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3,415,745

METHOD OF FLOCCULATING A WATER-BORNE OIL SLICK

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This invention relates to a method for the dispersion of water-borne oil slicks. Particularly, it relates to the dispersion of such oil slicks by the application thereto of an aqueous solution of a quaternary ammonium salt of an imidic reaction product of a vinyl monomer-maleic anhydride polymer and a polyamine.

Various techniques have been proposed for the removal or dispersion of oil "slicks" resulting from the spills, leaks and deliberate disposal of petroleum products in harbors, rivers, lakes, etc. The presence of oil slicks often creates a serious problem not only with respect to their unsightliness and deleterious effects on marine life, bathing beaches, etc., but also because of the fire hazards they create. The oil slick problem is increasing in frequency due in part to the replacing of the older coal-burning steamships with the diesel fueled vessels of today. Off-shore drilling rigs, seaside refineries and oil tankers likewise contribute to the incidents of oil leaks and spills and are constant sources of oil slicks or scums, creating a hazard to themselves as well as impairing the usefulness of any nearby water recreation areas.

Some of the early methods of surface oil removal included the application of solid absorbents to the slick, such as hay or straw, followed by the tedious task of gathering and removing the oil-soaked absorbing material. The disadvantages with respect to time, efficiency and cost of such a method are readily apparent. A more recent method, described in U.S. 3,198,731 to De Lew, involves the congealing of the oil to a stiff mass or gel by the application thereto of a congealing agent, such as a soap of a wool grease fatty acid, which is capable of forming a semi-rigid water-in-oil emulsion. This method, like the older ones, still requires a subsequent step of skimming the congealed oil off the surface of the water.

Still another oil slick removal method, described in French Patent No. 1,374,257, involves the use of an inclined conveyor belt made of a nonabsorbent oleophilic material. The oil is skimmed from the surface of the water at the foot of the conveyor and removed from the belt at the top of the incline by means of a scraper blade. While the foregoing methods attempt to solve the oil slick problem by actual removal of the oil from the water, it has also been known that floating oil could be dispersed in the water by application of a surface-active agent to the slick. Surfactants employed by the prior art, such as polyalkylene oxides and alkyl aryl sulfonates, have proven to be fairly effective in initially dispersing or emulsifying the oil, thereby eliminating the surface scum, but have been less than satisfactory in that the oil has often been found to reform on the surface of the water within a few days. Such reappearance of the slick is especially a problem in more or less quiescent waters

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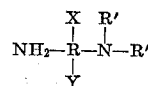
where currents are minimal and insufficient to carry off the dispersed oil.

It has now been found that the application to a water-supported oil slick of a quaternary ammonium salt of a tertiary amine-containing, imidic reaction product of a monovinyl monomer-maleic anhydride polymer and a polyamine will effect rapid and lasting removal, through flocculation, of the oil from the surface of the water. Suitable vinyl monomer-maleic anhydride polymers for preparation of the flocculant of this invention are those having an average molecular weight in the range of about 600 to 100,000 preferably 600 to 50,000, and containing a molar ratio of vinyl monomer to maleic anhydride of about 1 to 4:1 preferably 1 to 3:1. Suitable vinyl monomers are polymerizable monovinyl compounds of 2 to about 12 carbon atoms and include, for instance, alpha-olefins such as ethylene, propylene, isobutylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene and dodecylene; vinyl ethers such as methylvinyl ether, ethylvinyl ether, n-butylvinyl ether and isobutylvinyl ethers; and vinyl aromatics such as vinyltoluene, styrene and the like. Mixtures of, as well as single, vinyl monomers are contemplated and intended to be included herein and in the claims by the terminology "monovinyl compound." The preferred monomer is styrene. If desired, maleic acid can be used instead of maleic anhydride in formation of the polymer.

The vinyl monomer-maleic anhydride polymer can be prepared by known methods. A preferred method is by solution polymerization where the monomers are polymerized in a suitable solvent employing as the polymerization catalyst a free-radical catalyst, such as a peroxide, preferably benzoyl peroxide or dicumyl peroxide, at a temperature of about 75 to 300° C. or more. Suitable solvents include the aromatic hydrocarbon solvents, such as cumene, p-cymene, xylene, toluene, etc. Other suitable solvents are the ketones, such as methylethyl ketone.

