WHO SAYS OIL AND WATER DON’T MIX?

Beverage emulsion science 101
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An emulsion is a mixture of two or more liquids made up of molecules that possess lipophilic (fat-loving) and hydrophilic (water-loving) properties. These liquids are immiscible, meaning they are not normally capable of forming a uniform mixture by simple mixing. Hence the expression, “Oil and water don’t mix.” In the absence of emulsifiers, the two liquids would separate rapidly.

Types of emulsifiers

The beverage industry uses a variety of emulsifiers. The most popular ones are gum acacia (also known as gum arabic), modified starch and quillaja extract.

Gum acacia

Gum acacia is a naturally derived gum made of hardened sap exuded mainly from two species of the acacia tree: Acacia senegal and Acacia seyal. The gum is harvested commercially from wild trees primarily found throughout the Sahel region of Africa, with Sudan alone accounting for more than 50% of global output. Acacia senegal is tapped for gum by cutting holes in the bark, from which a product called kordofan, or Senegal gum, is exuded. Seyal gum comes from Acacia seyal, a species more prevalent in East Africa, and is collected from naturally occurring extrusions on the bark.

The mixture of glycoproteins and arabinoglactan in gum acacia imparts both emulsifying and viscosifying properties, making it a strong food and beverage emulsifier.

Introduction to Gum acacia from TIC Gums

TIC PRETESTED™ Gum Arabic FT (gum acacia) is an emulsifier made from wild harvested gum acacia. It is minimally processed without the use of chemical modification, enzymes, or filter aids. Gum acacia is a highly versatile ingredient as it is non-hygroscopic, low viscosity and highly soluble at room temperature. In addition, it is stable across a broad pH range (2-10) and temperatures as it is resistant to both heating and freezing. It is also highly compatible with other ingredients and does not contribute to the taste or colour of the final product. Gum acacia can be offered in spray dried or instant soluble (pre-hydrated) forms, and is certified organic.

Starch emulsifiers

Conventional OSA-modified starches are one of the most common beverage emulsifiers. They are modified by the addition of 1-Octenylsuccinic anhydride (OSA), creating the lipophilic property of conventional OSA starch. Modified starches are colourless and neutral in taste. They have good cold water solubility, and excellent emulsifying properties to stabilise lipids.

Emulsions can be categorised as oil-in-water or water-in-oil. In each case, one of the liquids is smaller in proportion to the other, with the smaller component being dispersed into the larger. For example, an oil-in-water emulsion contains more water. Water forms the continuous phase and oil is the dispersed phase, making the emulsion water soluble. Emulsifiers used in such emulsions are commonly termed oil-in-water emulsifiers. Citrus flavours, some natural colours and certain vitamins are oil soluble. Addition of these ingredients into beverages requires an oil-in-water emulsifier to form an emulsion before subsequent dilution. An oil-in-water emulsifier creates a thick layer around the oil droplets that keeps them suspended in water, keeping the mixture homogenous.
All starches are made up of two types of building blocks: amylose or amylopectin, with the ratio of one to the other varying with the starch source (Table 1). Due to their linear structure, amylose molecules tend to associate tightly in linear bundles, which form a thick gel that is not stable in a beverage emulsion. Therefore, starches high in amylose are not used in the beverage industry. Instead, starches high in amylopectin are used. These starches exhibit more of a “branching” structure that prevents gelling (Figure 1). Commonly used conventional OSA starches (Figure 2) are derived from waxy maize corn and contain 99% amylopectin, making them more stable in beverages.

Ingredion’s PURITY GUM® Ultra starch is an example of a specialty OSA starch that was developed using an Ingredion patented technology. It can be used to create very stable high oil emulsions (up to 24% oil load) across a broad pH range (2-8).

**Quillaja extract**

Quillaja extract is an aqueous extraction from the inner bark of an evergreen tree called Quillaja Saponaria Molina (family Rosaceae). This evergreen tree is native to several South American countries like Chile (see sidebar, page 4). It has been used as an emulsifier and foam stabiliser for years in foods and beverages, as well as in personal care and pharmaceutical products. The major components of quillaja extract are saponins, tannins and polyphenols.

The saponins are the active components and are extracted through a water process that does not use chemicals (Figure 3). Simply put, the tree branches are ground up, steeped in water, and go through a series of fine filtrations.

The liquids are filtered out, leaving 20% solids, of which, about 14% is saponin and the remainder is made up of tannins and polyphenols.

Ingredion’s Q-NATURALE® emulsifier is a highly purified extract. Its extraction process uses no chemicals thus making it a sustainable and renewable solution for beverage emulsions.

