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(54) **Title:** AN ENVIRONMENTALLY FRIENDLY DISPERSION SYSTEM USED IN THE PREPARATION OF INVERSE EMULSION POLYMERS

(57) **Abstract:** A water-in-oil emulsion composition and method of production is disclosed. The composition may comprise a monomer phase, an organic phase, at least one initiator, and an inverting phase. The monomer phase may further comprise at least one monomer, water, ammonium chloride, sodium 2-acrylamido-2-methyl-1-propanesulfonate, tetrasodium ethylenediaminetetraacetate, and at least one water soluble ethylenically unsaturated monomer. The organic phase may further comprise at least one hydrophobic solvent, lecithin, and a polyoxyethylene derivative of a sorbitan ester. The at least one monomer may be selected from the group consisting of an acrylic monomer, an acrylamide monomer, and combinations thereof.



AN ENVIRONMENTALLY FRIENDLY DISPERSION SYSTEM USED IN THE PREPARATION OF INVERSE EMULSION POLYMERS

FIELD OF THE INVENTION

5 This invention pertains to water-in-oil emulsion polymerization. More particularly, the invention pertains to an environmentally friendly, oil phase system used for making water-in-oil emulsion polymers.

BACKGROUND

10 Inverse emulsion polymerization is a process that produces high molecular weight, water-soluble polymer in a convenient package for application. In the process an aqueous monomer solution is emulsified within an inert hydrocarbon phase containing surfactants that promote water-in-oil ("w/o") emulsions. The resulting droplets are polymerized yielding polymer particles that are dispersed throughout the hydrocarbon phase and stabilized by surfactant.

15 Over time various emulsification systems have been discovered and utilized. In U.S. Patent No. 3,284,393, Vanderhoff and Wiley espouse the use of conventional w/o emulsifiers such as, sorbitan monooleate, sorbitan monostearate, hexadecyl sodium phthalate, cetyl or stearyl sodium phthalate, and metal soaps.

20 U.S. Patent No. 3,826,771, to Anderson and Frisque, also teaches the use of conventional w/o emulsifiers, showing the use of sorbitan monostearate in all of the examples.

U.S. Patent No. 4,024,097, to Slovinsky and Hurlock, introduced partially esterified lower N,N'-dialkanol substituted fatty amides, salts of fatty tertiary amines, quaternary salts of fatty tertiary amines, alkali metal salts, and alkyl or alkyl aryl sulfates and sulfonates as w/o emulsifiers that yielded lattices with smaller particle size distributions and improved storage
25 stability.

In U.S. Patent No. 4,147,681, to Lim et al., w/o emulsifiers with a HLB of at least 7 were used and many examples were cited. Lim and U.S. Patent No. 4,672,090, to Chan, made use of a system comprising a polyoxyethylene derivative of a sorbitan ester, sorbitan monooleate, and alkanolamide.

30 In U.S. Patent No. 4,906,701, to Clark, an inverse emulsion system utilizing polyoxyethylene sorbitol esters, polyoxyethylene fatty alcohols with a HLB of 7-9, and glycerides was revealed.

U.S. Patent No. 5,206,316, to Chuang, revealed the use of nonionic oil-soluble surfactant and a compound selected from, N-alkyl lactams, and an alkylated polymer of a N-vinyl lactam.

With this in mind, it was desired to create an environmentally friendly oil phase system useful for making inverse emulsion polymers. The adopted definition of environmentally friendly are the rules that govern offshore chemical use in the North Sea. The environmental impact of a chemical is defined by three tests: bioaccumulation, biodegradation and toxicity. In order for a chemical to be used without restriction offshore in the North Sea it must satisfy two of the following three criteria:

1. Biodegradation must be greater than 60%, if less than 20% it is automatically marked for substitution.
2. Bioaccumulation as measured by octanol/water partitioning coefficient ($\log P_{o/w}$) must be below 3 (or have a molecular weight >700).
3. Toxicity to the most sensitive marine species (typically *Skeletonema*) must be greater than LC50 or EC50 of 10 ppm.

