Patented July 11, 1933 1,917,252

UNITED STATES PATENT OFFICE

BENJAMIN R. HARRIS, OF CHICAGO, ILLINOIS

EMULSION

No Drawing. Application filed September 11, 1930, Serial No. 481,348. 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 on Aug. 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 these compounds in very small quantities, as they may be considered to concentrate at the water-oil interface of the emulsion rather than be 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 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 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 water-oil 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 determinant 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 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.

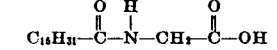
If this treated margarine spots the paper to the same extent as the untreated margarine from which the former was prepared, then the lipophile and hydrophile groups of the compound are not balanced. The number and size of spots on the paper or the added weight can be readily determined.

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", and in the light of the entire disclosure.

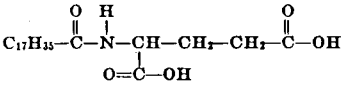
As will appear from my co-pending applications, it is not as a general rule, advisable to employ nitrogenous compounds as an anti-spatterer, even though their anti-spattering behavior may be very satisfactory. This is due to the fact that many nitrogenous compounds are very apt to liberate from themselves when used in margarine and other types of emulsions, objectionable substances such as choline or other objectionable amines. I state for this reason in the co-pending application above set out, that I prefer to avoid the use of nitrogenous compounds. I have now discovered that many nitrogenous compounds can be used with satisfaction providing the nitrogenous compounds selected are of such a character that no objectionable taste and odor can in any way be developed during conditions incident to the manufacture, storage, and use of margarine. I have found that if the molecular structure is devoid of the nitrogenous linkage —O—X—O— $(CH_2)_x$—N— (wherein "O" represents oxygen, "X" stands for phosphorous or sulphur, in the form of their oxygenated acid radicals such as phosphoric, sulphuric, etc., "C" represents carbon, "H" is hydrogen, "*w*" is a small whole number, and "N" is trivalent or pentavalent nitrogen, the terminal oxygen indicated being linked directly to carbon) it is satisfactory for my purpose.

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

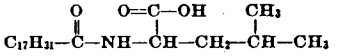
Palmityl glycine,



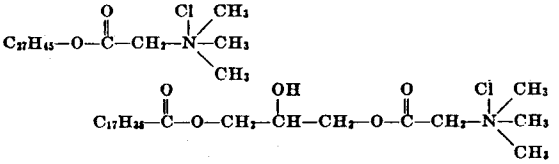
Stearyl creatinine, (sodium salt),
Stearyl glutamic acid,



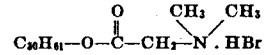
Stearyl peptone,
Palmityl leucine,



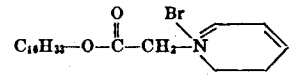
Cholesteryl ester of betaine chloride,



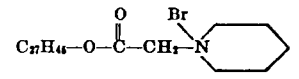
Melissyl dimethyl-aminoacetate hydro bromide,



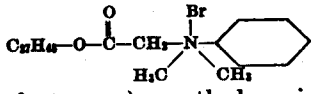
Palmityl ester of betaine chloride
Cholesteryl ester of betaine chloride
(Carbopalmitoxy) methyl pyridynium bromide,



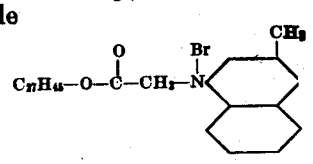
Melissyl ester of betaine bromide
Melissyl ester of betaine chloride
(Carbocholesteroxy) methyl pyridinium bromide,



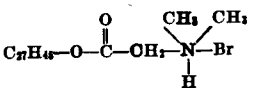
(Carbocholesteroxy) methyl dimethylphenyl-ammonium bromide



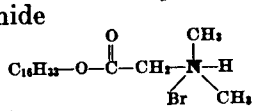
(Carbocholesteroxy) methyl quinaldinium bromide



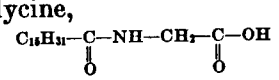
Cholesteryl dimethyl-aminoacetate hydrobromide



