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(54) Title: STABILIZATION OF PAINT STRIPPER FORMULATIONS

(57) Abstract: The present invention is directed to an oxidant containing paint stripper composition, stabilized or inhibited against oxidative attack, comprising an oxidant, an emulsifier, and an amphiphilic antioxidant component.



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STABILIZATION OF PAINT STRIPPER FORMULATIONS

FIELD OF THE INVENTION

The field of the invention relates to oxidant containing paint stripper compositions. In one aspect, it relates to peroxide containing paint stripper compositions containing a peroxide component, an organic emulsifier and stabilizers and processes for preparing stabilized paint stripper compositions.

BACKGROUND OF THE INVENTION

At one time, strong acids and halocarbon solvent-based compositions were employed in stripping various protective coatings from metal and other substrates. For some time now, chlorinated solvents have been disallowed for use in stripper formulations. New ways of removing paint coatings, e.g., from aircraft, both military and commercial, had to be developed. One example of a water-based stripper product is disclosed in U.S. Patent No. 6,465,405, incorporated herein by reference. This patent describes compositions in the form of an emulsion with benzyl alcohol, carboxyl methyl cellulose, wax, and a pigment in the continuous or oil phase, and an organic acid, water, peroxide (optional), and an emulsifier in the dispersed or water phase. However, when peroxide was used in the stripper, the '405 patent teaches that a pH of less than about 3 should be maintained to prevent the peroxide from decomposing.

One problem with low pH strippers is the potential for corrosion on metal substrates, such as aluminum aircraft substrates. In order to counter the corrosion problem, adding different solvents and corrosion inhibitors have been suggested. Also, stabilizers for the peroxide have been used to allow the peroxide to remain more stable.

Stabilizers are normally added to hydrogen peroxide solutions to combat decomposition of the hydrogen peroxide due to trace impurities, mainly dissolved metals. These compounds are usually sequestering agents and can take many forms. Many types of

compounds have been used to fill this function, such as diols, quinones, stannate salts, pyrophosphates, various aromatic compounds and amino carboxylic acids salts. However, many of the previously suggested compounds have various issues and challenges associated with them, such as toxicity, environmental impact and poor performance.

Examples of specific compounds that have been suggested for use in solutions to protect against hydrogen peroxide decomposition include sodium phenolsulfate; sodium stannate; N,N – lower alkyl aniline, sulfamic acid, sulfolane, and dinormal lower alkyl sulfones and sulfoxides; phosphonic acids and their salts; acrylic acid polymers; polyphosphates; polyamino polyphosphonic acids and/or their salts; and specific combinations (or blends) of such compounds. However, in addition to toxicity and environmental impact concerns, many of these suggested compounds or blends have other drawbacks. For example, use of the specific stabilizer(s) either require specific conditions to provide adequate hydrogen peroxide stability, such as specific pH levels, e.g., acidic conditions, or relatively low hydrogen peroxide concentrations, or have poor stability performance. The poor stability performance can either be poor stability performance generally or poor stability performance in specific formulations that contain other destabilizing organic components, e.g., surfactants and emulsifiers.

SUMMARY OF THE INVENTION

Paint stripping formulations used to strip epoxy or polyurethane coatings in the aerospace industry are typically in the form of a water-in-oil emulsion. The oil phase can include an organic solvent, e.g., an aromatic alcohol, a component that initiates removal of the coating, e.g., malic acid, and optionally additional organic co-solvents. The water phase can include an oxidant, such as peroxide, e.g., hydrogen peroxide, and water. In addition, the formulation typically includes suitable organic solubilizers or emulsifiers to stabilize the emulsion. The emulsifier is typically a polyethoxylated organic compound having at least ten ethylene oxide units.

It has been found that use of such paint stripper formulations containing hydrogen peroxide that have been stored for a period of time prior to use can result in decreased effectiveness and/or increased corrosion of the underlying substrate, e.g., aluminum substrate on aircraft.

It would be desirable to have a stabilized oxidant, e.g., peroxide, containing paint stripper formulation that has an improved shelf life, which maintains its effectiveness and does not result in increased corrosion over extended storage periods.

It has been found that even with sequestering agents many oxidant (e.g., peroxide) based formulations containing organic components (e.g, surfactants, solubilizers or emulsifiers) experience a downward pH drift over time and possibly an unacceptable short shelf life. It is believed that such a pH drift is a result of destabilization of the organic components as a result of oxidative attack by the oxidant. Further, with cleaning formulations it is believed that the destabilization of the organic surfactant results in a reduction in the cleaning performance normally provided by un-reacted surfactant. Similarly, it is believed that oxidative attack on the emulsifier (and/or other organic components) typically used in paint stripper formulations will destabilize the emulsifier and/or other organics and produce increased concentrations of acid, which tends to promote increased corrosion.

Some specifications for paint strippers include a requirement that the paint stripper have a pH near neutral, e.g., certain mil specs, to avoid corrosion problems for certain metal substrate associated with low pH condition. As such, it would be desirable to have a stable oxidant (e.g., peroxide) containing paint stripper formulation that has a pH near neutral (or other effective pH) and maintains its pH and effectiveness over extended storage periods.

