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SELF-PROPELLING FOOD MIXTURE

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This invention relates to a self-propelling food mixture and to a process for producing aerated food products.

Over a considerable number of years, it has been recognized that it is desirable to package food formulations together with a propellent gas in aerosol-dispensing containers so that they can be expelled to produce aerated food products. While many different foods and various propellent gases have been proposed therefor, only whipping cream, employing only nitrous oxide or mixtures of nitrous oxide with up to about 15% of carbon dioxide, appears to have met with commercial success. See Patents No. 2,120,297 of Reinecke, No. 2,294,172 of Getz and No. 2,435,682 of Getz, and the article on "Food Aerosols" by Earl Graham reported on pages 57–59 of the Proceedings of the Forty-Second Annual Meeting of the Chemical Specialties Manufacturers Association, December 5, 6, 7 (1955).

Generally, the propellants, such as nitrous oxide, carbon dioxide and the like, are in the form of pressurized gases and, preferably, are soluble to some extent in the food formulations. Such pressurized gases have certain inherent disadvantages. During use, the pressure in the container rapidly decreases so that the final dispensing pressure is far below the initial pressure. Therefore, in order to provide the desired final pressure, it is necessary that the gas occupy a large volume of the container, whereby the permissible volume of the food formulation in the container is approximately half to two-thirds of the total volume of the container. Also, when a pressurized gas is used as the propellant, there is danger of large pressure losses resulting from acidental valve release, from improperly positioned containers during discharge, and from slow leaks in the system, all of which quickly or eventually tend to render the package inoperable. Except for nitrous oxide, the other gases usually suggested for this purpose, such as carbon dioxide, hydrocarbons, difluoro-dichloromethane, and the like, impart a foreign flavor or taste to the food product, which is objectionable to at least some consumers, such as an acid-biting taste or a gasoline-like taste and/or a sensation in the mouth similar to that produced by organic vapors as gasoline or carbon tetrachloride.

A liquefied gas propellant would constitute an important factor in the development of food aerosols. A liquefied gas exists in the container as a liquid whose vapor pressure exceeds atmospheric pressure at the temperature at which the food formulation is to be discharged. A liquefied gas occupies a considerably less volume than a pressurized gas, whereby a much larger volume of the food formulation can be placed in the container. Since the pressure in the container is substantially the vapor pressure of the liquefied gas and is independent of the volume and of the free space in the container, the pressure in the container will be substantially constant throughout the discharge life of the system as long as liquid propellant is present in the container. Also, a liquefied gas provides a liquid reservoir whereby a potentially larger and constant supply of gas is available to guard against large pressure losses through accidental valve releases, leaks, and the like.

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Heretofore, the art has been unable to discover a liquefied gas propellant which was completely satisfactory for use with food formulation. In general, a suitable liquefied gas should have a vapor pressure of from about 4 to about 90 pounds per square inch at the temperatures at which the food formulation is desired to be discharged. It must be harmless to the packager and to the consumer and should present no unusual hazards during packaging, storage and use. It should be substantially inert chemically, i. e. it should undergo no change in properties which might render it useless as a propellant or harmful to the consumer during the life of the pressurized package under conditions likely to be encountered in shipping and in storage prior to its use. It should have no adverse effect on the odor, the flavor, the appearance, the texture, etc. of the discharged food.

While many food products naturally contain material amounts of fluorine, the United States Food and Drug Administration (FDA) prohibits the addition to foods of more than 1.4 parts per million (p. p. m.) of fluorine (Chemistry and Technology of Food and Food Products, Jacobs, vol. I (1944), page 485). Also, the generation of chlorine in any significant amounts in the presence of water yields hydrochloric acid which is corrosive to the containers. In the industry, corrosion tests on containers for aerosol-dispensible food formulations are generally run at 130° F., considered to be the probable upper limit of the range of temperatures to which the package is likely to be exposed for any considerable time before it finally reaches the consumer. Therefore, it is desirable that the propellent be non-corrosive and not produce material amounts of corrosive products or generate fluoride ion at a rate greater than about one part per million parts of the medium per year at 130° F. when in contact with neutral, basic and acidic aqueous media characteristic of foods and aerosol-dispensible food formulations.

