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Beverage Emulsions

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I. INTRODUCTION

Since the late 1990s, the beverage market in the United States had gone beyond providing beverages for refreshment to health and wellness claims. Beverages are also found to be the most successful and popular means of delivering functional benefits (1). These new beverages are flavored tea, flavored water, juice drinks, dairy-based juice drinks, and fortified beverages. In the United States, by the flavor category, the market statistic shows cola ranks first, and lemon-lime and orange are second and third, respectively. However, worldwide, orange flavor is the favorite of consumers (2). These citrus flavor products are based primarily on the essential oils from the peel of the fruits (e.g., orange oils, lemon oils, etc.). Like all essential oils, they are not water miscible. They cannot be mixed directly with a sugar solution to make a beverage. There are two methods of incorporating these flavors into soft drinks. The first method involves separating out the water-soluble fraction of the flavor from the essential oils by extraction and distillation. The second method involves converting the oil into a water-dispersible emulsion (i.e., a beverage emulsion).

Beverage emulsions are a unique class of emulsions. They are different from other food emulsions in that they are to be consumed in a highly diluted form, rather than in their original concentrate form. They are first prepared as an emulsion concentrate, which is later diluted in a sugar solution to produce the finished beverage—the soft drink. The soft drink prepared can be either a noncarbonated still drink or a carbonated drink. In soft drinks, the beverage flavor emulsion provides flavor, color, and cloudy appearance for the beverage, or just simply the cloudiness when the beverage cloud emulsion is used. These characteristics of beverage emulsions are what make them a unique class of emulsions. In the preparation of the finished beverages, the beverage emulsion concentrate is diluted in a sugar solution to produce the finished soft drinks; it is usually diluted several hundred times. The emulsions in both the concentrate and diluted forms must have a high degree of stability. They must be stable for at least 6 months, as required by the beverage industry. Other examples of emulsions consumed in a diluted form are coffee whitener and dairy cream for coffee. However, these emulsions are consumed almost immediately after dilution; the stability of the diluted form is required only for a short time. Therefore, dairy cream and coffee whiteners do not have the same stability problem as encountered by beverage emulsions for soft drinks. In this chapter, we will deal mainly with beverage emulsions for soft drinks.

II. DEFINITION

Beverage emulsions can be divided into two categories: beverage flavor emulsions and beverage cloud emulsions. Beverage flavor emulsions provide the beverage with flavor, cloudiness, and color as in certain formulas. Beverage cloud emulsions provide only cloudiness with no flavor. Both beverage emulsions are composed of an oil phase and a water phase, and they are classified as oil-in-water (o/w) emulsions. The oil phase consists of flavor oils and weighting agents. Flavor oils are usually composed of essential oils or citrus oils. Weighting agents can also be called density-adjusting agents, because they are added to flavor oils to increase the oil-phase density. They are materials that are oil soluble, which have no flavor of their own and have densities higher than the flavor oils. For beverage cloud emulsions, the oil phase contains only flavorless oils and the weighting agent. The flavorless oil can be orange terpenes or other flavorless oils, such as vegetable oils or edible waxes. The water phase usually consists of various types of hydrocolloid, acid, preservative, and coloring. The most commonly used hydrocolloids are gum arabic. During the shortage of gum arabic in the mid-1980s, blends of different hydrocolloids and modified food starches were developed for uses as gum arabic replacements.

III. INGREDIENTS

A. Oil Phase

1. Oils

In most of the beverage flavor emulsions, the flavor oils is the major component of the oil phase. It is responsible for providing the flavor and may produce some of the cloud in the beverage. The flavor oil in the emulsions is composed of several types of citrus oil in different proportion to produce a well-balanced flavor. Citrus oils are characterized by the presence of more than 90% of monoterpenes and a smaller amount of sesquiterpenes. They are not miscible with water. To compose a total flavor for a beverage, other flavor chemicals, such as alcohol, aldehyde, ketone, and esters, are compounded. These minor ingredients are responsible for the characteristic aroma and flavor profiles. These chemicals are important for the flavor of the products but have different degrees of solubility in water and do not behave as the typical oil phase in the emulsion (3).

In the beverage cloud emulsions, because terpenes possess little intrinsic odor or flavor, terpene hydrocarbons are used often as the oil component in the emulsions. Pure and deodorized vegetable oils are also commonly used with terpenes in the cloud emulsions. In addition to vegetable oils, edible waxes can also be used in the beverage cloud emulsions. When a stronger cloudifying strength is needed in some beverage flavor emulsions, terpene or vegetable oils are added to the flavor oils in order to produce more clouds in the emulsions (4,5).

Although citrus oils and other oils are important for the beverage emulsions, they also present a major problem for the emulsions because of their low density. In general, citrus oils have a specific gravity in the range of 0.845 to 0.890 g/cm^3. The specific gravity of a 10–12% sugar solution of soft drink is about 1.038–1.046 g/cm^3. The low specific gravity and insolubility of citrus oils in water indicate that it is difficult to mix the oils into the sugar solution to make a stable dispersion of the oils. Therefore, weighting agents are needed to add to the oils to increase the specific gravity.

2. Weighting Agents

Weighting agents are a group of materials added to the essential oils to increase their specific gravity and help to maintain a stable dispersion of the oil in sugar solution. In the beverage industry, weighting agents are also called density-adjusting agents. The criteria for a good weighting agent are as follows:

- Oil soluble, but relatively insoluble in sugar solution
- Has specific gravity sufficiently higher than that of essential oils

- Contributes no undesirable flavor, odor, or color to the finished product
- Approved by the food regulatory agency of the country in which the product is to be consumed

In the 1940s, brominated vegetable oil (BVO) was first used in soft drinks as the weighting agents for orange oils. In 1970, the United Kingdom and several other European countries withdrew their permission for the use of BVO. The United States and Canada restricted the permitted level of use to 15 ppm (6–10). These limitations have given the soft drink industry difficulty in producing flavor emulsions for soft drinks. Since then, a large variety of materials have been investigated for use as weighting agents for citrus oils.

As the result of the limitations placed on BVO use in 1970, the commonly used weighting agents are ester gum, sucrose acetate isobutyrate (SAIB), and damar gum. These materials have been approved individually by various countries; however, none has been approved universally by all countries.

Ester gum. Ester gum is a hard, pale-amber-colored resin produced by the esterification of pale wood rosin with food-grade glycerol and purified by steam stripping. Wood rosin is a solid resinous material which occurs naturally on the oleoresin of pine trees. There are three major sources for rosin (11):

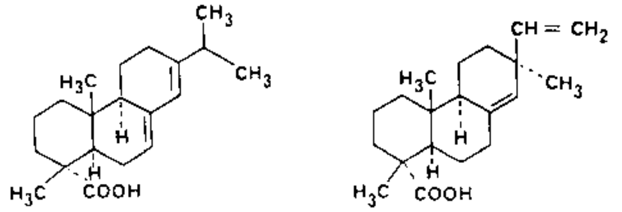
Gum rosin. Obtained by collection of the exudate of living pine trees followed by heating and stripping of the volatile terpenes and turpentine compounds

Wood rosin. Obtained by solvent extraction of aged pine stumps following by solvent refining of the extracted material

Tall oil. Obtained as a by-product of the Kraft process for wood pulp production followed by depitching and distillation

All three types of rosin are similar in nature and are composed of approximately 90% resin acids and 10% nonacidic neutral compounds.

The acid fraction is a complex mixture of isomeric diterpenoid monocarboxylic derivatives of alkylated hydrophenanthrenes having the typical molecular formula $C_{20}H_{30}O_2$. These acids are classified into two types: the abietic type and the pimaric type. The distribution of these resin acids can vary slightly according to botanical origin. Resin acids containing conjugated dienes and dehydro-, dihydro-, and tetrahydroabietic acids are classified as being of the abietic type. These differ from pimaric type acids in location of the double bonds and in type and configuration of the alkyl groups attached to C-13. The two double bonds of the abietic-type acids



(a) ABIETIC ACID

(b) PIMARIC ACID

Figure 1 The structural formulas of (a) abietic acid and (b) pimaric acid.

are conjugated, whereas those of the pimaric type cannot be because of the quarternary nature of the carbon atom at position 13. The presence of the conjugated double bond of abietic acid makes it readily oxidizable, isomerized by heat and acids. The structural formulas of abietic acid and pimaric acid are shown in Fig. 1. A typical analysis of gum and wood resins shows that the abietic acid content is in the range 55–68%.

In the neutral fractions of gum, wood, and tall oil rosins, one feature in common is that each is composed of approximately 60% of ester of resin and fatty acids. The resin acids are those found in the acid fraction of rosin. The fatty acids are those found in other neutral products. The fatty acids are predominantly the C-18 acids (i.e., oleic, linoleic, linolenic, and stearic). The alcohol portion of the esters is unidentified.

Ester gum is made by esterification of wood rosin with glycerol. The structurally hindered nature of the resin acid carboxyl group attached to a tertiary carbon atom makes it necessary to use higher temperatures or generally more drastic conditions to bring about esterification. This hindrance is, in turn, responsible for the unusual resistance of the ester linkage to cleavage by water, acid, or alkali. The ester gum with optimum physical properties is glycerol triabietate, which is produced from 3 mol of resin acid combined with 1 mol of glycerol. In commercial practice, it is difficult to obtain such a perfect ester. Commercially, the esterification process produces a mixture of monoglycerides, diglycerides, and triglycerides. Excess glycerol is removed by vacuum distillation and the remaining ester gum is steam-sparged until-odor free. Ester gum produced in this manner has the following typical properties (12):

Softening point (°C)	90
Color, USDA rosin scale	WG
Acid number	6.5
Density at 25°C (g/cm^3)	1.08

Ester gum is produced in flaked and rock forms in the past. The flaked form is easier to use. Because of the large surface area present on the flaked form, flaked-form resins are also prone to gradual oxidation. This usually induces darkening in color and decreasing solubility in terpenes and other organic solvents. In 1997, the manufacturer of ester gum started to produce the ester gum in pastilles shape and packaged in multilayered bags to protect the product. It is claimed that the barrier bag protected the product properties for at least 8 month (13).

