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EMULSIFIERS AND THE PRODUCTION OF EMULSIONS

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It is well known to use for the production of emulsions of an aqueous phase in a fatty phase, for instance in a mixture of fat, a fat soluble emulsifier consisting of oxidised and/or polymerised fatty oils. The emulsions produced in this manner have the drawback that they tend to exude the aqueous phase when the emulsion is subjected to working or mechanical treatment. This is particular obvious when emulsions solid at normal temperature are produced by means of emulsifiers of said kind. Thus it is desirable, for instance in the production of margarine, to subject the emulsion, after the fat has been caused to solidify, to a subsequent treatment in the nature of kneading or rolling, but, in case the substances mentioned above have been used for the emulsifier this can scarcely be effected without partially destroying the solid or soft margarine emulsion, i. e. the finely dispersed aqueous phase will partially coalesque to form greater drops of water, the margarine being "moist" and less durable.

One object of my present invention is the provision of a method of producing emulsions of an aqueous phase in a fatty phase by means of emulsifiers and being without the drawback mentioned above. Another object is the provision of emulsifiers for this purpose and a third object of the invention are the emulsifiers themselves.

More particularly my invention has for its object the production of emulsions under which term I desire to include, here as well as in the following description and claims, also the systems called dispersions such as margarine and the like, under the employment of emulsifying substances of two kinds each of which is known. One of these kinds of emulsifiers belongs to the class of emulsifiers which are triglycerides of unsaturated fatty acids in which lipophilc groups have been introduced into the fatty acid part thereof by oxydation by air or by polymerisation with other fatty acid chains having double bonds therein or by such oxidation in combination with polymerisation whereby oxygen atoms may participate in the formation of the links between the chains. The other kind of emulsifiers is esters of higher fatty acids with alcohols containing more than one alcohol group of which at least one is left unesterified. Again, it is an object of the invention to produce emulsifiers containing these kinds of emulsifying agents and adapted to produce emulsions freed from the drawback mentioned above. Still another object of my invention are these mixed emulsifiers themselves.

Further objects and purposes will appear from the following description and claims.

It is assumed that an important cause of the said drawback which has been experienced when emulsifiers consisting of oxidised and/or polymerised fatty oils are used as the only emulsifier is that the emulsifying agents within this class of emulsifiers are liquid or in some cases semiliquid, tenaceous substances. I have found that if in the film surrounding the individual drops of the aqueous phase a substance is incorporated which is solid at the temperature in question the stability of the emulsion against mechanical treatments will considerably increase. I obtain this according to my invention by adding to the emulsion and/or one or both of its components an emulsifier or emulsifiers belonging to the class of emulsifiers which are triglycerides of unsaturated fatty acids in which lipophile groups have been introduced into the fatty acid part thereof by oxidation by an oxygen containing gas or by polymerisation with other fatty acid chains having double bonds therein or by such oxidation in combination with polymerisation whereby oxygen atoms may participate in the formation of the links between the chains, as well as an emulsifier or emulsifiers which is or are an ester or esters of higher fatty acids with alcohols containing more than one hydroxy group of which at least one is left unesterified, the emulsifiers of the two kinds being added in such proportion that they would form when mixed in the same ratio outside the emulsion a mixture that will not be liquefied when heated from its solid condition to room temperature.

By this method the film surrounding the emulsified drops of the aqueous phase will obtain a degree of firmness, which will cause the emulsion to be able to endure mechanical treatment the better the higher the melting point of the mixture which is formed or would be formed by the emulsifiers added, when they were mixed outside the emulsion. This phenomenon may possibly be explained by the fact that both substances enter into the said film or take part in the formation thereof, although the film is not merely a mixture of the said substances having the melting point of the said mixture. It has been found, however, that there is a limit above which it will not be advantageous to rise the melting point which may be explained by the films surrounding the liquid drops being brittle, when the melting point of the composition is increased above a certain limit. It appears that this limit is about 60° C but it has not been exactly determined.