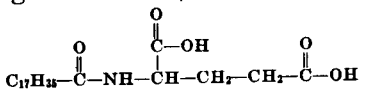
Palmityl ester of dimethylaminoacetic acid hydrobromide



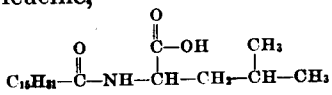
Palmito-glycine,



Stearyl glutamic acid,



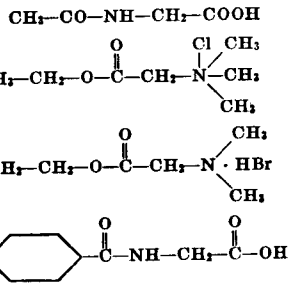
Palmito-leucine,



It will be noted that in every case, the anti-spattering agent has been produced by associating a lipophile group with a hydrophile group of a nitrogenous character.

However, the conclusion must not be drawn from this that any random combination of a nitrogenous group with a lipophile group will give an anti-spatterer.

Examples of molecules which contain nitrogenous hydrophile groups as well as lipophile groups, but which nevertheless, are not anti-spatterers are as follows:



In the above listed examples, 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 coact with the hydrophile group, and for this reason anti-spattering power is lacking. This matter is more fully discussed in my co-pending application, Serial No. 383,143.

A general method for the preparation of the anti-spattering agents with which the present application is concerned is to dissolve or suspend the nitrogenous 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 protected from contact with atmospheric moisture, 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 flo: culent 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.

In this procedure, other basic materials such as dimethyl aniline, quinoline, or quinaldine may be substituted for the pyridine. Also, the acylation may be carried out in a different anhydrous 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-spatters 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 derivatives thus obtained are also shown. These anti-spattering powers were determined by the method described in full in my co-pending application, Serial No. 383,143.

Hydrophyllic nitrogenous material	Acyl chloride	Pyridine	Comparative anti-spattering power
1 part glycine	4 parts palmityl chloride	50 parts pyridine	Fair
1 part creatinine	3 pts stearyl chloride	45 pts. pyridine	Moderate (sodium salt)
2 parts glutamic acid	4 pts. stearyl chloride	55 pts. pyridine	Very good
2 parts leucine	3 pts. palmityl chloride	60 pts. pyridine	Good
10 parts peptone (Merck's)	4 pts. stearyl chloride	60 pts. pyridine	Very 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 above described method, however the proportions of the reagents may have been varied.

The scope of my invention includes compounds, however prepared, when such compounds comprise lipophile and hydrophile groups and when the hydrophile group contains nitrogen, in a linkage other than $-O-X-O-(CH_2)_w-N-$ as herein described. Many other nitrogenous materials than those mentioned may be utilized to furnish the hydrophile function, for example, alanine, phenylalanine, tyrosine, tryptophane, arginine, other amino acids, and other nitrogenous substances with marked affinity for water.

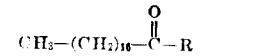
Many other materials than those mentioned may be utilized as sources of lipophile groups, for example: melissic acid, oleic acid, lauric acid, lauryl alcohol, palmityl alcohol, higher molecular weight esters and other substances with marked affinity for oils and fats, as pointed out more fully in my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

I may, for example, hydrolize a protein down to the amino acid stage by the use of a strong mineral acid or otherwise, then neutralize and dry the mixture and acetylate more or less by the general method described herein with the acyl chloride of a higher molecular weight fatty acid.

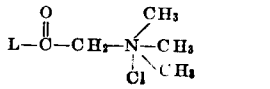
There are also many special methods available. Stearyl glycine, for example, may be prepared by heating together stearamide with choloracetic acid or with sodium chloracetate.

The nitrogenous substances of my invention may be represented by the formula

wherein "C" and "O" are carbon and oxygen respectively, "L" is the lipophile radical in the form of an alkyl or alkoxy group, or a derivative of an alkyl or alkoxy group and "R" represents the balancing nitrogenous hydrophile group. As pointed out previously herein, this group is to be devoid of a certain linkage which I have found objectionable. More specifically and with specific classes of compounds in mind my substances may be represented by the formula



wherein "R" represents an amino acid radical devoid of the objectionable linkage referred to. With reference to the betaine series, I may express my formula as follows:



Among the preferable compounds are also the peptones acylated with fatty acids of higher molecular weight, such as stearyl peptone, for example.