Hydrocarbon liquefied gases are unsatisfactory because they impart an objectionable (gasoline-like) taste to bland foods, and present a potential fire hazard in packaging and in certain applications, such as in the dispensing of pancake batter onto a hot greased skillet or grill. Chlorinated hydrocarbons, such as methyl chloride, are unsuitable because of their reactivity towards water and many food substances whereby they constitute potential and likely sources of appreciable and undesirable quantities of corrosive hydrochloric acid, and because they impart objectionable odor or taste to the food products. Highly halogenated compounds containing chlorine and a plurality of fluorine atoms are generally regarded as being inert, non-corrosive, relatively non-toxic and hydrolytically stable. Such terms, however, have meaning only within a definite frame of reference. Some of such highly halogenated compounds, such as dichlorodifluoromethane and sym-dichlorotetrafluoroethane, are recognized to be substantially non-corrosive and have been classified in group 6 of the Underwriters' Laboratories toxicity classification of refrigerants, i. e. compounds which appear to produce no injury when the vapors are in concentrations up to at least 20% by volume for durations of exposure of at least 2 hours. Carbon dioxide is classified in group 5, a group of more harmful compounds. However, it has been found that dichlorodifluoromethane and dichlorotetrafluoroethane do not have the desired hydrolytic stability to prolonged contact with aqueous media at the high temperatures to which many packaged foods are subjected, for example, at the temperatures prevailing in storage and in shipping in and through tropical and desert areas. Furthermore, these compounds adversely affect the taste of many foods and are unsatisfactory for general use with aerosol-dispensible food formulations.

It is an object of this invention to provide self-propelling food mixtures in which the propellant consists essentially of a liquefied gas and a process for producing aerated food products by the use of such propellant. A particular object is to provide such products and such process wherein the liquefied gas is non-corrosive to the container, is chemically inert, is non-toxic, is sufficiently stable to hydrolysis so that it does not increase the fluoride ion concentration of food formulations to an objectionable extent, and has no adverse effect on the odor, taste, appearance, body and texture of the dispensed food. Another object is to provide such products and such process in which the propellant is a mixture of said liquefied gas and a minor proportion of a pressurized gas to increase the pressure in the container, which pressurized gas is soluble in the liquefied gas and is also non-corrosive, chemically inert, non-toxic, comparably stable to hydrolysis, and free of adverse effects on the dispensed food. Other objects are to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished in accord with this invention which comprises charging an aerosol-dispensing container with an aerosol-dispensible edible food formulation which contains water as a constituent, then charging said container under a pressure corresponding to about 26 to about 90 pounds per square inch gage (p. s. i. g.) at 70° F., preferably about 26 to about 60 pounds, with a propellant of the group consisting of liquefied perfluorocyclobutane and mixtures of liquefied perfluorocyclobutane with a minor proportion of at least one of chlorotrifluoromethane, tetrafluoromethane and chloropentafluoroethane. Thereby, there is provided a self-propelling food mixture confined under pressure in an areosol-dispensing container, said food mixture consisting essentially of the food formulation and a propellant which consists of perfluorocyclobutane or a mixture of perfluorocyclobutane with a minor proportion of at least one of chlorotrifluoromethane, tetrafluoromethane and chloropentafluoroethane, the perfluorocyclobutane being mainly in liquefied form. To dispense the food formulation, the valve of the container is opened to release the pressure whereby the contents of the container are expelled under the pressure of the propellant. Preferably, the container is shaken to mix the contents thereof prior to releasing the pressure.