**How starches stabilise emulsions**

**Steric stabilisation**

There are always strong forces of attraction taking place between the oil particles in an emulsion. Therefore, it is important to counteract this force to maintain stability. Conventional OSA starches create repulsion between particles due to their larger size compared to synthetic surfactants. This is called steric stabilisation. It occurs when the uncharged molecules of starch form a thick uncharged layer — an interfacial layer — around the oil droplet. This layer adheres to the surface of the oil droplet, and is resistant to deformation or depletion.
Hydrophobic interactions

Hydrophobic means “water-fearing,” and it describes the natural tendency of uncharged substances to clump together in a water medium rather than dispersing, because this effect allows the fat molecules to have minimal contact with water. This repulsion between nonpolar substances and water explains the separation of a mixture of oil and water into its two components. However, once the conventional OSA starch layer is formed around the droplet, a short-range interaction takes place. As soon as the droplets get close enough, they repel each other, keeping the solution in suspension.

How quillaja stabilises emulsions

Quillaja uses a different process to stabilise emulsions than conventional OSA starches do. It uses micelles, similar to polysorbates or Tween surfactants. The formation of emulsions typically follows the same mechanism; the low molecular weight surfactant absorbs onto the interface quickly, therefore forming smaller particle sizes. These are surface-active materials (quillaja, polysorbates, etc) that form “anchors” that stick to oil droplets. Unlike the layer formed on oil particles by conventional OSA starches, micelles form a ball-like structure (Figure 4). Hydrophobic compounds can be incorporated into the micelle core, while the micelle itself is dispersed in the aqueous phase through the hydrophilic head. This is another type of defence mechanism unique to quillaja, and the bond it creates is difficult to break apart.

How gum acacia stabilises an emulsion

Gum acacia is a complex molecule which is predominantly carbohydrate and contains approximately 2-3% peptide moieties as an integral component of the structure. It consists of three main molecular weight fractions with various protein contents: arabinogalactan (AG), glycoprotein (GP), and arabinogalactan protein complex (AGP). The AGP fraction is made up of hydrophilic carbohydrate blocks, AG, linked to a protein chain, GP, and is widely accepted as the fraction most responsible for the emulsification properties of the gum.

The emulsification properties of gum acacia are a result of the amphiphilic character resulting from the presence of both polysaccharide and protein moieties. Gum acacia reduces the interfacial tension of an oil-in-water emulsion, thus improving the disruption of oil droplets during the homogenisation process. The protein moieties are hydrophobic and absorb to the surface of the oil droplets, while the polysaccharide components are hydrophilic and extend into the water phase, preventing flocculation and coalescence through both electrostatic and steric repulsion forces. The polysaccharide membrane formed around the oil droplets prevents them from aggregating thus creating a stable emulsion (Figure 5, page 5).

How weighting agents stabilise an emulsion

Weighting agents are food-grade oil-soluble ingredients, such as esterified wood rosins. They increase the specific gravity (density) of the flavouring oils used in citrus beverages and sports drinks, giving increased stability to the finished beverages. Without weighting agents, citrus beverages would tend to separate, leaving a ring of flavouring oils on the surface. Examples of weighting agents include brominated vegetable oil (BVO), ester gum and sucrose acetate isobutyrate (SAIB).
Drawbacks of weighting agents
Weighting agents have been used for a long time in the beverage industry, but they have drawbacks:

- Contribute to opacity in finished beverage, which, for clear applications, is not desirable
- Time-consuming to dissolve
- Usage levels are governed by regulation
- Cannot be used in additive-free beverages
- Questionable stability of SAIB in acidic pH and its tendency to decompose in citric and isobutyric acid

Weighting agents contribute to opacity in beverages and unwanted sediment in alcoholic beverages. Concerns about BVO stem from the fact that it contains bromine, the element found in brominated flame retardants, which is banned in Japan and Europe. Increased consumer demand for more “natural” food and recognisable ingredients has prompted several major beverage companies to completely remove such weighting agents from their products.

The makings of a good emulsion
To make a stable emulsion, it is important to consider several critical factors:

The emulsification process begins by making a slurry or solution using an emulsifier. The emulsifier, such as a conventional OSA starch or gum acacia, must first be hydrated; therefore, a standard emulsion recipe will have a water phase and an oil phase, as shown in Tables 2 and 3.

Water phase
The water phase involves the mixing of water-soluble ingredients. These do not require emulsification. If the mixture foams, it needs to sit for a few hours until the foam disappears.

