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(54) Title: STABILIZED FOAM CONTROL COMPOSITIONS FOR LUBRICATING COMPOSITIONS AND THEIR USE

(57) Abstract: The invention relates to stabilized foam compositions for lubricating compositions and their use in lubricating compositions, particularly metal working fluids.

WO 2004/080561 A2

STABILIZED FOAM CONTROL COMPOSTIONS FOR LUBRICATING COMPOSITONS AND THEIR USE

Background of the Invention

1. Field of the Invention

The invention relates to stabilized foam compositions for lubricating compositions and their use in lubricating compositions, particularly metal working fluids.

2. Description of the Related Art

Unwanted foam is encountered in a wide variety of processes and products. For example, foaming is often associated with processes that involve polymerization, paint processing and application, fermentation, sugar-refining, oil drilling and refining, food preparation, paper manufacture, sewage disposal, textile dying, printing, adhesive application and conversion of ores refined by flotation. Moreover, liquid coolants, metal working fluids, hydraulic fluids, lubricants, and gas adsorption fluids may foam with undesirable results.

There are many ways to eliminate or reduce foaming in a system. Typically, foam can be reduced or eliminated by optimizing the process conditions, using raw materials that have a low tendency for foaming, or, more typically, by adding a foam control agent to the product or at an appropriate step of the process.

If a foam control agent is used, there are two ways to apply the foam control agent. On the one hand, the foam control agent can be used as a process additive in order to suppress the formation of foam. An example of this is the use of foam control agents to control foam during the synthesis of water-based polymer latex dispersions and emulsions. A significant amount of foam, which negatively influences the reaction conditions and the properties of the polymer latex, may be generated during the actual synthesis of the latex dispersion or emulsion and/or during the pumping and drumming of the polymer latex. Thus, it is necessary to add a foam control agent at different steps of the process to control the build up of the foam.

A second way of using foam control agents involves adding the foam control agent as a component of a formulated product, which foams during the production or application of the product. In this case, the foam control agent is one of the many components used for formulating the end product. An example of this use of a foam a control agent is where the foam control agent is added, as an essential component, of a water-based paint or coating. Without a foam control agent, bubbles will form and remain in the paint or coating. When the paint or coating is applied to the substrate, the bubbles will dry on the substrate. Apart from the fact that these dried bubbles are not aesthetically pleasing, the substrate is also not well protected from the environment when these bubbles form.

Foam control agents generally are formulated with multiple components, although in some cases the foam control agent may be single liquid or solid. By varying the components of the foam control agent, their weight ratios, and/or by carefully changing the chemical properties of the foam control agent, one can obtain optimal foam control in a specific process or for a specific product.

Because processes and products that produce foam vary greatly and the reasons for foaming are diverse, the inhibition of foam in a particular system often requires a unique solution. Therefore, it has challenged those skilled in the art to develop foam control agents that have multiple uses.

Even if a foam control agent inhibits the formation of foam, there are often unwanted side effects caused by the use of the foam control agent that must be avoided in order for a foam control agent to be useful. The surface active properties of foam control agents may cause film defects, like craters or orange peel, to form when the end-product is used, even when then foam control agent is used in low dosages. This is particularly a problem when the foam control agents is used in water-based coating systems. This problem can be overcome by carefully formulating a foam control agent that will show a high degree of compatibility with the coating system. However, it requires detailed optimization procedures to effectively incorporate the foam control agent into the coating during its production.

The subject invention is particularly concerned with stabilizing foam that can be generated when lubricating compositions, particularly metal working fluids, are used. The foam is generated not only during the actual metal working process (e.g. drilling, sawing, cutting, etc.), but also during re-circulation, filtering and re-use of the diluted lubricant over prolonged periods of time. For this reason, foam control is needed over a long period of time, possibly weeks or months. Because only a limited dosage foam control agent can be used in the lubricant formulation without encountering problems, it is necessary to post-dose a suitable foam control agent directly into the water diluted lubricant fluid during actual use in order to maintain the high level of foam control that is needed. This often is a continuous dosage using dosing pumps. As is known, it is difficult to incorporate even small amounts of foam control agents into the metal working fluid under such circumstances without creating instability.

