CAKE EMULSIFIERS

NEW DEVELOPMENTS- ALPHA CRYSTALLINE GELS
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Emulsion & Emulsifiers

Oil and water are immiscible since the interaction results in high energy at the common surface. Through the physical action of mixing one can break up the oil into fine droplets which may be dispersed/ distributed into the water phase (Figure 1) to form a dispersion which may be called a emulsion. An emulsion is an unstable multiphase system containing at least two immiscible liquid phases. When the physical mixing action is stopped the oil droplets will coalesce and the oil and water will again separate into 2 different layers. To stabilize a emulsion, the droplets of the disperse phase must be as small as possible and as widely distributed as possible in the continuous phase. Further the viscosity of the continuous phase must be high to retard coalescence.

Ultimately to prevent such coalescing of oil droplets and subsequent layer separation, certain chemicals may be used which are known as emulsifiers. Emulsifiers are made up of molecules that have a non-polar (fatty acid) end which carries no charge and haS an affinity for oil and a polar (glycerol) end which carries a charge and has an affinity for water (Figure 2). Such a molecule can situate itself at the interface between oil and water. The polar end will immerse itself in the aqueous phase and the non-polar end will immerse itself in the lipid phase (Figure 3) and prevent coalescence of the oil droplets. This helps the two phases to stay intimately mixed and form a stable emulsion.

Emulsions may be characterized in two ways. In a first instance the oil droplets may be dispersed in the water leading to an oil in water emulsion. If on the other hand the water droplets are dispersed in the oil, then we have what is known as an water in oil emulsion (Figure 4). A foam is also a type of an emulsion where a gas is dispersed in a liquid phase or occasionally a solid phase.

The affinity of emulsifiers for either oil or water is measured by the HLB scale. If the HLB of an emulsifier system is between 3-6, it has an oil affinity and such an emulsifier will optimally stabilize a water in oil emulsion. On the other hand a emulsifier with a HLB value of 9-18 has a preference for water and therefore will optimally stabilize a oil in water emulsion.

Cake Batter:

A cake batter is a complex aerated emulsion of a shortening in an aqueous phase. In high fat batters, the emulsion is aerated by the inclusion of air into the fat phase which in turn is dispersed in the water phase (Figure 5). When the batter temperature rises during baking, shortening melts and the air migrates into the water phase.

On the other hand in low/no fat batters like sponge cakes the air is incorporated directly into the aqueous phase at the mixing stage.

The ideal aeration depends on both the number and size of the air bubbles in the foam. Proper aeration has to be accompanied by a system to stabilize the air bubbles. In cake batters emulsifiers stabilize the foam by forming a film around the bubbles and preventing coalescence. Improving batter viscosity retards bubble movement which further contributes to foam and batter stability.

Aeration combined with emulsification of the oil and water are two essential functions of emulsifiers in cake batter preparation. The optimum emulsifier combination for a cake batter is therefore one that can aerate if needed but more importantly has the ability to stabilize the foam as well as the subsequent fat-water emulsion by itís ability to finely disperse the shortening and help prevent coalescence of the fat dispersed in the water phase.

Emulsifier Development

The main functions of emulsifiers in the sweet goods sector of the baking industry are:

1. Optimizing distribution of oil in water dispersions and stabilizing the resultant emulsion.
2. Optimizing distribution of air and stabilizing the foam
3. Optimizing internal characteristics.
4. Improving shelf life
5. Optimizing development of reduced fat products
6. Optimizing use of liquid oils with low levels of Trans Fatty Acids

As cake baking has become a more precise industrial activity, baking emulsifiers have become a very important class of ingredients in the manufacture of cakes and other sweet goods. In the early days bakers used eggs and lecithin as providers of natural emulsifiers mainly due to the presence of phospholipids that have surface-active properties.

In the early 1920ís chemical emulsifiers made their first appearance in the form of mono-diglycerides. A mono-diglyceride is an ester formed when an acid combines with an alcohol.
Specifically a mono-diglyceride (Figure 6) is an ester which is formed when the fatty acid is a triglyceride fat which combines with a polyvalent alcohol - glycerol. Mono-diglycerides, the first chemical emulsifiers used in baking, contained about 40-50% of the monoglycerides- the component that is functional as an emulsifier.

Subsequently distilled mono-glycerides were developed since such emulsifiers contained 90-95% of the functional monoglyceride (Figure 7). The introduction of monoglycerides helped the cake baker increase the proportion of both fat and sugar in the batter and this resulted in rich, high ratio cakes with superior keeping qualities.

