

Patented July 11, 1933

1,917,249

UNITED STATES PATENT OFFICE

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EMULSION

No Drawing. Application filed August 15, 1930, Serial No. 475,623. Renewed October 5, 1932.

My invention relates in general to improved emulsions and emulsion improving substances. It relates more specifically to an improved non-spattering type of margarine and anti-spattering substances for use with margarine.

By means of my new products I am able to impart superior qualities to many types of emulsions, particularly emulsions of fats and oils used for culinary purposes, but I shall explain the same in connection with improvements in margarine. Those skilled in the art are referred to my prior application Serial Number 383,143, filed on August 2, 1929, for a more complete disclosure of certain details of the invention than is made herein. I wish also to call attention to my co-pending application Serial Number 475,622, filed August 15, 1930, as a continuation in part of application Serial Number 383,143, filed August 2, 1929.

In general the present invention represents a specific embodiment of the main invention disclosed in the co-pending application above referred to, and while the present disclosure is substantially complete in so far as it describes the invention and supports the claims, those interested in the art are referred to the co-pending case for a more complete disclosure of the basic concept of the invention.

The principal object of my present invention is to improve such forms of emulsions as margarine.

Another object is to reduce the spattering of margarine when used for frying purposes and generally improve its frying behavior.

Other objects and features of the invention will be apparent from a consideration of the following detailed description.

As was disclosed in my prior applications, I have discovered a large class of chemical compounds which may be used to impart improved characteristics to all types of water-oil emulsions, particularly those used for cooking purposes, and other types of culinary fat preparations. These substances have several characteristics in common which make them very valuable in their use with margarine. These substances are compatible with mild acids and in particular with lactic acid in the

concentration and under the conditions existing in margarine. In general they are difficultly soluble in oils and fats and aqueous media and in many cases are substantially insoluble. This makes it possible to use these compounds in most cases in very small quantities, as they may be considered to concentrate at the water-oil interface of the emulsion rather than be freely dissolved in either the water or oil phase. These substances are semi-colloidal or truly colloidal in character and are frequently colloiddally dispersible in aqueous and/or oleaginous media. They are, moreover, substantially non-volatile at margarine frying temperatures and so will remain in the margarine and perform their function during frying.

One of the most important characteristics of these compounds is the presence in the molecule of two types of groups in balanced relation to each other, one group being hydrophylic or water wetting in character, and the other group being lipophylic or fat wetting in character. These groups must exist in the molecule in such a state of balance that they will function at the water-oil interface in the intended manner. Presumably these substances orientate themselves at the interface, by reason of the balance of the two types of groups, but it is understood that the invention does not depend upon this explanation.

My prior application treats exhaustively of the manner in which the balance between the two groups may be determined so that without tests of any kind it is possible for the skilled colloid chemist to pick out compounds which can not function effectively as anti-spatterers, as well as compounds which clearly will be effective as anti-spatterers.

However, there are compounds of such character that the state of balance existing between the two groups in the molecule is preferably determined by a simple quick test.

The balance of the hydrophile-lipophile groups in the compound which I employ in my invention is one of the characteristics and determinants of the class of substances which I employ.

The test which I have chosen as a means for

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determining the hydrophile-lipophile balance in organic compounds, I call the "spoon test". It is carried out as follows: From 0.05 to 0.10 gr. of the material or substance in question is introduced into a porcelain mortar, wetted, and ground into a smooth paste with a pestle with a minimum proportion of water; two to five drops generally will suffice.

10 An ordinary margarine such for example as one made from vegetable oils, and fats, and cultured skimmed milk, and which possesses the usual property of spattering during frying is selected. Ten grams of this margarine are then introduced in small portions into the mortar and macerated thoroughly with the paste first prepared until the entire ten gram portion is thoroughly and uniformly intermixed with the material in the mortar. Two grams of this mixture are introduced into a tablespoon and held directly over a free flame such for example a Bunsen flame, one or two inches long in such a position that the point of the flame just about reaches the bottom of the spoon. A clean sheet of paper is placed on the bottom of the burner by inserting the stem of the Bunsen burner prior to lighting through a hole made in the center of the paper and allowing the paper to drop to the base of the burner to catch the margarine splashed out during the heating. The mixture in the spoon is heated until all of the water is boiled off and the ebullition ceases and the spots on the paper observed.

35 If this treated margarine spots the paper to the same extent as the untreated margarine from which the former was prepared, then the lipophile and hydrophile groups of the compound are not balanced. The number and size of spots on the paper or the added weight can be readily determined.