The use of ester gum (glyceryl abietate) in orange oil terpene fractions to obtain a stabilized orange drink was first proposed in 1967 (14). Ester gum is considered the best agent for creating cloudy emulsions when it is used in combination with other emulsifying agents (5). Because ester gum is prone to oxidation, hydrogenated abietic acid and esters were proposed for use in cloud emulsions but are still pending government approval (15). Glycerol ester of wood rosin or ester gum is approved by the United States, Canada, and a number of other countries as a food additive. As specified in the U.S. Code of Federation Regulations, Title 21, under Section 172.735 (Glycerol ester of wood rosin), ester gum is permitted for use in nonalcoholic carbonated beverages at 100 ppm. Ester gum is known in the European Union under food additive number E445. It has been evaluated by the Scientific Committee for Food of the EEC, who established an acceptable daily intake (ADI) of 12.5 mg/kg body weight/day. The JECFA (Joint Expert Committee on Food Additives) of the FAO/WHO listed ester gum in the codex Alimentary as E445, glycerol ester of wood rosin (16,17).

Sucrose Acetate Isobutyrate. Sucrose acetate isobutyrate (SAIB) is a mixture of sucrose esters containing approximately 2 mol acetate and 6 mol isobutyrate per mole of sucrose. The major constituent of the mixture is 6,6′-diacetyl- 2,3,4,1′3′4′-hexaisobutyryl sucrose. The structure formula of pure sucrose acetate isobutyrate is shown in Fig. 2. SAIB is manufactured by esterification of sucrose with acetic anhydride and isobutyric anhydride in the presence of a barium hydroxide catalyst. After the removal of unreacted acids and anhydrides by steam-stripping under vacuum, the crude product is decolorized with activated carbon and purified by molecular distillation (18).

Sucrose acetate isobutyrate is a tasteless, odorless, and colorless viscous substance. It has a viscosity of 100,000 cps and a specific gravity of 1.146 g/cm^3 at 25°C. SAIB is very soluble in various solvents, such as orange terpenes, ethanol, and median-chain triglycerides. Being fully saturated, it has excellent oxidative stability. The viscosity of SAIB decreases when it is mixed with a solvent and, similarly, the viscosity will drop from 100,000 to 105 cps when the temperature is raised from 30°C to 100°C (19). The typical

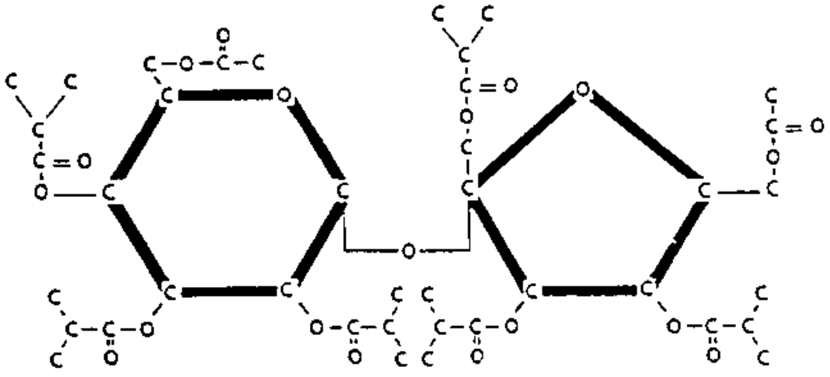


Figure 2 The structural formula of sucrose acetate isobutyrate (SAIB).

properties of SAIB are as follows:

Color, Gardner Scale:	1
Refractive index, n 20/D:	1.154
Specific gravity, at 25°C (g/cm^3)	1.146
Flash point, Tag closed cup (°C)	226
Solubility in water, at 25°C (wt%)	0.1
Shelf life (years)	2

A study conducted by Eastman Chemical Company determined the stability of SAIB in beverages. The study was performed at various values for the pH from 2.46 to 4.01 and for the temperature from 20°C and 40°C. SAIB was very stable under all conditions for 2 months. Minimal degradation of SAIB was observed in the beverages and beverage bases. The study was concluded. The stability of the emulsion containing acacia gum can be improved by the addition of six to eight parts per million of dioctyl sodium sulfosuccinate (DSS), based on the final beverage (20).

Sucrose acetate isobutyrate is metabolized to sucrose, acetic, and isobutyric acids. Metabolic studies indicate that the primary urinary metabolites in humans are lower aceylated sucrose and free sucrose. In 1968, a patent was issued in the United Kingdom for SAIB to be used for mixing with essential oils to facilitate the emulsification of these oils in water for the manufacture of soft drinks (21). Since then, many studies have been made on the biochemical effect and metabolism of SAIB in the rat and man. In general, the results of the studies show that the use of SAIB as a food additive is unlikely to constitute a toxicological problem with respect to its metabolitic fate in man (22–24). SAIB is now being used as a weighting agent in beverage emulsions in many countries. In June 1999, the United States Food Drug Administration

(FDA) approved SAIB for use in nonalcoholic beverages at a maximum level of 300 ppm in the finished beverage (25). SAIB is approved globally in more than 40 countries. In most of the countries of the European Union, the permitted level is 300 ppm or 300 mg/L. In the United States, SAIB can be listed as SAIB or sucrose acetate isobutyrate. In the European Union countries, SAIB is designated as E444 (26).

Damar Gum. Damar is the general name given to a group of natural exudates from shrubs of the *Caesalpinaceae* and *Dipterocarpaceae* families and other families belonging to the genera Dammar (27). These plants are indigenous to Malaysia, Indonesia, and the East Indies. The materials of the resins are known as Pale Bold Indonesia Dammar, Dammar Mata Kuching, or Cat Eye Dammar (28).

Damar resin contains an acidic fraction and a neutral fraction. The neutral fraction of the resin is subdivided into ethanol-soluble and ethanol-insoluble fractions, which are designated α-resene and β-resene, respectively. The β-resene has been shown to be a polymeric material of low molecular weight. The remainder of the resin is principally a complex mixture of neutral and acidic triterpenes. The main neutral triterpenes are dammadiennone, dammadienol, hydroxydammarenones, and hydroxyhopanone. All of these substances are tetracyclic compounds.

In the acidic fraction, the following acids have been identified: dammarolic acid, ursonic acid, and dammarenolic acid, dammar-enonic acid. Methyl esters mixture of the above acids are found with the acids (28,29).

Damar gum is completely soluble in essential oils, benzene, toluene, petroleum ether, carbon tetrachloride, and chloroform. It is partially soluble in ethanol and acetone, and it is insoluble in water. It has been used in coating varnishes for many years. Because of its high solubility in essential oils, it is used as a weighting agent for edible oil to produce beverage clouds emulsions (30). Damar gum can be used in the crude form if it is of top quality; small amounts of impurities that consist of insoluble materials, such as fine bark chips, can be removed by simple filtration after the solution is made. However, in most cases, the crude form will impart a terpene note to the product. A deodorized material can be made through solvent extraction (28,29,31) or by fractional distillation (32).

The typical characteristics of damar gum for use as weighting agent are as follows (27):

Appearance:	Off-white to pale yellow to brown
Weight loss:	5% at 105°C for 18 h
Melting point range:	90–110°C
Insoluble matters:	0.5%
Specific gravity:	1.05–1.08 g/cm^{3}at 20°C

Damar gum is permitted for use in beverages as an all-natural non-chemically modified vegetable gum resin; it is classified under the name AGATIS D'AMMARA (Classification N3), number 16 of the Single List of Natural Flavoring Substances, countersigned by 21 countries belonging to the Council of Europe.

Brominated Vegetable Oils. Brominated vegetable oil (BVO) was first used as the weighting agent for essential oils in beverages in the 1940s. It is made by the addition of bromine molecules to the olefinic bonds of the unsaturated fatty acid moieties of vegetable oils.

Commercial BVOs are made from vegetable oils with an iodine number of 80–90, such as olive oil, which produces a BVO with a specific gravity about $1.24\,g/cm^3$ at $20^{\circ}C$. Vegetable oils with an iodine number of 105–125, such as sesame oil, corn oil, soybean oil, or cottonseed oil, give a BVO with a specific gravity of about $1.33\,g/cm^3$ at $20^{\circ}C$. The BVO for beverage use is a dark brown color, viscous liquid with bland odor and bland taste.

It is the high specific gravity of BVO that makes it unique as an important weighting agent for citrus oils in soft drinks. It balances the specific gravity of citrus oils and, at the same time, provides cloudiness or opacity to the beverages. In 1966, the Joint FAO/WHO Expert Committee on Food Additives expressed particular concern about the possibility of bromine storage in body tissue when BVOs were used in food. In 1970, permission to use BVOs in soft drinks was withdrawn in the United Kingdom, after being permitted for use for some 30 years. In the same year, the U.S. government limited the use of BVO to 15 ppm in the finished beverage (6).