One of the most popular and conventional w/o emulsifiers, sorbitan monooleate, does not pass the biodegradation and bioaccumulation protocols that govern offshore chemical use in the North Sea. For the initial assessment procedure, one must use marine biodegradation data as outlined in Organization for Economic Cooperation and Development, Procedure OECD 306 or BODIS. Sorbitan monooleate has a BODIS result of 32%, which coupled with $\log P > 3$ prevents sorbitan monooleate from passing the test. Other governing bodies allow the use of other types of biodegradation data such as the OECD 301 series (freshwater) to prove a chemical's non-harm to the environment, but not for use in offshore applications. This prompted an investigation into other w/o surfactant systems that could be used to produce inverse emulsion polymers.

Lecithin is well known as an emulsifier and has been used in w/o emulsion technology in explosives. A number of publications illustrate this application including U.S. Patent Nos. 3,535,174; 4,308,081; 4,357,184; 4,473,418; 4,507,161; and 4,602,970. Of particular interest, U.S. Patent Nos. 4,943,389 and 5,008,037 indicate that lecithin can be an inferior emulsifier for w/o emulsions. The patents teach that lecithin can be made into a better w/o emulsifier after subjection to a thermal process. Although inverse emulsions using lecithin are well known in the literature, not all inverse emulsions can go through the polymerization process and provide usable product.

Accordingly, there is a need for an environmentally friendly, oil phase system used for making water-in-oil emulsion polymers. Desirably, the oil phase system is biodegradable

according to current environmental standards. More desirably, the oil phase system is comprised of substances recognized worldwide as generally safe for use.

SUMMARY OF THE INVENTION

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The present invention is directed toward a water-in-oil emulsion composition. The composition comprises an aqueous phase, an organic solvent, and lecithin. Additionally, the composition may optionally comprise a nonionic surfactant, and the nonionic surfactant may comprise at least one polyoxyethylene derivative of a sorbitan ester.

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The present invention is alternately directed toward a water-in-oil dispersion composition. The composition results from a polymerization. The composition comprises a polymer phase, an organic phase, at least one initiator, and an inverting phase. The polymer phase is created from a monomer phase. The polymer phase may further comprise water, an inorganic salt, and a polymer created from at least one water soluble ethylenically unsaturated monomer. The organic phase may further comprise at least one hydrophobic solvent and lecithin. The at least one water soluble ethylenically unsaturated monomer may comprise at least one of an acrylic monomer and an acrylamide monomer. The inverting surfactant may be added after the polymer phase is created from the monomer phase. The organic phase of the water-in-oil emulsion composition may additionally comprise a polyoxyethylene derivative of a sorbitan ester.

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The present invention is alternately directed toward a method for producing a water-in-oil polymer dispersion. The method comprises emulsifying an aqueous monomer solution in an organic phase, and polymerizing the aqueous monomer emulsion. The emulsifying forms an aqueous monomer emulsion. The polymerizing forms the water-in-oil polymer dispersion. The at least one monomer comprises at least one of an acrylic monomer and an acrylamide monomer, and the organic phase comprises lecithin and an organic liquid. The organic phase may additionally comprise a polyoxyethylene derivative of a sorbitan ester.

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These and other features and advantages of the present invention will be apparent from the following detailed description, in conjunction with the appended claims.

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DETAILED DESCRIPTION OF THE INVENTION

While the present invention is susceptible of embodiment in various forms, there is shown in the drawings and will hereinafter be described a presently preferred embodiment with the understanding that the present disclosure is to be considered an exemplification of the invention

and is not intended to limit the invention to the specific embodiment illustrated.

It should be further understood that the title of this section of this specification, namely, "Detailed Description of the Invention," relates to a requirement of the United States Patent Office, and does not imply, nor should be inferred to limit the subject matter disclosed herein.

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An embodiment of the present invention is an environmentally friendly oil phase system comprising an organic solvent and lecithin. The immiscible organic solvent can be a hydrocarbon solvent that is aliphatic or at least one oil derived from one or more natural products, and are at least 60% biodegradable after 28 days as determined by the Organization for Economic Cooperation and Development, Procedure OECD 306, its text incorporated by reference. One or more non-ionic surfactants may be used. A preferred non-ionic surfactant is comprised of polyoxyethylene derivatives of a sorbitan ester that have a HLB of 9–10.