The aerosol-dispensing container employed is of conventional form and construction well-known to the art, particularly those designed for dispensing food formulations. Such containers are generally constructed of metal and provided with manually operated valves for discharging the contents thereof. Representative containers are disclosed by Reinecke in Patent No. 2,120,297 and Getz in Patent No. 2,294,172. The specific form and construction of the container does not constitute any part of this invention.

The aerosol-dispensible food formulations, which are to be employed in this invention, are those which contain water as a constituent and include whipping cream, dessert toppings of all kinds, custards, cake frostings, syrups, ice cream mixes, cake batters, pancake batters, cheese spreads such as those of the cottage cheese type, mayonnaise, eggs, salad dressings such as French dressing, catsup, mustard, peanut butter, and the like. The particular food or food formulation is not important to this invention, so long as it is aerosol-dispensible; that is, it must be of such fluidity or viscosity that it can be readily discharged from an aerosol-dispensing container by a gas pressure in the range of from about 4 to about 90 pounds per square inch gage. While many foods are not aerosol-dispensible when in their normal state, they can be suitably modified or formulated to render them aerosol-dispensible by various techniques known to the art, as by the addition of edible fluidizing agents such as water or milk solids and/or edible emulsifying agents, or by physically reducing the particle size of any solids therein to less than about 200 microns. For best results, it will generally be desirable to include an emulsifying agent in the food formulation so as to render the formulation emulsifiable with the propellant. Ideally, the food formulation and the propellant, on mixing and shaking, should form a uniform emulsion to ensure a uniform discharged product (uniform in appearance, texture, body, etc.) throughout the period of discharge. When these emulsions are discharged, the steady evaporation of the liquefied gas propellant results in "aerated" products having better overrun (i. e. greater increased volume), more stable (more permanent) foamed structure and less bleed (less serum separation) than those obtainable with the conventional pressurized gas propellants.

Perfluorocyclobutane has the formula

$$\begin{array}{c} CF_2-CF_2 \\ | \quad\quad | \\ CF_2-CF_2 \end{array}$$

At normal atmospheric temperatures and pressures, it is a colorless, odorless gas, boiling at −6.04° C. (21.1° F.) at 760 mm. mercury pressure and freezing at −41.4° C. (−42.5° F.). It may be prepared as described by Downing et al. in Patent No. 2,384,821, and is obtainable in a purity satisfactory for use as a propellant for food formulations by fractional distillation of the crude product. It is easily liquefied at the pressures normally desired in pressurized conventional aerosol-dispensing containers, and, in liquefied form, has a vapor pressure of abut 26 pounds per square inch gage at 70° F. It is nonflammable in air in all proportions under all conditions of test. It has been found to be non-corrosive under normal conditions to ordinary metals of construction such as steel, cast iron, brass, copper, tin, lead, zinc and aluminum, and to practically all metals at temperatures up to 120° C. (248° F.) even in the presence of oils, water and/or methanol; e. g., cast iron, steel, stainless steel, Inconel, nickel, platinum, Babbitt metal, silver solder and soft solder.

Toxicological tests indicate perfluorocyclobutane to be non-toxic and to fall into group 6 of the Underwriters' Laboratories classification. For example, two guinea pigs were subjected to an atmosphere containing perfluorocyclobutane in a concentration of 1.9% by volume at room temperature for six hours—one exposure only. One of the animals showed no effect either during exposure or on subsequent observations for one week. Pathological studies indicated neither gross nor microscopic change. The other animal, although showing no effect during or after exposure, gave indications of slight focal congestion in the lung upon pathological examination.

Although substantially insoluble in aqueous and oil-based food formulations, perfluorocyclobutane is readily emulsified with those food formulations that are to be discharged as emulsions, and is chemically inert to the food formulations. It does not impart any objectionable or foreign flavor to the food formulations.