Other Weighting Agents. Since the use of brominated vegetable oil was banned or limited in different countries, the soft drinks industry has been faced with the problem of finding alternatives to replace BVO. In addition to ester gum, SAIB, and damar gum mentioned earlier, the following potential weighting agents have been proposed and are still being evaluated by the soft drink industry and metabolism and toxicology studies (4):

Sucrose octa-isobutyrate
Sucrose octa-acetate
Sucrose hepta-isobutyrate
Sucrose octa-propionate
Propylene glycol dibenzoate
Glycerol tribenzoate
Glycerol ester of hydrogenated rosin
Methyl ester of hydrogenated rosin

B. Water Phase

1. Water

In beverage emulsions, water is the major component. In most beverage emulsions, the water content is about 60–70%, and in certain formulations, it can be as high as 80%. The importance of good quality water in an emulsion is no less than that in soft drinks. Standard water treatment for soft drink water should be applied to the water intended for beverage emulsion. The treatment should remove colloidal and suspended matter, undesirable taste, odor, and micro-organisms. The carbonate hardness or alkalinity of water should be reduced. Highly alkaline water neutralizes the acid in the soft drink and causes the beverage to "go flat" and taste insipid. It will also affect the stability of the beverage emulsion due to the neutralization of the electrostatic charge carried by the emulsion particles. The effect of high water hardness or alkalinity on emulsion stability is much more obvious in the finished soft drink than in the emulsion concentrate because of the very high volume ratio of water to emulsion in the finished drink. Although there is no industrial standard set for hardness or alkalinity for water used in soft drinks, the major soft drink companies have been using the maximum hardness level at 50 mg of $CaCO_3$ per liter for cola drinks and 100 mg of $CaCO_3$ per liter for other products (33,34). For beverage emulsions, the water hardness level is recommended to have the same quality—not to exceed 50 mg of $CaCO_3$ per liter. Public municipal water supplies are not necessarily acceptable for soft drinks or emulsions without treatment. The water treatment at the public water plant is to produce safe potable water and it does not necessarily have the quality required for the soft drink industry. Public water companies depend on reservoirs for water supplies. Water quality varies, because different water sources feed into the reservoirs. Seasonal variation is another influence on the quality of the water in the reservoirs. The additional treatment applied to municipal water at the soft drink plant is to ensure that the quality of water used throughout the year is the same. In the preparation of beverage emulsion, the following steps further treat the raw municipal water: cartridge filtration (5 μm), cation exchange, anion exchange, and ultrafiltration (0.22 μm). This water must be of such quality described as "ultrapure" (35).

2. Hydrocolloids

Hydrocolloids are water-soluble biopolymers consisting of high-molecular-weight polysaccharides with rigid backbone and totally hydrophilic polyol (sugar) moieties. Some hydrocolloids serve as the stabilizer in the oil-in-water emulsions (36). The basic mechanisms for emulsion stabilization by hydrocolloids are viscosity effect, film formation, steric hindrance, and electrostatic interaction. These stabilization mechanisms will be discussed in detail later. To perform as an effective stabilizer for beverage emulsion, the hydrocolloid must have the following properties:

- Readily soluble with high solubility in cold water
- Low viscosity in water
- High emulsifying property
- Will not thicken or gel on aging

Gum Arabic. Gum arabic or gum acacia is the most well-known hydrocolloid for use in beverage emulsions. It is a dried exudate from the stems and branches of trees of the genus *Acacia*, which belong to the botanical family Leguminosae. About 80% of the acacia of commerce are from *Acacia senegal*, with *Acacia seyal* providing about 10%, with other minor species making up the difference. The best commercial grades designated for good uses are those giving clear, viscous, colorless, or pale yellow solutions that are as tasteless and odorless as possible (37). Gum arabic is a very complex substance with many unique features and properties. Supposedly, its chemical structure is composed of a main skeleton of 18–20 galactose units, with arabinose and rhamanose units limited to the side chains and uronic residues existing as sodium, potassium, and magnesium salts, which tend to give the molecule a buffering capability. The geometry is such that around 50% of these units are believed to be internal in the molecule (38). Composition ranges for the more commonly occurring Acacia species are as follows (37):

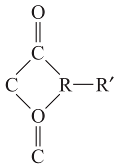
Ash	3–4 %
Nitrogen	0.14–1.11%
Glucuronic acid	9–16%
pH, solution at 25%	4.4
Intrinsic viscosity	12.1–20.7 ml/g
Molecular weight	$(312–950) \times 10^3$

Gum arabic is almost completely soluble in twice its weight of water and has very low viscosity in water with regard to concentration. A 30% solution has a viscosity of about 100 cps (39,40). Solutions of gum arabic show essentially Newtonian flow properties below about 40% concentration (41). The pH of a 10% gum solution is about 4.6–5.5. The addition of salts or electrolytes affects the consistency of the gum solution as does the pH. Gum arabic solutions become most viscous near pH 6–7. The high solubility and low viscosity allow for the preparation of solutions containing a high concentration of gum solids.

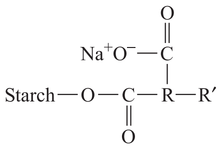
Gum arabic is well known as an emulsion stabilizer and emulsifier. It is most effective in stabilizing oil-in-water emulsions. It has been reported that gum arabic has a hydrophile–lipophile balance (HLB) value of 8.0 (42); another researcher gave it another value of 11.9 (43). These values indicate that gum arabic is an efficient emulsifier for oil-in-water emulsions. Gum arabic reduces the interfacial tension between oil and water and facilitates the formation of fine oil droplets in the emulsion (94). It has the ability to form an adsorbed film at the oil–water interface whose surface viscoelasticity is rather insensitive to dilution of the aqueous phase. The formation of a thick layer of film around emulsion droplets enable the flavor oil emulsion to be sterically stabilized both in a concentrate and in a diluted beverage (44). It has been reported that it is the protein-containing high-molecular weight-fraction which adsorbs most strongly at the oil–water interface and is probably mainly responsible for the emulsifying and stabilizing properties of the gum acacia (45). In a functionality study of fractionated gum arabic, it was reported that the higher-protein, high-molecular-weight fraction makes the best emulsions. All fractions except the lowest-molecular-weight fraction (about 5% of the whole gum) make reasonably good emulsions and perform well in model beverage (46).

Spray-dried gum arabic is a cleaned gum in a spray-dried powder form. It is used commonly for the preparation of beverage emulsions. In producing spray-dried gum, the raw gum is crushed, dissolved in water, foreign materials of the gum in solution removed by filtration or centrifugation, and then pasteurized and spray-dried into powder. A standard spray-dried gum arabic contains approximately 50% of particles less than 75 μm. A recent development in the gum industry is to make the powder into a fine granulated form for dust-free flowing and faster dissolution in water.

Modified Food Starches. The most widely accepted alternative to gum arabic for use as a beverage emulsion stabilizer is modified starches. They are a group of specially designed starch derivatives with balanced lipophilic and hydrophilic groups on the starch molecules. The starch derivatives are also converted to low-viscosity starches by acid degradation or by enzyme digestion. Caldwell and Wurzburg (47) and Richard and Bauer (48) developed the modification processes. The starch derivative is prepared by a standard esterification reaction in which the reagent and the starch suspended in water are mixed under alkaline conditions. The reagent is a substituted cyclic dicarboxylic acid anhydride having the following structural formula:



where R is a dimethylene or trimethylene radical and R′ is the substituent group, usually a long hydrocarbon chain. Examples are the substituted succinic acid anhydrides in which the substituent lipophilic chain is an alkyl or alkenyl group containing 5–18 carbon atoms. The acid ester of starch may be represented by the following structural formula:



$$\text{Starch}-\text{O}-\underset{\overset{\|}{\text{O}}}{\text{C}}-\overset{\overset{\text{Na}^{+}\text{O}^{-}-\overset{\overset{\text{O}}{\|}}{\text{C}}}{|}}{\text{R}}-\text{R}'$$

where R is a dimethylene or trimethylene radical and R′ is the substituent lipophilic group.

The octenylsuccinic acid anhydride-treated starches, generally referred to as sodium starch octenyl succinates, have been approved for food use by the U.S. FDA and by several other countries. The maximum level of the anhydride treatment allowed is 3%. The approximate degree of substitution is about 0.02 (49). These starches are widely used in the food and pharmaceutical products.

This type of modified starch is a white or yellowish-white bland-tasting, odorless powder. It is cold water soluble and the solution is very low in viscosity. At a concentration less than 20%, its solution has a viscosity about equal to that of gum arabic at the same concentration. The low viscosity of this starch in solution is an important attribute for it to be used as a beverage emulsion stabilizer. Another important property is the emulsifying power derived from the lipophilic modification of the starch molecules. In comparing the use of modified starch to gum arabic, modified starch is a cleaner material, as it contains fewer foreign substances. It is as easy to handle as gum arabic. The emulsion made with some of the earlier developed modified starch had the tendency to develop higher viscosity or form gel in storage at refrigerated temperatures due to retrogradation of the starch. This shortcoming has been overcome by recent developments (50,51).

There are several advantages to using modified starch as the stabilizer in the emulsions. The most important one is that the raw material for manufacturing this starch is corn, which is grown in several areas of the world and the overall supply is less likely to be affected by climatic conditions than that of gum arabic. The second is that in formulation, a smaller amount of modified starch than gum arabic can be used to stabilize the emulsions. A drawback of using modified starch is that it cannot be considered as natural an ingredient as gum arabic.

Gum Tragacanth. Gum tragacanth is known to have the excellent stabilization mechanisms of colloidal suspensions even at relatively low concentrations (of the order of 10 ppm). Gum tragacanth is commonly used with gum arabic as the stabilizer for emulsions because of its high viscosity. When it is used in conjunction with gum arabic, the mixture is a very effective stabilizer for emulsions. The viscosity of a solution of gum tragacanth and gum arabic tends to be lower than that of either constituent solution. A minimum viscosity is attained in a mixture consisting of 80% tragacanth and 20% arabic (52). The viscosity of gum tragacanth is most stable at pH 4 to 8 (53). In solution, it takes 48 h to develop to its maximum viscosity. The viscosity of the tragacanth solution is reduced by the addition of acids, alkalis, or electrolytes. It is also affected by the manner in which the solution is prepared.

Gum tragacanth is not a completely soluble gum. It is compatible with other plant hydrocolloids as well as carbohydrates and proteins. Because of the high price of this gum and its slow hydration rate with slow viscosity development, it is not commonly used commercially in beverage emulsions.

Other Hydrocolloids. Other hydrocolloids which have been reported to be useful in beverage emulsions are some ‘‘underutilized’’ species of Acacia, such as *Acacia verek* and gum arabic from the *Acacia senegal* species, and locust bean gum (54). The successful performance of these gums depends very much on their formulations. There are reports on using hydrocolloid materials such as propylene glycol alginate, xanthan gum, pectin, gellan gum, ghatty gum, and carboxymethylcellulose to enhance the stability of flavor and cloud emulsions. These materials are used as a thickener or blend of thickeners in diluted beverages. They cannot be used to replace gum arabic or modified starch in the emulsion concentrate. The beverage emulsions prepared using these hydrocolloid materials do not have the required stability for the emulsion concentrate and in the finished soft drinks. In general, polysaccharides are usually added to oil-in-water emulsions to enhance the viscosity of the aqueous phase, which produces desirable textural characteristics and retards the creaming of oil droplets. Nevertheless, at certain concentrations, polysaccharides have been shown to accelerate creaming instability by promoting droplet flocculation through the depletion mechanism (55,56).

