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AQUEOUS MIXTURE OF SURFACE ACTIVE AGENTS

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This invention relates to an aqueous mixture of surface-active agents which exert a synergistic action, neither surface-active agent alone being effective.

From a practical standpoint the manufacturer of a water-insoluble pesticidal agent must supply the agriculturist with a low-cost concentrate thereof in such form that by merely mixing with water at the point of use he will have an easily prepared pesticidal spray. It has been customary in the preparation of concentrates that such water-insoluble pesticidal agents be dissolved in an organic solvent therefor and to admix with the organic solution a water-soluble surface-active agent. As those skilled in the art are well aware, the specifications for an emulsifying and/or wetting agent in packaged goods which must withstand the effects of storage are exacting. The passage of time and changes of temperature encountered in normal storage often materially effect the emulsifying and/or wetting properties of the surface-active agent. Additionally the surface-active agent may react with the pesticidal agent or be otherwise affected by it over a period of time and thus cause the active ingredient to lose or materially lessen its pesticidal properties. Also in many instances while a particular water-insoluble pesticidal agent may be highly useful in combatting certain pests its usage has been limited or negatived by virtue of the particular organic solvent employed to solubilize it, e.g. oily films and/or objectionable odor or solvent residues after application and for other reasons those skilled in the art are thoroughly familiar.

In accordance with this invention it has been found that the combination of about 1 to 2 parts by weight of (*a*) alkali metal alkyl sulfate water-soluble anionic surfactant, about 1 to 3 parts by weight of (*b*) the condensation product of 1 mole of a mono-higher fatty acid ester of hexitol anhydrides, i.e. sorbitan ($C_6H_{12}O_5$), mannitan, sorbide ($C_6H_{10}O_4$), mannide etc. with 10 to 30 moles of alkylene oxide, and 2 to 6 parts by weight of (*c*) water provides a homogeneous water-soluble surface-active mixture which fulfills the rigorous requirement of emulsifying and/or wetting agents which must withstand storage as concentrates. Optimum results are obtained when the weight ratio of (*a*) to (*b*) to (*c*) is 1:2:3.

By "alkali metal alkyl sulfate" as employed herein and in the appended claims is meant water-soluble anionic surfactants of the structure $RO.SO_2.OM$ wherein R is a long chain alkyl radical (either straight or branched) containing from 8 to 18 carbon atoms as exemplified by octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, pentadecyl, cetyl, octadecyl, and the various isomeric forms thereof, and wherein M is an alkali metal such as sodium, potassium or lithium. It is preferred that R be a straight chain alkyl radical.

By "mono-higher fatty acid ester of hexitol anhydrides" as employed herein and in the appended claims is meant mono-esters of hexitol anhydrides and a higher fatty acid such as lauric acid, palmitic acid, oleic acid, ricinoleic acid, stearic acid and the like fatty acids containing from 12 to 20 carbon atoms. As exemplary of such esters are sorbitan mono-laurate, mannitan mono-laurate, sorbitan mono-palmitate, sorbitan mono-oleate, mannitan mono-oleate, sorbide mono-oleate.

By "alkylene oxide" as employed herein and in the appended claims is meant ethylene oxide and propylene oxide and mixtures thereof. These materials can be represented by the empirical formula $C_nH_{2n}O$ wherein *n* is a whole number from 2 to 3. The preferred alkylene oxide is ethylene oxide.

Typical mixtures of the surface-active agents of this invention comprise (in parts by weight)

	A	B	C
Sodium lauryl sulfate	1	1	2
1 mole of sorbitan monooleate condensed with 20 moles of ethylene oxide	2	1	2
Water	3	2	6

These aqueous mixtures of surface-active agents, i.e. compositions A, B and C, are clear liquids soluble in water.

The mixture of surface-active agents of this invention is characterized by excellent stability. To demonstrate such the following respective compositions (in parts by weight)

Components/Composition

	A	B	C	D	E	F	G
6-ethoxy-2, 2, 4-trimethyl-1, 2-dihydroquinoline	70	70	70	70	70	70	70
1 mole of sorbitan mono-oleate condensed with 20 moles of ethylene oxide	10	----	----	10	----	10	10
Sodium lauryl sulfate	5	5	----	----	----	----	----
Water	15	25	20	15	20	15	20
Dioctyl ester of sodium sulfosuccinic acid [1]	----	----	10	5	----	----	----
Triethanolamine lauryl sulfate [2]	----	----	----	----	10	5	----

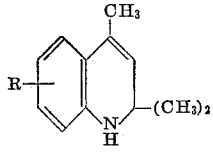
[1] Commercial water-soluble anionic wetting agent.
[2] Commercial water-soluble anionic emulsifying agent.

were prepared by initially mixing the sorbitan mono-oleate-ethylene oxide condensation product with a solution of the recited anionic surfactant in the water and passing the mix and 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline through a colloid mill. The resulting concentrates were then permitted to stand in closed containers under normal storage conditions. Compositions B, C, D, E, F and G after 2 days showed oiling out of 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline while composition A after standing 5 months showed no signs of oiling out of 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline. Further Composition A after standing for 5 months was still self-emulsifiable with water.