As the baking of cakes became more automated and the demands of the market called for cakes and sweet goods with a better quality and longer shelf life, emulsifier technologists developed a wide range of emulsifier products.

To address these needs there has been continuing development of emulsifiers and some of the important ones are summarized below:

* Long chained, saturated fatty acids have the best starch complexing ability (Figure 8). To increase shelf life of baked goods Glyceryl Mono Stearate (GMS) was made by utilizing saturated long chain stearic acid. Such fatty acids were either derived from animal sources like lard or saturated through hydrogenation of vegetable oils. This saturated acid was then reacted with Glycerol to give GMS with superior anti staling properties.

* It was noted that derivatives of monoglycerides with lipophilic tendencies had unique qualities to improve the quality of cake and other baked goods. Some of these products include PGMS (Figure 9) and PGE (Figure 10). PGMS is often used in American sweet goods baking. Another derivative emulsifier is PGE, and it is very commonly used by European craft bakers but to date has been sparingly used by the North American sweet goods baker. Nevertheless it has substantial potential to improve American sweet goods as will be discussed below.

Commercial product development of emulsifiers for the baking industry has been predominantly based on the chemical properties of surfactants. In the ongoing search to develop new products, concepts have now been developed based on physical properties of emulsifiers, in particular the crystalline behavior of emulsifiers.

Alpha crystalline emulsifiers

Monoglycerides are polymorphic since they can exist in 4 crystalline forms- alpha, alpha prime, beta and beta prime (Figure 11). Powdered emulsifiers exist in the beta crystalline form- very stable and moderately functional. The beta crystal is the most rigid and stable at low temperatures. Crystalline emulsifier molecules are oriented with the hydrocarbon chains in dense parallel layers (Figure 12). When heated in the presence of water, the hydrocarbons change from a solid to a liquid state with the water penetrating in between the polar groups of the bi-layers. On cooling the hydrocarbon chains crystallize, forming a sandwich structure of alternating surfactant and aqueous layers giving a alpha crystalline gel phase. The alpha crystal form is known to be much more functional (Figure 13) than the beta crystal. However this alpha gel is unstable and has a tendency to revert back to the beta crystalline form. Researchers have identified many reasons for the superior functionality of the alpha crystalline form. One major reason is that the liquid alpha crystalline form is more flexible than the rigid beta crystalline form and rearranges more easily during heating cycles. Thus alpha crystalline emulsifiers are able to form flexible and more protective films around the dispersed phase be it oil, air or water and preserve the emulsion (Figure 5).

At this stage it would be appropriate to clarify the term "alpha" (Figure 14). Occasionally emulsifier specification sheets specify a "alpha-monoglyceride content"- a figure that may be ambiguous. Monoglycerides can have the fatty acid moiety at C-1, such monoglycerides are called 1-monoglyceride, or at C-2 when it is called 2-monoglyceride. A practice has also grown of calling the 1-monoglyceride as _-monoglyceride and the 2-monoglyceride as _-monoglyceride. This practice may be misleading as it relates to the positional isomerism of the emulsifier rather than the critical crystalline structure being discussed here.

A traditional and preferred method for the optimum utilization of Monoglycerides has been through hydration. Such GMS hydrates helped to provide both aeration and emulsification. However it was noted that on ageing these monoglyceride hydrates had reduced functionality. Whilst it was generally understood by bakers that hydrated monoglycerides were easier to use and distributed more evenly, it is now realized that upon hydration the mono-diglycerides were converted into the more active and
functional alpha crystalline form. But since this crystal form is unstable it tends to change on storage to the more stable beta crystalline form which is less effective. The common practice of improving the functionality of powdered emulsifiers through hydration is a very imprecise way of forming the comparatively unstable but more functional alpha crystalline form.

Techniques have now been developed to convert the emulsifier to the alpha crystalline form under controlled conditions and more importantly to stabilize the emulsifier in this state for periods of up to one year. These techniques are based on optimum selection of raw materials, processing techniques, use of transition inhibitors as well as optimum blending of emulsifiers to both optimize functionality as well as alpha stability.

The concept of blending emulsifiers for optimal results has been used commercially for sometime now and a number of emulsifier blends are in use in the cake sector. To further this idea into the realm of alpha crystalline emulsifiers like monoglycerides, complimentary emulsifiers have to be selected which besides functional compatibility must also have the potential to preserve "alpha-stability".