Perfluorocyclobutane may be employed as a liquefied gas propellant with any aerosol-dispensible food formulation and is particularly useful with those formulations which contain water as a naturally occurring component or which are formulated with water as an added ingredient. Virtually all edible foods (with certain exceptions such as salad oils and cooking oils) containing appreciable quantities of water. Although foods may be classed primarily as fat-based (e. g., whipping cream) or sugar-based (e. g., custards) or protein-based (e. g., cheese spreads), they all contain water as a component, usually emulsified with the organic constituents, and may be considered to be aqueous-based foods for the purposes of this invention. The aqueous-based food formulations to which this invention applies may be homogeneous solutions or emulsions in which water is a component.

For a fluorinated hydrocarbon to undergo hydrolysis at a measurable rate corresponding to small parts per million per year, it is obvious that only minute quantities of water need to be involved. On this basis alone, it should be apparent that virtually all of the aerosol-dispensible food formulations contain relatively tremendous quantities of water, quantities which are small in proportion to the total quantity of food but which are very large compared to the stoichiometric quantities of water that need be involved in the hydrolysis of the propellant.

Surprisingly and unexpectedly perfluorocyclobutane is essentially completely inert under hydrolytic conditions of storage at temperatures of from 100–130° F., i. e. it generates fluoride ion at a rate less than 1 part of fluoride ion per million parts of aqueous medium per year at these temperatures. This substantially negligible rate of formation of fluoride ion is indicative of the high degree of chemical inertness and hydrolytic stability of perfluorocyclobutane towards aqueous food formulations under extreme conditions of storage. Normally, a pressurized food package will not be subjected to such a relatively high temperature for such a prolonged period of time. However, it is to be expected and perhaps it will not be too unusual to find that as much as a year may elapse between the packing of and the consuming of the containers' contents. Part of this time, particularly under certain conditions of shipping and storing these products, as in freight cars or warehouses in hot climates, the package may be subjected to temperatures as high as 100–130° F.

For an aerosol-dispensed food product to be acceptable to the consumer, it must have the expected appearance, odor, and flavor. In certain foods such as whipped cream, dessert toppings, and cake frostings, the appearance (including body and texture) of the food as dispensed is of prime importance to the consumer. Also since these, and indeed the majority of foods, are bland foods, any odor and flavor other than that expected by the consumer on the basis of past experience is likely to be rejected as unacceptable. This problem of off-taste is generally encountered with liquefied gas propellants in bland or delicately flavored foods. It is less often a problem in highly seasoned foods. However, since the majority of foods are essentially bland and/or are expected to have particular characteristic flavors, the acceptability of almost all foods which are to be consumed directly, will depend upon how closely such goods meet expectations. In fact, it might well be said that a foreign flavor is readily detectable by some in any food, bland or otherwise. In this respect, perfluorocyclobutane is universally satisfactory, being substantially odorless and tasteless and chemically inert, i. e. it does not give rise to objectionable odors and flavors while in storage in contact with the food formulations.

As an all-purpose liquefied gas propellant for food formulations, perfluorocyclobutane is substantially as good as or is superior to the convetnional pressurized gas propellants in dispensing such typical foods as cake frosting, cheese spreads and cake batters having the expected appearance, body and texture.

The pressure-temperature relationship of perfluorocyclobutane is such that the propellant is normally gaseous at the temperatures at which the food formulation is to be discharged, and yet is safely maintained as liquid in equilibrium with its vapor in conventional low pressure containers. By normally gaseous, is meant that its boiling point at atmospheric pressure lies below the normal discharge temperatures, which will usually range from home refrigeration temperatures of about 0–10° C. up to room temperatures. Over this temperature range, the vapor pressure of the propellant will ordinarily be from about 4 to about 30 pounds per square inch gage, which is sufficiently high to ensure adequate discharge of the aerosol-dispensible food formulations from the conventional low pressure containers.

