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REACTION PRODUCT OF MALEIC ANHYDRIDE UNSATURATED FATTY ACID ADDUCT AND POLYETHYLENE GLYCOL

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This invention relates to novel high molecular weight acidic ether esters of a surface active nature which are particularly effective detergents for cleaning operations where an acidic medium is desired.

It is well known in the detergent field that fatty acid soaps are excellent detergents when employed in soft water. When used in hard water, however, sodium and potassium fatty acid soaps interchange with the calcium ion and precipitate as an insoluble scum thereby being rendered inactive for detergent purposes. For this reason, fatty acid soaps in recent years have been supplanted by synthetic detergents such as the anionic alkyl aryl sulfonates and the non-ionic polyalkoxy ethers. These synthetic detergents are not precipitated in hard water and have good wetting and detergent properties. There are instances, however, particularly where fabrics are concerned, in which the use of these synthetic detergents leave the fabric harsh and brittle whereas soap when used with soft water leaves the fabric with a soft desirable "hand." This difference is apparently due to the fatty acid constituent of the soap which lubricates the fiber and leaves it with a soft feel. In addition, soaps when used under soft water conditions generally exhibit good solvating and emulsification power for removal of grease soils. The provision of a detergent which combines the desirable detergent properties of fatty acid soaps and the ionic and non-ionic synthetic detergents is thus highly desirable.

It is an object of the present invention to provide novel surface active agents having excellent detergent properties and which, while similar to fatty acid soaps in their effect on fabrics and in their ionic character do not precipitate in hard water.

The novel substances provided in accordance with the present invention consist of compositions which are essentially monoesters of unsaturated fatty acid-maleic anhydride adducts and polyethylene glycols having a molecular weight of from about 200 and not more than about 1000. The novel monoesters of the invention are made by heating the adduct with a suitable polyethylene glycol at a temperature of not more than about 120° C. in proportions of about 1 mole of adduct per mole of polyethylene glycol.

The adducts which are used for reaction with the polyethylene glycols to form the monoesters of the present invention are adducts of maleic anhydride with unsaturated fatty acids. These adducts are readily prepared by methods well known in the art which generally consist of heating approximately equivalent proportions of the reactants at temperatures from about 100 to 220° C. for periods ranging from several minutes up to several hours. The adducts contain, in addition to a carboxyl group, a dibasic anhydride functional group. The adducts react

with the polyethylene glycol through the anhydride functional group to form a monoester product having two free carboxyl groups therein.

The acids employed in making the adducts are the unsaturated acids of the fatty acid type having at least about 10 carbon atoms per molecule. Mixtures of such fatty acids can also be satisfactorily utilized. Representative acids which can be employed include oleic, linoleic, clupanodonic, undecylenic, erucic, dehydrated ricinioleic, eleostearic, beta liconic, arachidonic, licanic, linseed oil fatty acids, soya oil fatty acids, and dehydrated castor oil fatty acids. One preferred fatty acid mixture suitable for use in the invention is the acid mixture comprising refined tall oil fatty acids. Tall oil which is available commercially in various grades is the liquid residue obtained from digesting wood to wood pulp in the paper industry. It is a dark brown viscous liquid with the acid components thereof consisting essentially of 14 to 18 carbon acids. The unsaturated acids, oleic and linoleic acids, are the predominant acid components. Myristic acid, palmitic acid, heptadecanoic acid, stearic acid and linolenic acid are usually present as minor constituents. Tall oil when fractionally distilled yields various grades of fatty acid containing from about 95 to 99% fatty acids and from 4% to 0.2% unsaponifiables and from 5 to 0.2% rosin acid. Refined tall oil fatty acids are of this type.

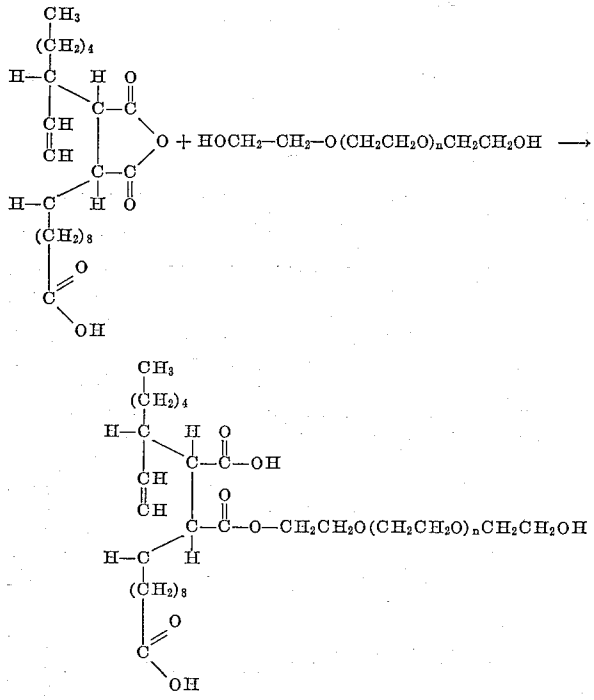
The polyethylene glycols which are employed in producing novel chemical substances of the present invention are polymers having the general formula:

$$HOCH_2—CH_2—O(CH_2CH_2O—)_nCH_2CH_2OH$$

wherein n is a numeral from about 4 to about 23. Polyethylene glycols are currently available in technical quantities and polymeric grades corresponding to molecular weight ranging from about 200 to 6000 or more. The polyethylene glycols employed in the present invention are those having a molecular weight from about 200 to not more than about 1000. Preferred polyethylene glycols are those having a molecular weight from about 300 to about 800.

To make the novel substances of the present invention the maleic anhydride unsaturated organic acid adducts are reacted with the polyethylene glycols in substantially equimolar proportions at a temperature ranging from about room temperature up to but not substantially exceeding 120° C. Preferably this esterification reaction is carried out at a temperature from about 85 to 95° C. for a period of time ranging from about 10 to 20 minutes. It is important that the esterification reaction be carried out for a relatively short period of time, generally not substantially more than about 20 minutes and at a temperature substantially not in excess of 120° C. in order to control and direct the esterification reaction. By controlling the time and temperature of the esterification reaction as indicated, the polyethylene glycol reacts with the adduct at the location of the anhydride functional group to form the desired monoester and simultaneously set free a carboxyl group so that the resulting monoester will contain two free carboxyl groups per molecule. No water is liberated during the partial esterification when conducted under the specified conditions. This reaction can be illustrated as follows, the adduct of maleic anhydride and

linoleic acid being used as representative of the adduct reactants.



As seen from the above reaction, the monoester products of the present invention have a unique structure wherein the ester linkage is located at an intermediate point along the fatty acid chain adjacent to a carboxyl group but remote from another free carboxyl group located at the end of the acid chain. The novel reaction products thus are combination nonionic and anionic compounds in that they contain a nonionic group (polyethylene glycol portion) which imparts water solubility and surface activity thereto and in addition contain anionic carboxyl groups which impart acidic properties to the product.

The invention is further illustrated by the following examples wherein the parts are by weight unless otherwise indicated.

EXAMPLE I

Approximately 141.2 grams (½ mole) of oleic acid are placed into a 500 milliliter 3-necked flask fitted with a reflux condenser, a thermometer and stirring apparatus. Approximately 49.0 grams (½ mole) of maleic anhydride is then added to the flask and the mixture heated by stirring to a temperature of about 210–220° C. and maintained at that temperature for about 3 hours. The resulting intermediate maleic anhydride-oleic acid adduct is cooled and to it is added approximately 300 grams (½ mole) of a polyethylene glycol (Dow Chemical Company Polyglycol E–600) having an average molecular weight of about 570–630. The mixture is then heated to a temperature of about 110–120° C. and maintained at this temperature for about 20 minutes. After cooling to room temperature the product is a red-brown slightly viscous transparent liquid, having a pH of about 2.5–3 in liquid form and a refractive index of 1.4708 at 26.5° C.

EXAMPLE II

Approximately 140.0 grams (½mole) of soya oil fatty acid are placed into a 500 milliliter 3-necked flask fitted with a reflux condenser, a thermometer and stirring apparatus. Approximately 49.0 grams (½ mole) of maleic anhydride is then added to the flask and the mixture heated with stirring to a temperature of about 210–220° C. and maintained at that temperature for about 3 hours. The resulting intermediate maleic anhydride-soya oil fatty acid adduct is cooled and to it is added approximately 300 grams (½ mole) of a polyethylene glycol (Dow Chemical Company Polyglycol E–600) having an average molecular weight of about 570–630. The mixture is then heated to a temperature of about 110–120° C. and maintained at this temperature for about 20 minutes. The product is then cooled to room temperature at which temperature it solidifies. The product has a pH of about 2.5–3 in liquid form and a refractive index of 1.4764 at 25.0° C.