It has been found without importance for the result obtained whether the substances belonging to each of the two groups of emulsifiers are added simultaneously or separately and whether they are added to one or the other or both of the components of the emulsion or to the emulsion being otherwise ready. In all cases there is not formed in the emulsion a simple mixture of the components with the said emulsifiers, but the latter will both tend to gather in the interface between the oily and the aqueous phase and both will partake in the construction of the film surrounding the emulsified drops of the aqueous phase irrespectively whether one or the other of the emulsifiers has been first added.

The lowest melting point of the real or fictious mixture of the emulsifiers of the two said groups of substances at which the effect aimed at can be obtained is the lowest temperature at which the emulsion is likely or sure to be subjected to physical or mechanical influences tending to break the emulsion. Thus, in order to make an improved stability of the emulsion observable at room temperature, the emulsifier of the ester class having free hydroxy groups is added in such a proportion that the ratio of the quantity thereof to the quantity of the emulsifier of the class of the oxydised and/or polymerised fats is so that the emulsifiers will form together a mixture, which is paste-like or solid at room temperature. According to an embodiment of the invention the ratio is chosen so that the said mixture will still be paste-like or solid at the melting point of the fat to be used for or used in the emulsion, in which case the water-binding power may be observed to a greater or less degree in all treatments of the emulsions taking place when the same is solid. In case the emulsifying agents are added to a component or both components the water phase is then caused to emulsify in fat or oil by a known emulsificating treatment. In case the emulsion is produced first without the aid of said emulsifying agents the same are afterwards introduced by agitation or kneading. For the use of the invention in the production of margarine it is most advantageous to chose the ratio of the two kinds of emulsifying agents so that the melting point of the mixture will be between 20° C and 60° C. It is advantageous in many cases to add one of the kinds of emulsifiers to at least one of the components from which the emulsion is to be produced, then producing the emulsion and finally introducing the other emulsifier in the emulsion.

It has now been found that emulsions produced in the said manner with the addition of oxidised and/or polymerised fatty oils as well as esters of higher fatty acids with di-, tri- or polyvalent alcohols or derivatives thereof, in which at least one free hydroxyl group is present in the alcohol group will possess properties also in other respects which for certain important purposes are more advantageous than the properties of emulsions produced by emulsifiers of the former group alone. These properties of the emulsions produced by the new methods in a way are brought closer to the properties of emulsions produced by means of emulsifiers, which are esters of higher fatty acids with di-, tri- or polyvalent alcohols or derivates thereof, in which there is at least one free hydroxyl group in the alcoholic group. In fact the properties of an emulsion containing emulsifiers belonging to both groups are in a way mixed properties, which is advantageous, because the properties of the emulsion obtained by emulsifiers of each of the said groups are capable of complementing one another as far as those properties concern, which are advantageous in the case of the production of margarine and similar emulsions, unfavourable properties of one of the emulsifiers being more or less balanced by a corresponding favourable property of the other emulsifier.

The question is especially of such properties as for instance the tendency to burn when the emulsion is used for frying something on a pan. It is well known that margarine containing esters of the kind mentioned above with free hydroxy groups in the molecule for the emulsifier is apt to show such tendency, whereas the same tendency is not present in margarine that has been produced by means of oxidised and/or polymerised fatty oils for the emulsifier. With respect to the tendency to spatter during frying the emulsifiers of the said classes are behaving oppositely, margarine produced by means of an emulsifier consisting of oxidised or polymerised fatty oils showing this drawback, whereas the same is not to be found in the case of margarine in the production of which emulsifiers of the other said class mentioned have been used. Other examples are the capability to maintain in finely distributed state the brown frying products produced during the frying process so that said brown frying products do not flocculate nor form flakes. Still another property is the capability of taking up water with formation of a finely distributed water-in-oil emulsion, when water is added to the margarine after the same has been deprived of the water emulsified therein by frying and has been fried so long as to make the fats and dry components take a brownish shade or colour. With respect to the former property the emulsifiers of the class of oxidised or polymerised fats are preferable, whereas the emulsifiers of the ester class are deficient in this respect. With respect to the latter property the emulsifiers of the ester class are superior and the other ones are inferior.

