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# PATENT SPECIFICATION

(11) 1255394

## DRAWINGS ATTACHED

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## (54) OIL SLICK DISPERSANTS

(71) We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to improved biodegradable oil slick dispersant compositions and methods involving their use.

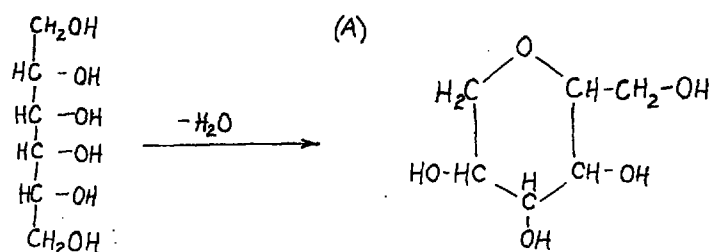
Water pollution occasioned by the discharge of oil into water resulting in the formation of objectionable oil slicks is a well-known hazard. Such oil slicks or films are undesirable not only from an esthetic standpoint but also because cohesive oil films represent a barrier to the transfer of oxygen from the atmosphere to support marine life, a serious hazard to marine fowl, as well as a serious short contaminant. The pollution of water by oil is sometimes inadvertently occasioned by the discharge of ballast water from oil tankers or from off-shore drilling operations. While the discharge of oil to the water in these situations is often inadvertent and is sought to be avoided, problems nevertheless do arise.

Various techniques have been advanced for solving the oil contamination problem. One solution involves the use of strong detergents to emulsify the oil with the water. However, the use of strong detergents or surfactants has resulted in severe damage to marine life.

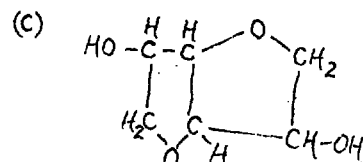
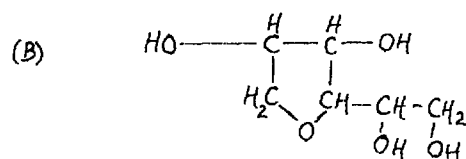
In accordance with the present invention, it has been found that intact cohesive oil films or oil slicks on water can be rapidly dispersed or the formation of such oil slicks from a mixture of oil and water can be prevented by contacting the oil slick or oil-water mixture with a dispersant system composed of a sorbitan monoacylate or a polyalkylene oxide derivative of a sorbitan monoacylate, or their mixture. Preferably, the dispersant system exhibits a hydrophilic-lipophilic balance number of about 14.0. The dispersant system can be applied to an oil slick either alone or in conjunction with a polar diluent. Highly desirable results are achieved by spraying the dispersant system directly and as uniformly as possible onto the surface of the oil slick using approximately 1 part by weight of dispersant per 10 to 100 parts by weight of oil followed by agitating the polluted area, if possible, to aid in the dispersion of the oil film. The active components of the dispersant system, namely, the sorbitan derivatives, are non-toxic to marine life and are readily biodegradable.

The accompanying drawing shows a series of curves which illustrate the efficiency of the dispersant system of the invention in comparison with other dispersant materials.

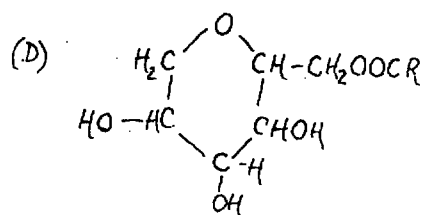
The sorbitan products employed in the formation of the oil slick dispersant system are formed, in the case of sorbitan monoacylates, through the reaction of a long-chain saturated or unsaturated hydrocarbon fatty acid with a mixture of polyalcohols formed by the dehydration of sorbitol, and in the case of polyoxyalkylene sorbitan monoacylates, through the reaction of the sorbitan monoacylates with a 1,2-alkylene oxide, such as ethylene oxide or propylene oxide. The dehydration of sorbitol to the intermediate sorbitan compounds proceeds according to the following equations:



