1,917,255

UNITED STATES PATENT OFFICE

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EMULSION

No Drawing. Application filed September 11, 1930. Serial No. 481,349.

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 on 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. They are difficultly soluble in oils and fats and aqueous media and in many cases are substantially insoluble. This makes it possible to use such compounds 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 colloidally dispersible in aqueous and or oleaginous media. They are, moreover, substantially non-volatile at water boiling 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 hydrophyllic or water wetting in character, and the other group being lipophyllic 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 apply 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 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.

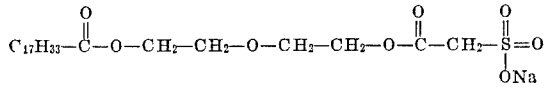
An ordinary margarine such for example as one made from vegetable oils, and fats and cultured skimmed milk and which possesses the usual property of spattering during frying is selected. Ten grams of this margarine are then introduced in small portions into the mortar and macerated thoroughly with the 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 as 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 ebullition ceases and the spots on the paper observed.

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.

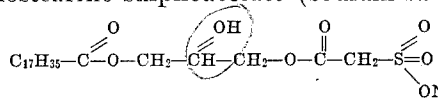
If the increase in weight of the paper or the number and character of the spots produced on the paper up until all the water has boiled off are less than that produced by similarly heating two grams of the original untreated margarine employed for the test, then the material or substance in question 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 relates to a class of substances of the general character described in my prior application. These substances which I claim herein are all sulphonic acid derivatives and have certain characteristics in common, as the following description will establish. Among the sulphonic acid derivatives which I have used successfully as anti-spattering agents, either in relatively pure form or admixed with other unobjectionable materials, and which may be used for the general improvement of emulsions are the following:

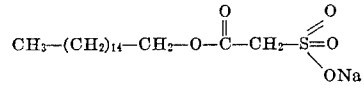
Oleyl diethyleneglycol sulphoacetate (sodium salt)



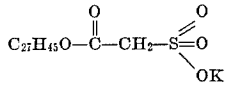
Monostearine sulphoacetate (sodium salt)



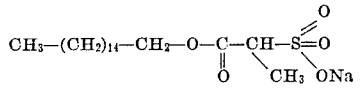
Palmityl sulphoacetate (sodium salt)



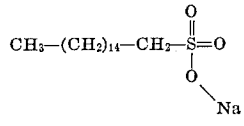
Cholesteryl sulphoacetate (potassium salt)



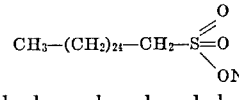
Palmityl sulphopropionate (sodium salt)



Palmityl sulphonic acid (sodium salt)



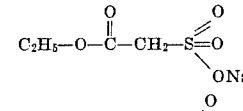
Ceryl sulphonic acid (sodium salt)

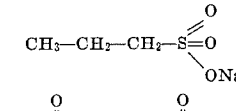


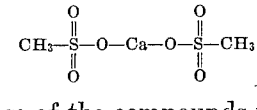
Stearyl diethyleneglycol sulphoacetate (sodium salt)

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 in the form of a sulphonic acid radicle or its derivative. However, the conclusion must not be drawn from this that any random combination of a sulphonic acid group with a lipophile group will give an anti-spatterer.

Examples of molecules which contain a sulphonic acid hydrophile group as well as a lipophile group but which nevertheless are not anti-spatterers are as follows:







In the case of the compounds indicated directly hereinabove, the hydrophile sulphonic

acid group dominates and is inadequately balanced by the lipophile group, that is, the lipophile characteristics of the latter are too weak to balance and coact with the sulphonic acid group.

Generally speaking I select for my lipophile group radicles of relatively high molecular weight. For example, the following material may be utilized as sources of lipophile groups: melissic acid, stearic acid, oleic acid, lauric acid, palmitic acid, lauryl alcohol, cholesterol, monostearyl glycerine (monostearine, so called), many higher molecular weight esters with esterifiable hydroxy groups and other substances with marked affinity for oils and fats, as pointed out more fully in my copending application Serial No. 383,143.

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 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 aqueous phase is much more tenaciously held in the margarine than otherwise.

Numerous methods are available for the introduction of the sulphonic acid group. In the case of aromatic sulphonic acids, of course, the standard sulphonation procedures employed for producing aromatic sulphonic acids may be used and if desired, the lipophyllic group may be introduced subsequently.

In the case of aliphatic sulphonic acids, and for that matter, even for the production of aromatic sulphonic acids, a reactive halogen may be caused to react with sodium sulphite or potassium sulphite or ammonium sulphite or some other sulphite in aqueous solution, if desired.

Another method is to introduce a sulphhydryl or disulphide or some other suitable sulphur group and then oxidize to the sulphonic acid with nitric acid or a permanganate or some other oxidizing agent.

As an example of one of these methods, I describe herewith the preparation of the sodium salt of cholesteryl sulpho-acetate; nine parts of cholesterol, nine parts of brom acetyl bromide, and forty parts of benzene were heated under a reflux condenser for two hours at the boiling point of the mixture. The reaction mixture was then washed repeatedly with hot water until it was substantially free of acid and freed of benzene by distilling from a steam bath. Seven parts of this reaction product were then treated with seven parts of sodium sulphite, (Na_2SO_3), dissolved in forty parts of hot water, for five hours at the temperature of boiling water and with continuous, vigorous agitation. This reaction mixture was washed several times with hot brine until free of sulphites, dried and finally purified by extracting the impurities with dry ethyl ether. Analysis showed that the product was the sodium salt of cholesteryl sulphoacetate in relatively pure form, with an admixture of sodium chloride.