3. Acids

Acid is an important ingredient in a soft drink because it provides the taste and controls the pH. In a beverage emulsion, acid plays an important role in controlling the pH to prevent the growth of micro-organisms. It is used to bring the emulsion to pH below 4.5. The reason is that most bacteria grow best at a pH range of 6.0–8.5, and pathogens do not grow well below pH 4.5.

Citric acid is used most commonly in beverage emulsions because it is closely related to citrus products and citrus flavor is the most popular flavor of beverage emulsions. There is an additional benefit of using citric acid because its sequestering power for chelating metallic ions may be present in water (57). Citric acid is usually produced in crystal or powder form and is readily soluble in water. Other acids, such as phosphoric acid, is used in cola emulsion but is not permitted in beverages which claim a fruit juice content. Malic, tartaric, acetic, and lactic acids have been used somewhat rarely as a replacement for citric acid for producing acidity.

4. Preservatives

Benzoic acid or sodium benzoate is added to beverage emulsion as a preservative. Other approved preservatives can also be used. Because of the low solubility of benzoic acid, its sodium or potassium salt is most commonly used. The preservative effect of benzoic acid is largely influenced by the pH. It is greatly increased by a corresponding decrease in pH because it is the undissociated form of benzoic acid which exhibits the preservative action. The preservation of beverages by benzoic is most effective when acidity is less than pH 4.5.

5. Colorings

FD&C colors are commonly used for citrus flavor emulsions. FD&C Yellow 6 and FD&C Red 40 are used for an orange shade. Natural colors, such as α- and β-carotenes and marigold extracts, are used for their yellow or orange shades. However, the stability of natural colors is never as good as the FD&C colors. In cola-flavored soft drinks, caramel color is used. Because of the high acidity in the beverage, the acid-stable double-strength caramel color is used. When the emulsion is a cloudifier, usually no colors are added. The natural color of cloudifiers is just milky white. Because titanium dioxide is an acceptable food additive, the water-dispersible form of it has been used to improve the opaque appearance of oil-in-water emulsion for short-term stability (58,59). Because of the high specific gravity of titanium dioxide it has the tendency to settle out in the beverage.

III. PREPARATION OF BEVERAGE EMULSIONS

In general, the preparation of a beverage emulsion can be divided into the following steps:

A. Step 1. Preparation of the Water Phase and Oil Phase

For the water phase, it is simple to dissolve the proper amounts of preservative, citric acid, coloring, and gum in water and make a complete solution. It is important to follow the proper order of the addition of these ingredients to assure their full dissolution in water. For the oil phase, the weighting agent is dissolved completely in the oil. The ratio of the weighting agent to the oil is governed by the legitimate permissible amount in the finished beverages. Usually, the maximum quantity of the permissible amount of weighting agent is used to fully utilize the benefit of the weighting agent.

B. Step 2. Prehomogenization

In this step, the oil phase is mixed with the water phase to make a crude emulsion or "premix." It breaks the oil phase into small oil droplets in the water phase. The quality of the premix of prehomogenization being supplied to the homogenizer can greatly influence the quality of the finished emulsion. A good premix fed to the homogenizer produces a better emulsion than a poor premix (60). The reason for this is quite easy to understand. At any given homogenizing pressure, a fixed amount of energy is available for transmission to the product; this energy is the means by which particle size reduction is achieved. If a significant portion of this energy is needed to reduce very large particles, then there will not be enough energy left over to work on the smaller particles and reduce them even further.

As a general rule, the premix should have a droplet size less than 20 μm to avoid a polydispersed final emulsion (61). In practice, it is preferable to have the premix droplet size smaller than 10 μm. Usually, this step can be achieved by the use of a high-speed mixer, colloid mill, homomixer, or making one pass through the homogenizer.

C. Step 3. Homogenization

This is the most important step of the process. In this step, the crude emulsion or premix is pumped through the homogenization valves of the homogenizer at high pressure. The high pressure forces the liquid to pass through the valves at a high velocity, which creates turbulence and cavitation forces that shatter the oil droplets into fine particles (62,63). Single-stage or two-stage homogenizers are usually used for this procedure. For beverage emulsions, a two-stage homogenizer is preferred. In a two-stage homogenizer, the second stage provides controlled back-pressure to ensure the optimum efficiency of homogenization. An additional benefit of the second-stage valve is its ability to delay or prevent reagglomeration of the particles after leaving the first stage. The second-stage valve also provides a means of controlling the viscosity of the product (64). The pressure setting for the first-stage homogenization valve usually varies from one emulsion to the other and is dependent on the composition of the emulsion. This first-stage pressure can vary from 2000 psi to 5000 psi, or from 140 to 350 kg/cm^2, and in certain cases, 7000 psig or 500 kg/cm^2. In general, the second-stage pressure is set between 300 and 500 psi (20 and 35 kg/cm^2) or set at 10% of the first-stage pressure.

Because beverage emulsions usually require either a very small average particle size and a very uniform particle size distribution, it is simply not possible to reach these goals in a single pass through a homogenizer. Generally, two passes of the emulsion through the homogenizer are performed in order to obtain a more uniform particle size distribution in the emulsion. Because beverage emulsions vary in their formulations, there is no set operational procedure for all emulsion preparations. However, the ideal operating procedures for each emulsion can be designed according to the basic principles of a stable emulsion.

IV. STABILITY PROBLEMS

In 1970, the use of BVO in soft drinks has been banned or regulated. The use of BVO in the soft drinks is limited to 15 ppm in the United States and a few other countries. In many countries, its use is completely prohibited. For this reason, the soft drink industry has been trying to find other appropriate materials to take the place of BVO for use as the weighting agent for citrus oils in beverage emulsions. Although ester gum, SAIB and damar gum can be used as the weighting agents in place of BVO, they have their shortcomings and limitations. All of these weighting agents do not have a specific gravity as high as that of BVO. The specific gravity of ester gum is 1.08 g/cm^3, that for SAIB is 1.15 g/cm^3, and that for damar gum is 1.05 g/cm^3. They all have government regulations on the amount can be used in beverages. Under these regulations and the low specific gravity of weighting agents, a stable beverage emulsion has become difficult to make than when BVO could be used without limitation.

The instability of beverage emulsion observed in both the concentrates and the finished soft drinks may lead to the following occurrences (65): creaming (ringing), flocculation, and coalescence.

A. Creaming

Creaming is a term adopted from the separation of cream from unhomogenized milk. In the soft drink industry, the common term for creaming of the soft drink in bottles is "ringing." This is because in the beverages, the flavor oil particles separate from the beverage and float to the top and it is seen as a white creamy ring at the neck of the bottle. Creaming or ringing is related to flocculation. It can be considered as a separation of one emulsion into two emulsion sections. One section is richer in the oil phase than the original emulsion, and the other section is richer in the water phase than the original emulsion. When creaming occurs in a bottle of beverage, the emulsion richer in the oil phase rises to the top and forms a creamy layer or just a ring at the neck of the bottle. It is not only unsightly to have the ring at the neck of the bottle but it indicates the breakdown of the distribution of the flavor oil in the bottle of beverage.

In relation to creaming, two other phenomena not commonly observed in bottles of soft drink are "lifting" and "striation." Lifting occurs when the emulsion in the bottle of beverage lifts up from the bottom and shows a clear layer of liquid at the bottom. Striation occurs when the emulsion in the bottle shows two or more distinctive layers of different degrees of cloudiness. It looks as if the emulsion in the bottle has separated itself into two or more different particle size or density fractions. Lifting and striation only show in bottles that have been held in an upright position undisturbed for a long period of time. They are more often seen in bottles that are kept in the refrigerator where the temperature is low and the Brownian movement and thermal convection of the emulsion particles are less active.

A rather special and rare situation found in soft drinks is "sedimentation." Sedimentation is also called "downward creaming" by the soft drink industry. It happens only when the weighting agent is overused or supersaturated in the oil. In such case, the excess weighting agent will separate gradually from the flavor oil and precipitate in the beverages (66). When the gum arabic or starch used in preparing the emulsion has not been purified properly, the impurities or foreign materials will precipitate as sediments.

B. Flocculation

Flocculation occurs when oil droplets of the dispersed phase form aggregates or clusters without coalescence. At this stage, the droplets still retain their original identities. The forces which draw these droplets together to form aggregates are primarily the long-range London–van der Waals forces and electrostatic forces around the droplets (67). From the creaming point of view, these aggregates behave as simple large droplets. The rate of creaming is accelerated in systems in which the density difference of the aggregates from the continuous phase is sufficiently large. In the emulsion concentrate, a perceptible increase in emulsion viscosity can be observed when flocculation occurs. Although flocculation generally changes the physical properties of the emulsion, the particle size distribution remains unchanged. In the finished beverage system, the droplet concentration is so low that the flocculation is often reversible. The aggregates can be readily redispersed because the interaction forces between the droplets are weak. This phenomenon can be observed by lightly shaking a bottle of beverage that has a ring in the neck. The ring quickly disappears after the shaking.

C. Coalescence

In this stage, there is localized disruption of the sheaths around neighboring droplets of the aggregates, and the oil droplets merge together to form a large droplet. This leads to a decrease of the number of oil droplets and eventually causes the breakdown of the emulsion. When a proper hydrocolloid is used in the water phase, the breakdown of the emulsion will seldom reach this stage. The reason is that the hydrocolloid, such as gum arabic, has a good film-forming ability and will form film around the oil droplets in addition to providing viscosity in the water phase (68). More about the film-forming property of gum arable will be discussed later in this chapter.

