

DISPERSANT FORMULATION FOR CLEANING UP OIL SPILLS

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to an oil dispersant formulation and a process for dispersing spilled oil on water. More particularly, a formulation of chemical surfactants and solvent results in a low toxicity dispersant which is effective at dispersing highly viscous oil at low concentrations under a wide range of weather conditions.

Description of the Related Art

One of the technologies used for oil spill response involves the use of chemical dispersants. The application of chemical dispersants is dependent on several factors: (1) weather conditions, (2) nature of the oil spilled, (3) area to be covered and (4) adequacy of equipment and supplies. Although it is highly desirable, it has not been possible to provide a single chemical dispersant formulation which will treat all oils under all conditions. For example, it is much more difficult to disperse a high-boiling viscous oil such as bunker oil as compared to a light crude oil. Furthermore crude oils and oil products vary widely in their properties including ability to be dispersed.

A desirable property for chemical dispersants used to treat oil spills is that the surfactant formulation of the dispersant results in very low oil-water interfacial tension such that the oil is effectively dispersed as fine oil droplets in water without coalescing even at low dispersant to oil ratios. Also, the dispersant formulation should be of minimal toxicity so that it does not add to the environmental damage caused by the oil spill.

Various dispersant formulations have been advanced for treating oil spills. U.S. Patent 3,793,218 discloses a dispersant formulation for dispersing oil slicks. U.S. Patent 4,560,482 relates to a dispersant composition for treating oils having viscosities of from 1000 to 10,000 cp in water.

It would be desirable to have a dispersant formulation which is economical, and effective on highly viscous hydrocarbons.

SUMMARY OF THE INVENTION

The present invention provides an improved dispersant formulation which is effective on highly viscous hydrocarbons and a improved process for dispersing an oil layer on water. The improved dispersant formulation which is effective on highly viscous oils comprises:

- (a) a sorbitan monoester of a C_{10} - C_{20} aliphatic monocarboxylic acid,
- (b) a polyoxyethylene adduct of a sorbitan monoester of a C_{10} - C_{20} aliphatic monocarboxylic acid, said adduct having from 6 to 30 ethyleneoxide units per mole of ester,
- (c) an alkali metal salt of a dialkyl sulfosuccinate wherein the alkyl group is a branched chain radical containing 4 to 13 carbon atoms provided that the critical micelle concentration at 25 °C is greater than 0.05 g/100ml,
- (d) a polyoxyethylene adduct of a sorbitan triester of a C_{10} - C_{20} aliphatic monocarboxylic acid having from 6 to 30 ethyleneoxide units per mole of triester or a polyoxyethylene adduct of a sorbitol hexaester of C_{10} - C_{20} aliphatic monocarboxylic acid, said having from 6 to 30 ethyleneoxide units per mole of hexaester, and

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(e) a solvent comprising at least one of a propylene glycol ether, ethylene glycol ether, water, alcohol, glycol and a paraffinic hydrocarbon.

The improved process for dispersing an oil layer on water comprises contacting the oil layer on the water surface with the dispersant formulation described above.

DETAILED DESCRIPTION OF THE INVENTION

In the sorbitan esters of C_{10} - C_{20} aliphatic monocarboxylic acids (component (a)), the aliphatic radical is straight or branched chain and saturated or unsaturated. Preferred aliphatic monocarboxylic acids moieties are C_{12} - C_{18} straight chain saturated or monoethylenically unsaturated. Sorbitan esters are prepared by dehydrating sorbitol followed by reaction with aliphatic monocarboxylic acid, and are available commercially from ICI under the trade name Span®.

Polyoxyethylene adducts of sorbitan monoesters of C_{10} - C_{20} aliphatic monocarboxylic acids (component (b)) have from 6 to 30, preferably 15 to 22, ethyleneoxide units per mole of ester. Such polyoxyethylene adducts are prepared by reacting the sorbitan esters of aliphatic monocarboxylic acids described above with 1,2-ethylene oxide. These polyoxyethylene adducts are available commercially from ICI Inc. under the trade name Tween®.

The alkali metal salt of a dialkyl sulfosuccinate wherein the alkyl group is a C_4 - C_{13} branched chain radical (component (c)) is an anionic surfactant. A preferred salt is sodium dioctyl sulfosuccinate commercially available from Mona Industries, Inc. under the trade name Monowet®. The critical micelle concentration for any given dialkyl sulfosuccinate is a function of nature of the alkyl group on the sulfosuccinate and the solvent employed. In the present dispersant formulation containing a major portion of paraffinic solvent,

the dialkyl sulfosuccinate surfactant has a critical micelle concentration at 25 °C of at least about 0.05 g/100 ml.

