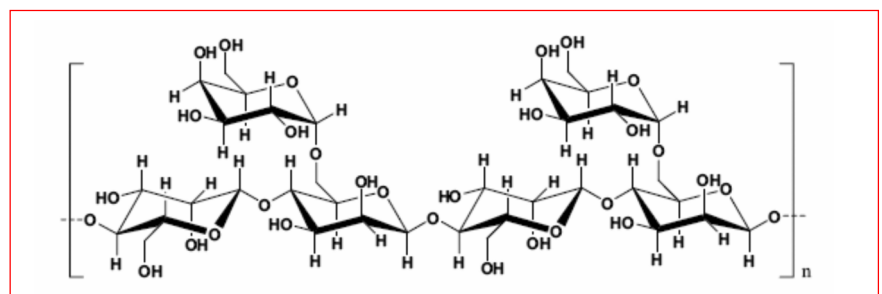


Figure 2: Guar gum polysaccharide

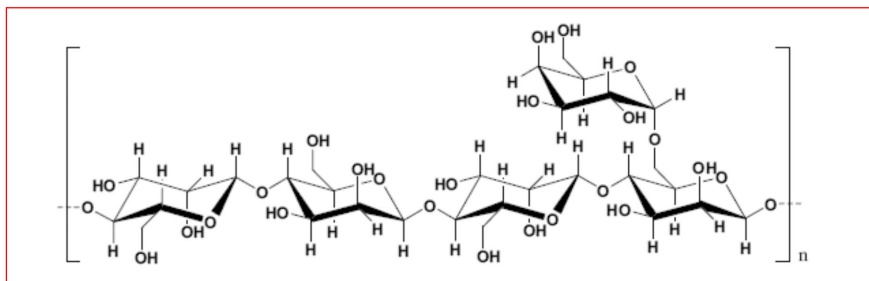


Figure 3: Locust bean gum polysaccharide

reduces free water within the system. This is accomplished by introducing many branched galactose side chains into the mixture.

Guar gum is often used in combination with carrageenan and locust bean gum to impart excellent properties to ice cream.

Locust Bean Gum [CAS No. 9000-40-2, E-410]

The locust bean has been known for its thickening properties since ancient times: the Egyptians used locust bean paste to glue bandages onto mummies. However, it was only early in the 20th century that locust bean gum (LBG) became an industrial product.

Also known as Carob bean gum, it is primarily the ground endosperm of the seeds from *Ceratonia siliqua* (L.) Taub., mainly consisting of high molecular weight (approximately 50,000-3,000,000) polysaccharides composed of galactomannans. The mannose:galactose ratio is about 4:1(9). It is approved for GRAS food substance under section 582.7343 in Title 21 set by the U.S. Code of Federal Regulations.

Unlike guar, LBG has to be heated to 80°C for full hydration usually achieved during pasteurization process of milk. Solutions of LBG are non-Newtonian and have zero yield value; thus, they flow as soon as slight shear is applied. In LBG, the ratio of mannose to galactose is higher than in guar gum thus, allowing the two gums to

interact synergistically so that together they make a thicker gel than either one alone.

When combined with xanthan, LBG yields pliable gels. In the presence of k-carrageenan, LBG forms gel. The synergy with kappa carrageenan provides noticeable advantages like reinforcement of the carrageenan gels, elastic texture and prevention of syneresis. Locust bean gum enhances aeration creates a pleasant texture with a good flavor release. Used alone, it can cause whey-off during processing, so it is usually used in combination with carrageenan and guar gum.

Xanthan Gum [CAS No. 11138-66-2, E-415]

Xanthan gum was discovered 50 years ago in Illinois (USA). It is a high molecular weight exocellular heteropolysaccharide and is produced as a secondary metabolite by a pure culture fermentation of a carbohydrate by microorganism *Xanthomonas campestris*. It is approved for GRAS food substance under section 172.695 in Title 21 set by the U.S. Code of Federal Regulations (21 CFR 172.695).

Chemically, xanthan gum consists primarily of 1, 4-linked β-D-glucose

backbone with side chains containing two mannose and one glucuronic acid on every other glucose at the C-3 position. Approximately half of the terminal mannose units carry a pyruvic acid residue and the non-terminal residue usually carries an acetyl group at C-6(8).

Xanthan gum can be used in food and pharmaceutical systems where excellent solubility and stability against varying pH at different concentrations of salts/enzymes/other ingredients is required. Xanthan gum is an acid-resistant thickener and stabilizer; its solutions are extremely pseudoplastic and exceed most common gums in this aspect. Viscosity is reduced with increasing shear; viscosity is regained after shear is released.

Xanthan gum is soluble in hot and cold water, highly resistant to temperature variations. It has high stabilizing properties, excellent freeze/thaw and compatible with almost all commercial thickeners and stabilizers. It can be dispersed by blending with skim milk, corn syrups or non-fat milk solids. It is always used in combination with other gums. It is synergistic with LBG and guar gum, which reduces the levels of LBG and guar required.