V. STABILIZATION OF BEVERAGE EMULSIONS

For a beverage emulsion, the most critical criterion of stability is its stability in the finished beverage, where the emulsion concentrate is further dispersed in sugar solution. The stability of the emulsion in the concentrate is much easier to achieve than in the finished beverage. This is because, in the concentrate, the viscosity is high due to the high concentration of a hydrocolloid, which acts as a stabilizer. In the beverage, the emulsion concentrate is redispersed in sugar solution at a very high dispersion ratio. The dispersion ratio could vary from 1/300 to 1/1000 depending on the flavor strength or the cloud strength in the emulsion concentrate. It can almost be described as the emulsion concentrate being dispersed in a second water phase i.e., from a gum-solution water phase to a sugar-solution water phase. The following discussion will emphasize the principles involved in stabilizing beverage emulsions in sugar solutions such as ready-to-drink beverages.

A. Stokes' Law

The "Ringing Test" is the most popular method used to evaluate the stability of beverage emulsions in soft drinks. It is a simple test in which bottles of soft drinks containing the beverage emulsion are held in an upright or horizontal position for observation of ringing. If the emulsion in the soft drink bottle is not stable and will ring, it will form ring faster in the horizontal position than at the upright position. The reason is simply that the oil droplets in the bottle have a much longer distance to travel to the top surface than in the bottle at horizontal position. The rate of ringing or creaming of an oil droplet in sugar solution may be determined by equating the force of gravitation with the opposing hydrodynamic force as given by Stokes' law:

$$\nu = \frac{2gr^2(\rho_2 - \rho_1)}{9\eta_1} \tag{1}$$

In Eq. (1), ν is the rate of creaming or sedimentation, g is the acceleration of gravity, r is the droplet radius, ρ_2 is the density of the oil phase, ρ_1 is the density of the water phase, and η_1 is the viscosity of the water phase. In an o/w emulsion or a soft drink, the oil density, ρ_2, is lower than that of the water phase, ρ_1. The resulting sign, ν, is negative; hence, creaming or ringing will occur.

As an example of the use of Stokes' law, consider the case of the orange flavor emulsion used to make a beverage. Orange oils are the major components of orange flavor. Typically, orange oils have a density of $0.846\,\mathrm{g/cm^3}$ and the sugar solution in the soft drink has a density of $1.040\,\mathrm{g/cm^3}$ for a 10% sugar solution or $1.048\,\mathrm{g/cm^3}$ for a 12% sugar solution. Applying these density data to Stokes' law, the resulting ν carries a negative sign, which indicates that the emulsion will ring in the bottle. Stoke's law shows that the velocity of a droplet, ν, is directly proportional to the density difference between the oil phase and the water phase and to the square of the radius of the droplet. It is also inversely proportional to the viscosity of the water phase. The equation clearly shows that if one can make orange oils with a density equal to that of the sugar solution, there will be no creaming or ringing in the finished beverage because when $\rho_2 = \rho_1$, $\rho_2 - \rho_1 = 0$ and, therefore, $\nu = 0$. Because orange oil is lighter in density than the sugar solution in the soft drink, weighting agents must be added to orange oil to increase the density. However, the government regulates the use of weighting agents. These regulations make it impossible to adjust the density of the orange oil to equal to that of the sugar solution. For example, an equal weight of ester gum added to orange oil can only bring the density of orange oil from 0.85 to 0.95 g/cm^3. A density of 0.95 g/cm^3 is still a large difference from 1.05 g/cm, the density of a 12% sugar solution. According to Stokes' law, an emulsion with these components will cause a ringing problem in the soft drink. Because of the consumer's preference for the strength of the orange flavor and the 10–12% sugar sweetness level in the beverages, there is little a beverage processor can do to narrow the density difference between the oil phase and the water phase, because the amount of weighting agent added to the orange oil is reaching the regulated limit in the finished beverage. The exception is in making diet drinks, where artificial sweeteners are used and the density of the water solution is almost equal to 1.

As shown in Stokes' law, if $\rho_2 - \rho_1$ and η_1 equal to constants, where gravity, g, is also a constant, the velocity of an oil droplet moving upward will be in direct proportion to r^2. It demonstrates that reducing the droplet size is one effective way to control the creaming velocity when the adjustment of oil density has reached the maximum limit permitted. For instance, in a bottle of beverage, a particle 0.1 mm in diameter will travel upward at a velocity 100 times slower than a particle 1.0 mm in diameter. This example shows the importance of controlling the particle size, keeping it small.

B. Adsorption at Interfaces

Most beverage emulsions are made with a water phase composed of gum arabic or other hydrocolloids and water. It has been known for many years that gum arabic solution produces a film at the oil–water interface. Shotton and White reported that gum arabic solution formed a film on paraffin oil and showed this interfacial film to be viscoelastic (68). Dickinson et al. reported that gum arabic forms film and stabilizes an oil-in-water emulsion containing gum arabic and *n*-tetradecane. They also reported that the surface rheology of gum arabic films is relatively insensitive to dilution of the aqueous phase (69). In the case of modified starch, such as sodium starch octenyl succinates, because it contains both lipophilic and hydrophilic groups, the starch molecules are attracted to the oil–water interface and form a film about the oil droplets (49).

Because citrus oils are most commonly used in beverage emulsions, we conducted a study of the characteristics of films formed at the interface of orange oil droplets dispersed in a gum arabic solution. In order to simulate closely to the conditions of commercial beverages, the orange oil was weighted with ester gum to a density of 0.95 g/cm. The study was repeated using modified starch, sodium starch octenyl succinates, in the water phase. The films formed by both gum arabic and modified starch are viscoelastic. Under the microscope, they appeared as elastic interfacial film or shield on the oil droplets. The elastic property of the films formed by gum arabic and modified starch on orange oil droplets are seen on the shrunk bubble of oil droplet shown in Figs. 3 and 4 (70). The film or shield protects droplets from coalescence when they collide with each other. Aging of the interfacial film in the gum or starch solution seemed to strengthen the film on the droplets (68,70).

Finished beverages were prepared using emulsions containing orange oil with ester gum as the weighting agent with gum arabic or modified starch according to the standard formula and procedure. The aging study of these emulsions in the finished beverage was conducted by storing them on a shelf at ambient temperature for 6 months with weekly checking of their particle size changes. The results show that there was no ringing in the bottle with no significant change in particle size as analyzed by Coulter Model LS-130 particle analyzer (70). In this study, the orange oil/gum arabic emulsion in the beverage had a mean particle size of 0.364 μm when freshly prepared and 0.410 μm after being aged for 6 months. The orange oil/modified starch

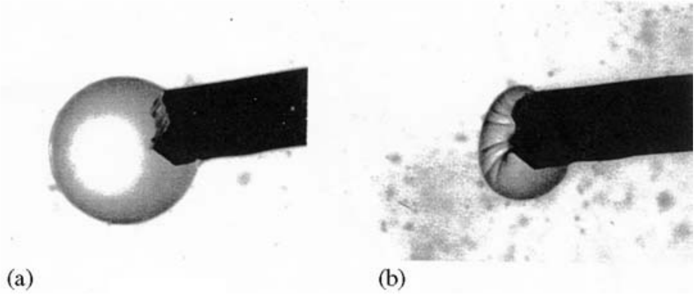


Figure 3 Orange oil droplet in gum arabic solution: (a) full oil droplet; (b) oil droplet shown with wrinkled membrane after oil had been partially withdrawn. (From Ref. 70 with permission.)

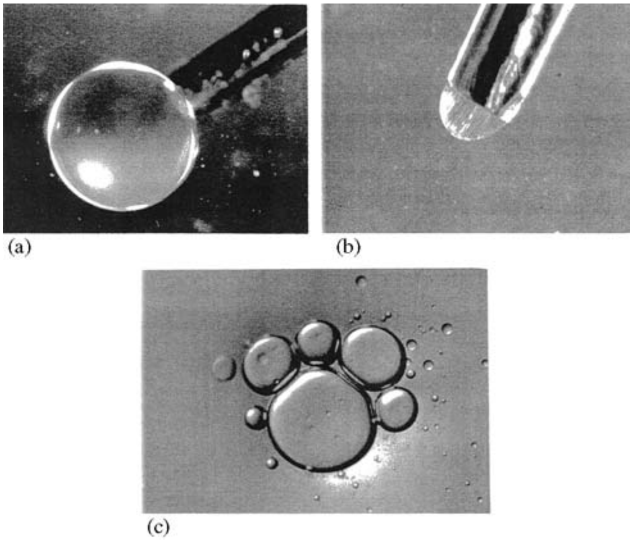


Figure 4 Orange oil droplet in sodium octenyl succinated starch solution: (a) full oil droplet; (b) oil droplet shown with wrinkled membrane after oil had been partially withdrawn; (c) orange oil droplets with membrane aged in sodium succinated starch solution and showed no coalescence. (From Ref. 70.)

emulsion in the beverage had a mean particle size of 0.264 μm when freshly prepared and 0.320 μm after 6 months of aging. The changes are so small and the effect to the emulsion stability in beverage is negligible. The histograms of these two emulsions in beverages when freshly prepared and after 6 months in storage are shown in Figs. 5 and 6. These histograms show that there is no significant change in the particle size distribution patterns.