It is moreover well known that liquid emulsions produced by mono- or diglycerides are but little stable. It has been found, however, that emulsions produced by oxidised and/or polymerised fatty oils as well as esters of higher fatty acids with di-, tri- or polyvalent alcohols in the alcohol group of which there is at least one hydroxyl group free and in which the emulsifiers of the latter class are added in the quantity stated above will possess a stability in the liquid state which is sufficient for such purposes as for instance the production of margarine.

It has moreover been found that with respect to the durability of the foam formed by the emulsion, for instance during its use for frying purposes, emulsions produced in accordance with the present invention will also possess properties which depend on the melting point of the mixture that is formed or would be formed in case the emulsifiers were present in the mixed state outside the emulsion, being the better the higher the melting point.

In view of the fact that emulsifiers of the two closses in question may be added to the emulsion or the components thereof in the form of a mixture in which the emulsifiers are incorporated in a ratio within the limits mentioned above, the invention will comprise also such mixed emulsifiers. Such emulsifiers are produced by mixing the emulsifying agents of the two kinds in such ratio that a mixture is obtained which will not pass into liquid state until the temperature is raised above room temperature, and emulsifying agent of the class of esters having free hydroxy groups being chosen which will melt above room temperature.

According to a particularly preferable embodiment of the invention the emulsifying agents of the ester class having free hydroxy groups melt above abt. 40° C. and the mixture above abt. 30° C. The two components in the proportions securing the said final melting point the ratio being fixed by one or two experiments on the small scale, are molten together and left to cool.

By choosing suitable individuals of the two classes the hydrophilic and lipophilic properties of the two kinds of emulsifier may be varied in a way known per se, within wide limits, which alters at the same time the emulsifying, stabilising water-binding and anti-spattering effect. Thus mono glycerides are stronger water-binding than diglycerides. The mono-fatty acid-diglycerolesters, are more strongly water-binding and spattering prohibiting than mono glycerides. The same applies to other polyglycerol derivatives and to esters in which sulphuric or phosphoric acid groups are introduced. By way of example mono-stearic acid-glycose ether is pronounced spattering prohibiting. This applies also to other esters of carbohydrates. It is very good to choose for the ester having free hydroxy groups one in which the fatty acid chains are such in which hydrophilic groups are produced by oxidising by oxygen containing gases double bonds occurring therein or by interlinking by way of polymerisation such chains having double bonds therein.

The ratio between the emulsifiers of the two classes in question depends on the melting point of the emulsifier that is an ester of a higher acid with di-, tri- or polyvalent alcohols having at least one alcoholic hydroxyl group free. Using a mixture of 1 part by weight of oxydised and polymerized soya bean oil and two parts by weight of soya bean oil monoglyceride a substance will be obtained which is liquid at room temperature. Using mono-glyceride of fully hardened arachide oil the melting point being about 60° C. a substance will be obtained which is solid at room temperature even when the amount of the mono-glyceride be reduced to half the amount of oxydised or polymerised oil.

To illustrate the connection between consistency and melting point and the various mixtures of emulsifiers some examples are mentioned in the following showing mixtures of fatty acid glycerine esters of various melting point with soya bean oil, which is oxydised and polymerised by blowing with air at 250° C. until a degree of oxidation and polymerisation has been obtained at which the oil will be liquid only at about 100° C., but without the oxidation and polymerisation having been carried so far that the oil has gelatinized.

Fatty acid glycerine ester		Oxyd. and polym. soya bean oil, ratio	The mixture	
Kind and M. P.	Ratio	Ratio	M. P.	Relative [1] consistency 15° C.
Monoglyceride M. P. abt. 60° C.	200	100	55	17
	100	100	55	9
	100	200	53	1
Monoglyceride M. P. 40° C.	200	100	40	4
	100	100	40	2
	100	200	Abt. 35	0, 5
Mono fatty acid-polyglycerine M. P. 55° C.	200	100	Abt. 54	Abt. 5, 0
	100	100	Abt. 54	Abt. 2, 5

[1] States the reciprocal value of the volume (in ccm) of the impression produced by a sphere of 20 mm diameter weighted by 5.5 kgs.

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