While not being bound by any particular theory it is believed that the cause of the drop in pH, along with the commensurate increase in corrosion, is due at least in part to attack of one or both of the emulsifier and the aromatic alcohol dissolved in the water

phase by the oxidizer present. Emulsifiers such as Polysorbate 80 are nonionic and can contain as many as 20 ethylene oxide units on every molecule. Aromatic alcohols, such as benzyl alcohol, are primary alcohols and as such are vulnerable to direct oxidation by strong oxidizers, resulting in the production of organic acids. In the case of the emulsifier, it is believed that attack starts at an ethylene oxide group and proceeds in a step-wise chain reaction, induced by free radicals, until acid is generated in the final quenching step. It is believed that when combined with certain other compounds, unique combination of chemistries used to interrupt this sequence can be made to contribute to the composition's stability over a longer period of time.

In one aspect, the present invention is directed to a paint stripper composition comprising: an organic solvent component that includes an organic solvent, an oxidant component that includes an oxidant, water, an emulsifier component that includes an emulsifier, and an amphiphilic antioxidant component that includes at least one amphiphilic antioxidant and at least one hydrophilic antioxidant booster, where the molar ratio of amphiphilic antioxidant:booster is at least 1:1. The amphiphilic antioxidant component is present in an amount sufficient to improve the stability of the emulsifier, or the emulsifier and the organic solvent, against oxidative attack. In one embodiment, the oxidant component contains a peroxide.

In one embodiment, the oxidant component comprises a peroxide generating agent and a phosphonic acid based sequestering agent. In one embodiment, the peroxide generating agent is selected from the group consisting of hydrogen peroxide, magnesium peroxide, calcium peroxide, sodium perborate, and combinations thereof.

Preferably, the peroxide generating agent is hydrogen peroxide, magnesium peroxide, or a combination thereof. On most metal surfaces, including aluminum and its alloys, a decomposition reaction of the peroxide, e.g., hydrogen peroxide, takes place, generating an intermediate nascent oxygen which associates instantaneously, producing gaseous oxygen and water. The oxygen accelerates the stripping process by initiating the lifting of the softened protective coating and allowing new quantities of the

paint stripping composition to penetrate the metal-coating interface. As such, it is advantageous to prevent or reduce decomposition of the peroxide during storage of the paint stripper composition. In embodiments of the invention, it is contemplated that the peroxide generating agent can include any compound that contains or provides a peroxide group that is capable of creating the above described effect when present in the paint stripping composition.

It is believed that the amphiphilic antioxidant component according to the invention can protect (or reduce oxidative attack on) not only the organic emulsifier from oxidative attack by the oxidant, e.g., peroxide, present in the composition, but will also protect other organic compounds, e.g., organic solvents, that are present in the water phase with the oxidant, that are otherwise vulnerable to oxidative attack by the oxidant. Thus, in one aspect of the invention, the amphiphilic antioxidant component is present in the paint stripper composition in an amount sufficient to reduce (or inhibit) the level of oxidative attack by the oxidant on any oxidizable organic components present in the water phase of the composition. These oxidizable components can include, e.g., the emulsifier, organic solvents, other organic species that are present in the water phase. In embodiments, the amphiphilic antioxidant component is present in the paint stripper composition in an amount sufficient to inhibit oxidative attack by the oxidant on organic species and to inhibit downward pH drift of the composition, i.e., protect the oxidant from decomposition.

In embodiments of the invention, the paint stripper composition can include from about 0.1 to about 30% by weight and preferably from about 0.3 to about 15% by weight of peroxide generating agent based upon 100% weight of total composition.

In an embodiment, the peroxide generating agent is hydrogen peroxide.

In an embodiment of the invention, the paint stripper composition contains a stabilized oxidant composition. In one embodiment, the stabilized oxidant composition is combined with at least one emulsifier and, optionally, other common components used in paint stripping formulations. In embodiments of the invention, the stabilized paint

stripper formulation will (substantially) maintain its pH and effectiveness over extended storage periods.

In another aspect, the invention is directed to a peroxide based paint stripping composition, stabilized against oxidative attack of an emulsifier, containing a peroxide generating agent (e.g., hydrogen peroxide), an emulsifier and stabilizers.

In one embodiment, the peroxide based paint stripper composition comprises: (1) an aqueous peroxide composition that comprises (a) a peroxide generating agent, (b) a peroxide stabilizer component, (c) an amphiphilic antioxidant component, and (d) water; and (2) a emulsifier component.

In one embodiment, the peroxide based paint stripper composition comprises: (1) an aqueous peroxide composition that comprises (a) a peroxide generating agent, (b) a peroxide stabilizer component, and (c) water; and (2) a stabilized emulsifier composition that comprises (a) an emulsifier component and (b) an amphiphilic antioxidant component.

In one embodiment, the peroxide generating agent is hydrogen peroxide. In an embodiment, the peroxide stabilizer component is a complexing agent based on phosphonic acid, its salts or degradation products thereof.

In one embodiment, the peroxide composition comprises: (a) hydrogen peroxide in an amount from about 20 to about 70 wt%, based on the peroxide composition, (b) at least one diphosphonic acid compound, its salts or degradation products thereof in an amount from about 10 to about 60 wt%, based on the amount of hydrogen peroxide, and (c) water. In one embodiment, the diphosphonic acid compound is 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP). In one embodiment, the peroxide composition further comprises: (d) an amphiphilic antioxidant component.