It is important to define some of the nomenclature used within this disclosure. A monomer phase within a hydrocarbon solvent is an inverse emulsion because such a composition is a liquid dispersed within another liquid. During polymerization, the liquid droplets become solid particles that are dispersed within the hydrocarbon solvent, creating a dispersion. Formally, a dispersion is solid particles dispersed within another phase. Acknowledgement of difference between an emulsion and a dispersion is important when dealing with the invention at hand.

The final component is lecithin, which can be obtained from sources such as soybean lecithin. The United States Food and Drug Administration has given lecithin the status of Generally Recognized As Safe ("GRAS"), and the European body OSPAR that governs offshore chemical use in the North-East Atlantic has given lecithin the status of Poses Little Or NO Risk ("PLONOR"). Chemicals with PLONOR status are inherently acceptable for use in the North Sea.

Inverse emulsion polymers can be created with lecithin and the polyoxyethylene derivative of a sorbitan ester dispersion system. Evidence of the environmentally friendly oil phase system is shown in Table 1, which shows the environmental profile for an aliphatic hydrocarbon solvent and two surfactants that can be used in the dispersion system.

Table I: Environmental profile of dispersion system components.

component	Toxicity EC ₅₀ (ppm)	Bioaccumulation log P _{o/w}	Biodegradation, t = 28 days
aliphatic hydrocarbon	>1800	>3	100
POE(4)-sorbitan monostearate	165	<3	27
POE(5)-sorbitan monooleate	20	<3	52

In an embodiment, the organic solvent may be an aliphatic hydrocarbon. The aliphatic
5 hydrocarbon may be derived from a natural product.

In an embodiment, the organic solvent may be a fatty ester. The fatty ester may be
derived from a natural product.

In an embodiment, the organic solvent may be at least 60% biodegradable after 28 days.

In an embodiment, the polyoxyethylene derivative may have a hydrophilic-lipophilic
10 balance within the range from about 9 to about 10.

In an embodiment, the lecithin has not been subject to a thermal process.

In an embodiment, the aqueous phase is selected from at least one of a brine solution, an
acid solution, a water soluble polymer solution, a gel, and a solid.

The polymer created by the invention may be anionic, cationic, nonionic, amphoteric, or a
15 betaine-containing polymer.

There are several envisioned uses for the invention. First, the invention may be used to
produce inverse emulsion polymers that could be used as friction (drag) reducers during pressure
pumping operations, or an acid gellant in a crude oil recovery process. As an acid gellant, the
invention could be used to produce stable gelled acid, and as a friction reducer when applied in
20 low doses to fluids in turbulent flow. The invention could improve acid fracturing by allowing
deeper penetration of the acid. The invention may be used as a hydrate inhibitor, as a clay
stabilizing agent, or as a de-emulsifier. The invention may also improve pressure pumping by
suppressing turbulent flow and minimizing the energy loss between the fluid and its
surroundings. The invention may be particularly useful in the treatment of a subterranean
25 formation of an oil production operation and/or a gas production operation, *i.e.*, those
applications that attempt to pump crude oil to the surface at steady state. Background
information related to the aforementioned applications can be found in U.S. Patent Application
Publication No. 2010/0056399, paragraphs [0048]–[0079], which are hereby incorporated by
reference.

Another use of the invention involves its use as an environmentally friendly acid emulsifier. The emulsion would act to retard the action of acid on acid-soluble formation rock, again typically found in the crude oil recovery process. Because the invention is environmentally friendly, its user would be less of a threat to the environment than perhaps other emulsifiers.

Several other envisioned uses of the invention include its use as an environmentally friendly dispersion system useful for the preparation or packaging of friction reducer, a scale inhibitor, or a hydrate inhibitor, depending on a particular application.

The following examples are meant to be illustrative and not limit the invention.

EXAMPLES

General Procedure:

The following is a general procedure for the preparation of a sodium 2-acrylamido-2-methyl-1-propanesulfonate and acrylamide copolymer. The continuous phase is prepared by dissolving the emulsifying surfactants in the hydrocarbon solvent. The dispersed phase is prepared by dissolving sodium or ammonium chloride in acrylamide and water. 2-Acrylamido-2-methyl-1-propanesulfonic acid sodium salt solution is then added to the monomer phase followed by tetrasodium ethylenediaminetetraacetate. After all of the solids are dissolved, the monomer phase is added to the oil phase and the emulsion is formed with adequate mixing. Typically a 1 kg emulsion is subjected to 60 seconds of mixing with a high shear rotor/stator laboratory mixer set at 5000 rpm. After the high shear mixing, the initiators are added and the system mixed with overhead stirring at 650 rpm while purging nitrogen. The reaction begins at around 43°C and is run isothermally for approximately 3 hours. At the end of three hours, the temperature is increased to 70 °C for one hour to lower residual monomer levels. After cooling to approximately 38–40 °C, the inverting surfactant is added to help the dispersion break when it is dispersed into an aqueous solution.