Oil phase
The oil phase involves mixing ingredients such as flavours and weighting agents. One of the most popular flavours in the beverage industry is citrus-based oil such as orange oil. Low agitation is used to mix. Certain ingredients take many hours to dissolve.

TABLE 2: A standard starch-based recipe

<table>
<thead>
<tr>
<th>WATER PHASE</th>
<th>%</th>
</tr>
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<tbody>
<tr>
<td>Water</td>
<td>75.55</td>
</tr>
<tr>
<td>Sodium benzoate</td>
<td>0.15</td>
</tr>
<tr>
<td>(preservative)</td>
<td></td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.30</td>
</tr>
<tr>
<td>Conventional OSA</td>
<td>12.00</td>
</tr>
<tr>
<td>starch</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>OIL PHASE</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange oil 1 fold</td>
<td>5.76</td>
</tr>
<tr>
<td>Orange oil 5 fold</td>
<td>1.44</td>
</tr>
<tr>
<td>Ester gum</td>
<td>4.80</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100.00</td>
</tr>
</tbody>
</table>

TABLE 3: A standard gum acacia-based recipe

<table>
<thead>
<tr>
<th>WATER PHASE</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>74.55</td>
</tr>
<tr>
<td>Sodium benzoate</td>
<td>0.15</td>
</tr>
<tr>
<td>(preservative)</td>
<td></td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.30</td>
</tr>
<tr>
<td>Gum acacia</td>
<td>15.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>OIL PHASE</th>
<th></th>
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<tr>
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<td>5.00</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Pre-emulsion
The water phase is added to the oil phase in the pre-emulsion stage. This is done with a high-shear mixer.

Homogenisation
The last step is homogenisation, which is usually done using a high-pressure two-stage homogeniser at about 3,500/500 psi. The mixture may need a number of passes through the homogeniser. The amount of pressure and number of passes will vary, depending on the emulsifier, the type of oil phase and the finished application. If you are formulating a clear beverage, you want small oil particle sizes and would need higher pressure with more passes. For a cloudy beverage, lower pressure and fewer passes are required.

Significance of oil droplet particle size
There is an ideal particle size for every beverage. If the oil droplets are too big, they will separate faster (Figure 6). Most beverages require oil particles of 0.30 to 0.40 micron to stay in the stable range. Particle size also affects the opacity of a beverage. Larger particles make beverages cloudy; smaller particles make beverages clear. A balance between beverage opacity and stability is required.

Viscosity
One of the main limitations of conventional beverage emulsifiers is that a significant quantity is needed to stabilise the high oil loads of flavours, colours, actives and nutrients used in formulating beverages. Higher amounts of emulsifiers can cause increased viscosity during processing.

As an example, in a gum acacia stabilised emulsion, you would need a higher dosage of gum acacia compared with modified starch to stabilise the oil.

This increases the emulsion viscosity and restricts the maximum oil load in the emulsion, which can lead to lower yield due to emulsion loss. Alternative new emulsifiers, like starch-based PURITY GUM® Ultra starch and quillaja-based Q-NATURALE® emulsifier, have been developed to allow for high oil levels while maintaining an optimal viscosity for processing and beverage stability.

pH sediment
Most beverages have a pH of 3 to 4. If the pH range is lower than that, sedimentation may occur. The lower the pH, the quicker sediment will begin appearing. Many factors such as impurities and destabilised weighting agents can cause sediment problems as well. Some emulsifiers, such as PURITY GUM® Ultra starch, are stable at pH levels as low as 2.0, which make them ideal in highly acidic beverage systems.

As you can see, finding the optimal ingredient, formulation and processing conditions for stable emulsion systems — and more importantly, stable, appealing and great-tasting beverages — is as much a science as an art.

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Figure 7 sums up the characteristics of a stable emulsion.
**How an emulsion destabilises**

There are three ways an emulsion will destabilise:

- Gravitational separation or creaming
- Flocculation
- Coalescence or Ostwald ripening

**Creaming**

When creaming occurs, a small layer of oil droplets forms on top of the emulsion (Figure 8). As oil droplets are less dense than the water in the emulsion, they float to the top. It looks like a layer of whipped cream, so this effect is called “creaming.” If you were to shake the emulsion, the layer might mix back eventually.

**Flocculation**

In flocculation, multiple droplets stick together to form clusters. These clusters behave like large droplets. Individual droplets retain their shape and adhere to one another.