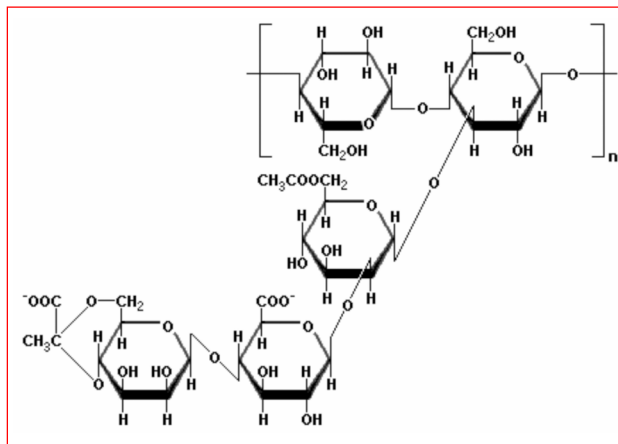


Fig. 4: Xanthan gum polysaccharide

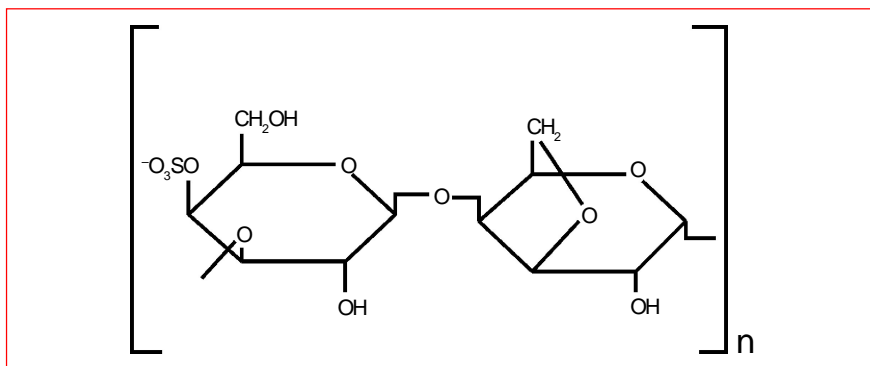


Fig. 5: Carrageenan building unit

Carrageenan [CAS No. 9000-07-1, E-407]

Carrageenan is an anionic polysaccharide, extracted principally from the red seaweed *Chondrus crispus*. It is approved for GRAS food substance under section 172.620 in Title 21 set by the U.S. Code of Federal Regulations (21 CFR 172.620).

Carrageenan is a high molecular weight polysaccharide made up of repeating galactose units and 3,6 anhydrogalactose, both sulfated and nonsulfated. The units are joined by alternating α -1-3 and β -1-4 glycosidic linkages(8, 10).

Three main structural types exist: Iota, Kappa and Lambda, differing in solubility and rheology. The primary differences which influence the properties of kappa, iota and lambda carrageenan are the number and position of the ester sulfate groups on the repeating galactose units. Higher levels of ester sulfate lower the solubility temperature of the carrageenan and produce lower strength gels or contribute to gel inhibition. Carrageenan solutions are typically clear and of alkaline pH. All solutions are pseudoplastic with some degree of yield value.

Lambda is non-gelling. Kappa can produce brittle gels; Iota can produce elastic gels. Kappa and iota solutions require heating for proper hydration. All solutions show a reversible de-

crease in viscosity at elevated temperatures. Carrageenan is compatible with most nonionic and anionic water-soluble thickeners. It is strongly synergistic with locust bean gum and strongly interactive with proteins.

It is used as a gelling and stabilizing agent and as viscosity builder in foods, especially in milk-based systems such as ice cream, frozen desserts, chocolate milk, whipped cream etc. Due to the presence of the half-ester sulfate groups, a reaction occurs with charged amino-acid chains of proteins to form stable gels. Because of its ability to interact with milk proteins, it is widely used in milk based applications such as in ice creams to prevent whey separation and in milk gels to obtain the desired consistency. For low fat and soft serve ice cream compositions, kappa carrageenan is often used for its gel forming functionality and its reactivity with casein. A kappa-iota blend is sometimes preferred, to keep kappa from forming a brittle gel. Lambda blends can be used for ice creams with sufficient fat to stabilize without gelling.