If the increase in weight of the paper or the number and character of the spots produced on the paper up until all the water has boiled off are less than that produced by similarly heating two grams of the original untreated margarine employed for the test, then the material in question has balanced hydrophile-lipophile groups. The expression "balanced lipophile and hydrophile groups" used in the claims is to be interpreted in terms of the above described "spoon test".

My present invention has to do with a certain class of compounds of this general character, these new compounds all being characterized by the presence of hydroxy groups attached to carbon, and the hydrophylic function being exercised primarily by such hydroxy groups. These compounds contain at least one —OX group linked to carbon, wherein "O" represents oxygen and "X" stands for an edible cation.

Examples of some of the hydroxy substances which I have used as anti-spattering agents, many of them not known heretofore,

and the preparation of many of which is described herein, are as follows:

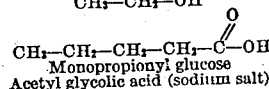
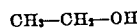
"Stearic acid ester of glucose"
"Stearic acid esters of polyglycerols"

Stearyl sucrose 70
Palmityl lactose
Stearyl tartaric acid
Stearyl citric acid (sodium salt)
Digitonin
Digitonin cholesteride 75
Stearyl glycolic acid (sodium salt)
Stearyl malic acid
Palmityl mucic acid
Stearyl mannitol

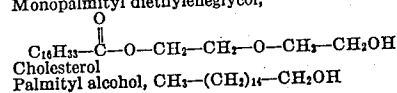
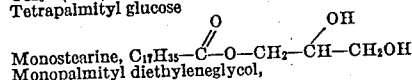
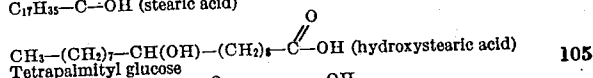
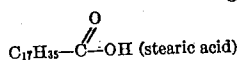
It is to be noted that in every case, the anti-spattering agent has been produced by associating a lipophile group with a hydrophile group wherein the hydrophile function is supplied primarily by hydroxyl groups, or by hydroxyl groups wherein the hydrogen is replaceable by metal. However, the conclusion must not be drawn from this that any random combination of hydroxyl groups or their metal derivatives with a lipophile group will give an anti-spatterer.

Examples of molecules which contain —OX groups as well as a lipophile group, but which nevertheless are not anti-spatterers are as follows:

Class A



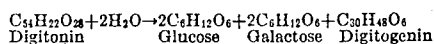
Class B



In the case of compounds of both Class "A" and Class "B", anti-spattering powers are lacking because of inadequate balance between the lipophile and hydrophile groups. In the case of compounds of Class "A", the hydrophile group dominates and is inadequately balanced by the lipophile group, that is, the lipophile characteristics of the latter are too weak to adequately balance and co-act with the hydrophile group. In the case of substances of Class "B", the reverse situation exists and anti-spattering power is absent because the lipophile group is dominant and is inadequately balanced by the hydrophile group.

Glucosides and glucoside-like substances, such as some of the saponins, in which the lipophyllic and hydrophylic functions are qualitatively balanced, represent anti-spatter-

terers in which the hydrophylic function is dependent largely, if not entirely, on —OX groups. Digitonin is a case in point. As is well known, digitonin yields four molecules of sugar on hydrolysis, as indicated hereinbelow:



Digitonin is an effective anti-spatterer in which, apparently the large accumulation of hydroxyl groups, furnished particularly by the sugar residues, supplies sufficient hydrophylic character to balance the digitogenin.

The saponin sterides, again, are anti-spatterers, in which hydroxyl groups play the principal, if not the entire hydrophylic role. Digitonin cholesteride, prepared according to the method of Windaus (Hoppe-Zeyler's Z. fur Phys. Chem. V. 65 (1910) pp. 110 to 117), is a good example of a saponin steride acting as an anti-spatterer.

In general, I use relatively small proportions of the anti-spattering agents, up to 2% and in some instances as little as .1%, or less, but sufficient to effectively improve the frying behavior of the margarine; however, larger proportions may be used if desired.

I do not by any means restrict the use of these anti-spattering agents to margarine, inasmuch as they have many useful colloidal properties and can function as wetting, detergent, penetrating, emulsifying, frothing and foaming agents in the arts where such materials are employed. In fact, even in margarine, they function in other ways than merely to improve the frying characteristics.