2,2,4-trimethyl-1,2-dihydroquinolines, such as 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline which is a water-insoluble yellow oily liquid, have been found to be useful in the control of common apple scald and Anjou pear scald and for preserving the nutritive value of feeds and forage plants, particularly alfalfa. However their usage has been curtailed by virtue of the organic solvents (usually high molecular weight alcohols such as decyl alcohol and dodecyl alcohol) employed to make concentrated solutions thereof because of injury to the treated surface as well as objectionable odors and/or oily films characterizing the residues after application in the field. Further to date, no-water-soluble surface-active agent in admixture with such concentrated organic solutions has provided a concentrate capable of withstanding the effects of storage. The aqueous surface-active mixture of this invention is soluble in 2,2,4-trimethyl-1,2-dihydroquinolines such as 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline and provides solventless concentrates which are self-emulsifiable in water. Concentrates containing 0.5 to 8.0 but preferably 1.5 to 2.5 by weight of 2,2,4-trimethyl-1,2-dihydroquinoline per 1 part by weight of the aqueous surface-active agent mixture of this invention exhibit good stability in storage and excellent self-emulsi-

fying properties when admixed with water at the point of use.

The aqueous surface active mixture of this invention aforementioned is useful in preparing emulsifiable concentrates of other 2,2,4-trimethyl-1,2-dihydroquinolines as for example those disclosed in U.S. 2,562,970 (issued August 7, 1951) of the structure



wherein R is hydrogen, a hydrocarbon radical or a hydrocarbonoxy radical (e.g. methyl, ethyl, isopropyl, n-butyl, isobutyl, hexyl, phenyl, benzyl, methoxy, ethoxy, propoxy, isoamyloxy, phenoxy, benzyloxy, etc.) containing not more than 7 carbon atoms.

While this invention has been described with respect to certain embodiments it is to be understood that it is not so limited and that variations and modifications thereof obvious to those skilled in the art can be made without departing from the spirit or scope of this invention.

What is claimed is:

1. A homogeneous mixture of surface-active agents for emulsifying and dispersing water-insoluble substances in water which mixture is water-soluble and contains from about 1 to 2 parts by weight of (*a*) an alkali metal alkyl sulfate water-soluble surfactant of the structure $RO.SO_2.OM$ wherein R is a long chain alkyl radical containing 8 to 18 carbon atoms and wherein M is an alkali metal, about 1 to 3 parts by weight of (*b*) the water-soluble condensation product of a mono-higher fatty acid ester of hexitol anhydride with 10 to 30 moles of alkylene oxide of the empirical formula $C_nH_{2n}O$ wherein *n* is a whole number from 2 to 3 per mole of ester, and 2 to 6 parts by weight of (*c*) water.

2. The composition of claim 1 wherein the weight ratio of (*a*) to (*b*) to (*c*) is 1:2:3.

3. An emulsifiable concentrate containing 0.5 to 8.0 parts by weight of a 2,2,4-trimethyl-1,2-dihydroquinoline and 1 part by weight of the composition of claim 1.

4. An emulsifiable concentrate containing 1.5 to 2.5 parts by weight of 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline and 1 part by weight of the composition of claim 2.

5. An emulsifiable concentrate containing 1.5 to 2.5 parts by weight of 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline and 1 part by weight of a mixture of (*a*) sodium lauryl sulfate, (*b*) water-soluble condensation product of 1 mole of sorbitan mono-oleate with 10 to 30 moles of ethylene oxide, and (*c*) water, the weight ratio of (*a*) to (*b*) to (*c*) being 1:2:3.

6. A homogeneous mixture of surface-active agents for emulsifying and dispersing water-insoluble substances in water which mixture is water-soluble and contains from about 1 to 2 parts by weight of sodium lauryl sulfate, about 1 to 3 parts by weight of the water-soluble condensation product of one mole of sorbitan mono-oleate with 10 to 30 moles of ethylene oxide, and 2 to 6 parts by weight of water.

References Cited in the file of this patent

UNITED STATES PATENTS

Re. 24,184	Sanders et al.	July 24, 1961
2,372,807	Brown	Apr. 3, 1945
2,509,233	Kaberg et al.	May 30, 1950
2,562,970	Thompson	Aug. 7, 1951
2,845,380	Mayhew et al.	July 29, 1958
2,870,058	Loder	Jan. 20, 1959
2,872,368	Sanders et al.	Feb. 3, 1959
2,898,267	Lindner	Aug. 4, 1959
2,946,721	Hyatt et al.	July 26, 1960

OTHER REFERENCES

Schwartz et al.: "Surface Active Agents and Detergents," Interscience Publishers, Inc., N.Y. 1958, vol. II, pp. 205, 209, 231, 232–235, 238–241, 318–322, 380–381, 383, 607, 611, 652–656. Esp. pertinent pages of Schwartz et al., disclosing enhanced effects arising from surfactant adjuvation of residual plant sprays, are on pages 652–656.