In embodiments of the invention, the emulsifier component comprises one or more polyethoxylated organic emulsifiers having at least ten ethylene oxide (EO) units. In other embodiments, the emulsifier has at least 15, or at least 20, EO units.

In one embodiment, the emulsifier is a polyethoxylated sorbitan ester. Examples of suitable polyethoxylated sorbitan esters can include polyethoxylated sorbitan monolaurate, polyethoxylated sorbitan monopalmitate, polyethoxylated sorbitan monostearate, polyethoxylated sorbitan tristearate, and polyethoxylated sorbitan monooleate; trioleate polysorbates; and any combination of any of the foregoing. In one embodiment, the emulsifier is polyethoxylated sorbitan monooleate or Polysorbate 80.

In an embodiment, the amphiphilic antioxidant component comprises at least one amphiphilic antioxidant and at least one antioxidant booster. In one embodiment, the at least one amphiphilic antioxidant is present in an amount from about 0.5 to about 20 wt%, or about 1 to about 15 wt%, about 1 to about 10 wt%, or about 1.5 to about 6 wt%, based on the amount of emulsifier. In one embodiment, the at least one amphiphilic antioxidant is present in an amount from about 0.5 to about 20 wt%, or about 1 to about 15 wt%, about 1 to about 10 wt%, or about 1.5 to about 6 wt%, based on the amount of oxidizable organic components, e.g., emulsifiers and organic solvents, contained in the water phase of the paint stripper composition.

In one embodiment, the at least one amphiphilic antioxidant includes alpha-tocopherol. In another embodiment, the amphiphilic antioxidant component comprises at least two amphiphilic antioxidants, wherein alpha-tocopherol is the primary (i.e., majority) amphiphilic antioxidant.

In one embodiment of the invention, the molar ratio of amphiphilic antioxidant to antioxidant booster is at least 1:1. In an embodiment, the antioxidant booster includes at least one hydrophilic compound having antioxidant or radical scavenging properties. In embodiments, the ratio of amphiphilic antioxidant to antioxidant booster is at least

2:1, or at least 3:1, or at least 5:1, based on the molecular weight of the materials (molar ratio). In embodiments of the invention, the antioxidant booster is chosen from lipoic acid, caffeic acid, cinnamic acid, nicotinic acid, picolinic acid, ferulic acid, coumaric acid, rosmarinic acid, derivatives thereof, and combinations thereof. In one embodiment, the booster is picolinic acid.

The paint stripper formulation can include an organic solvent component and a component that initiates paint removal. In an embodiment of the invention, the organic solvent is an aromatic alcohol. In embodiments of the invention, the aromatic alcohol is chosen from benzyl alcohol, phenoxy propanol, phenoxy ethanol, and any combination of any of the foregoing. In one embodiment, the aromatic alcohol is benzyl alcohol. In one embodiment, the aromatic alcohol is present in an amount from about 5 to 50 wt%, based on the paint stripping formulation. The component that initiates paint removal can be a hydroxycarboxylic acid, e.g., malic acid.

The paint stripper formulation can also include one or more of the following additional additives such as an aromatic ether, e.g. benzyl ether, an aromatic hydrocarbon co-solvent, and a second hydroxycarboxylic acid, such as glycolic acid, depending on the specific application.

The paint stripper formulation can also include other additives selected from the group consisting of coupling agents, chelating agents, corrosion inhibitors, rheology modifying agents, evaporation retardants, additional stabilizers and combinations thereof.

In embodiments of the invention, the pH of the paint stripping formulation is in the range of 4 to about 12, or 4 to about 11, or 4 to about 9.5. In embodiments, the oxidant, e.g., hydrogen peroxide, is present in an amount from about 0.1 to about 30 wt%, or about 0.3 to about 15 wt%, or about 0.5 to about 8 wt%, based on the entire formulation. In embodiments, the peroxide stabilizer is present in an amount sufficient to provide the solution with a hydrogen peroxide stability of at least about 50%, more preferably at least about 60%, and most preferably at least about 65%, after 16 hours at about 97°C.

In embodiments, the emulsifier is present in an amount from about 0.04 to about 10 wt%, or about 0.1 to about 5 wt%, or about 0.5 to about 3 wt%, based on the entire formulation. In embodiments, the amphiphilic antioxidant component is present in an amount sufficient to provide the peroxide solution (in the water phase) with pH stability decrease (total pH drop) of less than about 2, or less than about 1.5, or less than about 1, after 24 hours at about 94°C.

In one embodiment, the paint stripper composition comprises: (1) hydrogen peroxide in an amount of 0.1 to about 8 wt%, based on the total composition; (2) HEDP, its salts or degradation products thereof in an amount from about 10 to about 60 wt%, based on the amount of hydrogen peroxide; (3) an emulsifier in an amount of 0.1 to about 5 wt%, based on the total paint stripper composition; and (4) at least one amphiphilic antioxidant molecule (as described herein) in an amount from about 0.5 to about 20 wt%, based on the amount of emulsifier, and at least one antioxidant booster (as described herein), wherein the molar ratio of amphiphilic antioxidant molecule to antioxidant booster is at least 1:1.