An illusration of another one of these methods is the preparation of palmityl sulphonic acid, (sodium salt), which I prepared as follows:

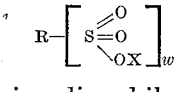
I treat twenty-five parts of palmityl mercaptan with a hot solution of fifty parts of potassium permanganate in eight hundred parts of water at a temperature of approximately 95°, adding the permanganate solution in four successive portions with stirring to avoid too violent a reaction. The mixture is heated at 100° C. for three hours and the remaining potassium permanganate is reduced with oxalic acid but not in excess.

The mixture is filtered hot and the manganese dioxide is washed with hot water. The filtrate and washings are cooled and filtered at 40° to remove oily impurities.

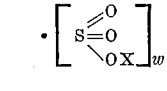
On cooling and salting out with sodium chloride, the potassium salt of palmityl sulphonic acid separates out.

Of course, I do not limit myself to the above described methods of preparing these anti-spatterers, nor to the particular substances mentioned above, which are merely illustrative embodiments of my invention. Aromatic as well as aliphatic sulphonic acids may be employed to furnish hydrophyllic groups.

My emulsion improving substances may be represented by the structural formula



in which "R" is a lipophile radical of relatively higher molecular weight, "S" reprecents sulphur linked to carbon, "O" stands for oxygen, "X" stands for innocuous cations, and "*w*" is a whole number. The lipophile radical "R" may be an ester group of higher molecular weight while the hydrophile portion of the molecules, represented by



is preferably a sulphoacetic acid group. Among the most satisfactory of compounds of this class, I wish to express a preference for higher molecular weight esters of sulphoacetic acid, wherein the lipophile function is performed primarily by at least one stearyl group. Salts of monostearine sulphoacetate, and particularly the sodium salt of monostearine sulphoacetic acid are very valuable for my purpose. I have found, for example, that when from one tenth to one half percent of sodium monostearine sulphoacetate is added to margarine in a suitable manner, spattering is almost entirely prevented, and other improvements secured.

The compounds described above are of unusual importance in connection with their use with water-oil emulsion 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.

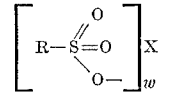
My emulsion improvers may be introduced into the margarine in a number of ways, as long as a satisfactory dispersion is obtained. For instance, the main constituents of margarine are edible oils and fats and cultured milk, and the anti-spattering or improving compounds may be introduced either into the 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 in 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 sulphonic acid derivatives 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 behavoir of which is improved by the addition thereto of the novel materials of my invention herein described. Margarine is used in the sense in which this term is employed in the U. S. Revised Statutes, including the recent Haugen amendment, extending the meaning of the term for tax purposes to include substances not emulsified with cultured milk. Examples of other types of products besides the conventional margarine of commerce are puff paste, renovated butter and any like fatty-aqueous compositions which may be used in frying.

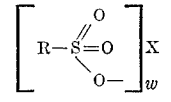
What I claim is new and desire to protect by Letters Patent of the United States is:—

1. A non-spattering margarine including an oleaginous material and aqueous material and having included therein a proportion of an improving agent comprising a chemical compound characterized by a coaction in its molecule of balanced lipophile and hydrophile groups and represented by the formula



in which "R" is a lipophile radical having more than 18 carbon atoms, "S" represents sulphur linked to carbon, "O" stands for oxygen, "X" stands for innocuous cations, and "*w*" is a whole number, at least one.

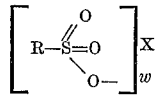
2. A non-spattering margarine including oleaginous material, and aqueous material and having included therein a proportion of an improving agent comprising a chemical compound characterized by a coaction in its molecule of balanced lipophile and hydrophile groups and represented by the formula



in which "R" is a lipophile radical comprising an ester group having more than 18 carbon atoms, "S" represents sulphur linked to carbon, "O" stands for oxygen, "X" stands for innocuous cations, and "*w*" is a small whole number.

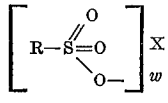
3. A non-spattering margarine including oleaginous material and aqueous material and having included therein a proportion of a carboxylic ester of sulphoacetic acid, having balanced lipophile and hydrophile groups wherein the lipophile group has more than 18 carbon atoms.

4. A non-spattering margarine including an oleaginous material and an aqueous material and having included therein a proportion of a chemical substance characterized by a co-action in its molecule of balanced lipophile and hydrophile groups and represented by the formula



in which "R" is a lipophile radical having more than 18 carbon atoms, "S" represents sulphur linked to carbon, "O" stands for oxygen, "X" stands for innocuous cations, and "*w*" is a whole number at least one, said substance being substantially insoluble in oleaginous and aqueous media, substantially non-volatile at water boiling temperatures, and compatible with mild acids.

5. A non-spattering margarine including oleaginous material, and an aqueous material and having included therein a proportion of a chemical substance characterized by a co-action in its molecule of balanced lipophile and hydrophile groups and represented by the formula



in which "R" is a lipophile radical comprising an ester group having more than 18 carbon atoms, "S" represents sulphur linked to carbon, "O" stands for oxygen, "X" stands for innocuous cations, and "*w*" is a small whole number, said substance being substantially insoluble in oleaginous and aqueous media, substantially non-volatile at water boiling temperatures, and compatible with mild acids.

6. A non-spattering margarine having oleaginous and aqueous media and having included therein a proportion of cholesteryl sulphoacetate.

7. A non-spattering margarine having an oleaginous phase and an aqueous phase and having included therein a proportion of an improving agent, comprising a chemical substance having balanced hydrophile and lipophile groups, in which the hydrophile function is imparted to the molecule primarily by a sulphonic acid radical, and in which the lipophile group is in the form of an ester of a fatty acid and wherein said lipophile group has more than 18 carbon atoms.

In witness whereof, I hereunto subscribe my name this 8th day of August, 1930.

BENJAMIN R. HARRIS.