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EMULSIFIER-WAX COMPOSITIONS

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The present invention is directed to petroleum wax and oil compositions containing emulsifying agents, more particularly, to a combination of at least two such agents in order to provide an effective wax-like or oil-like material. These materials which are anhydrous can be used to produce emulsions by heating the mixture to a fluid state and adding water as directed in the examples below.

The incorporation of the emulsifiers in either the petroleum waxes or oils produces a new article of commerce which has not been available before. In the case of the wax systems the product has the appearance of wax. The emulsifiers do not sweat out the wax system because they are homogenously dispersed throughout the wax.

Various types of emulsifying agents have been used to produce the oil in water type of emulsions of waxes and oils and have been effective for commercial applications. However, these emulsifying agents are mixtures of water and oil soluble compounds which do not lend themselves to the incorporation with petroleum waxes and oils. It is desirable that the emulsifiers be homogenous with the petroleum wax and oil so that a product is produced from which the emulsifiers do not sweat out to the surface and do not materially alter the physical properties of the wax or oil.

In the past the water-repellent and/or the waterproofing qualities of wax have been altered by the emulsifiers to the extent that the effectiveness of the wax has been markedly decreased. Furthermore, the usual emulsifiers do not permit the formation of emulsions from the high melting point type of micro-crystalline waxes 190°–200° F., nor would they produce a homogenous product which would be similar to the product herein described.

The present invention is intended and adapted to overcome disadvantages of prior emulsifying agents, it being among the objects of the present invention to provide a homogenous solution of a plurality of emulsifying agents and oils and waxes.

It is also among the bojects of the present invention to provide a combination of such emulsifying agents and waxes or oils, which compositions are self-emulsifiable and are stable over long periods of storage without separation of the emulsifying agent.

It is further among the objects of the present invention to provide aqueous emulsions with such oil or wax solutions with said emulsifying agents, which are stable under various weather conditions, including very high temperatures as well as very low temperatures.

It is still further among the objects of the present invention to provide such emulsions which are stable in hard water and which are resistant to alkalies and acids.

In practicing the present invention, it was found that a combination of two or more emulsifying agents gave better results than one agent alone. In particular it was found that a combination of three agents, namely, glyoxalidine or salts thereof, a glyceride-amine condensation product and a fatty acid in various ratios provides an execellent emulsifying agent for oils and waxes. It was also found that a combination of the first two said agents gives good results. By providing certain ratios of fatty acid to the other two constituents, the combination is completely soluble in various types of waxes. As a result, self-emulsifying waxes are produced by the present invention.

The glyoxalidine is formed by condensing an alkylpolyamine or an alkylolpolyamine in which there are from 2 to 6 amino groups and the alkyl group being ethylene or propylene, with a fatty acid having 12 to 18 carbon atoms. In the condensation some amide is formed, usually not over about 30–50%. Salts of the glyoxalidines may be used, such salts being formed by reaction with a lower fatty acid having 1 to 4 carbon atoms or the common inorganic acids.

The glyceride-amine condensation product is formed by the reaction of an animal or vegetable oil with an alkylolamine. Preferably the oil is of the coconut type containing a substantial proportion of lauric acid in combination. The alkylolamine is the mono-, di-, or triethanol or propanolamine. The oil should have a low free fatty acid number, preferably below 1%, but up to 5% is tolerated; if the free fatty acid is too high, esters may be formed and the product become too hydrophobic. In the product some free amine may remain unreacted.

These two substances are blended in about equal proportions by weight, providing an excellent emulsifier for mineral oils. However, the solubility thereof in waxes, particularly microwaxes, is limited, and to overcome this the blend is modified by the addition of a fatty acid or mixture of fatty acids having 12 to 18 carbon atoms. The ratio of the fatty acid to the blend or mixture is about 40–65 to 60–35; for the various types of waxes the ratios vary within the stated range. In the harder waxes the larger amounts of the fatty acids are used and in the softer waxes the lower amounts are used. The blend with the fatty acid makes the emulsifier homogeneous and completely wax soluble.

The following are specific examples of the operation of the invention:

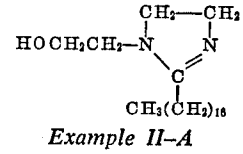
Example I–A

A glyoxalidine is produced by condensing an alkylol polyamine with a fatty acid. The following composition was used.