The preferred manner of carrying out the polymerization is by what is known as incremental feed addition. By this method, the monomers and catalysts are first dissolved in a portion of the solvent in which the polymerization is to be conducted and the resulting solution fed in increments into a reactor containing solvent heated to reaction temperature, usually the reflux temperature of the mixture. When an aromatic solvent is employed as the solvent for the polymerization, the formation of the polymer causes a heterogeneous system, the polymer layer being the heavier layer and recoverable by merely decanting the upper aromatic solvent layer and drying. On the other hand, when a ketone is the solvent, the polymer formed is usually soluble in the solvent media so that recovery of the product necessitates a stripping operation.

The polyamines to be reacted with the vinyl monomer-maleic anhydride polymer to produce the flocculating agent of the present invention include those represented by the following structural formula:



where X is hydrogen or



Y is hydrogen or



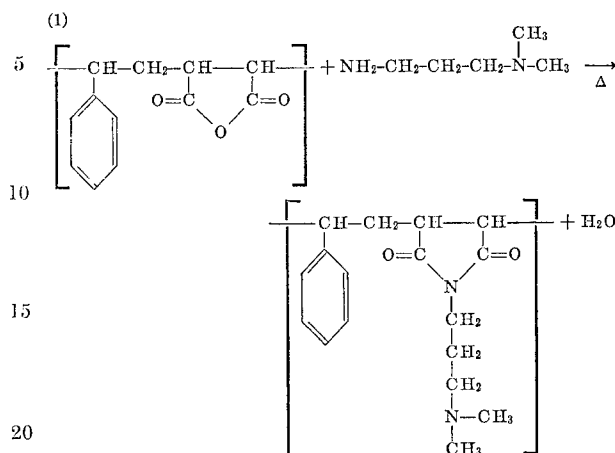
R is alkylene, including cycloalkylene of 1 to about 10, preferably about 2 to 6 carbon atoms, and R' is a monovalent hydrocarbon radical, preferably alkyl, including cycloalkyl, of 1 to about 8, preferably 1 to 2, carbon atoms. Thus, suitable polyamines include dihydrocarbylaminoalkylamines, bis(dihydrocarbylamino)alkylamines and tris(dihydrocarbylamino)alkylamines. As examples of those polyamines containing only one tertiary amine group, may be mentioned dimethylaminoethylamine, dimethylaminoethylamine, dimethylaminopropylamine, dimethylaminobutylamine, diethylaminopropylamine, diethylaminoamylamine, dipropylaminopropylamine, methylpropylaminoamylamine, propylbutylaminoethylamine, etc. As examples of suitable polyamines containing two or three tertiary amine groups may be mentioned, bis(dimethylamino)propylamine, bis(dimethylamino)ethylamine, tris(diethylamino)-amylamine, bis(methylpropylamino)butylamine, tris(methylethylamino)-butylamine, etc.

Reaction of the polyamine with the vinyl monomer-maleic anhydride polymer can be effected by heating at imide-forming temperatures, either with or without catalyst, a mixture of the reactants. The ratio of reactants and the duration of the reaction can be controlled so as to effect imidation of about 80 to 100, preferably at least about 90 or even 95, percent of the maleic anhydride units in the polymer. A temperature of about 125° C. is usually necessary to effect the imidation reaction but temperatures above about 350° C. are generally not utilized in that they may cause undesirable side reactions or degradation of the product. Preferred reaction temperatures are in the range of about 150 to 200° C. The reaction may be carried out in bulk or in the presence of a suitable mutual solvent for the reactants. Total reaction time will vary depending on the particular reactants employed, but will usually range from about 1 to 5 hours.

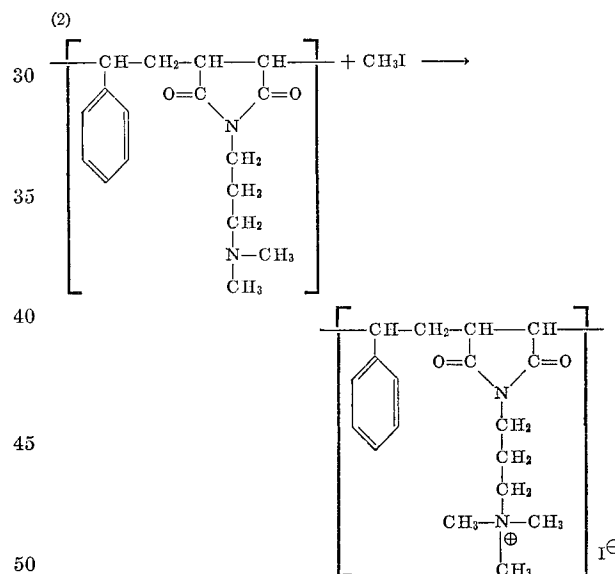
The quaternary ammonium salt of the imidic reaction product can be prepared by treatment of the polymeric imide with an alkyl halide. Suitable alkyl halides are, for instance, the monohalogenated alkanes, including cycloalkanes, having 1 to about 4, preferably 1 to 3, carbon atoms, the halogen having an atomic number of 17 to 53, i.e., being chlorine, bromine or iodine. Quaternization can be effected by known methods such as by contacting, for instance at room temperatures, the imidic reaction product with the alkyl halide in solution in a suitable mutual solvent. Elevated temperatures, for example, up to about 100° C. or more, can be employed if suitable equipment is used to maintain the relatively low boiling alkyl halide in solution. As suitable solvents, may be mentioned ketones, e.g., acetone and methylethyl ketone; aromatic hydrocarbons, e.g., benzene and toluene; ethers, e.g., diethyl ether and methyl phenyl ether; etc. Reaction times depend upon reactant proportions, reaction temperature, the desired extent of quaternization, etc., will vary anywhere from a few minutes to several hours, or even days. At room temperature the quaternization reaction will generally be complete within a period of a few hours to overnight. The quaternary salt used in the method of the present invention is one in which about 30 to 100, often about 50 to 80, percent of the total tertiary amine, i.e., dihydrocarbylamino, groups are quaternized with the alkyl halide.

