

## CALCIUM CITRATE-VEGETABLE OIL COMPOSITIONS

This invention relates to semi-solid to solid, normally liquid vegetable oil compositions and the use thereof, particularly in the food industry.

### CROSS REFERENCE

Commonly assigned U.S. patent application Ser. No. 07/704,500, filed May 23, 1991, which describes certain calcium citrate salt crystals.

### BACKGROUND OF THE INVENTION

Vegetable oils are most desirable natural forms of lipids to be used for diet purpose. The role of lipids, i.e. fats, which are saturated or comprise trans unsaturated fatty acid glycerides in blood circulatory problems is well known. The use of vegetable oils which are comprised of cis-unsaturated fatty acid triglyceride in lieu of the aforesaid saturated fats or trans-unsaturated fatty acid triglycerides has been highly recommended to avoid the blood circulatory problems of the latter fats.

One of the difficulties in implementing this recommendation is the physical form of the desirable vegetable oils, i.e. liquid form, which is not always adaptable for many food uses. In the past, vegetable oils have been converted to the more useful semi-solid to solid state by hydrogenation which results in conversion of the vegetable oils to saturated fat and trans-unsaturated fatty acid glycerides. Therefore, the use of the desirable vegetable oils has been seriously limited in the food industry to only those situations where the liquid oil can be employed.

The dietary importance of low-fat, low-calorie, no cholesterol foods is well-documented in not only the scientific literature but also in the lay press. Considerable research effort has been, and is now being, expended to meet the requirements of new food technology. Thus, low fat food products such as cheeses, mayonnaise, salad dressings, margarines and the like have been developed based on non-fat substitutions in whole or in part for the fat content of classical foods. Such products necessitate new food additives and constituents of the new dietary food compositions. These new additives and constituents are mainly designed to improve appearance, color, mouth-feel, and induce other properties to assure public acceptability of the new dietary compositions. To be successful, such additives and constituents should be food acceptable and compatible with the compositions in which they are employed. For example, titanium dioxide has been used as a whitener in low fat compositions and is found to be compatible in these compositions. However, the food-acceptability of titanium dioxide has been challenged and is rejected in many countries, especially in Europe.

### SUMMARY OF THE INVENTION

The present invention provides new and useful vegetable oil calcium citrate salt compositions which are readily adaptable for use in food compositions, particularly as opacifiers, whitening agents and partial fat substitutes. These and other uses of the present new salt compositions are described hereinafter.

The invention provides semi-solid to solid oil-calcium citrate compositions which are readily adaptable for use in the food industry, thus providing the benefits of natural vegetable oil and mineral oil which heretofore was

not possible. The products thus produced can be made to range from a somewhat viscous consistency, e.g. mayonnaise consistency, to a solid consistency (similar to lard) by simply adjusting the level of calcium citrate employed in the compositions.

### DETAILED DESCRIPTION OF THE DRAWINGS

In the accompanying drawings, FIG. 1 is a plot of viscosity of olive oil at varying concentrations of the specific calcium citrate employed in the present new oil compositions of the inventions (the unfilled circle plot) and commercial calcium citrate, hydrated (the square plot) and the dehydrated form (the black circle plot).

FIG. 2 is a plot of viscosity of the present new compositions against concentration of calcium citrate for soyabean oil (the unfilled square plot) and canola oil (the black square plot).

### DETAILED DESCRIPTION OF THE INVENTION

The present new compositions comprise a finely divided calcium citrate salt of the formula



wherein n is a value from 2.5 to 2.95, preferably from 2.61 to 2.92, and an aqueous slurry (1% by weight) of said salt in water at 25° C. showing a pH value of from about 4 to about 7, and preferably from about 4 to about 5.5.

In general, these calcium citrate crystals are prepared by spray drying a neutralization mixture prepared by neutralizing citric acid with a slurry of calcium oxide/or hydroxide in water, e.e., a slurry of calcium hydroxide under controlled conditions to assure the production of the present new calcium citrate salts. Calcium carbonate can be used to neutralize citric acid, but slow additions and/or large reaction vessels are required to prevent overflow of the reaction mixture due to liberation of carbon dioxide. Temperature, slurry solid content and agitation time before spray drying are critical parameters in determining the physical characteristics of final product.

In particular, the calcium citrate crystals are prepared by first neutralizing citric acid with calcium hydroxide while controlling the rate and conditions of the reaction as well as the degree of neutralization. In the present process, a calcium hydroxide aqueous slurry is reacted with a citric acid solution in water resulting in a strong exothermic reaction. The rate of reaction, concentration of reactants and reaction conditions are all important factors in producing calcium citrate salts of the desired pH values and particle size.

It is preferred to form two separate aqueous systems, one a solution of citric acid and the second, a slurry of calcium hydroxide, and then mix the uniform slurry of calcium hydroxide with the aqueous citric acid. The temperature of the mixture is not allowed to exceed about 60° C. The pH of the slurry so produced after thorough mixing should fall within the range of 4-6 and, if needed, should be adjusted to this range of pH. The slurry is then used in the spray-drying step.

The produced calcium citrate salts are very insoluble in water providing about 0.1% by weight solution at ambient temperature and slightly more soluble in hot water. During preparation of a batch and while waiting for spray drying of the batch, the salts are present in the