In principle, all that is needed for the food formulation to be discharged from the container is a positive pressure differential between the contents of the container and the outside atmosphere. However, the more viscous the food formulation the greater this pressure differential has to be in order to obtain a practical rate of discharge. For relatively fluid food formulations of low viscosity such as whipping cream, dessert topping, some chocolate syrups and salad dressings, catsup, mustard and the like, a few pounds of positive pressure suffice. With more highly viscous food formulations such as peanut butter spreads, cake batters, cake frosting, marshmallow topping, cheese spreads, etc. a greater pressure differential is needed. In general, a pressure within the container of about 60 lbs./sq. in. gage is sufficient to ensure adequate discharge of the most viscous aerosol-dispensible food products. Where such high internal pressures are needed, they may be obtained by a mixture of the perfluorocyclobutane with a minor proportion of at least one more volatile auxiliary propellant, selected from chlorotrifluoromethane, tetrafluoromethane and chloropentafluoroethane. The auxiliary propellant advantageously may be in the form of a pressurized gas because only small proportions thereof are needed to obtain substantial boosts in the initial pressure. Also, since these auxiliary propellants are soluble in the liquefied perfluorocyclobutane, they are lost from the system less rapidly than insoluble gases and thus exert their booster effects over a longer period of time. Chlorotrifluoromethane and tetrafluoromethane are preferred as the auxiliary propellants or booster gases.

The maximum permissible pressures are limited by the strength of the particular container. In general, in the conventional metal container of the aerosol industry, a pressure of about 90 lbs./sq. in. gage at 70° F. or 125 lbs./sq. in. gage at 130° F. is the upper allowable limit to meet Interstate Commerce Commission requirements for shipping most food products. The auxiliary propellant usually will be in a proportion sufficient to increase the pressure in the container to about 40 to about 90 pounds per square inch gage at 70° F., preferably about 40 to about 60 pounds, but may be used in smaller amounts to obtain pressures between 26 and 40 pounds when such intermediate pressures are desired. The pressures exerted by mixtures of liquefied perfluorocyclobutane and the booster gas are dependent upon the mole fractions of the propellent components and their partial pressures. The proportion of each component of the mixture which is required to produce a desired pressure at any given temperature can be calculated by one skilled in the art from known data or readily determined empirically. Usually, the mixtures employed will consist of about 99% to about 90% by weight of perfluorocyclobutane and about 1% to about 10% by weight of the more volatile propellant, preferably about 98% to about 96% of perfluorocyclobutane and about 2% to about 4% of the more volatile propellant. For example, a mixture consisting of 96% by weight of perfluorocyclobutane and 4% by weight of chlorotrifluoromethane will provide a pressure of about 60 pounds per square inch gage at room temperatures; 99% of perfluorocyclobutane and 1% of chlorotrifluoromethane provides a pressure of about 40 p. s. i. g.; and 93–92% of perfluorocyclobutane and 7–8% of chlorotrifluoromethane provides a pressure of about 90 p. s. i. g.

The auxiliary propellants (chlorotrifluoromethane, tetrafluoromethane and chloropentafluoroethane) are colorless, odorless gases under normal conditions, are nonflammable in any mixture with air, are unusually inert chemically, and are non-corrosive to ordinary metals of construction, e. g., steel, cast iron, brass, copper, tin, lead, zinc and aluminum, under normal conditions. Preliminary toxicological tests indicate that they fall in Group 6 of the Underwriters' Laboratories classification, i. e. no evident toxicity. Their resistance to hydrolysis and generation of fluoride ion in the presence of water is of the order of that for perfluorocyclobutane and very much greater than that of dichlorodifluoromethane. They do not impart any objectionable taste to the food formulations.