The foregoing discussion of the preparation of the polymeric imide and its quaternary salt may be better understood by reference to the chemical equations presented below, wherein dimethylaminopropylamine exemplifies the polyamine and methyl iodide is used as the quaternizing agent. Thus, the reaction at elevated temperatures between a styrene-maleic anhydride polymer and

dimethylaminopropylamine proceeds at the maleic anhydride unit of the polymer to form an imide as follows:



Subsequent reaction of the dimethylaminopropylamide of the styrene-maleic anhydride polymer (product of Equation 1) with methyl iodide results in the formation of a quaternary salt of the imide as follows:



The flocculant used in the present invention, i.e., the quaternary ammonium salt of the polymeric imide, is, for economic reasons, preferably applied to the oil-slick as an aqueous solution containing, say, at least about 0.01, preferably about 0.1 to 3, weight percent of flocculant. The solubility of the flocculant of the present invention in aqueous media is excellent over an extremely wide pH range; thus, the flocculant solution may be acidic, basic or neutral.

Oil slicks which may be effectively flocculated by application of the imidic reaction product of the present invention are those comprised of mineral oil hydrocarbons boiling primarily in the range of about 175° F. to 1000° F. and include, for example, gasoline, diesel oils, lube oils, crude oils, and the like. Application of the flocculant may be by any suitable means such as by spraying over the surface of the slick, or, when the source of the oil is known, by injecting the flocculant at the point of oil entry into the water. Both fresh and salt water supported slicks can be effectively removed by the method of the present invention.

The following examples serve to further illustrate the method of the present invention. Parts and percentages are by weight.

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EXAMPLE I

The effectiveness of the various agents described in Table I, to follow, was measured in terms of the length of time required for each to completely disperse or flocculate a water-supported film of a hydrocarbon fuel oil containing 55 percent gas oil, 30 percent light cycle oil and 15 percent water-white distillate. To 250 cc. of a saturated solution of sodium chloride in water, contained in a Pyrex crystallization dish 7¼" in diameter and 4" high, were added at room temperature 5 cc. of the above fuel oil mixture. In each run 3 drops of a 0.1 percent aqueous solution of the indicated surfactant or flocculant were applied to the center of the oil slick and the time required for the slick to "break" was measured. The flocculants of the present invention, K, L and M, were provided as 0.1 percent solutions in dilute acetic acid. Results are given in Table I.