Polyoxyethylene adducts of sorbitan triesters or sorbitol hexaesters of C₁₀-C₂₀ aliphatic monocarboxylic acids (component (d)) contain from 6 to 30, preferably 15 to 22 ethyleneoxide units per mole of triester or hexaester. The sorbitol adduct is prepared by reacting ethylene oxide with sorbitol followed by esterification and are commercially available from ICI, Inc.

The solvent (component (e)) is at least one of a propylene glycol ether, ethylene glycol ether, alcohol, glycol, water, and a paraffinic hydrocarbon. One embodiment relates to a mixture of propylene glycol ether and paraffinic hydrocarbon. Another embodiment relates to a mixture of at least one of (1) a propylene glycol ether, ethylene glycol ether, alcohol, glycol and water, and (2) a paraffinic solvent. It is feasible to use the propylene glycol ether or ethylene glycol ether with water, alcohol or glycol. It is also feasible to use only water, alcohol or glycol with paraffinic solvent. The nature of the alcohol or glycol is not critical. Preferred alcohols are C₂ to C₁₃ alcohols and preferred glycols are C₂ to C₈ glycols. Examples of component (e)(1) include propylene glycol n-butyl ether, dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol n-propyl ether, propylene glycol phenyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, ethylene glycol n-butyl ether, ethylene glycol phenyl ether, ethylene glycol methyl ether, , hexyl alcohol, octyl alcohol, butyl alcohol, ethylene glycol, propylene glycol and butylene glycol. Especially preferred are propylene glycol n-butyl ether, dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, tripropylene glycol methyl ether, propylene glycol n-propyl ether and propylene glycol phenyl ether. Glycol ethers are available from Dow Chemical Co. under the trade name Dowanol®. Preferred paraffinic components (e)(2) are isoparaffinic solvents. Especially

preferred solvents are isoparaffinic solvents wherein the isoparaffin content is at least about 50 vol.%, based on paraffinic solvent. Such solvents are available from Exxon Chemical Co. under the trade name Isopar®.

While not wishing to be bound to any theory, it is believed that when any given solvent set forth above, e.g., glycol ether, water, alcohol or glycol, is combined with paraffinic solvent, especially isoparaffinic solvent, the nature of the given solvent is not as important as when the given solvent is the sole solvent (without added paraffinic solvent). When combined with isoparaffinic solvent, the role of the given solvent relates to the solubility and hence stability of the surfactant package as well as impacting performance of the dispersant formulation in terms of its dispersant effectiveness. In some applications, it may be feasible to use a paraffinic hydrocarbon as the sole solvent component, especially when the paraffinic solvent is an isoparaffin. Use of isoparaffin alone as solvent may result in the dispersant formulation being hazy, but this may be acceptable under some applications.

The concentration ranges for components (a) through (e) in the dispersant formulation are as follows: (a) 1-9 vol.%; (b) 2-17 vol.%; (c) 5-34 vol.%; (d) 2-25 vol.%; and (e) 90-15 vol.%, based on dispersant formulation. The amount of component (e) is preferably 30 to 80 vol.%, based on dispersant formulation. The amount of paraffinic solvent is from about 30 to 100 vol.%, based on total solvent, preferably from 60-98 vol.%.

The present dispersant formulations containing a mixture of co-solvents have the advantage of dispersing highly viscous hydrocarbons, i.e., hydrocarbons having a viscosity greater than 10,000 cp at 15° C. Such viscous hydrocarbons such as heavy crudes, weathered crudes and bunker oil are difficult to disperse because of the cohesiveness of the oil which resists the spreading and breakup of the oil as well as the penetration mixing of the dispersant formulation.

In addition these formulations have low environmental impacts and can be sprayed over wide temperature ranges. Viscosity properties can be adjusted to favor aerial spraying over a wide temperature range, and evaporation losses are minimal which means that nearly all the solvent will reach the oil slick to aid surfactant penetration of the oil. It is preferred that the viscosities for the dispersant formulations be greater than about 70 cp at 68° F. Oil slick dispersal can be achieved by spraying the dispersant formulation directly on the slick through one or more spray nozzles. Dispersal action can be achieved under normal water motion, i.e., in a presence of wave action.

An important property of a dispersant formulation for use on oils spills is the ability to disperse the maximum amount of oil per unit of dispersant. The ability to effectively disperse oil at low dispersant to oil ratios (DOR) provides both economic and environmental benefit. By lowering the amount of dispersant per unit of oil, there is less need for resupplying the application system thereby saving time. The present formulations are effective at low dispersant to oil ratios.

While not wishing to be bound to any theory, it is believed that component (e)(1) acts to solubilize the surfactant package. Therefore the least amount of component (e)(1) is that effective to maintain the surfactant package in solution without haze or phase separation of the dispersant formulation. Generally the minimum amount of component (e)(1) is about 2 vol.%, based on total solvent. In addition to its solubility properties, component (e)(1) may act synergistically with component (e)(2) to improve effectiveness of the dispersant formulation.

