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EMULSIONS AND PROCESS OF MAKING THE SAME

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This invention relates to aqueous emulsions of fatty material and to processes of forming the same, and has for its principal object the provision of emulsions of increased stability.

It has heretofore been proposed to produce stable aqueous emulsions by positively charging fat emulsions formed in the usual way, and having a negative charge, by the addition of acid reacting substances or heavy metal ions. However, this process can be carried out only if the charge reversal is effected in the presence of a protective colloid, for example glue, gelatine, starch, mucin, and the like. It will be appreciated, however, that the inclusion of such colloids is seriously disadvantageous for many purposes, and under some circumstances may render the product entirely useless.

It is a feature of the present invention that emulsions of high percentage and increased stability may be formed from emulsifiable fatty substances without the addition of special protective colloids. More specifically the invention contemplates the mixing of two different colloidal electrolytes, one of which has a colloidal cation and the other a colloidal anion, the mixture being effected substantially in electro-equivalent quantities, whereby a water insoluble electro-neutral compound is formed. One of the colloidal electrolytes or any other desired colloidal electrolyte may then be added to the compound in excess, until the reaction substance provides a stable emulsion with water. For certain uses it is preferable to produce these emulsions with inert fatty substances. Thus one of the colloidal electrolytes may be added to the inert fat before admixture with the other electrolyte. The operation may also be carried out by adding the inert fatty substance to the water insoluble electro-neutral compound, the fatty substance being dissolved therein, particularly when this fatty substance contains no hydrophilic groups.

Among the electrolytes with colloidal cations which have been found particularly useful may be mentioned the quaternary ammonium compounds, belonging to the aliphatic, aromatic, aliphatic-aromatic, hydro-aromatic, and heterocyclic series, for example alkyl and alkaline pyridinium salts, and the corresponding compounds of pyridine derivatives and substitution products, and the more simply formed tetra-alkyl ammonium salts act similarly provided there is an alkyl residue sufficiently long to impart a surface active character to the cation.

Use can also be made of alkyl iso-urea, or alkyl iso-thiourea salts, for example lauryl isothiourea halogenide.

Products with surface active cations may also be obtained by the condensation of alkyl halogenide with hexa-methylene-tetramin.

Further, alkyl pyridinium, alkyl chinolinium,

and alkyl i-chinolinium derivatives substituted in the nucleus by halogen atoms or alkyl groups have proved to be useful. Also the secondary nitrogen containing organic bases not being derived from pyridine can be used.

As representative of colloidal electrolytes with colloidal anions, the following may be named: alkyl esters of polybasic strong mineral acids, for example dodecyl, hexadecyl, octadecenyl, and octadecyl sulphuric acid and/or the corresponding alkaline salts, the alkaline salts of fatty acids, the free fatty acids, Turkey red oil products, and the like. If the chain of the product with surface active cations is long enough, electro-neutral compounds can also be produced with naphthalene and benzol derivatives which contain one or more carboxyl groups, SO_3X or SO_4X groups.

The invention of course contemplates the employment of more than one colloidal electrolyte of either positive or negative character; thus mixtures of several different electrolytes having colloidal cations may be reacted with one or more electrolytes having colloidal anions in electro-equivalent quantities to form the water insoluble compound. Similarly, a mixture of several colloidal electrolytes may be added to the electro-neutral compound to form the emulsion. For the formation of the electro-neutral compounds can be further used the naphthene sulphonic acids, sulphonated naphthenic acids, naphthene soaps, oleyl taurin and similar derivatives of taurin with long aliphatic chains (Igepon T), fatty alcohols, camphor sulphonic acid salts, pine oil and turpentine oil.

The emulsions produced in this manner are considerably more stable than those produced by the use of only one component of the electro-neutral fat. As compared with emulsions produced with metallic charges, the emulsions contemplated by the present invention which are formed on an organic basis contain no constituents which can impart a harsh feel to textiles.

The process of the present invention is also particularly advantageous by reason of the fact that all reaction by-products and contaminating matter of the commercial fatty substances may be removed from the water insoluble electro-neutral compound by the simple expedient of washing with hot water. Since for the purpose of emulsifying the electro-neutral compound, only relatively small quantities of substances with surface active anions or surface active cations are necessary, these substances being difficult to purify, the commercial products obtained contain scarcely any inorganic salt, a fact which considerably promotes the stability of the emulsions. Another practical advantage is the fact that very dilute solutions of fatty substances can be converted to high percentage products by simple

reciprocal precipitation. The following examples are given to indicate the manner in which the process may be carried out and are intended to be merely representative and not restrictive of the scope of the invention.