One of these additional improvements is that the margarine is much less likely to leak and suffer from so-called "weeping" by virtue of the fact that the anti-spattering agent improves the emulsion in such a way that the water phase is much more tenaciously held in the margarine than otherwise.

A general method for the preparation of the anti-spattering agents with which the present application is concerned is to dissolve or suspend the hydroxy substance, freed of moisture, by drying or otherwise, in dry pyridine, with heating if necessary, cooling this mixture and introducing into it the required amount of acyl chloride with agitation, either as such or dissolved in an inert solvent such as chloroform or carbon tetrachloride, care being taken throughout to exclude moisture as far as possible and to cool so as to control the heat of the reaction. The mixture is then allowed to stand at room temperature or is agitated at room temperature for six or eight hours or longer, and is then poured into iced dilute sulphuric acid or some other acidulating agent. The product generally separates out, in the case of the acyl chloride of solid fatty acids, as a flocculent solid and in cases where acyl chlorides of liquid fatty acids have been used, generally speaking, as a liquid or

semi-liquid material. It may then be washed several times with water or with brine at room temperature or with the application of heat and finally separated from the water and dried.

A case in point is the method by which I prepare an anti-spattering ester of glucose. I prepare the "stearic acid ester of glucose" as follows: Four parts of glucose (anhydrous) were dissolved in thirty parts of dry pyridine, by warming. This solution is cooled and seven parts of stearyl chloride are added to it in small portions, with simultaneous agitation and cooling. This mixture is allowed to stand at room temperature for twenty-four hours and is then poured into iced, dilute sulphuric acid. The solid material is washed several times with water and dried. This crude product which consists principally of monostearyl glucose, shows a relative anti-spattering power of approximately 90% when introduced into margarine in the proportion of one-half of one percent.

In this procedure other basic materials such as dimethyl aniline, quinoline, or quinoline may be substituted for the pyridine. Also, the acylation may be carried out in a different medium or in an aqueous medium using a basic material such as calcium hydroxide or carbonate to take care of the hydrochloric acid formed during the course of the reaction.

The products may be purified, if desired, by recrystallizing from solvents.

Some of the anti-spatterers of the class described herein which I prepared by the pyridine method are listed hereinbelow, with the proportions of the reacting materials used, indicated. The comparative anti-spattering powers of the fatty acid esters thus obtained are also shown. These anti-spattering powers were determined by the method described in full in my co-pending application, Serial Number 383,143.

Hydrophile hydroxy substance	Acyl chloride	Pyridine	Comparative anti-spattering power of the product
8.5 parts sucrose	8 parts stearyl chloride	60 pts. pyridine	Good
5 pts. tartaric acid	10 pts. stearyl chloride	60 parts pyridine	Fair
5 pts. citric acid	9.5 pts. stearyl chloride	60 pts. pyridine	Moderate (sodium salt)
8 pts. lactose	7 pts. palmityl chloride	60 pts. pyridine	Good
2 pts. malic acid	4 pts. stearyl chloride	50 pts. pyridine	Good
4 pts. mannitol	6½ pts. stearyl chloride	50 pts. pyridine	Very good
4 pts. mucic acid	6 pts. palmityl chloride	55 pts. pyridine	Good

I do not, of course, limit my invention to the products obtained by using the above listed reagents in the proportions indicated, nor do I even limit my invention to products obtained by the specific method above de-

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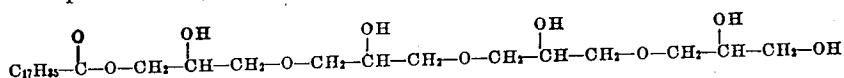
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scribed, as the proportions and the reagents may be varied. The scope of my invention includes compounds, however prepared, when such compounds comprise balanced lipophile and hydrophile groups and when their lipophile function is exercised by at least one —OX group.

Many other materials than those mentioned may be utilized to furnish the hydrophile function, for example, saccharic acid, gluconic acid, glucuronic acid, lactic acid, xylose, galactose, fructose, maltose, rhamnose, sorbitol, dulcitol, arabitol, and other hydroxy substances with marked affinity for water.

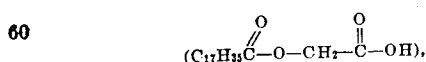
Many other materials than those mentioned may be utilized as sources of lipophile groups, for example, melissic acid, oleic acid, lauric acid, lauryl alcohol, palmityl alcohol, high molecular weight esters and other substances with marked affinity for oils and fats as pointed out more fully in my co-pending application, Serial No. 383,143.