EXAMPLE III

Approximately 578 grams (2 moles) of refined tall oil fatty acids and 196 grams (2 moles) of maleic anhydride are charged into a two-liter, 3-necked reaction flask fitted with a reflux condenser, a thermometer and mechanical stirrer. The reaction mixture is heated to approximately 215° C. with agitation and held within the range of 215 to 225° C. for a period of three hours after which the product is cooled. The product, designated herein as Intermediate A, is a dark reddish brown liquid having a pH at 100% concentration of 3–3.5 and an index of refraction at 22° C. of 1.4871. Extraction of an aliquot sample with water shows no free maleic anhydride to be present.

The tall oil fatty acids employed had the following inspection:

Acid value	192–196
Saponification value	195–198
Rosin acids, percent	1.0
Unsaponifiables, do	1.0
Total fatty acids, do	98
Specific gravity at 25° C	—0.9
Viscosity, S.U.S., at 100° F	—94
Flash point, Open Cup, ° F	—380

Approximately 290 grams (0.75 mole) of the above Intermediate A product and 150 grams (0.75 mole) of a polyethylene glycol (Dow Chemical Company Polyglycol E–200) having an average molecular weight of about 190–210 are then charged into a one-liter reaction flask equipped with a thermometer and mechanical stirrer. The reaction mixture is then heated to 120° C. and held for a period of 20 minutes before cooling to room temperature. The product is a reddish brown liquid having surface active properties.

EXAMPLE IV

Approximately 232 grams (0.6 mole) of Intermediate A from Example III and 180 grams (0.6 mole) of a polyethylene glycol (Dow Polyglycol E–300) having an average molecular weight of 285–315 are charged into a 1 liter three necked flask equipped with a stirrer and thermometer. The reaction mixture is then heated to 120° and held for a period of twenty minutes and cooled to room temperature. The final product is a clear reddish liquid.

EXAMPLE V

Approximately 193 grams (0.5 mole) of Intermediate A from Example III and 200 grams (0.5 mole) of a polyethylene glycol (Dow Polyglycol E–400) having an average molecular weight of 380–420 are charged into a 1 liter flask equipped with a mechanical stirrer and thermometer. The reaction mixture is heated to 120° C. with agitation and held at this temperature for approximately twenty minutes and then cooled to room temperature. The resultant product is a reddish brown liquid with surface active properties.

EXAMPLE VI

Approximately 193 grams (0.5 mole) of Intermediate A from Example III and 300 grams (0.5 mole) of a polyethylene glycol (Dow Polyglycol E–600) having a molecular weight of 570–630 are charged into a 1 liter reaction flask equipped with a thermometer and mechanical agitation. The reaction mixture is heated to 120° C. and held at that temperature with agitation for a period of twenty minutes and than cooled to room tem-

perature. The final product is a reddish brown liquid with surfactant properties.

EXAMPLE VII

Approximately 129 grams (.35 mole) of the Intermediate A from Example III and 333 grams (.33 mole) of a polyethylene glycol (Dow Polyglycol E–1000) having an average molecular weight of 950–1050 are charged into a 1 liter reaction flask equipped with a thermometer and mechanical stirrer. The reaction mixture is heated with stirring to a temperature of 120° C. and held at this temperature for a period of 20 minutes, and is then cooled to room temperature. The final product is a yellow waxy solid.

EXAMPLE VIII

The properties of representative substances of the invention are tabulated in the table below:

Table

Compound	Surface Tension @ 0.1% conc., dynes/cm.	pH of concentrated product	Acid Value	Dilution of conc. product to cloud with H_2O, percent product/ percent H_2O	Compatibility with H_2O after made to pH 6 with KOH	Refractive Index	Appearance
Example III	36	3.0	181.2	16/84.0	(infinite)	1.4804	Reddish Brown Liquid.
Example IV	35	3.0	146.5	16/84.0	do	1.4774	Do.
Example V	36.4	3.0	127.0	18/82	do	1.4726	Do.
Example VI	34.9	3.4	108.5	24/76	do	1.4750	Reddish Brown Viscous Liquid.
Example VII	35.6	4.0	85.7	75/24	do	1.4613	Yellow Waxy Solid.

The foregoing data clearly shows the desirable surface activity, water compatibility and acidic properties of the novel chemical reaction products of the present invention. The new compositions do not precipitate from hard water as do fatty acid soaps when made neutral or slightly basic. In addition, the new surfactants are compatible with other nonionic and anionic surfactants in almost any proportion.