Example I

700 grams of paraffin oil or soft paraffin are emulsified while cold with 140 grams of the alkaline salt of dodecyl sulphuric acid ester (30% fat content) in a boiler provided with rapidly actuated agitating mechanism. Commercial lauryl pyridinium bisulphate (40%) is added thereto in such a quantity that the resulting paste develops the maximum viscosity. When this point is reached, the salt water can be removed by heating and the electro-neutral compound, which occludes the paraffin, is converted into a positively charged, high percentage emulsion by the further addition of lauryl pyridinium bisulphate. A negatively charged high percentage emulsion can also be produced by the addition of the dodecyl sulphuric acid ester or an equivalent compound.

Example II

60 grams of oleic acid are agitated while cold with 450 grams of commercial lauryl pyridinium bisulphate (40%) whereby a glass-like gel is produced, which remains uniformly dissolved in clear water to form a positively charged emulsion.

Substantially as described in Example I one first can add only a part of the technical lauryl pyridinium bisulphate (40%) and wash the unsoluble complex compound with water to obtain fats being free of salts and acid.

Example III

3000 grams of Marseilles soap with an 84% fat content are dissolved in a large quantity of hot water until a freely flowing solution is formed. 3000 grams of commercial lauryl pyridinium bisulphate (40%) which is heated to generally the same temperature, is added abruptly to the solution. The resulting mass is further heated in the agitator until the foam disappears and the fat separates as a greenish black substance on the surface. The aqueous phase, which contains the sodium bisulphate and all the impurities, should now be separated off at as high a temperature as possible. The resulting reaction product is a viscous, sticky, dark green mass at room temperature, a thin layer of which is transparent, and which is insoluble in hot and cold water. A lighter product, having in general the same characteristics is obtained if use is made of equivalent quantities of oleic acid.

Example IV

As in Example III Marseilles soap is mixed with commercial lauryl pyridinium salt. 20 grams of the reaction mass are agitated with 80 grams of lecithin obtained from the residue of soy bean oil. 100 grams of commercial lauryl pyridinium bisulphate (40%) are added thereto. The resulting product is a dark although clear oil which produces extremely stable emulsions with water.

Example V

50 grams of mineral oil are agitated in the cold with 50 grams of commercial lauryl pyridinium chloride. 50 grams of the intermediate product obtained according to Example III, and finally 45 grams of commercial lauryl pyridinium bisulphate (40%), are then added.

Example VI

600 grams of commercial octadecyl sulphuric acid (80%) and 1000 grams of commercial lauryl pyridinium bisulphate (40%) are allowed to react on each other.

The result is an insoluble, viscous electro-neutral fat which can be emulsified with fatty alcohol sulphonates and Turkey red oil to form negatively charged emulsions. Similarly stable but positively charged emulsions may be obtained by the use of cation active substances.

Example VII

400 grams of neat's-foot oil are well agitated with 40 grams of an electro-neutral compound formed of beta-naphthol sulphonate of sodium; the resultant material is thereupon treated with 120 grams of commercial lauryl pyridinium bisulphate (40%).

Example VIII

200 grams of mineral oil are heated and 30 grams of sulphonated castor oil are added thereto. The resultant mixture is then treated with 70 grams of commercial lauryl pyridinium bisulphate (60%) with constant agitation. When the mass is cold, an additional 60 grams of lauryl pyridinium bisulphate (60%) are added to the reaction product.

Example IX

To 250 parts of the electro-neutral compound obtained according to Example 2, 750 parts of paraffin oil are added and then lauryl pyridinium bisulphate (40%) is further added till the proportion 60 parts oleic acid: 450 parts of lauryl pyridinium bisulphate (40%) is reached again.

Example X

100 parts of fatty alcohol isolated from wool fat (hydroxyl No. 100) are melted and still hot added to 100 parts of lauryl pyridinium bisulphate (40%). A precipitate is obtained which agglomerates while stirring. The product is washed with hot water until the inorganic salts are wholly removed, then 700 parts of paraffin oil are added to the dry mass and, by further addition of 100 parts of lauryl pyridinium bisulphate (40%) or of a corresponding quantity of another cation-active fatty compound, a substance containing a high percentage of fatty substance is produced which gives very stable emulsions being absorbed completely by the leather in the cold.

Example XI

To 20 parts of hexamethylene tetrammonium-stearyl bromide (75% active substance) so much sodium salt of acid sulphuric esters of normal primary alcohols of 6-12 carbon atoms is added, that the viscosity reaches its maximum. The resulting compound containing lyophobic aliphatic chains at both ends of the molecule is insoluble in water and can be freed from the unavoidable by-products and from the inorganic salt formed at the reaction. The pure electro-neutral compound for example can be dissolved in 60 parts of paraffin oil. A small addition of one of the named cation active or anion active fat substances can be added to this solution, which then forms a negatively or positively charged concentrated emulsion which is easily dilutable in more water. For example 10 parts of sodium salt of acid sulphuric esters of normal primary alcohols of 6-12 carbon atoms are sufficient to obtain a negatively charged concentrated emulsion. For

obtaining a positively loaded emulsion about 10 parts of lauryl pyridinium bromide, e. g., are sufficient.