Because gum arabic or modified starch is heavier than water, a layer of hydrated gum arabic or starch will provide an added weight to the oil droplet and actually change the density of the total droplet—the oil droplet plus the hydrocolloid film—to a higher value. When an oil droplet is smaller, the percentage of weight contributed by the hydrocolloid layer to the total droplet weight will be larger than that for a larger droplet. This further indicates that to achieve emulsion stability in the finished beverage, the oil droplets of the emulsion should be made small. When oil droplets are small, they will gain more of the additional weight benefit contributed by the gum or starch layer on the particles. This theory answers partially the question commonly asked in the industry: "Why in orange oil weighted with a weighting agent to a density of only about 0.95 g/cm^3 could the emulsion

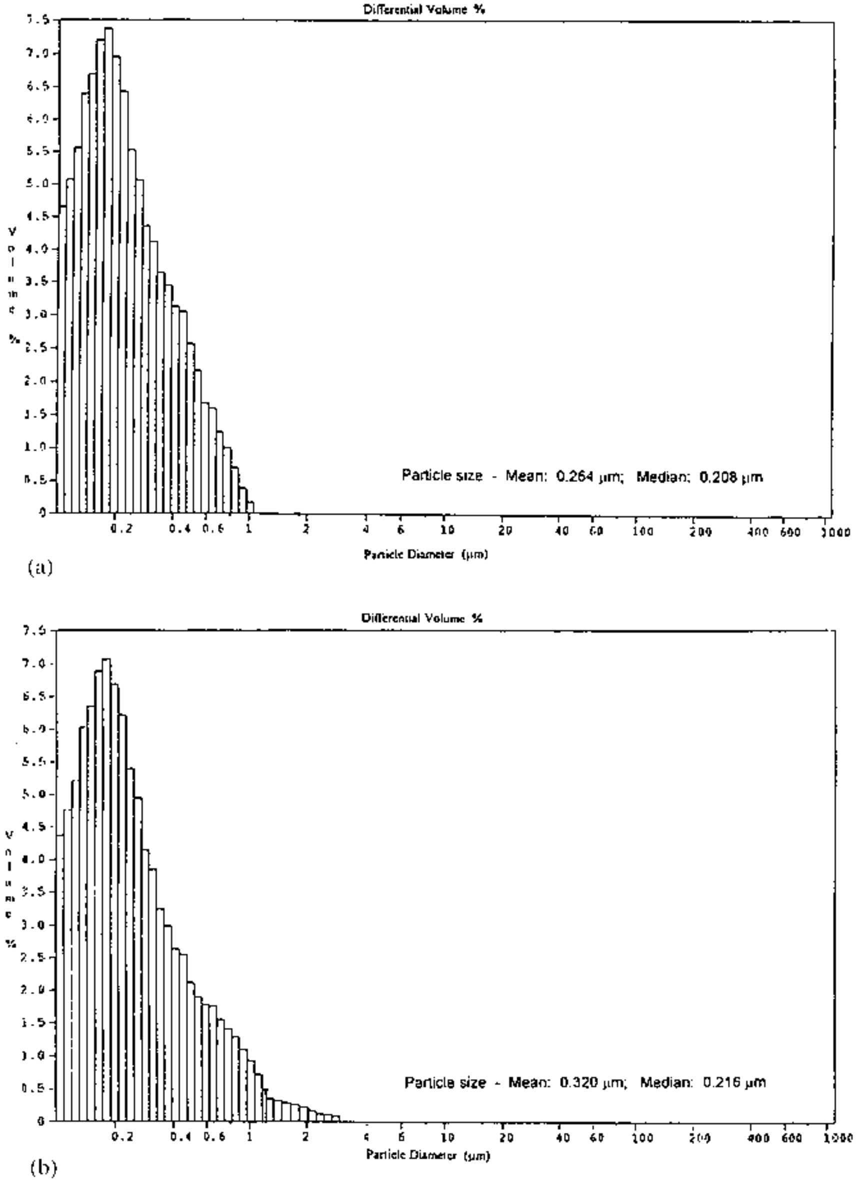


Figure 5 Particle size distribution histogram of an orange oil/gum arabic emulsion in beverage stored at room temperature: (a) 2 days old and (b) 6 months old. (From Ref. 70.)

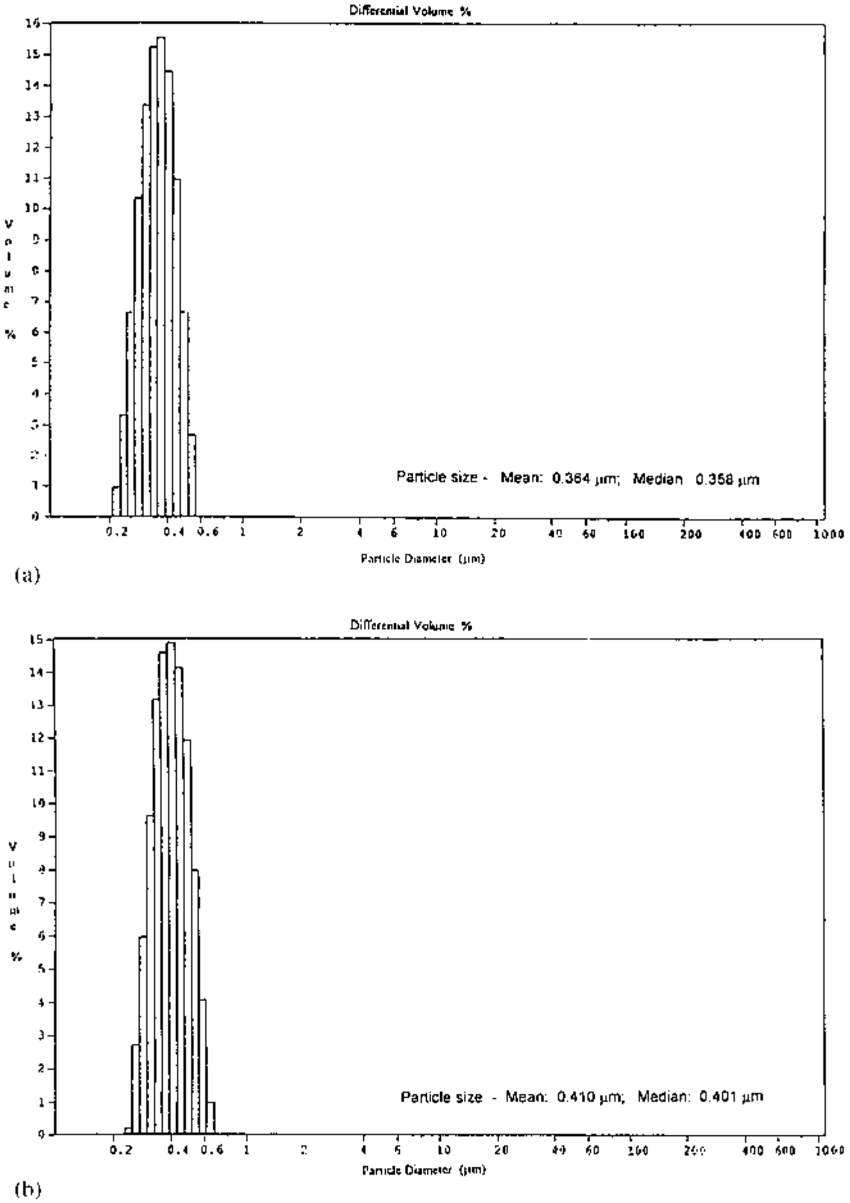


Figure 6 Particle size distribution histogram of an orange oil/modified starch emulsion in beverage stored at room temperature: (a) 2 days old and (b) 6 months old. (From Ref. 70.)

still be made stable in a solution of density of 1.05 g/cm^3?" This is because the additional weight of the film brings up the density of the particle close to that of the sugar solution when the particles are small enough to take the advantage of the weight of film.

The formation of the interfacial film by gum arabic or other hydrocolloid polymers on the oil droplets also helps to stabilize the emulsion in another way. It is the hydrocolloid material adsorbed on the surface of the oil droplets which prevents oil droplets from coalescence and the formation of larger droplets. Coalescence may eventually lead to emulsion breakdown. It may be described as the adsorbed hydrocolloid layer on droplets keeping the droplets far enough apart such that the van der Waals attraction force is minimized (67,71). In this way, the droplets will remain dispersed. When an emulsion is stabilized sterically by adsorbed polymers, the mechanism is considered "polymeric steric stabilization" (72,73).

In many classic emulsions in which emulsifiers or surfactants are used, the emulsifiers are adsorbed on the interface of oil droplets as a closely packed monomolecular film and reduce the surface tension. In citrus-flavor beverage emulsions, Walford proposed using a blend of Atmos 300/Tween-80 (HLB 11.5) to prepare a stable clouding agent (74). Kaufman and Garti studied the use of a different combination of Span/Tween emulsifiers to stabilize oil-in-water emulsions (75). They reported that the type of emulsifier, the required HLB, oil concentration, amount of emulsifier, and the method of preparation affect emulsion stability. However, because of flavor and their non-natural status, little or no emulsifier is being used in the present commercial beverage products. In citrus-flavor soft drinks, which have a delicate flavor, the off-flavor imparted from the emulsifier can be detrimental to taste.

In the beverage emulsion, when gum arabic or sodium starch octenyl succinate is used, they perform as an emulsifier but in a weaker manner as compared to true emulsifiers. It is because these hydrocolloids do not have the distinctive polar and nonpolar groups that, the real emulsifiers have (42,43,49).

C. Electrostatic Interaction

In an oil-in-water emulsion, the oil particle may acquire an electric charge through the ionization of an adsorbed surface charged group. In beverage emulsions, gum arabic is used in the water phase. Gum arabic is an acidic polysaccharide. The carboxyl (COO−) ions are at the periphery of the molecule and are very active in creating an anionic environment (76). Surface charge may also be acquired through the adsorption of the dissolution of small ions in the water phase. Anions have a greater tendency to be adsorbed than cations, because cations are normally more hydrated and prefer to stay in the aqueous bulk solution. The electrical charge may also be acquired through a possible friction mechanism. An empirical physical rule may be applied to this theory. It states that a substance having a high dielectric constant is positively charged when in contact with another substance that has a lower dielectric constant (77). Because water has a dielectric constant higher than oil, oil droplets will have a negative charge. These charges cause a repulsive force among the oil droplets which prevents flocculation, therefore contributing to the stability of emulsion.