The novel substances of the present invention can be used in a variety of applications where surface active agents find utility. These new substances have detergent properties and can be advantageously employed in cleaning applications wherein acidic cleaning media is desired such as, for example, in the cleaning of felts in paper mill operations.

Those modifications and equivalents which fall within the spirit of the invention and the scope of the appended claims are to be considered part of the invention.

We claim:

1. As a composition of matter, a monoester of substantially equimolar proportions of a maleic anhydride unsaturated organic at least 10 carbon atom containing fatty acid adduct and a polyethylene glycol having a molecular weight from about 300 to about 800, the said monoester being formed by opening of the anhydride functional group of the said adduct and reaction of the polyethylene glycol therewith to form simultaneously the monoester and a free carboxyl group.

2. As a composition of matter, a monoester of substantially equimolar proportions of an adduct of maleic anhydride and an unsaturated organic fatty acid containing at least about 10 carbon atoms and a polyethylene glycol having a molecular weight from about 200 to about 1000, the said monoester being formed by opening of the anhydride functional group of the said adduct and reaction of the polyethylene glycol therewith to form simultaneously the monoester and a free carboxyl group.

3. As a composition of matter, a monoester of substantially equimolar proportions of a polyethylene glycol having a molecular weight from about 200 to about 1000 and an adduct of maleic anhydride with a mixture of

unsaturated organic at least 10 carbon atom containing fatty acids, the said monoester being formed by opening of the anhydride functional group of the said adduct and reaction of the polyethylene glycol therewith to form simultaneously the monoester and a free carboxyl group.

4. The composition of claim 3 wherein the mixture of organic acids comprises refined tall oil fatty acids.

5. The composition of claim 3 wherein the mixture of organic acids is soya oil fatty acids.

6. As a composition of matter, a monoester of substantially equimolar proportions of a maleic anhydride-oleic acid adduct and a polyethylene glycol having a molecular weight from about 200 to about 1000, the said monoester being formed by opening of the anhydride functional group of the said adduct and reaction of the polyethylene glycol therewith to form simultaneously the monoester and a free carboxyl group.

7. The method of producing a chemical reaction product which comprises reacting at a temperature of not more than about 120° C. and for a period of time not substantially exceeding about 20 minutes, substantially equimolar proportions of a polyethylene glycol having a molecular weight from about 200 to about 1000 and a maleic anhydride unsaturated organic at least 10 carbon atom containing fatty acid adduct.

8. The method of producing a chemical reaction product which comprises reacting at a temperature from about 85 to 95° C. for a period of time not substantially exceeding about 20 minutes substantially equimolar proportions of a polyethylene glycol having a molecular weight from about 200 to about 1000 and a maleic anhydride unsaturated organic at least 10 carbon atom containing fatty acid adduct.

9. The method of producing a chemical reaction product which comprises reacting at a temperature from about 85 to 95° C. for a period of time not substantially exceeding about 20 minutes substantially equimolar proportions of a polyethylene glycol having a molecular weight from about 300 to about 800 and a maleic anhydride unsaturated organic at least 10 carbon atom containing fatty acid adduct.

10. The method of producing a chemical reaction product which comprises reacting at a temperature of not more than about 120° C. and for a period of time not substantially exceeding about 20 minutes substantially equimolar proportions of a polyethylene glycol having a molecular weight from about 200 to about 1000 and an adduct of maleic anhydride with a mixture of unsaturated organic at least 10 carbon atom containing fatty acids.

11. The method of producing a chemical reaction product which comprises reacting at a temperature of not more than about 120° C. and for a period of time not substantially exceeding about 20 minutes substantially equimolar proportions of a polyethylene glycol having a molecular weight from about 200 to about 1000 and an adduct of maleic anhydride and tall oil fatty acids.

12. The method of producing a chemical reaction product which comprises reacting at a temperature of not more than about 120° C. and for a period of time not substantially exceeding about 20 minutes substantially equimolar proportions of a polyethylene glycol having a molecular weight from about 200 to about 1000 and an adduct of maleic anhydride and soya oil fatty acids.

13. The method of producing a chemical reaction product which comprises reacting at a temperature of not more than about 120° C. and for a period of time not substantially exceeding about 20 minutes substantially equimolar proportions of a polyethylene glycol having a molecular weight from about 200 to about 1000 and an adduct of maleic anhydride with oleic acid.

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