The improved dispersant formulations are further illustrated by the following examples, which include a preferred embodiment of the invention.

Example 1 - Dispersant Effectiveness

This example is directed to the advantages of using a combination of isoparaffinic solvent and co-solvent. A dispersant formulation containing 15.2 vol.% polyoxyethylene(20) sorbitan trioleate, 9.8 vol.% of polyoxyethylene(20) sorbitan monooleate, 5.4 vol.% sorbitan monooleate and 19.6 vol.% of sodium dioctyl sulfosuccinate was prepared. The balance (50%) of the dispersant formulation is solvent. The dispersant effectiveness was measured using the IFP technique described as follows.

The IFP dilution test is a well-known laboratory procedure to measure dispersant effectiveness. The physical apparatus for the test involves a cylindrical glass container for holding a test solution and an oscillating hoop that fits inside the container. The glass container has two ports: (1) an inlet port located just below the experimental water level and (2) an outlet port that is located near the bottom of the vessel and contains an overflow arm extending upward to determine the depth of the test solution in the container. Clean seawater is introduced by a peristaltic pump into the glass container through the inlet port. Overflow water (containing oil droplets) leaves the container through the exit port and is collected in a flask. The oscillating hoop is suspended 20-35 mm beneath the water's surface and moves up and down with a 15 mm vertical path by an electromagnet controlled by an electronic timer. The frequency of the oscillation can be varied in the range of 6.66-20 cycles/minute. For tests designed to evaluate dispersant effectiveness, the following experimental protocol is followed: the glass container is filled with sea water, a specified amount of oil is poured onto the water surface inside a 10 cm diameter vertical ring, dispersant is added onto the surface of the oil, the oscillating hoop is started, and water flow through the peristaltic pump is started at a specified flow rate (e.g., to produce a dilution or turnover rate of 0.5/hour). Outflow water is collected for specified periods of time (e.g., 0-30 minutes, 30-60 minutes, and

60-120 minutes) and analyzed for oil content. Oil content in the collected samples follows the equation (1):

$$x = x_0 e^{-Dt} \quad (1)$$

where x = oil concentration at time t ,

x_0 = initial dispersed oil concentration in the experimental beaker, and

D = dilution rate.

The percentage of washed-out oil (P) at time t is:

$$P = 100(1 - x/x_0) = 100(1 - e^{-Dt}). \quad (2)$$

Dispersion effectiveness can be determined from the equation:

$$E = 100 [(P_d - P_c) / P_c] \quad (3)$$

where E = dispersant effectiveness (%),

P_d = percentage of washed-out oil at time t in solution with dispersant d ,
and

P_c = percentage of washed-out oil at time t in control solution without dispersant.

The results for a No. 6 bunker oil (200°C+ fraction having a viscosity of about 37,000 cP @ 10 s⁻¹ shear rate) are shown in Table 1.

TABLE 1

<u>Solvent</u> ⁽¹⁾	<u>% Dispersed</u>
Isopar M	84.6
Exxsol D80 ⁽²⁾	57.9
Ethylene glycol n-butyl ether	46.1
Propylene glycol n-butyl ether	72.0
Dipropylene glycol n-butyl ether	74.4
Tripropylene glycol n-butyl ether	71.5
Propylene glycol n-propyl ether	33.6
Dipropylene glycol n-propyl ether	59.6
Dipropylene glycol methyl ether	49.3
Tripropylene glycol methyl ether	61.5
Ethylene glycol phenyl ether	60.3
Propylene glycol phenyl ether	71.8
Isopar M (45 vol. %)/Dipropylene glycol n-butyl ether (5 vol. %)	87.0
Isopar M (40 vol. %)/Dipropylene glycol n-butyl ether (10 vol. %)	80.0
Isopar M (25 vol. %)/Dipropylene glycol n-butyl ether (25 vol. %)	77.0
Exxsol D80 (25 vol. %)/ Dipropylene glycol n-butyl ether (25 vol. %)	51.9
Isopar M (25 vol. %)/Exxsol D80 (25 vol. %)	77.0
Isopar M (25 vol. %)/Tripropylene glycol methyl ether (25 vol. %)	85.1
Isopar M (40 vol. %)/Ethylene glycol n-butyl ether (10 vol. %)	72.7
Isopar M (47.5 vol. %)/Ethylene glycol phenyl ether (2.5 vol. %)	78.6
Isopar M (47.5 vol. %)/Propylene glycol phenyl ether (2.5 vol. %)	87.8
Isopar M (47.5 vol. %)/Propylene glycol n-propyl ether (2.5 vol. %)	89.9
Isopar M (45 vol. %)/Propylene glycol n-propyl ether (5 vol. %)	52.3
Isopar M (47.5 vol. %)/Water (2.5 vol. %)	75.5

⁽¹⁾ Dispersant formulation in 50 vol.% solvent.