In the self-propelling food mixtures of this invention, the propellant may be emulsified with the food formulation or it may be present as a separate and discrete layer. The quantity of propellent employed should be such as to provide a liquid phase of propellant initially and throughout the discharge life of the package. This quantity may be from about 3% to about 10% by weight of the total contents of the container, preferably, from about 5% to about 10% by weight. Materially larger quantities, while operable, are wasteful. Conventionally, the aerosol-dispensing container is incompletely filled with liquid so that there is a small free space above the liquid contents thereof. This free space is occupied by vapors of the propellent. Such vapors constitute a minor proportion of the propellent, whereby the perfluorocyclobutane is mainly in liquefied form and, when the auxiliary propellants are present, they are mainly in solution in the liquefied perfluorocyclobutane.

In order to more clearly illustrate this invention, preferred modes of practicing it, and the advantageous results to be obtained thereby, the following examples are given in which the propellent compounds were pure, as obtained by careful fractional distillation, their infrared spectra showing no detectable impurities, and in which the proportions are by weight except where otherwise specifically indicated.

EXAMPLE 1

A whipping cream concentrate of the following composition was prepared:

Component:	Weight percent
Heavy cream	70
Skim milk	18.12
5% gum tragacanth solution [1]	5.25
Sucrose	6.25
"Dricoid" [2] stabilizer-emulsifier	0.38

[1] Emulsifying agent and food preservative.
[2] Understood to be an algin-emulsifier composition recommended by the manufacturer as a stabilizer-emulsifier for ice cream and pressurized whipping cream.

90 grams of the above formulation was added to a 6 oz. aerosol can. Air was purged from the can by passing perfluorocyclobutane vapor through the contents of the can. The can was capped with a foam valve and liquefied perfluorocyclobutane (10 grams) was added to the can through the valve by means of a conventional pressure loader. The pressure within the can was approximately 26 lbs./sq. in. gage at room temperature. The mixture was shaken briefly by hand and then discharged at room temperature. A fluffy light-bodied cream having good foam structure was obtained. As judged by a panel of 13 tasters, there was no foreign flavor in this product—the taste was that of fresh whipped cream.

When essentially the same pressurized food formulation was employed but with sym-dichlorotetrafluoroethane as the liquefied gas propellant, all in a panel of 7 tasters found the discharged whipped cream to have an unacceptable foreign flavor.

In a similar experiment, where isobutane was employed as the liquefied gas propellant, 6 out of 7 tasters found the flavor of the discharged whipped cream objectionable.

Similarly, Example 1 was repeated employing 10 grams of dichlorodifluoromethane as the liquefied gas propellant instead of perfluorocyclobutane. The flavor of the discharged whipped cream was rated objectionable by 8 out of 12 tasters.

Results of the taste tests are summarized below in tabular form. The designation "gas" means pressurized gas propellant; "liq." means liquefied gas propellant.

Taste test—Whipping cream

Propellant	Type	Objectionable flavor
1. N_2O/CO_2	Gas	No.
2. CHF_3	do	No.
3. $CClF_3$	do	No.
4. CF_4	do	No.
5. N_2	do	No.
6. CH_4	do	No.
7. Isobutane	Liq	Yes.
8. $CHClF_2$	Liq	Yes.
9. CCl_2F_2	Liq	Yes.
10. $ClF_2C–CClF_2$	Liq	Yes.
11. 1,1,1-chlorodifluoroethane	Liq	Yes.
12. Chloropentafluoroethane	Liq	No.
13. Perfluorocyclobutane	Liq	No.

EXAMPLE 2

To 300 parts of a commercially available cake frosting mix, whose exact composition was not determined but which is understood to consist essentially of sugar, dried egg-white (or an egg-white substitute), was added 235 parts of water, 8 parts of glyceryl monostearate and enough vanilla extract to season, and the mixture was stirred to a creamy consistency.

308 grams of the above masterbatched cake frosting mix was added to a 16 oz. aerosol can, and purged of air by perfluorocyclobutane vapor. The can was capped with a foam valve. Then 30 grams of liquefied perfluorocyclobutane was added, as described in Example 1. (The total charge in the 16 oz. can represents an 80% fill.)