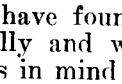
While I have not set forth in detail the compounds covered by the specific formula set out above, those skilled in the art will readily understand from the manner in which the formula is expressed which of the compounds shown in the tables are covered by such formula, together with additional compounds not disclosed which may be produced in accordance with the invention and function satisfactorily as anti-spatterers.

As to the specific application of the invention to margarine or other emulsions and oleaginous culinary emulsions, it is clear that there are many nitrogenous compounds devoid of the linkage described containing balanced hydrophile and lipophile groups. It is impractical and unnecessary to list each particular combination which can be used in accordance with my invention. Moreover, while I leave something to the skill of persons applying my invention, the description is sufficiently exhaustive, particularly when considered with respect to the prior applications, to enable those skilled in the art successfully to 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 materials of my invention herein described. The term "margarine" includes all forms of margarine type of emulsions intended for culinary and table use, either containing animal or vegetable fats, and either churned with cultured milk, sweet milk, water or other types of oleaginous material. Examples of margarine within the meaning of the term, in addition to the usual margarine of commerce, are puff paste, renovated butter, and any like fatty-aqueous composition which may be used in frying.

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

1. A non-spattering margarine having aqueous and oleaginous media, and having included therein a proportion of a nitrogenous substance represented by the formula



wherein "C" and "O" are carbon and oxygen, respectively, "L" is the lipophile radicle with more than 18 carbon atoms in the form of an alkyl or alkoxy group, or a derivative of an alkyl or alkoxy group and "R" represents a balancing nitrogenous hydrophile group devoid of the linkage

$$-O-X-O-(CH_2)_w-N-$$

wherein "O" represents oxygen; "X" stands for phosphorous or sulphur in the form of

their oxygenated acid radicals; "C" represents carbon; "H" is hydrogen; "*w*" is a small whole number; and "N" is trivalent or pentavalent nitrogen, the terminal oxygen indicated being directly linked to carbon.

2. A non-spattering margarine having aqueous and oleaginous media, and having included therein a proportion of a nitrogenous substance represented by the formula

wherein "C" and "O" are carbon and oxygen, respectively, "L" is the lipophile radicle with more than 18 carbon atoms in the form of an alkyl group of higher molecular weight and "R" represents a balancing nitrogenous hydrophile group devoid of the linkage

$$-O-X-O-(CH_2)_w-N-$$

wherein "O" represents oxygen; "X" stands for phosphorous or sulphur in the form of their oxygenated acid radicals; "C" represents carbon; "H" is hydrogen; "*w*" is a small whole number; and "N" is trivalent or pentavalent nitrogen, the terminal oxygen indicated being directly linked to carbon.

3. A non-spattering margarine having aqueous and oleaginous media, and having included therein a proportion of a nitrogenous substance represented by the formula

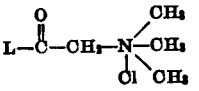


wherein "C" and "O" are carbon and oxygen, respectively, "L" is a lipophile group with more than eighteen carbon atoms and "R" is a balancing betaine radicle devoid of the linkage

$$-O-X-O-(CH_2)_w-N$$

wherein "O" represents oxygen; "X" stands for phosphorous or sulphur in the form of their oxygenated acid radicals; "C" represents carbon; "H" is hydrogen; "*w*" is a small whole number; and "N" is trivalent or pentavalent nitrogen, the terminal oxygen indicated being directly linked to carbon.

4. A non-spattering margarine having aqueous and oleaginous media, and having included therein a proportion of a nitrogenous substance represented by the formula



wherein "C", "O", "H", "N" and "Cl" represent carbon, oxygen, hydrogen, nitrogen and chlorine respectively and "L" is a balancing lipophile group with more than 18 carbon atoms.

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

BENJAMIN R. HARRIS.