34.73 parts of hydroxy ethylethylene diamine
94.66 parts of stearic acid (e.g. hydrogenated tallow or veg. fatty acids)

The stearic acid is melted in a steam jacketed kettle which is fitted with a variable speed agitator. When the acid is all melted and the temperature has reached 70° C., the amine is slowly poured into the reaction kettle. The mixture is slowly agitated as the temperature is raised to 150°–180° C. The reaction mixture is kept at 150°–180° C. until the free fatty acid content is below 5% and at least 9 to 12 parts of water of condensation has been released. This usually takes from 3 to 7 hours. The reaction product is a wax-like substance which is soluble in hot hydrocarbons (e.g. wax and oil).

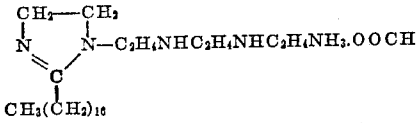
The product probably has the following structural formula:



Example II–A

In order to prepare a salt of the glyoxalidine, the product of Example I–A is reacted with a suitable acid. For

instance, tetraethylene pentamine is condensed with a fatty acid such as stearic, to form the glyoxalidine. This intermediate product is reacted with an acid such as formic, to form the salt which probably has the following structural formula:



The following composition was provided:

	Parts by weight
Tetraethylene pentamine	63.1
Stearic acid (hydrogenated tallow or vegetable fatty acids)	94.6

The stearic acid is melted and heated to 70° C. in a steam jacketed kettle fitted with a variable speed stirrer. The amine is slowly added as the reaction mixture is slowly agitated. After all the amine has been added the reaction temperature is raised to 150°–180° C., and the system is kept at this temperature until the free fatty acid is below 3% and from 9 to 12 parts of water of condensate has been removed. This usually takes from 3 to 7 hours.

This product is more hydrophylic than that of Example I. The reaction product usually contains some unreacted amine and ordinarily about 2% or 3% thereof is present. However, much larger amounts of free amine can be tolerated.

Example II–B

In order to form the salt of the product of Example II–A, the following composition is used:

	Parts by weight
Reaction product (Example II–A)	45
Formic acid (85%)	4–9.0

The reaction product from Example II–A is melted to 75°–100° C. and the formic acid is slowly poured into the agitated glyoxalidine. The system is kept at 75°–100° C. until the mixture is homogenous.

Example III

The second type of emulsifying agent is the condensation product of an amine and a triglyceride. The reaction is believed to be an ammonolysis reaction which is carried out in the presence of an alkaline catalyst. The following composition is typical:

	Parts by weight
Diethanolamine	50
Crude Manila coconut oil	50
Potassium carbonate	1

The coconut oil is heated to 60°–70° C. in a steam jacketed vessel and the amine is added with constant slow agitation. The potassium carbonate is then added, the temperature is raised to 140° C. and the system is kept there until the reaction mixture is completely soluble in water. This requires from 2 to 7 hours. The product is a viscous liquid which is completely soluble in water and not soluble in hydrocarbons. In general, any amine may be used with any glyceride, but for our end use a glyceride having the lower fatty acids C_{10} to C_{14} were found to give the best results. It was also found that better results are obtained if the free fatty acid content of the glyceride is below 5%.

Any one of the products of Example I is blended with the type of compounds illustrated in Examples II–A, II–B or III. Such blends are partially soluble in waxes and oils. In order to render them completely soluble, a third component is used to couple the blend into the wax and particularly the hard type of wax. The coupling agents used are fatty acids having 12 to 18 carbon atoms. The character and amount of fatty acid required varies with the type of wax used. Lower fatty acids such as lauric, or unsaturated fatty acids such as oleic, tend to make the final emulsion quite fluid. When stearic acid is used, the viscosity of the final emulsion is increased. As a result, emulsifying agents are provided ranging from those which are soluble in hydrocarbons in limited quantities up to those which are completely soluble.

Example IV–A

An emulsifying agent which has limited solubility in wax or oils is as follows:

	Parts by weight
Coconut oil—diethanolamine condensate (Example III)	50
Hydroxy ethyl ethylenediamine—stearic acid condensate (Example I)	50

The proportions may be varied from about 60–40 to about 40–60. The reaction product as prepared in Example I is melted to 80°–90° C. and the condensate from Example III is poured in and the mixture is agitated until clear. The product is allowed to cool to room temperature and it resembles a soft wax. This mixture is only partially soluble in wax or oil. It can be used to emulsify mineral oils with good results.