Example 1:

Table II below illustrates the formulation for this example prepared by following the general procedure outlined above. The resulting latex had a bulk viscosity of 693 cP when measured as Brookfield viscosity at room temperature with a #2 spindle at 30 rpm. The viscosity of an inverted 1% product solution in synthetic Nalco water was 277 cP using the same technique. The reduced specific viscosity ("RSV") of a 450 ppm polymer solution in 1-molar sodium nitrate was 20.3 dL/g using an Ubbelohde viscometer and the equation $RSV = (1/c)[t/t_0 - 1]$ where c = concentration, t_0 = time of flow for solvent, and t = time of flow for polymer solution.

Table II: Ingredients used for making NaATBS-acrylamide copolymer of Example 1.

MONOMER PHASE	wt %
acrylamide solution(49.5% in water)	38.737
water	14.247
sodium chloride	3.903
2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt solution(58% in water)	14.441
tetrasodium EDTA	0.017
OIL PHASE	
hydrocarbon solvent	22.774
soy lecithin	1.952
POE (4) sorbitan monostearate	1.952
INITIATORS	
2,2'-azobisisobutyronitrile	0.023
2,2'-azobis(2,4-dimethylvaleronitrile)	0.003
INVERTING SURFACTANT	
ethoxylated fatty alcohol	1.951
TOTAL	100.000

Example 2:

Table III below illustrates the formulation for this example prepared by following the general procedure outlined above, except adding the post-treatment chemicals indicated in the table. The resulting latex had a bulk viscosity of 494 cP when measured as Brookfield viscosity at room temperature with a #2 spindle at 30 rpm. The viscosity of an inverted 1% product solution in Sugar Land, Texas, tap water was 238 cP using the same technique. The reduced specific viscosity of a 450 ppm polymer solution in 1-molar sodium nitrate was 19.9 dL/g.

Table III: Ingredients used for making NaATBS-acrylamide copolymer of Example 2.

MONOMER PHASE	wt %
acrylamide solution (49.5% in water)	42.096
water	4.254
ammonium chloride	4.000
2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt solution (58% in water)	15.798
tetrasodium EDTA	0.020
OIL PHASE	
hydrocarbon solvent	25.500
soy lecithin	2.267
POE (5) sorbitan monooleate	1.733
INITIATORS	
2,2'-azobisisobutyronitrile	0.023
2,2'-azobis(2,4-dimethylvaleronitrile)	0.009
POST-TREATMENT	
sodium metabisulfite	0.200
ammonium thiosulfate	1.000
INVERTING SURFACTANT	
ethoxylated fatty alcohol	3.100
TOTAL	100.000

Example 3:

Table IV below illustrates the formulation for this example prepared by following the
5 general procedure outlined above, except adding the post-treatment chemicals indicated in the
table. The resulting latex had a bulk viscosity of 1200 cP when measured as Brookfield viscosity
at room temperature with a #3 spindle at 30 rpm. The viscosity of an inverted 1% product
solution in synthetic Nalco water was 254 cP when measured as Brookfield viscosity at room
temperature with a #2 spindle at 30 rpm. The reduced specific viscosity of a 450 ppm polymer
10 solution in 1-molar sodium nitrate was 17.5 dL/g.

Table IV: Ingredients used for making NaATBS-acrylamide copolymer of Example 3.