TABLE I

Treating Agent	Description	Time Required for Oil Film to Break, Seconds
A.....	100% butyl cellosolve half-ester of styrene-maleic anhydride polymer of about 1,600 mol weight; molar ratio of styrene to maleic anhydride of 1/1.	10
B.....	Ammonium salt of 75% butyl cellosolve half-ester of 1/1 styrene-maleic anhydride polymer of about 1,600 mol. weight.	8
C.....	Ammonium salt of 50% butyl cellosolve half-ester of 1/1 styrene-maleic anhydride polymer of about 1,600 mol. weight.	5
D.....	Ammonium salt of 50% butyl cellosolve half-ester of 2/1 styrene-maleic anhydride polymer of about 1,700 mol. weight.	5
E.....	Ammonium salt of 65-70% n-propanol half-ester of 2/1 styrene-maleic anhydride polymer of about 1,700 mol. weight.	6
F.....	Ammonium salt of 55-60% allyl alcohol half-ester of 2/1 styrene-maleic anhydride polymer of about 1,700 mol. weight.	8
G.....	Commercial nonionic surfactant, reported to be a 10-12% aqueous solution of a polyethoxylate.	12
H.....	Anhydrous ammonia treated 3/1 styrene-maleic anhydride polymer of about 1,900 mol. weight.	6
I.....	Commercial condensation product of 1 mole of C ₁₃ to C ₁₈ primary alkanol and 15 moles of ethylene oxide.	18
J.....	Commercial condensation product of a C ₁₆ secondary alcohol with 12 moles of ethylene oxide.	15
K.....	Methyl iodide quaternary salt (61%) of 98% dimethylaminopropylimide of 3/1 styrene-maleic anhydride polymer of about 1900 mol. weight.	4
L.....	Methyl iodide quaternary salt (45%) of 94% dimethylaminopropylimide of 1/1 styrene-maleic anhydride polymer of about 20,000 mol. weight.	3
M.....	Methyl iodide quaternary salt (95%) of 100% dimethylaminopropylimide of 1/1 styrene-maleic anhydride polymer of about 45,000 mol. weight.	1
N.....	Condensation reaction product of 1 mole of C ₁₀ to C ₁₄ primary alkanol and 7 moles of ethylene oxide.	7

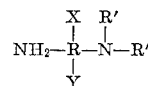
As evidenced by the data presented in Table I, the quaternary ammonium salts of the imidic reaction products of the present invention, i.e., flocculating agents K, L and M, were the fastest acting of all the treating agents tested. Further observation of the sample dispersions revealed that after about one month oil films had reformed on the surface of all of the samples which had been treated with surfactants, including that dispersed with commercially available treating agent G which is advertised and sold specifically as an oil slick dispersant, and only those samples treated with flocculants K, L and M in accordance with the method of the present invention were free of such oil slick reformation.

It is claimed:

1. A method of flocculating a water-borne oil slick which comprises applying to said oil slick a quaternary ammonium salt of a tertiary amine-containing, imidic reaction product of (A) a vinyl monomer-maleic anhydride polymer having an average molecular weight of about 600 to 100,000 and a molar ratio of vinyl monomer to maleic

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anhydride of about 1:1 to 4:1, said vinyl monomer being a monovinyl compound of 2 to about 12 carbon atoms and (B) a polyamine corresponding to the formula:



where X is hydrogen or



Y is hydrogen or



R is alkylene of 1 to about 10 carbon atoms and R' is a monovalent hydrocarbon radical of 1 to about 8 carbon atoms, about 80 to 100 percent of the maleic anhydride units of said polymer being imidated with said polyamine.

2. The method of claim 1 wherein the quaternary ammonium salt is applied as an aqueous solution containing at least about 0.01 weight percent of said salt.

3. The method of claim 1 wherein the vinyl monomer is styrene.

4. The method of claim 3 wherein the polyamine is a dialkylaminoalkylamine.

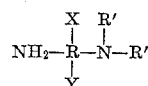
5. The method of claim 4 wherein the dialkylaminoalkylamine is dimethylaminopropylamine.

6. The method of claim 4 wherein the tertiary amine-containing, imidic reaction product is quaternized with a monohalogenated alkane having 1 to about 4 carbon atoms, the halogen having an atomic number of 17 to 53.

7. The method of claim 6 wherein about 30 to 100 percent of the tertiary amine groups are quaternized with the monohalogenated alkane.

8. The method of claim 7 wherein the monohalogenated alkane is methyl iodide.

9. A method of flocculating a water-borne oil slick which comprises applying to said slick an aqueous solution containing at least about 0.01 weight percent of a quaternary ammonium salt of a tertiary amine-containing, imidic reaction product of (A) a styrene-maleic anhydride polymer having an average molecular weight of about 600 to 100,000 and a molar ratio of styrene to maleic anhydride of about 1:1 to 4:1 and (B) a polyamine corresponding to the formula:



where X is hydrogen or



Y is hydrogen or



R is alkylene of about 2 to 6 carbon atoms and R' is an alkyl radical of 1 to 2 carbon atoms; at least about 90 percent of the maleic anhydride units of said polymer being imidated with said polyamine; and about 30 to 100 percent of the tertiary amine groups of said imidic reaction product being quaternized with a monohalogenated alkane having 1 to 3 carbon atoms, the halogen having an atomic number of 17 to 53.

References Cited

UNITED STATES PATENTS

3,157,595 11/1964 Johnson et al. 210-54

MICHAEL E. ROGERS, Primary Examiner.

U.S. Cl. X.R.

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