In one aspect, the invention is directed to a method for preparing a stabilized peroxide based paint stripping formulation, which comprises: 1) preparing a stabilized emulsifier composition by combining an emulsifier component with an amphiphilic antioxidant component; and 2) combining the stabilized emulsifier composition with a peroxide composition. In one embodiment, the amphiphilic antioxidant component comprises at least one amphiphilic antioxidant molecule and at least one antioxidant booster, wherein the amphiphilic antioxidant molecule and antioxidant booster are added separately to the emulsifier component. In one embodiment, the amphiphilic antioxidant molecule and antioxidant booster are first combined prior to adding to the emulsifier component. In one embodiment, the peroxide composition comprises hydrogen peroxide, a phosphonic acid based sequestering agent, e.g., HEDP, and water. The amounts of each of the different components can be as specified herein in the specification.

Additional objects, advantages and novel features will be apparent to those skilled in the art upon examination of the description that follows.

BREIF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a graph showing the effect of the invention on pH drop.

FIGURE 2 is a graph showing the effect of the invention on peroxide stability.

FIGURE 3a is a graph showing the effect of the invention on turbidity of a cleaning solution.

FIGURE 3b is a graph showing the effect of the invention on peroxide stability.

FIGURE 4a is a graph showing the effect of the invention on pH drop.

FIGURE 4b is a graph showing the effect of the invention on peroxide stability.

FIGURE 5 is a graph showing the effect of the invention on pH drift.

FIGURES 6a-c are photographs showing the effect of the invention on cleaning ability.

FIGURE 7 is a graph showing the effect of the invention on cleaning efficiency.

FIGURE 8 is a graph showing the effect of the invention on pH drift.

FIGURE 9 is a graph showing the effect of the invention on pH drift.

FIGURE 10 is a graph showing the effect of the invention on pH drift.

FIGURE 11 is a graph showing the effect of the invention on pH drop for a simulated paint stripper composition.

FIGURE 12 is a graph showing the effect of the invention on peroxide stability for a simulated paint stripper composition.

FIGURE 13 is an HPLC graph showing a HPLC analysis of simulated paint stripper compositions.

DETAILED DESCRIPTION OF THE INVENTION

Without being bound by any particular theory, it is believed that over time and at ambient conditions of temperature and humidity that oxidative attack on an organic component, e.g., an emulsifier component, takes place in formulations containing both hydrogen peroxide and the organic component. The reaction pathway is thought to proceed through two or more steps culminating in the formation of an organic acid species which results in the drop of pH of the formulation. The first step of this process, however, is thought to start with oxidative attack on the organic in the formulation. The by-products of this first reaction are thought to provide the reactants for the next step in the continued oxidation of organics that result in acid formation. The first indication of this attack is a drop in pH of the emulsion. Some small amount of emulsifier may be oxidized at first and not result in a change in pH early on. A drop in pH over time indicates that emulsifier is being attacked and therefore emulsion stability has degraded. Further, the drop in pH is actually only occurring in the water droplets that eventually will impact the metal substrate when they penetrate far enough. Preventing the drop in pH is desirable in order to prevent corrosive attack of the substrate and therefore preserve the integrity of the substrate surface, for example, an aircraft fuselage or wing structure.

In one embodiment, the invention is directed to a stabilized emulsifier composition, stabilized or inhibited against oxidative attack, comprising an emulsifier component and

an amphiphilic antioxidant component. In an embodiment of the invention, the stabilized emulsifier composition is included in a paint stripping formulation containing an oxidant component, e.g., hydrogen peroxide solution.

In another aspect, the invention is directed to a stabilized oxidant composition comprising an oxidant and an amphiphilic antioxidant component. In one embodiment, the stabilized oxidant composition further comprises a sequestering agent stabilizer, e.g., a phosphonic acid based sequestering agent, such as HEDP. In an embodiment, the oxidant is a peroxide, e.g., hydrogen peroxide. In an embodiment of the invention, the stabilized oxidant composition is combined with at least one emulsifier and, optionally, other common components used in paint stripping formulations to make a formulation with the emulsifier protected against oxidative attack.

In another aspect, the invention is directed to a peroxide based paint stripping composition, stabilized against oxidative attack of an emulsifier, containing a peroxide component, an emulsifier and stabilizers. In one embodiment, the peroxide is hydrogen peroxide.

The hydrogen peroxide used to prepare the paint stripping composition can be in the form of a stabilized hydrogen peroxide solution, which solution comprises a relatively high concentration of hydrogen peroxide, e.g., at least about 20 wt% hydrogen peroxide, based on the stabilized hydrogen peroxide solution, and a sequestering agent, e.g., a phosphonic acid based sequestering agent, such as HEDP. An example of a commercially available stabilized hydrogen peroxide solution is Peroxy-Blend® PB-30 (from AkzoNobel). In one embodiment, the stabilized hydrogen peroxide solution is combined with an amphiphilic antioxidant component prior to being combined with an emulsifier. In another embodiment, an emulsifier is combined with an amphiphilic antioxidant component prior to being combined with the stabilized hydrogen peroxide solution.

In one embodiment, the peroxide based paint stripping composition comprises: (1) an aqueous peroxide composition that comprises (a) a peroxide component, (b) a peroxide stabilizer component, (c) an amphiphilic antioxidant component, and (d) water; and (2) an emulsifier component and an organic solvent component.

In one embodiment, the peroxide based paint stripping composition comprises: (1) an aqueous peroxide composition that comprises (a) a peroxide component, (b) a peroxide stabilizer component, and (c) water; and (2) a stabilized emulsifier composition that comprises (a) an emulsifier component and (b) an amphiphilic antioxidant component.