As mentioned earlier, dispersed oil droplets may acquire an electric charge through the ionization of surface groups. Oppositely charged ions (counterions) are preferentially attracted toward the surface, and ions of the same charge (co-ions) are repelled from the surface. The region of unequal counterion and co-ion concentrations near the charged surface is called the electrical double-layer. The double layer may be regarded as consisting of two regions: an inner region of strongly adsorbed ions and an outer region where ions are diffusely distributed according to a balance between electrical forces and random thermal motion (78). At some point in the double-layer region, corresponding more or less to the potential at the zone of shear, the electrical potential is called the zeta potential (83). The determination of the zeta potential is important in the study of emulsion stability. It is an important parameter for both achieving emulsion stability and destroying emulsion stability. Gum arabic solutions generally have a zeta potential about $-23\,\mathrm{mV}$ (71,79,80). However, one cannot categorically state that an emulsion will or will not be stable at a given zeta potential, as some other factors should be taken into consideration. It is especially true in the case of beverage emulsion; two other important factors are the density difference between the two phases and the droplet sizes. It should be stressed that the zeta potential reflects both the electrolyte's presence in the system and the dissociated ions accompanying the original colloid particles. When a cation electrolyte is added to an emulsion containing a dispersed phase carrying negative charges, the electrolyte will be adsorbed and neutralize the zeta potential. This, in turn, will cause aggregation to occur due to the London–van der Waal's forces. This electrolyte effect on emulsion stability is much more evident in soft drinks than in the emulsion concentrates, because the emulsion concentrate contains a high concentration of gum arabic and gum arabic is known to produce stable emulsions over a wide range of pH and in the presence of electrolytes (68,70). In soft drinks, the emulsion is in a very diluted form and the gum arabic concentration is very low; therefore, the electrolyte effect is more obvious.

In the adsorption and desorption of electrolyte ions causing the change of zeta potential, the higher the valency of the ions, the greater

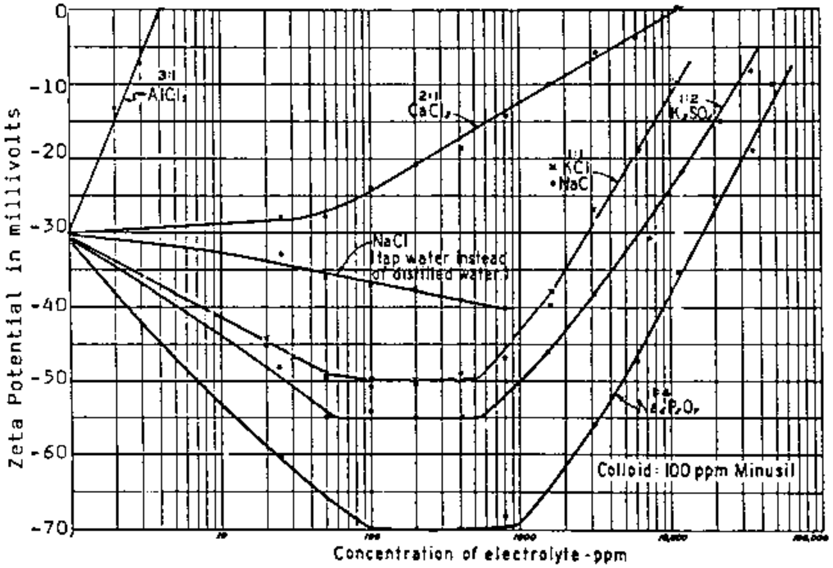


Figure 7 The effect of electrolytes on the zeta potential of a colloidal dispersion. (Courtesy of Zeta-Meter, Inc., New York.)

the effect of compressing the electrical double layer around the droplets and changing the zeta potential (81); that is, the higher the cation valence, the lower the zeta potential, and the higher the ion concentration, the greater the decrease in the negative zeta potential (82). Trivalent ions, such as aluminum ions, have 10–100 times the effect of equivalent concentrations of divalent ions, like calcium, which have 10–100 times the effect of equivalent concentrations of univalent ions. The effect of different electrolytes on the zeta potential of a colloidal dispersion is shown in Figure 7 (83). For the above reason, the soft drink industry usually uses only treated water to make emulsions and the finished beverages.

VI. PARTICLE SIZE CHARACTERIZATION

To achieve good emulsion stability, it is important to control the oil droplet size. This is especially true for beverage emulsions because their particles have to be stable in both the concentrate and the diluted finished soft drink. This means that the same oil phase must be stable in two water phases of different composition. In controlling the particle size, it is essential to know the average size of the oil phase particles and the size distribution of these

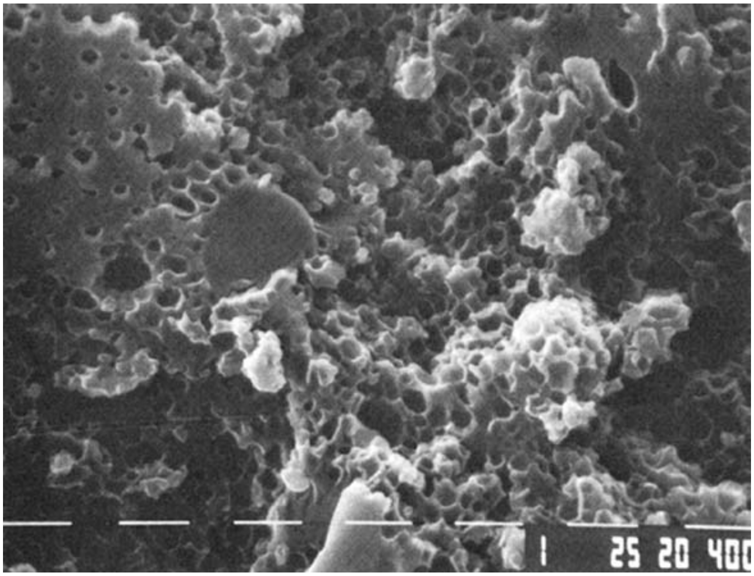


Figure 8 Scanning electron microphotograph of a dehydrated stable beverage emulsion concentrate.

particles in the emulsions. Two emulsions may have the same average particle size and yet have dissimilar stability because of the difference in their distributions of particle size.

A scanning electron microscopic photograph of a dehydrated stable emulsion that originally contained 70% moisture is shown in Fig. 8. In this microphotograph, the holes are the sites of oil droplets. Because the emulsion was dried at room temperature, the droplets did not change in size. The holes represent the actual size of the droplets. They show that almost all of the droplets have a diameter smaller than 1 μm.

For the beverage emulsion, the determination of particle size distribution serves two purposes: One is to estimate the quality of the emulsion concentrate and the other—even more important—is to predict the stability of the emulsion when it is made into the finished beverage at a future date. The latter is for quality control. It is to predict the stability of an emulsion by comparing its particle size data with the quality control standard established previously for this product.

There are many methods available for the determination of particle size and size distribution. Groves and others (84,85) have reviewed these methods of particle characterization. Groves' review emphasizes those methods that have practical use for emulsions containing smaller particles.

The beverage industry commonly uses the following methods for product development and quality control: optical microscopic method, transmittance measurement, and laser diffraction technique.

A. Optical Microscopy

The optical microscope is one of the most valuable tools for observing the microstructure of emulsions (86). It is invaluable for a quick examination of the emulsion when there is no other particle size measurement instrument available. Although the microscope is mainly used for examination of the oil particles, it is also useful for checking the gum solution. If there are insoluble materials or underdissolved gum particles in the solution, they can be seen under microscope. Because beverage emulsions are oil particles dispersed in a transparent liquid and they have very similar refractive indexes, a conventional bright-field optical microscope is not suitable for examining oil-in-water emulsions. A microscope equipped with a phase-contrast attachment is best for this purpose. A microscope equipped with a dark-field attachment can be used also. Both phase-contrast and dark-field microscopes will enhance the edge contrast of the image of oil droplets (87). When using the phase-contrast microscopy, an experienced technician can view and estimate the particles down to 0.5 μm at 1000 × magnifications with a micrometer. The theoretical limit of resolution of an optical microscope is about 0.2 μm, but, in practice, it is difficult to obtain reliable measurements below about 1 μm. The experience of routine use of an optical microscope is essential in particle characterization, even if it is used only to examine the state of dispersion for making crude measurements. In practice, it is common to use a microscope in conjunction with other instrumental analysis. Using an optical microscope for objective measurement is almost impossible. A statistically significant count of particles, allowing a 5% error and at 95% confidence level, would need 2960 particles. In general, the emulsion has to be diluted before being placed on the microscope slide. Brownian movement of particles usually is a problem for particle counting under the microscope. To slow down the Brownian movement, a gelatin solution, low-viscosity sodium carboxymethylcellulose (CMC) solution, or glycerin in water are commonly used to dilute the emulsion in place of pure water.

B. Light-Scattering Determination

In general, two types of light scattering method are used: (a) angular light scattering, where the intensity of the scattered light is measured as a function of the scattering angle, and (b) transmittance or turbidity measurement, where the intensity of the transmitted light is measured. In principle, the angular light-scattering method contains more information, but turbidity measurement is easier to carry out using a spectrophotometer (88,89). For routine particle size analysis or stability tests, where precision is not highly critical, turbidity provides a convenient monitor of the state of the emulsion. However, turbidity measurement only translates to average particle size.

In the soft drink industry, turbidity or transmittance measurement is used as a quick method to check the quality of the emulsion. Some other methods are measuring the spectral absorption of diluted emulsion at two wavelengths, such as 850 nm and 450 nm, or 800 nm and 400 nm, and using the ratio of the readings as stability indices (90,91).

C. Laser Diffraction Technique

The particle counting technique has been known for many years in emulsion science and pharmaceutical research (92). Providing adequate care in sampling and preparing the electrolyte solution, particle size analysis can produce accurate and reproducible results (84,92). In our study we found that there is good corelationship of the data of emulsion particle size distribution obtained from the particle size analysis with the stability of the emulsion in beverage (65). It is generally agreed that the particle size analyzer is capable of making a unique and valuable contribution to the subject of particle size characterization (84,93). With the development in the laser diffraction technique, several instrument manufacturers have developed more sensitive and accurate particle size analyzers. These instruments can determine particle size down to 0.01 μm with the upper size limit to 1000 μm. It is important to have an instrument with the upper size limit at 1000 μm as to make it useful for determine the oil droplet size in premix or crude emulsions. These instruments measure particle size distributions by measuring the pattern of laser light scattered by the particles in the sample. Arrays of photodetectors detect and measure the intensity of the scattered light. Each particle's scattering pattern is characteristic of its size. The pattern measured by the instrument is the sum of the pattern scattered by each constituent particle in the sample. When the duration of the measurement is long enough that the flux pattern accurately represents the contributions from all particles, an analysis of the resulting pattern will yield the particle size distribution of the sample. Because the measurement procedure is fully automated, once the emulsion sample has been placed in the instrument, it takes only a few minutes to complete. The data generated have proven to be invaluable for quality control and troubleshooting the processing of the emulsion.