MONOMER PHASE	wt %
acrylamide solution (49.5% in water)	41.200
water	2.7617
ammonium chloride	3.9100
2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt solution (58% in water)	15.4600
tetrasodium EDTA	0.0170
OIL PHASE	
hydrocarbon solvent	24.9480
soy lecithin	2.7300
POE (4) sorbitan monostearate	1.6000
POE (5) sorbitan monooleate	2.4500
INITIATORS	
2,2'-azobisisobutyronitrile	0.0200
2,2'-azobis(2,4-dimethylvaleronitrile)	0.0020
POST-TREATMENT	
sodium metabisulfite	0.1800
sodium thiosulfate pentahydrate	0.9700
INVERTING SURFACTANT	
ethoxylated fatty alcohol	3.7500
TOTAL	100.000

All patents referred to herein, are hereby incorporated herein by reference, whether or not specifically done so within the text of this disclosure.

5 In the present disclosure, the words "a" or "an" are to be taken to include both the singular and the plural. Conversely, any reference to plural items shall, where appropriate, include the singular.

From the foregoing it will be observed that numerous modifications and variations can be effectuated without departing from the true spirit and scope of the novel concepts of the present invention. It is to be understood that no limitation with respect to the illustrated specific
10 embodiments or examples is intended or should be inferred. The disclosure is intended to cover by the appended claims all such modifications as fall within the scope of the claims.

CLAIMS

1. A water-in-oil emulsion composition comprising:
 - an aqueous phase;
 - an organic solvent; and
 - lecithin.
2. The composition of claim 1, wherein the organic solvent is an aliphatic hydrocarbon.
3. The composition of claim 1, wherein the organic solvent is a fatty ester, the fatty ester derived from a natural product.
4. The composition of claim 1, wherein the organic solvent is at least 60% biodegradable after 28 days.
5. The composition of claim 1, wherein the composition additionally comprises a nonionic surfactant, the nonionic surfactant comprised of a polyoxyethylene derivative of a sorbitan ester.
6. The composition of claim 5, wherein the polyoxyethylene derivative has a hydrophilic-lipophilic balance within a range from about 9 to about 10.
7. A water-in-oil dispersion composition, the composition resulting from a polymerization, the composition comprising:
 - a polymer phase, the polymer phase created from a monomer phase;
 - an organic phase;
 - at least one initiator; and
 - an inverting surfactant;wherein the polymer phase comprises: water, an inorganic salt, and a polymer created from at least one water soluble ethylenically unsaturated monomer;
wherein the organic phase comprises: at least one hydrophobic solvent and lecithin;
wherein the at least one water soluble ethylenically unsaturated monomer comprises at least one of an acrylic monomer and an acrylamide monomer; and
wherein the inverting surfactant is added after the polymer phase is created from the monomer phase.
8. The composition of claim 7, wherein the organic phase additionally comprises a polyoxyethylene derivative of a sorbitan ester.

9. A method for producing a water-in-oil polymer dispersion, the method comprising the following steps:
emulsifying an aqueous monomer solution in an organic phase, the aqueous monomer solution comprising at least one monomer, the emulsifying forming an aqueous monomer emulsion, and
polymerizing the aqueous monomer emulsion, the polymerizing forming the water-in-oil polymer dispersion;
wherein the at least one monomer comprises at least one of an acrylic monomer and an acrylamide monomer;
wherein the organic phase comprises lecithin.
10. The method of claim 9, wherein the organic phase additionally comprises a polyoxyethylene derivative of a sorbitan ester.
11. The composition of claim 1, wherein the aqueous phase comprises at least one of a brine solution, an acid solution, a water soluble polymer solution, a gel, and a solid.
12. The composition of claim 1, wherein the composition additionally comprising a monomer phase, the monomer phase polymerized to form a water-in-oil polymer dispersion.
13. A method of using the composition of claim 12, wherein the composition is injected in a treatment of subterranean formation of at least one of the following: an oil production operation and a gas production operation.
14. The method of claim 13, wherein the water-in-oil polymer dispersion is useful as a friction reducer.
15. The method of claim 13, wherein the water-in-oil polymer dispersion is useful as a scale inhibitor.
16. The method of claim 13, wherein the water-in-oil polymer dispersion is useful as a hydrate inhibitor.
17. The method of claim 13, wherein the water-in-oil polymer dispersion is useful as an acid stimulation agent.
18. The method of claim 13, wherein the water-in-oil polymer dispersion is useful as a gelling agent for hydraulic fracturing fluid.

19. The method of claim 13, wherein the water-in-oil polymer dispersion is useful as a clay stabilizing agent.
20. The method of claim 13, wherein the water-in-oil polymer dispersion is useful as a de-emulsifier.