In one embodiment, the peroxide stabilizer component comprises a phosphonic acid based stabilizer. By the term "phosphonic acid based stabilizer" is intended to include compounds having at least one phosphonic acid group in its structure, including compounds in their acid form or salts thereof, as well as decomposition products of such compounds.

The phosphonic acid based stabilizer can include commercially available compounds which include a phosphonic acid group in their structure. Non-limiting examples of such stabilizers include 1-hydroxy-1,1-ethylidene diphosphonate commercially available as DEQUEST 2010, amino tri(methylene-phosphonic acid) available as DEQUEST 2000 and DEQUEST 2000LC; amino tri(methylene-phosphonic acid)pentasodium salt available as DEQUEST 2006; 1-hydroxyethylene-1,1,-diphosphonic acid commercially available as DEQUEST 2010; 1-hydroxyethylene-1,1,-diphosphonic acid tetrasodium salt available as DEQUEST 2016 and DEQUEST 2016D; ethylene diamine tetra(methylene phosphonic acid) available as DEQUEST 2041; ethylene diamine tetra(methylene phosphonic acid) pentasodium salt available as DEQUEST 2046; hexamethylenediamine tetra(methylene phosphonic acid) potassium salt available as DEQUEST 2054; diethylenetriamine penta(methylene phosphonic acid) available as DEQUEST 2060S; diethylenetriamine penta(methylenephosphonic acid)trisodium salt available as DEQUEST 2066A; diethylenetriamine penta(methylenephosphonic acid)pentasodium salt available as DEQUEST 2066; diethylenetriamine

penta(methylene phosphonic acid)pentasodium salt commercially available as DEQUEST 2066C2; bis-hexamethylene triaminepenta(methylenephosphonic acid) chloride salt commercially available as DEQUEST 2090A; tetrasodium salt of 1-hydroxy ethylen (1,1-diphosphonic acid) commercially available as DEQUEST SPE 9528, as well as other materials sold under the DEQUEST tradename, particularly DEQUEST 2086, DEQUEST 3000S, as well as DEQUEST 6004.

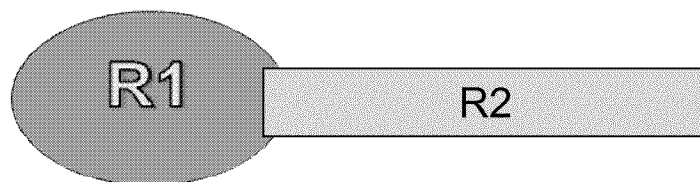
The peroxide composition is preferably added to the formulation that will also contain an emulsifier (e.g., a paint stripping formulation) in an amount to provide a paint stripping formulation having an initial hydrogen peroxide concentration of from about 0.1 to about 20 wt%, more preferably about 0.3 to about 15 wt%, and most preferably about 0.5 to about 8 wt%, based on the entire paint stripping formulation.

The paint stripping formulation is preferably prepared by combining the hydrogen peroxide solution with at least one emulsifier and at least one organic solvent.

In an embodiment, the amphiphilic antioxidant component comprises at least one amphiphilic antioxidant. By amphiphilic antioxidant is meant a surfactant like compound/molecule having a hydrophilic head that has antioxidant or radical scavenging properties and a hydrophobic tail. In an embodiment, the amphiphilic antioxidant is of a type and in an amount such that it is capable of self assembling into micelles with at least one of the emulsifiers present in the composition.

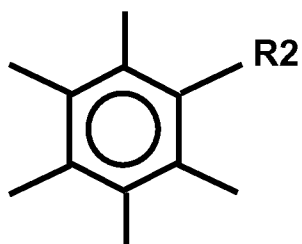
The amphiphilic antioxidant compound/molecule structure can vary provided that it has antioxidant or radical scavenging properties that make it preferentially subject to attack by the oxidant present in the solution in comparison to the emulsifier contained in the paint stripper formulation.

The general structure of the amphiphilic antioxidant compound/molecule is illustrated below, where R1 is the hydrophilic head group and R2 is the hydrophobic tail.



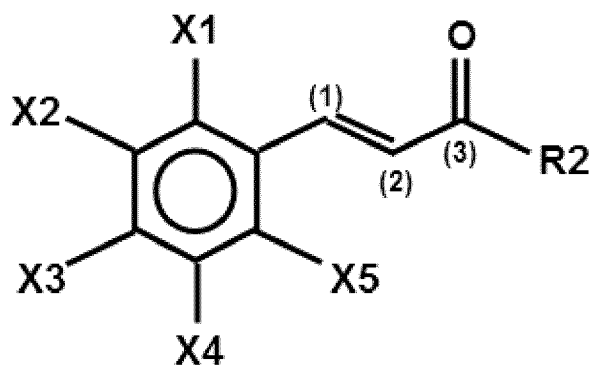
R1 can be selected from any group of polar head configurations also having appropriate radical scavenging capabilities. R1 can be chosen from moieties that are highly polar or hydrophilic, as well as moieties that contain alkyl chains and are less hydrophilic, provided that it provides appropriate radical scavenging functionality to protect or inhibit attack of the surfactant by the oxidant.