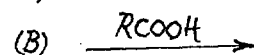
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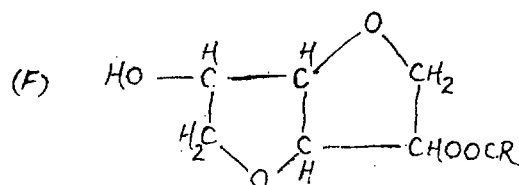
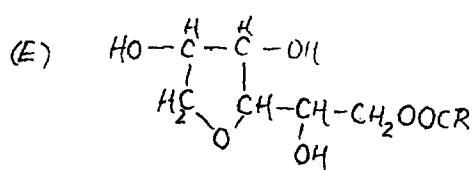
The above materials (products A, B, C) are all formed during the dehydration reaction. Sorbitan monoacylates are secured by reacting compounds A, B or C, or their mixtures with a fatty acid according to the following equation.



(A)



(C)



As noted in Equation II, the esterification reaction involving a long-chain monocarboxylic acid is quite specific as only certain of the available hydroxyl groups on the sorbitan material are subjected to the esterification reaction. The term "sorbitan monoacylates" as used herein is meant to denote compounds D, E, and F, alone or in admixture.

Polyoxyalkylene sorbitan monoacylates are formed by contacting sorbitan monoacylates (compounds D, E or F, or their mixtures) with a 1,2-alkylene oxide thereby reacting one or more of the remaining hydroxyl groups on the sorbitan monoacylate

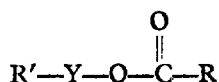
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10

10

$$\text{CH}_3$$

For the sake of simplicity, useful sorbitan monoacylates or polyoxyalkylene sorbitan monoacylates may be denoted by the following generalized formulas:


$$\text{-(CH}_2\text{-CH(CH}_3\text{)-)}_m\text{A}^n \text{ wherein m varies from 5 to 17, and n is a monoglycyl or diglycyl}$$

The present dispersant compositions are composed of either sorbitan monoacylates, polyoxyalkylene sorbitan monoacylates, or their mixtures. It has been found that it is highly desirable for these compounds to be used in the dispersant system in such a manner that the hydrophilic-lipophilic balance (HLB) number of the dispersant system varies between 13.5 and 14.5, preferably about 14.0. For the purposes of the present invention, the hydrophilic-lipophilic balance number is determined according to the following equation.

$$HLB = \frac{\begin{array}{l} \text{(Mol. Wt. of Hydrophilic} \\ \text{compound used in Synthesis} \\ \text{of Component A)} \end{array}}{\begin{array}{l} \text{(Mol. Wt. Component A)} \end{array}} (20) \text{ (Wt. \% of A} \\ \text{in Dispersant)} + \frac{\begin{array}{l} \text{(Mol. Wt. of hydrophilic} \\ \text{compound used in Synthesis of} \\ \text{Component B)} \end{array}}{\begin{array}{l} \text{(Mol. Wt. Component B)} \end{array}} (20) \text{ (Wt. \% of B} \\ \text{in Dispersant)}$$

In summary, HLB number is ascertained by dividing the molecular weight of the hydrophilic compounds employed in the synthesis of a given compound by the

5 molecular weight of that compound and multiplying the result by 20. In situations  
where a plurality of materials are employed in the dispersant system, the HLB number  
for the total system is the summation of the HLB numbers of the individual com-  
ponents multiplied by the weight percent of that particular component of the total  
dispersant system. For example, the HLB number of the lauric acid ester of com-  
pound A of equation I would be determined by dividing the molecular weight of the  
sorbitan material, (the hydrophilic portion of the molecule) namely, compound A, which  
has a molecular weight of 164 by the molecular weight of sorbitan monolaurate (com-  
pound D) which is 346 and multiplying the result by 20. Thus the HLB number for  
10 compound D of equation II wherein R is the alkyl portion of the lauric acid material  
is 9.5. As is evident from the method employed in calculating HLB value, the HLB  
number of any given compound can be increased by adding polyoxyethylene or poly-  
oxypropylene radicals to the compound or by diminishing the molecular weight of  
15 the alkene or alkenyl portion of the monoacid employed in the synthesis of the initial  
sorbitan monoacylate.