Example IV–B

In order to render IV–A soluble in various waxes it is compounded with a fatty acid. For example, if an emulsifying agent is required for microcrystalline waxes which is soluble in the wax, the following example should be followed:

	Parts by weight
IV–A	42.7
Stearic acid	57.3

Both components are melted together at 80°–90° C. to form a miscible system. This mixture is an efficient emulsifying agent for microcrystalline waxes and is also soluble in the wax.

Example IV–C

In order to make IV–A soluble in paraffin wax the following ratio of fatty acids to IV–A was found desirable:

	Parts by weight
IV–A	50.0
Oleic acid	27.7
Stearic acid	22.3

The oleic acid is used here so that the final wax emulsion would be more fluid. The above three mentioned compounds are melted together at 90° C. to form a clear solution and then cooled.

Example IV–D

For scale waxes the following ratio was found to be soluble in the wax:

	Parts by weight
IV–A	62.50
Oleic acid	18.75
Stearic acid	18.75

The above components are melted together to form a homogeneous system at 90° C.

Example IV–E

The following is an emulsifier suitable for microcrystalline waxes:

	Parts by weight
Coconut oil—diethanolamine condensate of Example III	50
Reaction product II–A	50
Stearic acid	162

This mixture is melted together to form an emulsifier which is soluble in micorcrystalline waxes.

Example IV–F

An emulsifier containing a glyoxalidine salt is as follows:

	Parts by weight
Coconut oil—diethanolamine condensate of Example III	50
Reaction product II–B	50
Stearic acid	162

These compounds are melted together to form a homogeneous system which is soluble in waxes.

The above examples of emulsifier systems can be varied considerably. For example, the ratio of amine-glyceride condensate to the glyoxalidine does not have to be 1:1. The coupling acids may be acids other than stearic or oleic (e.g. palmitic or lauric). Acids other than formic may be used to form the salt of the glyoxalidine (acetic or hydrochloric).

The following are examples of the production of emulsions of oils and waxes in accordance with the present invention.

Example V.—Mineral oil emulsions

	Parts by weight
(1) White mineral oil (Bayol oil)	100
(2) Emulsifier IV–A	3–10
(3) Water	300

The oil is heated to 80°–90° C. and then emulsifier IV–A is added to the oil. The water is heated to 80°–90° C. and is slowly added to the oil-emulsifier system which is being agitated with a high speed agitator (>400 r.p.m.). After all the water has been added, the emulsion is cooled to room temperature while it is being agitated.

The emulsion produced in this manner is a stable and fluid emulsion. It is not adversely affected by hard water, alkalies (NaOH) or acids. This emulsion can be used where high alkalinity exists (e.g. in viscous emulsions) for it is stable in 10% caustic soda solutions. Hard water of 1000 p.p.m. as calcium carbonate does not affect the emulsion nor do systems having a pH of 3.

Example VI.—Microcrystalline wax emulsions

	Parts by weight
Microcrystalline wax	100
Emulsifier IV–E	15
Formic acid (85%)	2
Water	300

The wax is melted in a suitable container fitted with a high speed agitator. When the wax is all molten and the temperature is about 90° C., emulsifier IV–E is added and is dissolved in the wax. A clear homogeneous solution of the emulsifier in the wax is thus obtained. (The wax may be allowed to solidify and the emulsifier will remain homogeneous in the solid wax. Thus, a self-emulsifiable wax may be prepared in this manner.) When the wax-emulsifier system is homogeneous and the temperature is 90° C., the heated water (at 90° C.) is slowly added to the agitated wax. After approximately ⅓ of the water has been added, the formic acid is introduced into the system. The temperature is maintained at 90° C. while the rest of the hot (90° C.) water is being added to the mixture which is being agitated. After all the water has been added the emulsion is cooled to room temperature while it is being agitated. The emulsion may be passed through a colloid mill to decrease the average particle size; in such case it should be passed through hot (90° C.).

The emulsion produced in this fashion is an acid-stable fluid emulsion. Depending on the type of microcrystalline wax used the emulsions produced in this manner may be used as pulp additives in paper or paperboard making to obtain various properties (e.g. water resistance, grease proofing, etc.).