In embodiments of the invention, examples of useful structures for R1 are as follows:



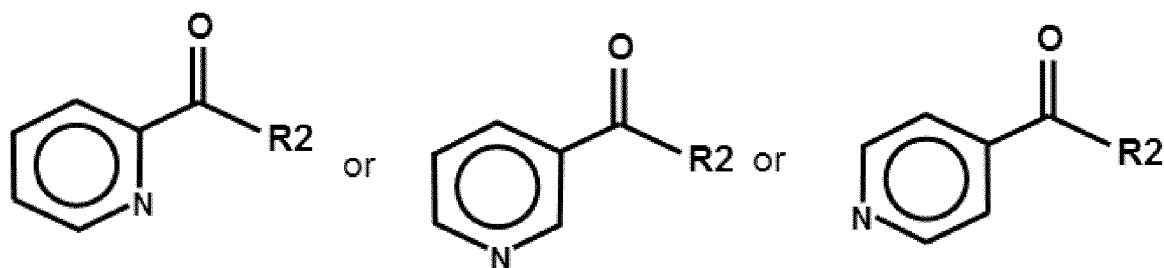
Wherein X1 through X5 can be H, OH, CH₃ or any combination thereof. In embodiments of the invention, O may be used to join a CH₃ group to the resonant ring structure. In one embodiment, OH groups are at the X1, X3, and X5 positions.

Or:

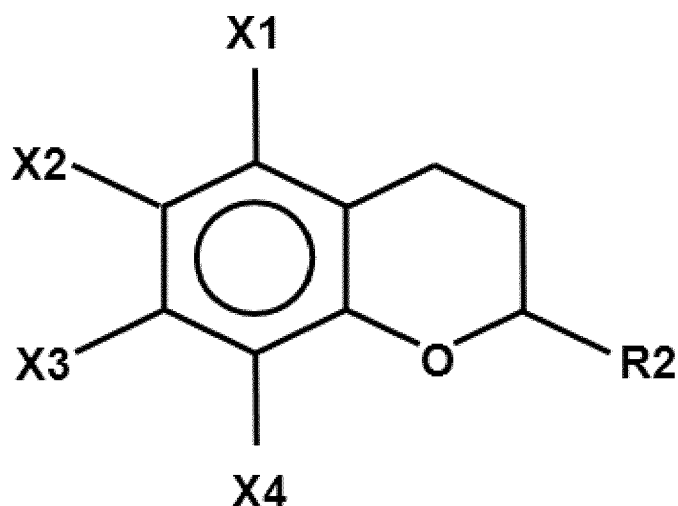


Wherein R1 can also have the configuration previously noted with an extension optionally containing either a double bond between carbons 1 and 2 shown in illustration, or a pendant oxygen attached to the carbon noted at position 3, or combinations of both making up the structure of R1. X1 through X5 can be as described above.

In other embodiments, R1 can include other polar head group configurations exhibiting radical scavenging or antioxidant behavior such as, for example, the following structures:



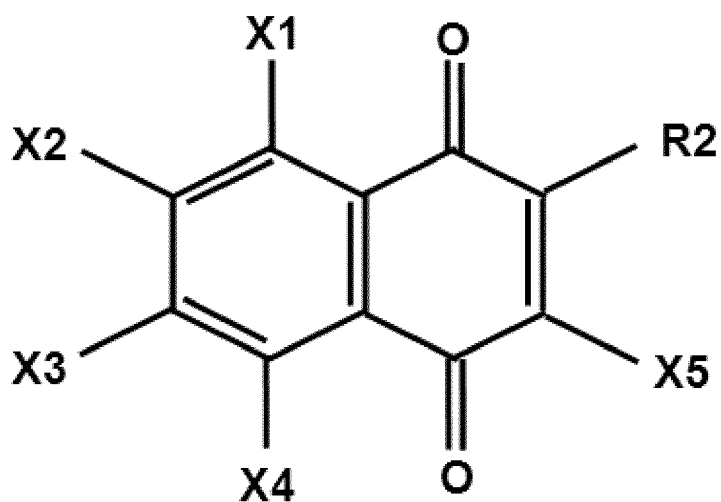
In yet other embodiments, other functional head groups with radical scavenging or antioxidant behavior include hetero-cyclic grouping common to natural vitamins such as Vitamin E, for example, having the following structure:



Wherein X1, X2, X3, and X4 can be H, OH, or CH₃ or any combination of those that serve to enable the inhibitory performance of the molecule.

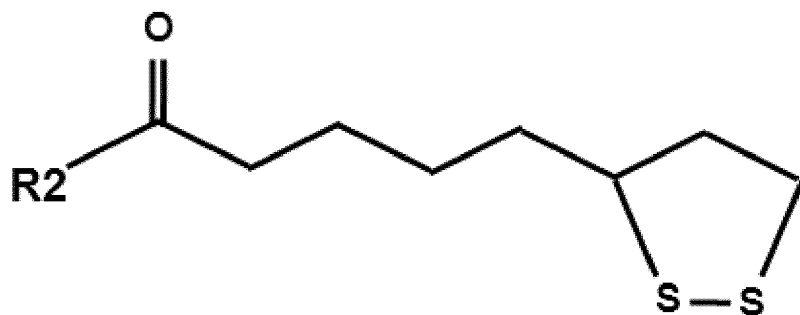
In embodiments of the invention, more than 2 rings may be employed. In embodiments, at least one ring can be a resonant structure. In embodiments of the invention, rings may be 6 member or 5 member rings, with complete saturation or un-saturation up to resonant structures (e.g., benzene ring).