Alginates

(Alginic acid E-400, CAS no. 9005-32-7, 21 CFR 184.1011) (Sodium alginate E-401, CAS no. 9005-38-3, 21 CFR 184.1724) (Potassium alginate E-402, CAS no. 9005-36-1, 21 CFR 184.1610) (Ammonium alginate E-403; CAS no. 9005-34-9, 21 CFR 184.1133, Calcium

Alginate E-404, CAS no. 9005-35-0, 21 CFR 184.1187)

Among the most versatile of the hydrocolloids, alginates (salts of alginic acid) are used in a wide variety of applications as thickeners, stabilizers and gelling agents. The first scientific studies on the extraction of alginates from brown seaweed were made by the British chemist E.C. Stanford at the end of the 19th century. Commercial varieties of alginate are extracted from brown algae (Phaeophyceae) seaweeds including the giant kelp *Macrocystis pyrifera*, *Ascophyllum nodosum* and various types of *Laminaria*.

Chemically, they are chain-forming heteropolysaccharides made up of blocks of β -(1 \rightarrow 3)-linked D-mannuronic acid and α -(1 \rightarrow 3)-linked L-gulonic acid residues(11).

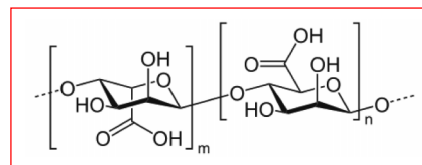


Fig. 6. Alginate building unit

Alginates have been used for a vast range of applications for more than 50 years. Through selection of grade and formulation, the flow characteristics of alginates can be controlled; from free-flowing (low viscosity) to drip-free (high viscosity). The aqueous solutions of alginates have shear-thinning characteristics, also called pseudoplasticity. The viscosity of an alginate solution depends on the concentration of alginate and the length of the alginate molecules, i.e. the number of monomer units in the chains. The longer the chains the higher the viscosity at similar concentrations. Viscosity of alginate solution is inversely proportional to temperature. Alginates form thermally stable cold setting gelling agents in the presence of calcium ions.

Alginates are also the preferred additive to ice-creams and dairy products in many countries, thereby competing with carrageenans in this complex market. Alginates add a type of body and texture to ice cream other gums don't easily duplicate. Alginates are cold-soluble and cold-setting. Further, alginate is heat and freeze/thaw stable. As a thickening and gelling agent, alginate offers a broad range of flow properties for aqueous and milk based systems.

Gelatin [CAS No. 9000-70-8, E-441]

Gelatin is mostly derived from animal collagen, isolated from animal skin and bones. It can also be extracted from fish skins. Boiling hydrolyzes the collagen and converts it into gelatin. Two processes are used, an acid process gives Type A gelatin and an alkaline process gives Type B gelatin(10, 12). Their properties are similar, but Type A can negatively interact with other anionic polymers, such as carrageenan.

Chemically, gelatin is a heterogeneous mixture of single or multi-stranded polypeptides; gelatin contains many glycine, proline and 4-hydroxyproline residues.

Gelatin is primarily used as a gelling agent forming transparent elastic thermoreversible gels on cooling below about 35°C, which dissolves at low temperature to give 'melt in the mouth' products with excellent flavour release. In addition, the amphiphilic na-

ture of the molecules gives them useful emulsification (whipped cream) and foam stabilizing properties. It is used, as well, in fat-reduced foods to simulate the mouth-feel of fat and to create volume without adding calories. Gelatin solutions show visco-elastic flow.

Although gelatin is by far the major additive used for gelling, current concerns about the possibility of such an animal derived product causes Creutzfeldt-Jakob Disease (CJD)(10). Additionally, the need generated by vegetarians and certain religions has recently encouraged the serious search for alternatives.

CONCLUSION

Although ice cream manufacture is not new, there are always new developments. Since manufacturers are always looking to create a new frozen item, they are constantly challenging food technologists to create new textures or to develop a system that will allow an inclusion that was not possible before.

The development of new machinery also allows creations that were not possible before and therefore creates new stabilization challenges.

Since all the desired properties in ice cream such as low melt down, good flavor release, excellent texture, homogeneity etc. cannot be shaped by a particular hydrocolloid, it is always essential to go for a blend of stabilizers or stabilizer & emulsifier, which can

meet the requirements of ice cream maker.

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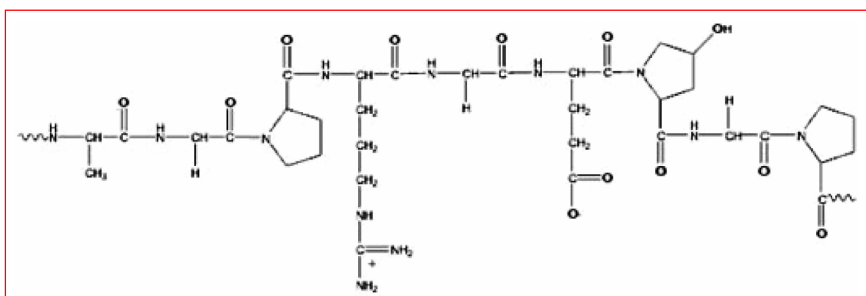


Fig. 7. Gelatin building unit