Example XII

5 50 grams of naphthene sulphonic acids (sulphonated naphthenic acids) are dissolved in much water, about 1000 grams. After adding 45 grams of lauryl pyridinium bisulphate (40%) a completely insoluble electro-neutral compound is precipitated which, having been washed thor-
10 oughly, can be emulsified in the above stated manner.

Example XIII

15 50 grams of naphthene soaps are dissolved in about 1000 grams of water. By addition of 35 grams of lauryl pyridinium bisulphate (40%) or of 15 grams of lauryl thiourea bromide (100%), the electro-neutral compound precipitates which
20 can be emulsified as described in the above examples.

Example XIV

1385 parts of lauryl pyridinium bisulphate (40%) are added to 300 parts of pine oil which
25 was previously heated nearly to the boiling point. After settling the watery salt solution beneath can be separated. An oil containing only very little electrolytes is obtained which can be dispersed by any method using small quantities of
30 emulgator.

The emulsions obtained by the foregoing processes may be used for the most widely varying purposes in the textile, leather, paper, and like industries, for example as revivifiers, for produc-
35 ing spinning fats, and the like. These emulsions can also be used as cold wetting agents, particularly when, for the purpose of securing solubility, use is made of large quantities of fatty alcohol sulphate of an unsaturated character or the
40 previously mentioned naphthalene or benzol derivatives, and no foreign fat is added to the reaction components to form the electro-neutral fat. The emulsions are particularly advanta-
45 geous in the oiling of leather if the electro-neutral compounds contain well-known leather fats and oils which are not yet emulsifiable, but which are emulsified with substances which form surface active cations.

As compared with leather fats employed heretofore, the present emulsions are not only more
50 stable, but also permit of the oiling of leather in the cold, thus protecting the material. In addition the treatment liquids are much more completely utilized, are absorbed much more rapidly,
55 and do not cause darkening. If the leather has been dyed before oiling, the resistance of the dye to water is greater than if oiling agents produced in the conventional manner are employed. Finally these emulsions are highly resistant to the
60 action of calcium and chromium salts and acids, wherefor preliminary de-acidification of the leather is superfluous, and thus the danger of exceeding the neutralization point is avoided.

Having thus described the invention, what is
65 claimed as new and desired to be secured by Letters Patent is:

1. The process of making stable aqueous emulsions which comprises reacting a compound selected from the group "A" consisting of high
70 molecular alkyl esters of polybasic strong mineral acids, high molecular free fatty acids, alkaline

salts of high molecular fatty acids, and Turkey red oils with a compound containing a long aliphatic chain and selected from the group "B" consisting of quaternary ammonium salts of the aliphatic series, alkyl iso-urea salts, alkyl isothiourea salts, alkyl pyridinium compounds in substantially electro-equivalent amounts to form a substantially water insoluble compound, separating the thus formed compound from the by-products, and incorporating with said compound a compound selected from the groups "A" and "B" in an appreciable quantity sufficient to form a stable emulsion with water.

2. The process of making stable aqueous emulsions which comprises reacting a compound selected from the group "A" consisting of high molecular alkyl esters of polybasic strong mineral acids, high molecular free fatty acids, alkaline salts of high molecular fatty acids, and Turkey red oils with a compound selected from the group
20 "D" consisting of high molecular alkyl pyridinium compounds in substantially electro-equivalent amounts to form a substantially water insoluble compound, separating the thus formed compound from the by-products, and incorporating with said compound a compound selected from the groups "A" and "D" in an appreciable quantity sufficient to form a stable emulsion with water.

3. The process of making stable aqueous emulsions which comprises reacting a compound selected from the group "A" consisting of high molecular alkyl esters of polybasic strong mineral acids, high molecular free fatty acids, alkaline salts of high molecular fatty acids, and Turkey red oils with a compound containing a long aliphatic chain and selected from the group
35 "B" consisting of quaternary ammonium salts of the aliphatic series, alkyl iso-urea salts, alkyl isothiourea salts, and alkyl pyridinium compounds, in substantially electro-equivalent amounts to form a substantially water insoluble compound, separating the thus formed compound from the by-products and adding to said compound a compound selected from the groups "A" and "B" in an appreciable quantity sufficient to form a
45 stable emulsion with water, and incorporating a substantially inert fat at any stage of the process.

4. The process of making stable aqueous emulsions which comprises reacting dodecyl sodium sulphate with dodecyl pyridinium bisulphate in substantially electro-equivalent amounts to form a substantially water-insoluble compound; separating the thus formed compound from the by-products and incorporating with said compound an appreciable quantity of dodecyl pyridinium sulphate sufficient to form a stable emulsion with water.

5. The process of making stable aqueous emulsions which comprises reacting sodium oleate with dodecyl pyridinium bisulphate in substantially electro-equivalent amounts to form a substantially water-insoluble compound; separating the thus formed compound from the by-products and incorporating with said compound an appreciable quantity of dodecyl pyridinium sulphate sufficient to form a stable emulsion with water.

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