In other embodiments, R1 can have a structure of the active end of Vitamin K1, for example, the following structure:

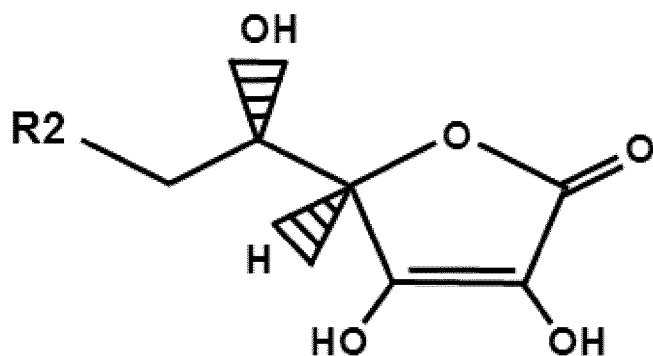


Wherein X1, X2, X3, X4 and X5 can be H, O, CH₃, or any combination thereof.

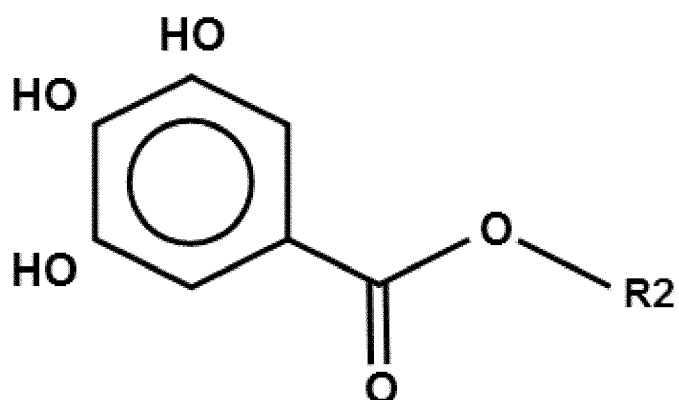
In yet other embodiments, R1 can have a polar structure found in Lipoic acid, for example, the following structure:



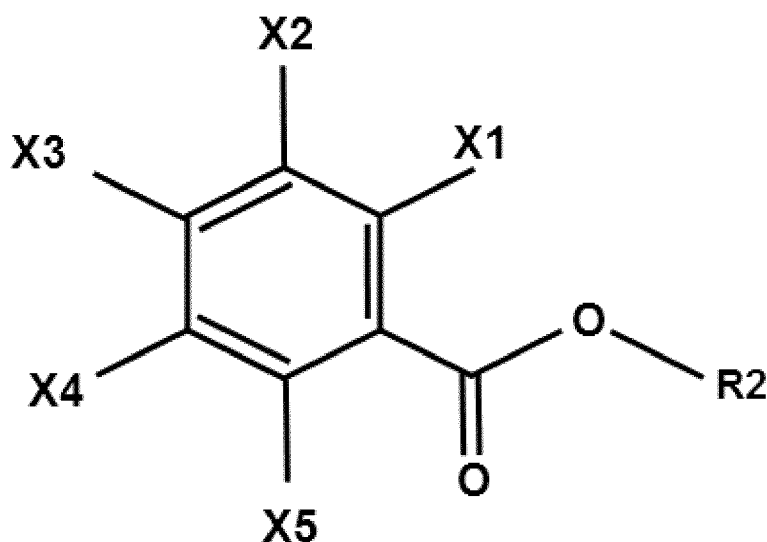
Or R1 can have a structure found in Ascorbic acid, or Vitamin C, for example, the following structure:



In embodiments of the invention, the gallate moiety is another example of a functional group that can act as both hydrophilic head group and antioxidant structure, for example, the following structure:



Or the following structure:



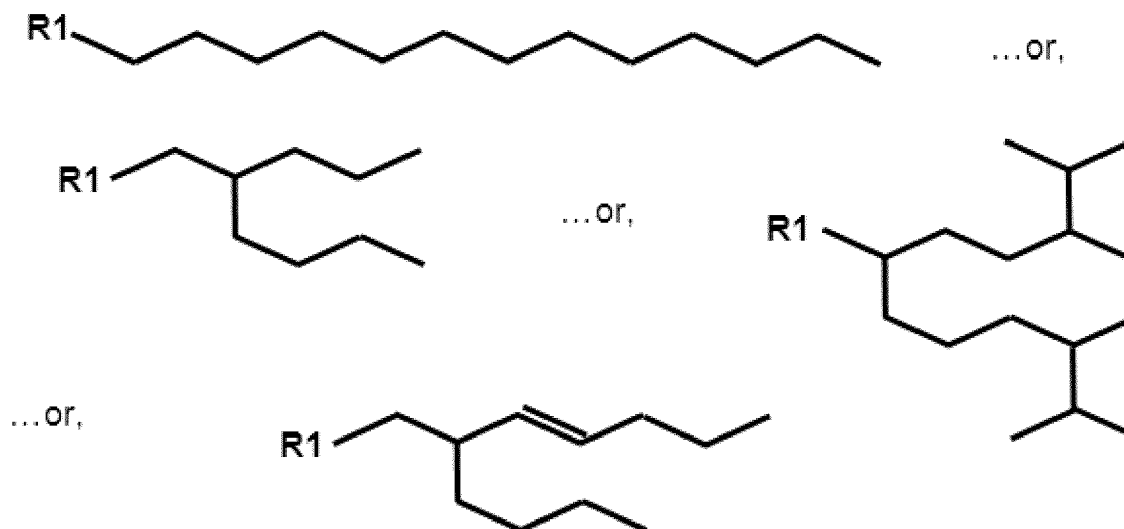
Wherein X1, X2, X3, X4 and X5 can be H, O, CH₃ or any combination thereof.