It is particularly difficult to stabilize lubricating compositions against foaming, because they are typically subject to high shear forces and pressure during use and only small amounts of foam control agent can be used without creating stability problems. Furthermore, prior to use, metal working compositions normally are diluted with water and of surfactants and wetting agents, which are needed for, among other things, rapid spreading of the metal working fluid onto the metal surface. As a result, the foam that is generated during the use is strongly stabilized.

Formulators of metal working lubricants/fluids try using raw materials that will not stabilize foam too strongly, but this not always possible. They also attempt using higher levels of foam control agent or highly hydrophobic foam control agents formulated into the neat lubricant, but this also causes problems. The main problem is that higher dosages of the foam control agents cannot be incorporated in the neat lubricant, which means that over time (this can be hours to weeks), the foam control agent will separate again from the lubricant composition. This may show up as, for instance, turbidity or, in the worst case, complete phase separation. Upon dilution of the neat lubricant composition, the consequences of this instability are (1) loss of foam control activity, (2) problems with respect to wetting of the metal surface, (3)

formation of flocs or creaming of the foam control agent in the diluted lubricant system causing, again, wetting problems and problems during cleaning/filtration for the diluted fluid, (4) breaking of the emulsion which reduces the cooling and lubricating effects.

All citations referred to under this description of the "Related Art" and in the "Detailed Description of the Invention" are expressly incorporated by reference.

Brief Summary of the Invention

The present invention relates to a process for preparing a stabilized foam control composition for lubricating compositions comprising:

(a) combining a mixture of components comprising:

component (a) which comprises at least one active foam control agent; and

component (b) which comprises at least one lubricating oil,

such that the amount of active foam control agent is from about 0.01 weight percent to about 70 weight percent, based upon the weight of said lubricating oil; and.

(b) mixing (a) and (b) with sufficient energy to create a mixture, which does not show full liquid-liquid phase separation or solid phase separation as determined by visual observation for at least 1 minute after mixing at ambient temperature.

The stable foam control compositions for lubricating compositions are prepared by combining an active foam control agent with at least one or more lubricating oils, and mixing these components with sufficient energy or force to create a mixture that is stable at ambient temperature. The manner of mixing components is not critical, as

long as sufficient energy is used to produce a stable product. Sufficient stability can be achieved by high-speed mixing, high-shear mixing, homogenization, mixing with equipment having rotor blades, etc., which, in some cases, may require increased pressure or temperature.

The resulting foam control compositions for lubricating compositions are stable at room temperature, i.e. they do not undergo liquid-liquid phase separation or solid phase separation. Because the lubricating compositions are stable at room temperature, a higher dosage of the foam control compositions for the lubricating composition can be used without encountering miscibility or compatibility problems.

The invention also relates to lubricating compositions, particularly metal working fluids, which are prepared by mixing the stable foam control compositions for lubricating compositions and the lubricating composition.

The resulting lubricating compositions are stable at room temperature, i.e. they do not undergo liquid-liquid phase separation or solid phase separation, and are stabilized against foam under use conditions.

The stabilized metal working fluid or lubricant foam control compositions and metal working fluids or lubricants are typically diluted with water prior to use.

Definitions

For purposes of defining this invention, "active foam control agent" means a chemical that is capable of inhibiting foam.

For purposes of this invention "high energy" means an amount of energy per unit volume sufficient to produce a stable "foam control composition". Typically, the amount of energy per unit volume required to produce a stable "foam control composition" is at least 10^5 J/m^3, preferably from 10^6 to 10^9J/m^3, most preferably from 10^6 to 10^8/m^3. This corresponds to pressure differences of 10 bars to 1000 bars

if a high-pressure homogenizer is used to produce the stabilized foam control agent composition.

For purposes of defining this invention, a "stabilized foam control composition for a lubricating composition" is mixture that contains at least one active foam control agent and at least one lubricating oil, such that the mixture does not show full liquid-liquid phase separation, or settling or creaming of a solid phase as determined by visual observation for at least 1 minute, preferably for at least 30 minutes, most preferably for at least 120 minutes, at ambient temperature.