The active ingredients of the active dispersant system may be applied directly  
to the cohesive oil slick to produce its dispersion; however, it is desired that the  
active ingredients be employed in conjunction with a solvent. Normally, solvents  
make-up from 0 to 95 weight percent, preferably 70 to 90 weight percent of the total  
composition. Useful solvents include: water;  $C_2-C_{10}$  alkyl alcohols such as ethanol,  
20 isopropanol, n-pentanol and 2-ethyl hexanol; aromatic and alkyl substitute aromatic  
hydrocarbons, such as benzene, toluene, ethyl benzyl neo-pentyl benzene, heavy aro-  
matic naphtha refinery streams and xylene. Water and lower alkanols are the pre-  
ferred solvent materials as they do not create any marine toxicity problem.

25 Normally, from 1 to 10 parts by weight of the total dispersant system, that is,  
active ingredients plus any solvent used, is employed per 100 parts by weight of oil.  
Oil slick dispersal can be achieved by spraying the total dispersant system directly onto  
the oil slick. In effect, the dispersant system works at the oil-water interface and by the  
gentle application of the dispersant system onto the film, the break-up and dispersion  
30 of the film quickly results. It is desirable that the dispersant be applied onto the oil  
slick with a small diameter hose equipped with a spray nozzle to supply a uniform  
fine spray for efficient distribution. Preferably the dispersant system is applied from  
a work boat as opposed to applying the material from a distant tanker or pier. For  
large yields, mechanical modifications of this arrangement may be more appropriate.  
35 For example, the dispersant may be applied more efficiently to a larger area by a  
simple pipe manifold to which is affixed a plurality of spray nozzles. This applicator  
may be rigged from the side or the bow of the work boat in order to increase the  
area sprayed upon each pass of the boat.

After application of the dispersant system onto the oil film, vigorous agitation  
40 such as that secured with a high velocity water hose or with a powerful propeller, is  
recommended although such agitation is not essential to the efficient use of the disper-  
sant system. Oil slick formation can be avoided in the first instance using the present  
dispersants by introducing the dispersant into a conduit or pipe that may contain oil-  
water mixtures prior to the passage of the oil-water mixture to the main body of drain-  
45 age water.

#### EXAMPLE 1

A series of tests were conducted to demonstrate the effectiveness of the disper-  
sant materials of the present invention in comparison with other commercially avail-  
able dispersant materials. In each of the tests two cubic centimeters of a mixture com-  
posed of 10 parts by weight of Southern Louisiana crude oil and one part by weight  
50 of dispersant system was mixed with 100 cubic centimeters of sea water and was  
shaken vigorously for five minutes using a mechanical shaking device. These mix-  
tures were then poured into colorimeter cells for measurement of turbidity as de-  
termined by light transmission measurements. The basis for the tests is the fact that  
the decay of light transmission versus time is a measure of the stability of the dis-  
persion with the more stable dispersion transmitting less light thus indicating a more  
55 effective dispersant system. The dispersant system of the present invention was com-  
posed of 9 wt. % of sorbitan monooleate (available as SPAN\* 80 from Atlas Chemi-  
cal Co.) and 91 wt. % of a 20 mole polyoxyethylene adduct of sorbitan monooleate  
(available as TWEEN\* 80 from Atlas Chemical Co.). The system had an HLB  
60 value of 14.0.