**Coalescence or Ostwald ripening**

In coalescence, two droplets merge into one after collision, partially due to insufficient interfacial coverage of emulsifier. Extensive coalescence leads to the formation of an oil layer in the emulsion. Hence, this emulsion has physically separated. In Ostwald ripening, small droplets get smaller and smaller while large droplets get larger and larger. This is commonly caused by increased oil solubility in the water phase (Figure 9).
How emulsions are used in beverages

Other than delivering flavour, emulsions can also be used to create colour by delivering a natural colourant, such as beta-carotene, or to add nutrients, such as omega-3 fatty acids or vitamin D. In addition, emulsions of neutral oils (alone or with flavour) are used to add turbidity, which is desired in some soft drink applications. Emulsifiers are used to hold these oils in suspension and to stabilise the concentrated emulsion during storage and transport, as well as in the final beverage.

Concentrated emulsions are typically produced in bulk quantity and shipped to beverage manufacturers to produce the final beverages, so they do not have to create the emulsions from scratch. The emulsions are added to beverage syrup typically containing water and corn syrup or sweetener (Figure 10). This practice saves companies from shipping more water than necessary, allowing their operation to be more efficient and sustainable. Therefore, a desirable emulsifier needs to deliver both flavour (or colour) and turbidity effectively, maximise the oil load and minimise water usage in emulsion concentrates.

The challenge faced by beverage formulators is that if they want to add more flavour, colour or nutrients, they are increasing the oil load. But to stabilise that high oil load, higher amounts of emulsifiers are also required. Adding conventional emulsifiers causes higher viscosity in processing, resulting in excessive emulsion loss and poor emulsion dispersion in the end application. Conversely, reducing the ratio of emulsifier-to-oil increases the risk of emulsion instability.

FIGURE 10: Typical beverage manufacturing flow process
**New-age emulsifiers with superior emulsification power**

Under Ingredion’s multidisciplinary research and development programme, scientists are constantly formulating new ingredients, advancing breakthrough technologies and expanding production capabilities. The company’s legacy of pushing the frontiers of the starch molecule has led to the development of unparalleled emulsifying solutions for beverages.

**Ultra performance**

The unique molecular structure of PURITY GUM® Ultra starch provides lower interfacial tension, greater specific surface coverage and steric stabilisation. As shown in Figure 10, conventional OSA starch emulsions contain 12% oil and 12% starch, whereas PURITY GUM® Ultra starch emulsifier contains 24% oil and 8% starch.

As seen in Table 4, at 24% oil load, neither conventional OSA starches nor gum acacia is able to provide a stable emulsion with practical viscosity at the usage levels tested. At 12% oil load, conventional OSA starches and gum acacia can produce stable emulsions, but the emulsifier usage level is at least three to four times more than PURITY GUM® Ultra starch.

**Small particle size**

PURITY GUM® Ultra starch produces narrow particle size distribution of less than one micron and produces excellent emulsion stability at different ageing conditions.

An independent study confirms the superior performance of PURITY GUM® Ultra starch*: “This new modified starch used in the study was capable of forming stable emulsions with small droplet sizes (0.30 micron)” at oil : starch ratios of 12:4 and 24:8 (Table 4).

* Journal of the American Oil Chemists’ Society, 2011 Vol. 88, 47-55

**Figure 11:** Ultimate performing starch for ultimate process savings

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**PURITY GUM® Ultra starch**

**Three times the emulsifying power**

PURITY GUM® Ultra starch offers up to two to three times the emulsifying power of conventional beverage emulsifiers. It is capable of doubling the emulsion oil load, which in turn doubles the beverage manufacturing volume that can be produced from the same amount of emulsion, reducing processing costs dramatically. This specialty starch also allows for the removal of weighting agents, which may make up a substantial portion of the cost of an emulsion, without major loss in beverage turbidity. In addition, PURITY GUM® Ultra starch reduces water in the emulsion concentrate by 55%, cutting shipping and inventory costs and reducing the carbon footprint (Figure 11).
Additional benefits
At high oil loading with low usage levels, PURITY GUM® Ultra starch offers benefits in addition to cost:

- Produces equivalent beverage turbidity to gum acacia emulsions, providing a lower-cost solution
- Stabilises weighting agent-free beverage emulsions
- Provides flexibility of formulating at different oil and starch usage levels

Traditional systems
If high oil load systems are not preferred, PURITY GUM® Ultra starch can also be used in more conventional emulsion formulations. For example, using this emulsifier at standard oil load (4% to deliver 12% oil) also creates a stable emulsion.