Shaking to mix and then releasing the valve at room temperature yielded an 88% discharge of the contents of the can as a firm white cake frosting having excellent texture and taste.

A control experiment was performed using an 85/15% mixture of nitrous oxide and carbon dioxide (3 grams) as a pressurized gas propellant in place of the subject liquefied gas propellant. A full pressure of 100 p. s. i. g. developed after the can was shaken to obtain good mixing and solution of the gases. The discharged product was in the form of a liquid paste which did not resemble a frosting and hence was judged to be inferior and unacceptable to the consumer in regard to appearance and texture.

EXAMPLE 3

A blank cheese paste was prepared by blending 1.5 pounds of cream cheese with 0.5 pint of single cream. Portions of this paste were placed in conventional aerosol cans and pressurized according to the standard methods with various propellants. The cheese spread in each can was discharged and tested for flavor. Liquefied perfluorocyclobutane contributed no foreign taste whatsoever to the product. The 85/15% mixture of nitrous oxide and carbon dioxide as a pressurized gas propellant was also judged satisfactory in this test. However, isobutane and sym-dichlorotetrafluoroethane, as liquefied gas propellants, imparted a strong foreign flavor to the discharged product that made it unpalatable. The same cheese spread, discharged by 1,1-difluoroethane as the propellant, was objectionably flavored to some tasters.

A mixture of propellants, consisting of 96% by weight of liquefied perfluorocyclobutane mixed with 4% by weight of chlorotrifluoromethane, was satisfactory in this test. The discharged product had a curdy appearance and had no detectable off-taste.

EXAMPLE 4

A pressurized maple syrup was packaged in a 4 oz. plastic coated glass bottle (a standard package for aerosols) using 127 grams of commercial syrup and 14 grams of perfluorocyclobutane as a liquefied gas propellant. In this system, the propellant forms the bottom layer, and the dip tube of the standard foam valve was cut off so that the tip of it was just above the syrup-propellent interface. When the valve was released, a steady discharge of syrup was produced.

EXAMPLE 5.—HYDROLYTIC STABILITY TESTS

The method employed involves storing liquefied propellant in contact with an aqueous solution in conventional aerosol containers at constant temperature. At the end of the test period, the aged containers were cooled, opened and the aqueous contents filtered. The fluoride ion content of the filtrate in parts per million was determined by a colorimetric method using thorium nitrate as reagent and sodium alizarin sulfonate as indicator, and calculated as parts per million per year. The analytical procedure was checked against controls of known fluoride ion content.

The test containers were 6 ounce (unless otherwise noted) lacquer-lined tinplate cans capped with lacquer-lined blank caps. In each test, the quantities of propellant and water were sufficient to have each present at least partly in the liquid state at the test temperatures. The controls contained aqueous solution but no propellant. The quantity of fluoride ion produced in the propellent-aqueous systems, less that of the controls, was taken as the fluoride ion content of the samples.

Typical results are given in Tables I and II below:

TABLE I

Hydrolytic stability of perfluorocyclobutane

[Charge: 100 g. aqueous solution plus 10 g. perfluorocyclobutane.]

Test	Aqueous solution	Temp., ° F.	Time, months	Fluoride ion	
				Found	P. p. m./time extrapolated
1	Water	130	6	0.09	0.18/yr.
2	3% sodium bicarbonate	130	6	0.43	0.86/yr.
3	3% acetic acid	100	3	Nil	Nil.

In a similar series of tests, using 100 g. aqueous solution plus 6 g. perfluorocyclobutane at a storage temperature of 70° F., the quantity of fluoride ion produced at the end of 4 months of storage was in each test nil (i. e., substantially zero).

TABLE II

Hydrolytic stability of dichlorodifluoromethane

[Charge: 100 g. aqueous solution plus 11 g. dichlorodifluoromethane.]