The activity of the invention composition was compared with two commercially

\* registered Trade Mark.

available oil slick dispersant systems namely, Biocleanosol\* and Polycomplex A-11, and two other dispersant systems composed of commercially available emulsifiers. The commercial emulsifier systems labelled B and D on Figure 1 consist of the following constituents: Composition B was composed of 50 wt. % heavy aromatic naphtha (HAN), 10 wt. % of a tertiary amine formed by condensing 15 moles of ethylene oxide with one mole of a primary stearic acid amine (Armour Ethomeen S/15), and 40 wt. % of an alkyl aryl polyether alcohol (Rohm & Haas Triton\* X-45). Composition B has an HLB value of 10.6. Composition D was composed of 50 wt. % HAN, 10 wt. % of Armour Ethomeen\* S/15, and 40 wt. % of Renex\* 697 (a polyoxyalkylene alkyl aryl ether sold by Atlas Chemical Industries). Composition D had an HLB value of 9.8. The control experiment was identical to the other experiments with the exception that a dispersant was not present.

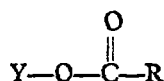
As can be seen by referring to Figure 1, the dispersant system falling within the scope of the invention was remarkably superior to other emulsifiers and to commercially available materials that are sold as oil slick dispersants. The curves shown on Figure 1 readily illustrate that the oil-water dispersion formed utilizing the composition of the present invention was much more impervious to separation than any of the other materials tested.

#### EXAMPLE 2

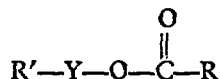
The effectiveness of the dispersant systems of the instant invention were also tested in the field. In offshore drilling operations, the oil recovered is sometimes contaminated with sea water. The water and oil are separated using typical decanting operations and the water which contains minor amounts of oil is discharged into the sea. Because the decanting operation is not completely effective, oil slicks develop because of the discharge of the oil into the sea. In the test, a dispersant system composed of 52 wt. % water, 20 wt. % isopropanol and 28 wt. % of the mixture of Example 1 having an HLB value of 14 was used. In the test, the dispersant system was injected into the oily water effluent line which passed the water from the separation vessel to the sea. The oily water effluent rate was about 2500 barrels per day and the oily water contained approximately 1000 parts per million of oil. The dispersant system was injected into the effluent line at a rate of about 8 gallons per day, the dispersant system being used at a rate of about 10 parts of dispersant per 100 parts by weight of oil. Using this technique, the oil slick normally surrounding the drilling rig was completely removed. The biodegradability and nontoxicity of instant dispersant systems was demonstrated using classic Warburg (registered Trade Mark) Respirometer tests and with bio assay tests using live tropical fish.

#### WHAT WE CLAIM IS:—

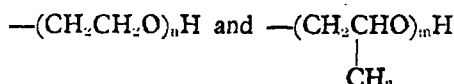
1. A method of dispersing an oil slick on water or preventing the formation of an oil slick on water from a mixture of oil and water which comprises contacting the slick or the oil-water mixture with a dispersant system containing a compound having the general formula



or



or a mixture of such compounds, wherein Y is a mono- or bicyclic sorbitan radical as hereinbefore defined, R is selected from monovalent alkyl and alkenyl radicals having from 8 to 20 carbon atoms, and R' is a radical having the general formula selected from the group consisting of



wherein n varies from 6 to 30 and m varies from 5 to 14.

\* registered Trade Mark.

available oil slick dispersant systems namely, Biocleanosol\* and Polycomplex A-11, and two other dispersant systems composed of commercially available emulsifiers. The commercial emulsifier systems labelled B and D on Figure 1 consist of the following constituents: Composition B was composed of 50 wt. % heavy aromatic naphtha (HAN), 10 wt. % of a tertiary amine formed by condensing 15 moles of ethylene oxide with one mole of a primary stearic acid amine (Armour Ethomeen S/15), and 40 wt. % of an alkyl aryl polyether alcohol (Rohm & Haas Triton\* X-45). Composition B has an HLB value of 10.6. Composition D was composed of 50 wt. % HAN, 10 wt. % of Armour Ethomeen\* S/15, and 40 wt. % of Renex\* 697 (a polyoxyalkylene alkyl aryl ether sold by Atlas Chemical Industries). Composition D had an HLB value of 9.8. The control experiment was identical to the other experiments with the exception that a dispersant was not present.