PURITY GUM® Ultra starch benefit summary
PURITY GUM® Ultra starch significantly enhances manufacturing productivity, reduces capital expenditure and decreases environmental impact:

- Reduced variable manufacturing costs, lower warehousing costs, reduced shipping weights
- Greater asset utilisation, potentially postponing capital expenditure in concentrate emulsion production
- Reduced carbon footprint, aligning with modern corporate sustainability initiatives

Q-NATURALE® emulsifier
Making clear beverage possible
Formulators are constantly challenged to develop and improve clear-type beverages like near water, sports drinks or functional beverages to meet consumers’ thirst for more natural and better-for-you options. Q-NATURALE® emulsifier was developed to support this demand in several ways.

<table>
<thead>
<tr>
<th>TABLE 4: Performance comparison of PURITY GUM® Ultra starch vs. typical beverage emulsifiers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PRODUCT</strong></td>
</tr>
<tr>
<td>REGULAR OIL LOAD (12%)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>HIGH OIL LOAD (24%)</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
Delivering clarity and nutrients

There are a few methods of adding oil-soluble flavours and nutrients to clear-type beverages. A common method is to use solvents and/or synthetic surfactants such as polysorbates to solubilise the oil-soluble flavours and nutrients so that they are easily dispersible in the beverage. Some drawbacks of this method are incomplete flavour profile (reduced authenticity) and potential off-taste if excessive surfactant is used.

An alternative method is to emulsify the oil-soluble flavour, making the oil droplets sufficiently small that minimal light is scattered, rendering the beverage clear. This method requires the formulator to optimise the emulsion formula and process until the oil droplet size is less than 0.20µm. It is important to note that weighting agents are absent in such a formula as they impart undesirable beverage turbidity. In the absence of a weighting agent, emulsion stability is primarily managed by achieving a small oil droplet size.

Q-NATURALE® emulsifier exhibits good performance in this type of non-weighted emulsion for clear beverages. The active component in Quillaja extract, saponin, allows this emulsifier to act as a surfactant. Because saponin is very surface active, the micelles form rapidly around the oil droplets once they are mixed together, creating a stable emulsion. Typical emulsifiers used in the industry produce emulsions of oil droplet size of 0.30 micron, on average, using standard processing. But emulsions produced with Q-NATURALE® emulsifier can be less than 0.20 micron, on average, using similar processing conditions (Table 5).

Stabilising natural colours effectively

The replacement of artificial colours with natural colours in beverages is a growing trend. This can be challenging given the poorer stability of natural colours. Stabilising oil-soluble natural colours, such as beta-carotene, in beverages requires emulsion formula expertise and the emulsion is expected to maintain stability after processing and throughout shelf life.

Q-NATURALE® emulsifier was found to be ideal for beta carotene emulsions. Such emulsions can deliver the desired light stability and avoid staining PET beverage bottles. Beta-carotene emulsions suitable for clear beverages can also be formulated using Q-NATURALE® emulsifier.

Q-NATURALE® emulsifier uses a no-chemical extraction process that aligns with consumers’ demand for improved labelling. It has a low viscosity, is similar to water, and does not require hydration prior to use.

### Table 5: Emulsion performance comparison of Q-NATURALE® emulsifier vs. typical beverage emulsifiers

<table>
<thead>
<tr>
<th>EMULSIFIER</th>
<th>Q-NATURALE® emulsifier</th>
<th>GUM ACACIA</th>
<th>CONVENTIONAL OSA STARCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>OIL : EMULSIFIER RATIO</td>
<td>4 : 1</td>
<td>1 : 1.5</td>
<td>1 : 1</td>
</tr>
<tr>
<td>WEIGHTED OIL LEVEL</td>
<td>up to 50%</td>
<td>up to 12%</td>
<td>up to 12%</td>
</tr>
<tr>
<td>DISSOLUTION OR HYDRATION TIME</td>
<td>none</td>
<td>1 day</td>
<td>1 day</td>
</tr>
<tr>
<td>MEAN PARTICLE SIZE (MICRON)</td>
<td>0.15</td>
<td>0.35</td>
<td>0.28</td>
</tr>
<tr>
<td>BEVERAGE EMULSION STABILITY</td>
<td>1 year</td>
<td>1 year</td>
<td>1 year</td>
</tr>
</tbody>
</table>
**Application flexibility**

Use Q-NATURALE® emulsifier to deliver flavours, colours and actives in these applications (Figure 12):

- Carbonated beverages
- Fruit and vegetable juice drinks
- Energy drinks
- Sports drinks
- Fortified waters
- Ready-to-drink teas
- Clear and cloudy beverages

**FIGURE 12:** The power of Q-NATURALE® emulsions

**Summary**

As you can see, oil and water DO mix and stay that way with the right emulsifiers. Ingredion experts are pushing the frontiers of emulsion science. Engage the beverage innovation experts at Ingredion in your next project.