There are a class of emulsifiers are known as alpha tending which when hydrated convert to the alpha crystalline form. Some examples of alpha tending emulsifiers include PGMS, PGE, SSL and DATEM.

Propylene Glycol Monostearate (PGMS) is a type of Propylene Glycol monoester. This emulsifier is an ester where propylene glycol is combined with a fatty acid. The resultant product consists of both mono and di-esters. The mono ester component (e.g. PGMS) is a alpha tending emulsifier particularly functional as a aerating emulsifier in combination with monoglycerides. Purification through molecular distillation is critical in optimizing such a blend.

Polyglycerol esters (PGE) are emulsifiers in which the fatty acid is combined with a polyglycerol. The HLB of PGE depends on the degree of polymerization of the glycerol moiety and have wide acceptance and use in the European sweet goods industry.

Based on this concept "alpha stable gels" comprising of monoglycerides and PGMS and/or PGE are now commercially available. They are complimentary both in functionality as well as in mutual "alpha" stabilization and have unique potential particularly in cakes and other sweet goods.

Some of the functional benefits of alpha stable gels are reviewed below (Figure 15):
Cakes:
A number of parameters define cake quality and these include-volume, texture and shelf life.

The cake baking process consists of 3 important stages-

* A cake batter is a complex foam/emulsion. Incorporation of air through whipping combined with optimal distribution is important. Cake quality depends not only on the aeration, but more importantly on the optimum number and size of the bubbles which define texture. Alpha crystalline emulsifiers are outstanding in their aeration potential. Traditionally cake batters have been mixed in a multistage process. Use of emulsifiers in a alpha crystalline configuration facilitates "all-iní one or two stage mixing.
* During the baking stage the batter is heated and the liquid emulsion phase is transformed, viscosity is changed, the air bubbles expand, moisture is lost and finally the internal and external cake structure are set. The stability of the bubbles and uniform expansion helps optimize the volume. Maintenance of emulsion stability and batter viscosity during the baking process is positively influenced by the proper selection of alpha stable emulsifier gels.

* Storage characteristics of a cake which is influenced by the staling cycle. The shelf life depends both on the well known starch retrogradation effect, but also on moisture retention and on optimum internal characteristics.

An alpha stable gel made up of optimally blended alpha tending monoglycerides and PGE has a superior effect on a cake. Long chain fully saturated monoglycerides are known to have the best starch complexing ability. PGE is alpha tending and increases batter viscosity, thus contributing to bubble stability. PGE has dual capabilities to function as a water in oil as well as a oil in water emulsifier and in combination with monoglycerides can stabilize the oil-water cake batter emulsion at various stages of the baking cycle. The proportion of the monoglycerides and alpha tending emulsifier like PGE can be modified to suit high or low fat batters. Thus in low fat cakes, alpha tending emulsifiers can not only help in direct aeration of the aqueous stage but also in stabilizing the aqueous foam by forming a interfacial film around the air bubbles. In low fat batters alpha stable gels high in PGE can also help by giving a smooth feel and a thick batter viscosity typically seen in high fat batters.

Shelf Life:

The shelf life of sweet goods is dependent on

* Control of starch retrogradation- Control of starch retrogradation is reflected by the Amylose complexing potential. As Fig. shows saturated, distilled monoglyceride are the best complexing abilities. It has also been reported that hydrated alpha crystalline monoglycerides have the best steric fit with amylose. The inside of the amylose helix is lipophilic as are alpha stable monoglyceride gels.

* Optimization of fat distribution and moisture retention- Alpha crystalline gels containing polyglycerol esters have the ability to optimize plasticity and moisture retention

Icings :

Icings generally consist of a sugar, shortening and water. Icings may be low fat, medium fat or high fat. Icings may be aerated or non-aerated.

Non aerated icings depend on high shortening levels to give a smooth mouthfeel. This can be complimented by the addition of alpha crystalline polyglycerol esters. PGE in combination with distilled monoglycerides can also control synerisis during the freeze thaw cycle.

Aerated icings and other whipped products need a emulsifier which can give volume, texture and foam stability and protection against synerisis in freeze thaw situations. Alpha crystalline monoglycerides and other alpha tending emulsifiers like PGMS are known to be superior aeration agents (Figure 16) as well as are outstanding in their ability to stabilize foams.