Example VII.—Emulsions of paraffin waxes

	Parts by weight
Paraffin wax (M.P. 130/3° F.)	100
Emulsifier IV–C	20
Aluminum acetate powder	10
Water	300

The paraffin wax is melted in a kettle which is fitted with a high speed agitator. When the temperature is about 90° C., emulsifier IV–C is dissolved in the wax so that a clear homogeneous solution is obtained (the solution of the emulsifier in the wax may be solidified to form a homogenous solid which can be used as a "self-emulsifying wax"). After the wax and emulsifier is melted and the temperature is 90° C., the hot (90° C.) water is slowly added to the agitated wax. When ⅓ of the water has been added the aluminum acetate is added to the agitated system. Then the rest of the hot (90° C.) water is added to the emulsion which is still maintained at 90° C. After all the water has been added the emulsion is either passed through a colloid mill (hot at 90° C.) or it is cooled down to room temperature with constant agitation. The emulsion prepared in this manner is on the acid side and is very efficient water proofing agent for textiles and paper.

Such an emulsion is quite weather stable. In a test the emulsion was heated to 130° F. and held at said temperature for 64 hours; the emulsion remained stable and fluid. In a freeze-thaw test the emulsion was cooled and held at a temperature to cause it to become completely frozen; on thawing out it remained stable and fluid.

The emulsions are effective water proofing agents. Tests were made in accordance with AATCC Water Absorption Test No. 21–52 on cotton gabardine, wool flannel and heavy woolen felt. 2% of wax on the weight of the fabric was deposited on the fabrics from a 2% emulsion. The water absorption was compared to untreated control fabrics with the following results:

	Percent water absorbed on weight of fabric	
	Treated	Control
Cotton Gabardine	23	63
Wool Flannel	25	93
Heavy Woolen Felt	32	200

In AATCC Spray Test No. 22–52 cotton gabardine was treated with the emulsion as set forth above; the treated fabric had a rating of 95–100, whereas the untreated control had a rating of 0–20.

Example VIII.—Petrolatum emulsions

Emulsifier IV–B is soluble in petrolatum type waxes and an effective emulsion can be prepared using Emulsifier IV–B.

	Parts by weight
Petroleum wax	100
Emulsifier IV–B	15
Boric acid	2
Water	270

The petrolatum is melted in a steam jacketed vessel fitted with a high speed agitator. After the petrolatum is all melted and the temperature is 90° C., emulsifier IV–B is dissolved in the wax. The emulsifier is completely soluble in the wax, and the wax may be solidified to form a homogenous solid or self-emulsifiable wax. The water is heated to 90° C. and about ⅓ is added to the wax-emulsifier system as it is being agitated. While the emulsion is still at 90° C. the solid boric acid is poured in. The rest of the water is then slowly added. After all

the water has been added the finished emulsion is cooled to room temperature as it is being agitated or the hot (90° C.) emulsion may be passed through a colloid mill and then cooled.

The emulsion as prepared in the above manner is slightly alkaline (pH 7.5–8) but is acid and alkali stable. The emulsion may be used as a pulp additive to decrease water or grease penetration in the finished board.

Example IX.—Scale wax emulsion

Scale waxes may be made self-emulsifiable by using emulsifier IV–D. The emulsion may have the following composition:

	Parts by weight
Scale wax	100
Emulsifier IV–D	10
Potassium carbonate	2
Water	300

The scale wax is melted in a steam jacketed vessel fitted with a high speed agitator. When the wax is at 90° C., emulsifier IV–D is dissolved in the wax. (The emulsifier is soluble in the wax and the wax may be solidified and a homogenous solid results which can be used as a self-emulsifying wax.) After the emulsifier has been all dissolved in the wax and the temperature is at 90° C., the hot (90° C.) water is slowly added until about ⅛ of the water has been added. Then the potassium carbonate is added followed by addition of the rest of the water. After all the water has been added the emulsion can either be passed hot (90° C.) through a colloid mill or cooled directly to room temperature as it is being agitated.

The emulsion prepared in this manner is an alkali stable emulsion which can be precipitated by the addition of acids. Scale wax emulsion can be used as pulp additives or sizing agents for paper or textiles.