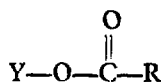
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#### EXAMPLE 2

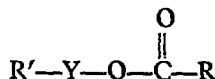
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#### WHAT WE CLAIM IS:—

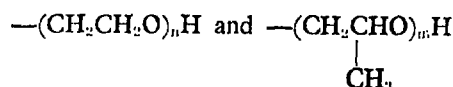
1. A method of dispersing an oil slick on water or preventing the formation of an oil slick on water from a mixture of oil and water which comprises contacting the slick or the oil-water mixture with a dispersant system containing a compound having the general formula



or



or a mixture of such compounds, wherein Y is a mono- or bicyclic sorbitan radical as hereinbefore defined, R is selected from monovalent alkyl and alkenyl radicals having from 8 to 20 carbon atoms, and R' is a radical having the general formula selected from the group consisting of



wherein n varies from 6 to 30 and m varies from 5 to 14.

\* registered Trade Mark.



(14)

2. The method of claim 1 wherein said dispersant system has an HLB number of from 13.5 to 14.5.

3. The method of claim 1 or claim 2 wherein said dispersant system has an HLB number of about 14.0.

5 4. The method of any of claims 1—3 wherein  $n$  varies from 15 to 22. 5

5. The method of any of claims 1—4 wherein  $R$  has from 12 to 18 carbon atoms.

6. The method of any of claims 1—5 wherein  $R'$  is a polyoxyethylene radical.

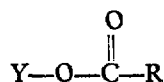
7. The method of any of claims 1—5 wherein  $R'$  is a polyoxypropylene radical.

10 8. The method of any of claims 1—7 wherein from 1 to 10 parts by weight of the dispersant system is employed per 100 parts by weight of oil. 10

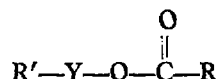
9. The method of any of claims 1—8 wherein said dispersant system contains a mixture of sorbitan monooleate and a polyoxyethylene adduct of sorbitan monooleate.

10. The method according to any preceding claim wherein the oil is crude oil.

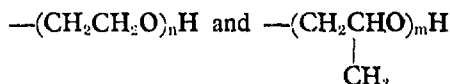
15 11. A dispersant system composition comprising a mixture of a sorbitan monoacylate having the formula: 15



and a polyoxyalkylene sorbitan monoacylate having the formula:



20 wherein  $Y$  is a mono- or bicyclic sorbitan radical,  $R$  is selected from the group consisting of monovalent alkyl and alkenyl radicals having from 8 to 20 carbon atoms, and  $R'$  is a radical having the general formula selected from the group consisting of: 20



wherein  $n$  varies from 6 to 30 and  $m$  varies from 5 to 14, said dispersant system having an HLB number of from 13.5 to 14.5.

25 12. The composition of claim 11 wherein  $n$  varies from 15 to 22. 25

13. The composition of claim 11 or claim 12 wherein  $R$  has from 12 to 18 carbon atoms.

14. The composition of any of claims 11—13 wherein  $R'$  is a polyoxyethylene radical.

30 15. The composition of any of claims 11—14 wherein said dispersant system has an HLB number of about 14.0. 30

16. The composition of any of claims 11—15 wherein said composition is admixed with a solvent, said solvent comprising 70 to 90 wt. % of the total solvent/dispersant composition.

35 17. The composition of claim 16 wherein said solvent is water. 35

18. The composition of claim 16 wherein said solvent is an alkyl alcohol having from 2 to 10 carbon atoms.

19. The composition of any of claims 11 to 18 substantially as herein described, and with particular reference to the accompanying drawing.

40 20. A method of dispersing an oil slick on water or preventing the formation of an oil slick on water from a mixture of oil and water according to any of claims 1 to 10 substantially as herein described, and with particular reference to the accompanying drawings. 40

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\* C L M S \*