For purposes of defining this invention, a lubricating composition is defined as any lubricating composition, e.g. a metal working fluid, a functional fluid, a hydraulic fluid, etc., which contains a lubricant, and a foam control agent for a lubricating composition as defined herein.

Detailed Description of the Invention

The detailed description and examples will illustrate specific embodiments of the invention will enable one skilled in the art to practice the invention, including the best mode. It is contemplated that many equivalent embodiments of the invention will be operable besides these specifically disclosed.

Any active foam control agent known in the art, which inhibits foam formation in a lubricating composition, can be used to prepare the foam compositions of this invention. Typical active foam control agents include acetylene diols and ethoxylated acetylene diols, silicones, hydrophobic materials (e.g. silica), fatty amides, fatty acids, fatty acid esters, and/or organic polymers, modified siloxanes, polyglycols, esterified or modified polyglycols, polyacrylates, fatty acids, fatty acid esters, fatty alcohols, fatty alcohol esters, oxo-alcohols, fluorosurfactants, waxes such as ethylenebistereamide wax, polyethylene wax, polypropylene wax, ethylenebisstereamide wax, and paraffinic wax, ureum. The foam control agents can be used with suitable dispersants and emulsifiers. Additional active foam control

agents are described in "Foam Control Agents", by Henry T. Kerner (Noyes Data Corporation, 1976), pages 125-162.

Typical hydrophobic material that can used as the active foam control agent typically have a surface energy of from about 10 to about 40 dynes/cm^2, preferably from about 20 to about 30 dynes/cm^2. Preferably the hydrophobic material is precipitated hydrophobic silica or a hydrophobic wax having an average particle size of from 5 to 75 microns, preferably 10 to 15 microns. Precipitated hydrophobic silica is made by treating hydrophilic silica with silicone according to well-known methods. Such precipitated hydrophobic silicon can be purchased from Degussa, Georgia Kaolin, and J. M. Huber.

Typical silicone compounds that can be used as the active foam control agent include polydimethylsiloxanes, often trimethylsilyl terminated. Generally, which are sold commercially as fluids or emulsions (which contain water and a surfactant as well as the silicone compound). Examples of commercially available products, which contain silicone compounds and are effective, include DC 200 sold by Dow Corning Corporation and L-45-350 sold by Union Carbide.

The active foam control agent may be mixed with other components before it is mixed with the active component of the metal working fluid or lubricant. Some of the components that can be mixed with the active foam control agent include, for example, a secondary foam control agent, a carrier, an emulsifier, a stabilizing agent, a surfactant, and/or other materials. Secondary foam control agents modify the crystallinity, surface properties, solubility and roughness of the primary foam control agents.

Typically used as the carrier for the hydrophobic silica and silicone are vegetable oils, e.g. rapeseed oil, canola oil, and soybean oil, preferably soybean oil, particularly refined soybean oil.

The metal working fluid or lubricant foam control composition may also contain a wax, preferably a hydrophobic waxes include, for example, polyethylene, paraffin wax, ethylene bis stearamide, and the like. These waxes typically have a melting point greater than 100° C., preferably greater than 120° C.

It should be noted that some classes of chemicals, e.g. polyglycols and esterifed polyglycols, can be used both as foam control agents and lubricating oils. However, although the chemicals are of the same class, they have different chemical structures, molecular weights, and properties. Those skilled in the art will know which particular chemicals in a class can be used as foam control agents and which can be used as lubricating oils. Typically, the foam control agents are more hydrophobic and the lubricating oils are more hydrophilic.

Another way of distinguishing polyglycols and esterified polyglycols used as foam control agents, from those used as lubricating oils, is on the basis of cloudpoint. The cloudpoint is defined as the temperature at which a solution containing one percent of block copolymer, e.g. polyglycol, esterfied polyglycol, in water begins to phase separate. At temperatures below the cloudpoint, the block copolymer will completely dissolve in water. In order to be useful as foam control agent for metal working compositions, the cloudpoint of the block copolymer is typically lower than 50°C. This is because the metal working fluid is prepared, filtered, recirculated, and used at temperatures well below 50°C.