Test	Aqueous solution	Temp., ° F.	Time, months	Fluoride ion	
				Found	P. p. m./time extrapolated
4	Water	130	1	0.29	3.5/yr.
5	3% sodium bicarbonate	130	1	2.6	31.2/yr.
6	3% acetic acid	130	1	21.1	253/yr.

In a similar series of tests, charges consisting of 200 g. aqueous solution plus 12 g. dichlorodifluoromethane in 12 oz. cans which were stored for 3 months at 70° F. produced the following results: 0.06 p. p. m. in water; 0.09 p. p. m. in 3% $NaHCO_3$; 0.28 p. p. m. in 3% acetic acid.

Comparison of the above storage data shows that perfluorocyclobutane is hydrolytically more stable than dichlorodifluoromethane, particularly at temperatures greater than 70° F.

When cans containing water were pressurized with each of chlorotrifluoromethane, tetrafluoromethane, and chloropentafluoroethane to a pressure corresponding to 60 pounds per square inch gage at atmospheric temperature and then stored at 130° F. for 2 to 5 months, the fluoride ion generation was nil. Thus, these compounds were found to generate fluoride ion at a rate much less than 1 part per million per year.

It will be understood that the preceding Examples 1 to 4 have been given for illustrative purposes solely, and that this invention is not limited to the specific embodiments disclosed therein. On the other hand, the food formulations, the proportions of the propellants, the composition of the mixed propellants, and the techniques disclosed may be varied as desired within the limits hereinbefore set forth in the general description without departing from the spirit or scope of this invention.

It will be apparent that this invention provides a novel combination of an aerosol-dispensible food formulation and a novel propellant therefor which is chiefly in the form of a liquefied gas and which has many advantages over the propellants heretofore used and proposed for use with food formulations and which overcomes the problems presented by prior propellants. Also, this invention provides a process for producing and dispensing aerated food products by such novel propellants. Accordingly, this invention constitutes a valuable contribution to and advance in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A self-propelling food mixture confined under pressure in an aerosol dispensing container, said mixture consisting essentially of an aerosol-dispensible edible food formulation containing water as a constituent and a propellant for said food formulation which propellant is a member of the group consisting of perfluorocyclobutane which is mainly in liquefied form and mixtures of said perfluorocyclobutane with at least one of chlorotrifluoromethane, tetrafluoromethane and chloropentafluoroethane in a minor proportion sufficient to increase the pressure in the container up to about 40 to about 90 pounds per square inch gage at 70° F.

2. A self-propelling food mixture confined under pressure in an aerosol dispensing container, said mixture consisting essentially of an aerosol-dispensible edible food formulation containing water as a constituent and a propellant for said food formulation which propellant consists of perfluorocyclobutane which is mainly in liquefied form.

3. A self-propelling food mixture confined under pressure in an aerosol dispensing container, said mixture consisting essentially of an aerosol-dispensible edible food formulation containing water as a constituent and a propellant for said food formulation which propellant consists of a mixture of perfluorocyclobutane which is mainly in liquefied form and chlorotrifluoromethane in a minor proportion sufficient to increase the pressure in the container up to about 40 to about 90 pounds per square inch gage at 70° F.

4. A self-propelling food mixture confined under pressure in an aerosol dispensing container, said mixture consisting essentially of an aerosol-dispensible edible food formulation containing water as a constituent and a propellant for said food formulation which propellant consists of a mixture of about 96% by weight of perfluorocyclobutane which is mainly in liquefied form and about 4% by weight of chlorotrifluoromethane.

References Cited in the file of this patent

UNITED STATES PATENTS

2,435,682 Getz ---------------- Feb. 10, 1948

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,849,323 August 26, 1958

Edmond G. Young

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 55, after "vapors" insert -- such --; column 4, line 31, for "abut" read -- about --; column 8, line 47, for "blank" read -- bland --.

Signed and sealed this 4th day of November 1958.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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