⁽²⁾ Contains less than 50 vol.% isoparaffins

As shown in Table 1, when a single solvent is used, propylene glycol n-butyl ether, dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether, and Isopar M give the best performance with regard to % dispersed. However, the propylene glycol phenyl ether solvent may not be desirable for an oil spill dispersant because of the aromatic moiety. Isopar M may not be desirable because of the haze, but still could be used in those cases where haze is acceptable.

Solvent mixtures of glycol ether and Isopar are generally more effective than would be expected from either solvent alone. This indicates a synergistic effect of the solvent mixture. Furthermore, lowering the concentration of glycol ether in the solvent mixture relative to the Isopar component favors increased dispersal effectiveness. The amount of glycol ether in the mixture must generally be above about 2 vol.% in order to keep the surfactant package in solution. The amount of co-solvent is that sufficient to solubilize the surfactant package, i.e., that amount effective to clear up any haze in the final formulation without causing haziness or phase separation.

Other solvents besides glycol ethers can also be used to keep the surfactant package in solution, including alcohols, glycols and water. The amount of such solvents is that effective to clear up any haze in the final formulation. If the amount of co-solvent is too great, then the final surfactant formulation may again become hazy due to solubility problems with the surfactant package. The combination of Isopar M with co-solvent is more effective than the pure solvent alone (without Isopar). As noted above, the combination of solvents exhibits a synergism in many cases, i.e., the dispersant effectiveness is greater than one would expect from a mere combination of Isopar M with co-solvent. Even solvents which are soluble in water can be effective dispersants when mixed with Isopar M in small amounts. Furthermore, at low co-solvent concentrations, toxicological concerns over glycol ethers containing an aromatic moiety are much less.

CLAIMS:

1. An improved dispersant formulation effective on highly viscous hydrocarbons which comprises:

(a) a sorbitan monoester of a C_{10} - C_{20} aliphatic monocarboxylic acid,

(b) a polyoxyethylene adduct of a sorbitan monoester of a C_{10} - C_{20} aliphatic monocarboxylic acid, said adduct having from 6 to 30 ethyleneoxide units per mole of ester,

(c) an alkali metal salt of a dialkyl sulfosuccinate wherein the alkyl group is a branched chain radical containing 4 to 13 carbon atoms provided that the critical micelle concentration at 25 °C is greater than 0.05 g/100ml,

(d) a polyoxyethylene adduct of a sorbitan triester of a C_{10} - C_{20} aliphatic monocarboxylic acid having from 6 to 30 ethyleneoxide units per mole of triester or a polyoxyethylene adduct of a sorbitol hexaester of C_{10} - C_{20} aliphatic monocarboxylic acid, said having from 6 to 30 ethyleneoxide units per mole of hexaester, and

(e) a solvent comprising at least one of a propylene glycol ether, ethylene glycol ether, water, alcohol, glycol, and a paraffinic hydrocarbon.

2. The formulation of claim 1 wherein the solvent comprises a propylene or ethylene glycol ether, at least one of water, alcohol and glycol, and a paraffinic hydrocarbon.

3. The formulation of claim 1 wherein the solvent comprises a propylene or ethylene glycol ether and an isoparaffinic hydrocarbon.



4. The formulation of claim 1 wherein the paraffinic hydrocarbon is an isoparaffinic hydrocarbon.
5. The formulation of claim 1 wherein the amounts of components (a) to (e) are: (a) 1-9 vol. %, (b) 2-17 vol. %, (c) 5-34 vol. %, (d) 2-25 vol. % and (e) 90-15 vol. %.
6. The formulation of claim 1 wherein component (b) is a polyoxyethylene adduct of a sorbitan monoester of a C_{10} - C_{20} aliphatic monocarboxylic acid.
7. The formulation of claim 1 wherein component (d) is a polyoxyethylene adduct of a sorbitan triester of a C_{10} - C_{20} aliphatic monocarboxylic acid.
8. The formulation of claim 1 wherein the solvent is an isoparaffinic hydrocarbon.
9. The formulation of claim 8 wherein the isoparaffinic hydrocarbon contains at least 50 vol.% isoparaffins.
10. The formulation of claim 1 wherein component (d) is the polyoxyethylene adduct of a sorbitol hexaester of a C_{10} - C_{20} aliphatic monocarboxylic acid.
11. A method for dispersing an oil layer on water which comprises contacting the layer with the dispersant formulation of claim 1.
12. The method of claim 11 wherein the dispersant formulation is applied to the oil layer by aerial spraying or from a boat.