On the other hand, these block copolymers should become "active" at temperatures higher than 50°C when used as lubricating oils. This is because at the high temperatures present at the metal surface, the block copolymer should phase separate from the water phase and form a lubricating film. Therefore, block copolymers should have cloudpoints higher than 50°C when used as lubricating fluids.

Those skilled in the art will know what types of block copolymers, e.g. polyglycols and esterfied polyglycols, have cloudpoints that make them suitable as foam control agents and lubricating oils.

Optional components that can be mixed with the lubricating oil include, but are not limited to, bactericides, solvents (e.g. secondary/ tertiary alcohols, alkanols), anti-corrosive agents, friction modifiers, seal and swell agents, odor additives, colorants, agents to modify the physical characteristics, detergents, viscosity modifiers, and antiwear additives. Useful antiwear agents include, for example, zinc dialkyldithiophosphate, sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, benzyl iodide, fluoroalkylpolysiloxane, and lead naphthenate. Useful friction modifiers include, for example fatty alcohols, amines, borated esters, and other esters. Useful seal and swell components include dialkyl diesters such as dioctyl sebacate, aromatic hydrocarbons of suitable viscosity, and polyol esters. Viscosity modifiers include polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, and polyisobutylene. Phenols, quaternary ammonium salts, nitrogen derivatives of alcohols, thiocarbonates, thiocarbamates, etc. can be used as bactericides. The anti-corrosive agents include alkaline nitrates, phosphates, borates, etc.

The metal working fluids or lubricants are prepared by combining the lubricant, optionally with other components of the metal working fluid or lubricant. and subjecting them to sufficient high energy to produce a stabilized foam control composition.

The mixture can be stabilized by subjecting the mixture to high energy, e.g. with a blade impeller mixer, Harbil mixer, impingement mixer, high shear mixer, agitator mixer, homogenization (particularly a high pressure homogenizer), colloid mill, microfluidizer, ultrasonic mixing, melt mixer, magnetic mixer, rotary blade mixer, propeller mixer, and combinations thereof. Typically, the amount of energy required to produce a "stabilized "foam control composition" is 10^5 to 10^{10} J/m^3, preferably from 10^6 to 10^8 J/m^3.

The foam control composition for the lubricating composition can be used "neat", but is preferably mixed with a metal working fluid or other lubricating fluid, which can

also be used "neat". Preferably, these compositions are diluted with water, such that the weight ratio of water to foam control composition, or foam control composition blended with a lubricating fluid, is from 99:1 to 60:40, preferably from 97:3 to 80:20. The amount of active foam control agent can vary over broad ranges is typically is used in amounts of about 0.01 weight percent to about 70 weight percent, preferably about 0.1 weight percent to about 10 weight percent, most preferably about 0.5 weight percent to about 5 weight percent, based upon the total weight of lubricating oil(s), prior to dilution with water.

Examples

While the invention has been described with reference to a preferred embodiment, those skilled in the art will understand that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims. In this application all units are in the metric system and all amounts and percentages are by weight, unless otherwise expressly indicated.

Example 1
(Preparation of a foam control composition for metal working fluid)

Using a rotor-stator type homogenizing device (Ultra Turrax Model T18 Basic, which is supplied by IKA), a concentrated blend of 10 wt% of a polypropyleneglycol modified siloxane, containing 3 wt % of a hydrophobized silica and 90 wt% of a metal working fluid concentrate, composed of high pressure lubricating oils, surfactants and an anti-corrosive additive, was prepared. The Ultra Turrax was operated at a rotation speed of 10,000 rpm for 3 minutes.

A clear, low viscous mixture was obtained showing good stability as was confirmed upon storage of the mixture for two weeks at 40°C (accelerated aging/stability test).

Ten parts of the foam control composition were subsequently mixed with 90 parts of the neat metal working fluid concentrate while gently stirring using a common stirrer device. Both the homogenized, concentrated siloxane/metal working fluid blend and the diluted medium were clear and did not show any signs of liquid-liquid phase separation even after storage for two weeks at an elevated temperature of 40 °C.