Fig 16 below two examples of icing type foams demonstrate the superior ability of alpha tending emulsifiers to aerate:

	1	2
Alpha stable gel	2%	1%
Water	98%	49%
Powdered Sugar	-----	50%
Specific Gravity	0.10	0.22

Optimal blends of alpha tending emulsifiers may be made to suit specific needs. Thus a combination alpha stable gel of distilled monoglycerides and PGMS will optimize aeration and icing foam stability, prevent breakdown of water-oil emulsion and minimize synerisis particularly in frozen and refrigerated icings and fillings. A combination of monoglycerides and PGE may help improve appearance, sheen and most importantly mouthfeel of low fat icing.
This basic concept may help in the utilization of alpha stable emulsifiers in the development of superior icings, fillings and whipped toppings.

Trans Fatty Acids;

Animal fats like lard tend to be saturated and thus solid at normal room temperature. Vegetable oils are normally liquid at room temperature due to the unsaturated carbon in the fatty acid component of the oil. Oil manufacturers solidify such liquid oils by the process of hydrogenation. Essentially this involves adding hydrogen across the double bond to create a saturated carbon bond. Whilst a minor amount of trans fatty acids occur naturally in some foods, the commercial process of hydrogenation of unsaturated oils results in the formation of noticeable levels of trans fatty acids. There is now a growing awareness of the negative health effects of trans fatty acids. Consequently hydrogenated fats are now under review by various bodies including the FDA. This may result in labeling recommendations/ regulations requiring identification of the amount of trans fatty acid in baked products may .

Consequently there is growing interest in the use of liquid oils in cakes, sweet goods and icings and whipped toppings.
When liquid oil is used in cake batters, unique needs are identified:

* The emulsifier needs to have solubility/dispersibility not only in the aqueous phase but also in oil. Monoglycerides in the beta crystalline form do not satisfy this criterion but alpha stable monoglycerides as well as alpha tending emulsifiers like PGMS and PGE would fit this requirement

* Liquid oil tends to destabilize foams particularly protein based foams as found in cake batters. Emulsifiers in the alpha crystalline form can aerate as well as stabilize such foams

The unique potential of using alpha stable emulsifier gels is demonstrated best by the example in Fig. 17 below;

	1	2
	%	%
Powdered Sugar	63	61
Water	11	11
Liquid Oil	26	26
Alpha stable emulsifier gel	----	3
Specific Gravity	1.10	0.65

This test clearly shows the advantage in the use of alpha crystalline emulsifiers when using liquid non-hydrogenated oils not only in cakes but also in whipped toppings and icings.

* With the use of liquid oils, the distribution and emulsification of liquid oil in water becomes critical in cake batters. Alpha tending emulsifiers like polyglycerol esters are known to improve both the distribution of the liquid oil as well as the viscosity of the resultant emulsion. Alpha stable gels made with distilled monoglycerides are known to protect the dispersed liquid oil droplets by the formation of a flexible alpha crystalline film around the oil to preserve the traditional cake batter/foam.

Low fat cakes/ sweet goods:

Fat reduced bakery foods have not gained sufficient acceptance due to excessive deterioration in organoleptic properties. Alpha gels made with distilled saturated monoglycerides are excellent aerating agents for use in low fat sweet goods. Finer air distribution may result in better batter viscosity, which is critical in low fat batters.

A major drawback of low fat cakes has been the reduced tenderness of the baked product. Use of liquid oil instead of plastic shortening in low fat cakes/ sweet goods may assist in improving the tenderness. As described above the use of alpha stable emulsifier gels is of vital importance when using liquid oil because of their superior aerating end emulsion stabilizing potential. Alpha crystalline gels may also have a role as structuring agents when used in reduced fat baked products

Tortillas/ Bagels:

With the increased acceptance of tortillas by the general market, there is a increased need for improved flexibility on storage. Some reports indicate that the use of distilled monoglycerides has improved the shelf life of tortillas. Use of alpha stable gels of monoglycerides in combination with Polyglycerol esters will improve shelf life substantially not only because of the starch complexing of the distilled long chain monoglyceride but also because of the plasticity contributed by the polyglycerol esters. Similarly the shelf life of bagels may also be improved by selection of alpha stable emulsifier gels.

Other potential areas where alpha gels may be use include doughnuts, cookies, pies, muffins and other sectors of the sweet goods industry

The potential of alpha crystalline gels is now being seriously utilized for commercial development. Combination of alpha crystalline distilled monoglycerides with synergistic alpha tending emulsifiers has been shown to have outstanding potential in sweet good manufacture. New product concepts are being developed to utilize such technology to improve the quality of yeast raised baked products