Example X.—Heat stability of self-emulsifying waxes

Some of the self-emulsifying waxes tend to be sensitive to prolonged heating at elevated temperatures. For example, a self-emulsifying wax is prepared as follows:

	Parts by weight
Microcrystalline wax	100
Emulsifier IV–B	15

The wax is melted and heated to 180° to 190° F. Then emulsifier IV–B is dissolved into the wax. A clear solution is obtained. The wax is allowed to solidify and a homogenous solid wax results. The emulsifier will not sweat out of the wax at 130° F. The chemical properties of the self-emulsifying wax as prepared above are as follows:

Acid value	15.7
Free fatty acid as oleic —percent—	7.9
Saponification value	19.6
Ester value	3.7

If the above self-emulsifying wax is heated at 200° F., an emulsion can be prepared from the heated mixtures using boric acid even after 10 hours of heating. Heating at 200° F. over 10 hours prevents the formation of emulsions using boric acid but an alkali may be used to prepare an emulsion, e.g. borax or potassium carbonate. Prolonged heating causes a decrease in the acid value and an increase in ester values. Thus, if the above product were heated for 17 hours at 200° F., the specifications would be as follows:

Acid value	12.1
Free fatty acid —percent—	6.1
Saponification value	19.6
Ester value	7.5

Emulsifier IV–E in wax is not adversely affected by heating. Emulsions may be prepared using formic acid after heating over 20 hours at 200° F.

It has been shown that by compounding a fatty glyoxalidine, amine-glyceride condensate and a fatty acid, wax soluble emulsifying agents may be prepared. From the wax-emulsifier systems diverse emulsions may be prepared ranging from alkaline to acid emulsions. Depending on the acid or alkali or salt used the emulsion may tend to be cationic or anionic. If "water-proofing" is desired, aluminum salts (aluminum acetate) should be used. If an acid emulsion is required, formic acid or hydrochloric acid salts may be formed. Thus, by use of the proper emulsifier and wax, a variety of emulsions can be prepared.

Aqueous emulsions according to the invention are stable to acid, alkali and hard water. The wax and oil compositions are stable over long periods of time, and are easy to handle and may be stored in reduced areas. Shipping costs are reduced because water need not be transported. They are easily and readily emulsified with water and emulsions are reproducible from batch to batch, and no special dispersing equipment is necessary.

Although the invention has been described setting forth several specific embodiments thereof, the invention is not to be limited thereto as the examples were introduced for purposes of illustration only. It will be obvious to those skilled in the art that various changes in the details of operation in the proportions of constituents and in the characters of the waxes and oils may be made within the principles of the invention.

Among the many advantages of the invention is the lower material cost compared to that of prepared emulsions. Shipping costs are reduced as the large bulk of water in emulsions has been eliminated. Handling is simplified as the goods are packed in cartons and a reduced storage area may be used. Emulsions are easily and quickly prepared and they are reproducible from batch to batch; no special dispersing equipment is necessary. The compositions are available in a large variety of waxes and with a wide range of stability to pH.

What is claimed is:

1. A substantially anhydrous composition taken from the group consisting of hydrocarbon wax and oil compositions blended with a mixture of emulsifying agents in sufficient amount to form emulsions, said mixture consisting essentially of a substance taken from the group consisting of glyoxalidines and salts thereof with acids and the condensation product of a glyceride oil with an alkylolamine taken from the group consisting of mono-, di-, and tri-ethanol and propanol-amines, the amounts of glyoxalidine and condensation product being approximately equal.

2. A composition according to claim 1, in which said glyoxalidine is the product of substantially equimolecular quantities of an amine selected from the group consisting of alkyl- and alkylol-polyamines with a higher fatty acid, the alkyl groups having 2–3 carbon atoms and there being present 2–6 amino groups.

3. A composition according to claim 1, in which there is also present a free higher fatty acid in substantial amounts, said amounts being sufficient to increase the solubility of said mixture of emulsifying agents in waxes.

4. A composition according to claim 1, in which there is also present a free higher fatty acid in substantial amounts approximately equal to from about one-half to one and one-half times the sum of the other two constituents.

5. A composition according to claim 1, in which said glyceride oil is a coconut type oil.

6. A composition according to claim 1, in which said composition is emulsified with water and a water soluble acid, said composition being anionic.

7. A composition according to claim 1, in which said composition is emulsified with water and a water soluble alkali, said composition being cationic.

8. A composition according to claim 1, in which said composition is emulsified with water and a mineral acid.

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