For expressing the particle size distribution of an emulsion, it is preferable to use volume percentage distribution rather than population percentage distribution. The reason is that volume percentage distinctively shows the quantity in volume of the large particles present in the emulsion. It can be clearly illustrated in the following example. In one emulsion, there are 100,000 dispersed particles of 1 μm diameter and 100 particles of 10 μm diameter. By percentage in population, 100, 10-μm-diameter particles are only 0.1% in number of the total particle population. When expressed in volume percentage, these 10-μm-diameter particles represent 50% of the total volume of all the particles. This is because the volume of 100,000, 1-μm-diameter particles is equal to that of the 100, 10-μm diameter particles. In the beverage, if these 10-μm-diameter particles float to the surface and ring, it represents 0.1% of the particles population in the bottle. The percentage of 0.1% is almost insignificant in the ratio of the population. However, in reality, it represents 50% of the total oil volume and it presents a serious ringing problem.

There is another way to express the particle size distribution data—that is, the total "surface area," in square meter (m^2), of the particles in each size category (93). When one oil particle is broken to many smaller particles, the total area of these particles will increase according to their reduced size. However, this method of data presentation is not as commonly used as the volume percentage method. The reason is that it is not as easy and simple to associate the data with the quality of the emulsion as the volume percentage.

VII. STABILITY CRITERIA SETTING

To set the criteria of particle size distribution for determining the stability of an emulsion, one has to realize that the criteria are different for each emulsion because each emulsion has a different composition which influences the physical and chemical properties of the product. Examples of particle size distributions of a typical stable emulsion and an unstable emulsion of orange oil with ester gum in gum arabic solution are shown in Figs. 9 and 10. In Fig. 9, the particle volume percentage of the most critical channel, channel 2 (0.4–0.5 μm), is over 50%, and the total volume percentage of channels 1–5 (0.32–1.0 μm) is over 80%. In Fig. 10, the particle volume percentage of channel 2 is slightly over 30%, and the total volume percentage of channels 1–5 is only over 60%, and there is a heavy-tail portion of particles larger than 1.0 μm. Figure 11 is the composite picture of three histograms. The top one shows the particle size distribution in volume percent of an unstable emulsion. This emulsion was used to make a soft drink. On standing, this bottle of soft drink developed a ring in the

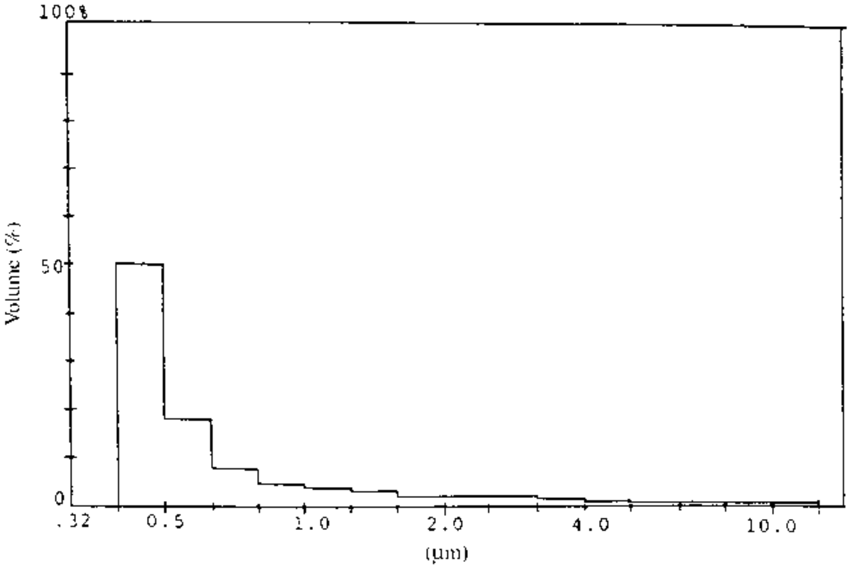


Figure 9 Particle size distribution histogram in volume percentage of a stable emulsion of orange oil plus ester gum in gum arabic solution.

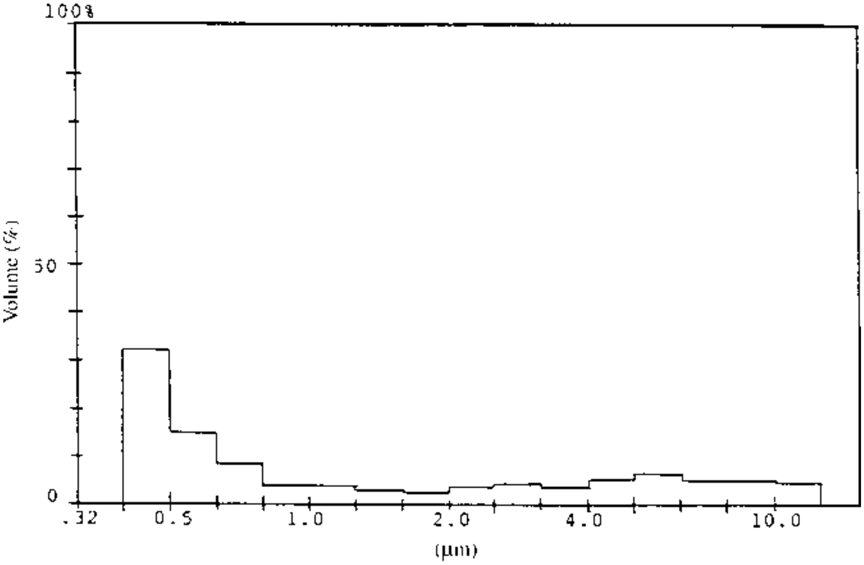


Figure 10 Particle size distribution histogram in volume percentage of an unstable emulsion of orange oil plus ester gum in gum arabic solution.

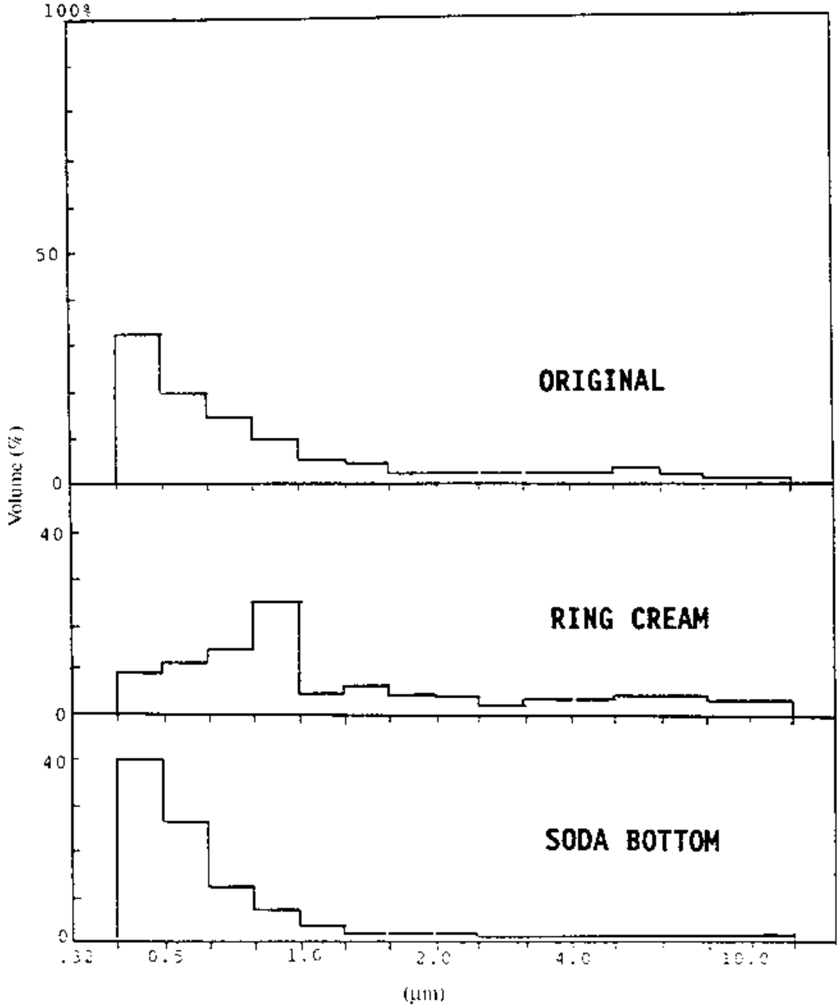


Figure 11 Particle size distribution histogram of (top) an unstable emulsion; (middle) the ringing cream section from a soft drink prepared from the above emulsion; (below) the stable section of the soft drink in the same bottle.

neck of the bottle. The particle size distribution in volume percent of the creamlike ringing material in the neck region is shown in the middle histogram. The bottom histogram shows the particle size distribution in volume percent of the stable emulsion in the nonringing portion of the bottle. The middle and bottom histograms clearly illustrate the particle size distributions difference of the stable portion and the unstable portion of the soft drink made of an unstable emulsion. It has been determined that the particle size distribution shown in the bottom histogram can be used as the criterion for stability for this particular emulsion. No matter which particle size distribution criterion is used, it is first necessary to collect a series of data with regard to the relationship of different particle size distribution patterns to their degrees of ringing. After these data have been obtained from the soft drink system, then the stability criteria can be developed.

VIII. SUMMARY

Beverage emulsions are a unique class of emulsion. They are prepared in the concentrated form first and then diluted in order to prepare the finished beverage. It has to be stable in both the concentrated and the diluted forms, as the water phases are of different compositions. The stability of the emulsion can be achieved by the application of colloidal chemistry principles.

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