I prepare the "stearic acid esters of poly-glycerols" as follows: Fourteen hundred parts of anhydrous glycerol and thirty parts of fused sodium acetate are mixed and heated at 275° centigrade for five hours with a stream of carbon dioxide gas bubbling through the mixture continuously. Nine hundred thirty parts of this reaction mixture are then treated with one hundred fifty-five parts of stearic acid and heated with continuous agitation for sixteen hours at 190 to 200° centigrade. The product is a tacky solid at room temperature, of a dark color, and emulsifies readily with water. It can be introduced in this form into margarine without further purification. This product is a mixture of various stearic acid esters of poly-glycerols, which in part, can be represented by monostearyl-tetraglycerol:



This material possesses appreciable anti-spattering power.

Still another method of preparation is the procedure by which I make stearyl glycolic acid: Five parts of monostearine are dissolved in fifty parts of glacial acetic acid. The mixture is warmed to 30° centigrade, and six parts of finely powdered potassium permanganate are added with vigorous agitation over a period of about two hours. The manganese dioxide is then removed by treating with four parts of oxalic acid dissolved in fifty parts of water containing five parts of sulphuric acid. The product,



may be extracted with a solvent like very light petroleum naphtha. This extract is then neutralized with sodium carbonate. The solvent

is evaporated off, leaving behind the sodium salt of stearyl glycolic acid.

The compounds described above are of unusual importance in connection with their use with water-oil emulsions of all kinds, but they have a particular adaptation for use with all culinary emulsion products such as margarine. Commercial margarine after being treated with my anti-spattering agent, when fried in a shallow pan exhibits improved frying behavior in that it allows its water to boil off quietly, fries in a pleasing and comparatively quiet manner with the formation of considerable turbid froth and foam after the manner of butter, reduces the tendency of the curd to stick to the bottom of the frying pan, and reduces the amount of material which escapes from the pan by spattering. Untreated margarine on the other hand when fried bumps turbulently, sputters noisily, and foams comparatively little. Also what little foam there is is transparent and of an entirely different character from that obtained from margarine previously treated with an anti-spatterer.

My emulsion improvers may be introduced into the margarine in a number of ways, as long as a satisfactory dispersion is obtained. For instance, the main constituents of margarine are edible oils and fats and cultured milk, and the anti-spattering or improving compounds may be introduced either into the oils or milk in any suitable manner. They may also be introduced into the churn during the production of the emulsion in its liquid state, care being taken to bring about the necessary dispersion. Or, the anti-spattering material may be used in a dry condition and mixed with the salt which is worked into the crystallized margarine, or the anti-

spattering material may be made into a paste with milk, and kneaded in, or blended into the margarine.

As to the specific application of the invention to margarine and other emulsions or oleaginous culinary preparations, it is clear that since there are many hydroxy compounds containing balanced hydrophile and lipophile groups, it is impractical and unnecessary to list each particular combination of groups which can be used in accordance with my invention. Moreover, while I leave something to the skill of persons applying my invention, my description is wholly sufficiently exhaustive, particularly when considered with respect to my prior applications, to enable those skilled in the art to successfully practice the same.

The term "non-spattering margarine" as used in the claims, is employed to designate a margarine, the frying behavior of which is

improved by the addition thereto of the novel compounds of my invention herein described. Margarine is used in the sense in which this term is employed in the U. S. revised statutes; in other words, it includes plastic emulsions of animal or vegetable fats, or mixtures thereof with sweet or ripened milk or water, either colored or uncolored.

Edible emulsions of oleaginous materials and brine, intended for human consumption are also included in the term margarine, or any like fatty aqueous composition which may be used in frying.

What I claim is new and desire to protect by Letters Patent of the United States is:—

1. A non-spattering margarine emulsion including an oleaginous phase and an aqueous phase, and having included therein a pro-

portion of a chemical substance having balanced lipophile and hydrophile groups, wherein the hydrophile group is represented by the radical of a class of substance consisting of saccharic acid, gluconic acid, glucuronic acid, lactic acid, xylose, galactose, fructose, maltose, sorbitol, dulcitol, arabitol, sucrose, tartaric acid, citric acid, polyglycerols, lactose, malic acid and mucic acid.

2. A non-spattering margarine emulsion comprising an oleaginous phase and an aqueous phase, and having included therein a proportion of a derivative of sucrose having balanced lipophile and hydrophile groups.

In witness whereof, I hereunto subscribe my name this 17th day of July, 1930.

BENJAMIN R. HARRIS.

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