A bench mark foam control agent, dosed at 1000 ppm to the neat metal working fluid, immediately caused turbidity of the metal working fluid concentrate and showed phase separation upon prolonged storage.

Example 2

(Preparation of a metal working fluid containing the homogenized foam control composition of Example 1)

The metal working fluid concentrate described in Example 1 was diluted with tapwater (weight ratio 5/95) to make a useable fluid.

A white-colored, low viscous mixture was obtained showing good stability as was confirmed upon storage of the mixture for two weeks at 40°C (accelerated aging/stability test).

The foaming characteristics of the diluted metal working fluid, with and without built-in foam control, were determined using a re-circulation test. The results of this test are shown in Table I.

Table I
(Foaming data of metal working fluid)

		Foam height (millimeters)[1] after time (seconds)				
Example	**FCA**	**>1 sec**	**2 sec**	**4 sec**	**6 sec**	**14 sec**
A	**None**	**100**	**100**	**110**	**120**	**140**
10	**Example 9**	**50**	**60**	**80**	**80**	**80**

The data in Table I indicate that the addition of the homogenized foam control agent of Example 1 strongly reduced foam formation of the diluted metal working fluid.

The unhomogenized foam control agents/metal working fluid mixture showed severe instability. For this reason the product did not pass the test and will never be tested with regards to inhibition of foam formation.

[1]Rounded off to the ten millimeters.

Claims

We claim:

1. A process for preparing a stabilized foam control composition for lubricating compositions comprising:

(a) combining a mixture of components comprising:

component (a) which comprises at least one active foam control agent; and

component (b) which comprises at least one lubricating oil,

such that the amount of active foam control agent is from about 0.01 weight percent to about 70 weight percent, based upon total weight of said lubricating oil; and

(b) mixing (a) and (b) with sufficient energy to create a mixture, which does not show full liquid-liquid phase separation and/or solid phase separation as determined by visual observation for at least 1 minute after mixing at ambient temperature.

2. The process of claim 2 wherein the lubricating oil is selected from the group consisting of fatty acid esters, fatty acid alkanol amides, mineral oils, polybutenes, polyalphaolefines, alkaline aromatics, polyglycols, fatty acid esterified polyglycols, and mixtures thereof.

3. The process of claim 3 wherein the active foam control agent is selected from the group consisting of acetylene diols and ethoxylated acetylene diols, silicone oils, modified siloxanes, polyglycols, esterified or modified polyglycols, fluorinated surfactants or chemicals, polyacrylates, fatty acids,

fatty acid esters, fatty alcohols, fatty alcohol esters, waxes, ureum and mixtures thereof.

4. The process of claim 3 wherein the amount of foam control agent is from about 0.1 to about 5.0 parts, based upon the weight of the lubricating oil.

5. A stabilized foam control composition for lubricating compositions prepared in accordance with claims 1, 2, 3, or 4.

6. A lubricating composition comprising the foam control composition for a lubricating composition of claim 5 and a lubricating composition.

7. The lubricating composition of claim 6 wherein the amount of foam control agent for the lubricating composition is from about 0.1 to about 5 parts by weight based upon the total weight of the lubricating composition.

8. The foam control composition for a lubricating composition of claim 5, which is diluted with water.

9. The lubricating composition of claim 6, which is diluted with water.

10. The lubricating composition of claim 7, which is diluted with water.

11. The foam control composition for a lubricating composition of claim 7 wherein the amount of water in the diluted metal working fluid or lubricant is from 80 parts by weight to 99 parts by weight based upon the total weight of the diluted metal working fluid or lubricant.

12. The lubricating composition of claim 8 wherein the amount of water in the diluted metal working fluid or lubricant is from 80 parts by weight to 99 parts by weight based upon the total weight of the diluted metal working fluid or lubricant.

13. The lubricating composition of claim 9 wherein the amount of water in the diluted metal working fluid or lubricant is from 80 parts by weight to 99 parts by weight based upon the total weight of the diluted metal working fluid or lubricant.