The previous description and listing of types of functional groups that can fulfill the requirement of the invention for the hydrophilic head group with antioxidant properties R1 is merely exemplary and not intended to limit the scope of the invention. It will be appreciated by one skilled in the art that other structures than those listed can fill the intended role described for the head group of the invention.

In embodiments of the invention, the R2 group or hydrophobic tail, can include a variety of configurations from a simple straight aliphatic chain to a complex branched configuration with an occasional double bond, which does not significantly decrease the overall level of hydrophobicity.

In embodiments of the invention, R2 can be a structure having a number of carbon atoms in the range of from C4 to C20, or C4 to C16, or C6 to C14.

Some non-limiting examples for R2 include the following:

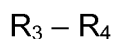


It will be appreciated by one skilled in the art that there are other structures or configurations that can be used for the R2 hydrophobic tail.

In one embodiment, the amphiphilic (or surfactant like) molecule(s) can be selected from naturally occurring compounds such as those found in plants and animal tissues. Examples of such compounds can include compounds, families of compounds and classes of compounds that include catechols, catechins, flavanoids, flavanols, or tannins. Additional examples include ubiquinol, co-enzyme Q-12 and Q-10, uric acid, methionine, glutathione, thymol, carvacrol, eugenol, plus water soluble and fat soluble vitamins.

In one embodiment, the amphiphilic antioxidant is alpha-tocopherol and the respective derivatives. In another embodiment, the amphiphilic antioxidant component comprises at least two amphiphilic antioxidants, wherein alpha-tocopherol is the primary (i.e., majority) amphiphilic antioxidant. In embodiments of the invention, the amphiphilic antioxidant is a tocopherol in a form selected from the group consisting of alpha, beta, delta, gamma, their respective derivatives, and combinations thereof. The derivatives can include, for example, acetate, nicotinate, or succinate derivatives.

In one embodiment of the invention, the amphiphilic antioxidant component comprises at least one amphiphilic antioxidant and at least one antioxidant booster, wherein the ratio of amphiphilic antioxidant to antioxidant booster is at least 1:1. In an embodiment, the antioxidant booster includes at least one hydrophilic compound having antioxidant or radical scavenging properties. In embodiments, the ratio of amphiphilic antioxidant to antioxidant booster is at least 2:1, or at least 3:1, or at least 5:1, based on the molecular weight of the materials (molar ratio). In embodiments of the invention, the antioxidant booster includes a hydrophilic organic compound having a structure as illustrated below:



wherein R_3 is a 5 or 6 member ring; wherein the members of the 6 member ring are all C or optionally where one ring member is N, and wherein one C has $-R_4$ as a substituent and the other carbon ring members can have a substituent group selected from -H, -OH, $-OCH_3$; and wherein the members of the 5 member ring are all C or optionally where up to 2 ring members are S, and wherein one C has $-R_4$ as a substituent; and

wherein R_4 is a carbon chain having a length from C1 to C5 and at least one carboxylic acid functional group. In one embodiment, R_4 has one carboxylic acid functional group that is a terminal group on the chain.

In one embodiment, the antioxidant booster having the formula above has a carbon chain tail having a length of C1-C5, contains a total of 6-10 carbon atoms and a total of 2-6 oxygen atoms, and has a molecular weight in the range from 120-225 g/mol.

In one embodiment, the antioxidant booster is chosen from lipoic acid, caffeic acid, cinnamic acid, nicotinic acid, picolinic acid, ferulic acid, coumaric acid, derivatives thereof, and combinations thereof.

In addition, combinations of the above mentioned amphiphilic (or surfactant like) molecules can be included in the amphiphilic antioxidant component. In one

embodiment, the amphiphilic antioxidant component comprises alpha-tocophol (as amphiphilic antioxidant) and picolinic acid (as antioxidant booster). In one embodiment, the alpha-tocopherol is present in an amount from about 0.5 to about 20 wt%, based on the amount of emulsifier, and picolinic acid is present in an amount from about 0.5 to about 20 wt%, based on the amount of alpha-tocopherol. In one embodiment, the alpha-tocopherol is present in an amount from about 1.0 to about 10 wt%, based on the amount of emulsifier, and the lipoic acid is present in an amount from about 1.0 to about 10 wt%, based on the amount of alpha-tocopherol. In an embodiment, the alpha-tocopherol is present in an amount from about 1.5 to about 6 wt% based on the amount of emulsifier, and the picolinic acid is present in an amount from about 1.5 to 6 wt%, based on the amount of alpha-tocopherol. In other embodiments, the weight percentages of the alpha-tocopherol can be based on the total organic compounds in the water phase that are capable of being oxidized by the oxidant in the composition.

Certain optional constituents which can be present in the inventive formulations are pH adjusting agents and/or pH buffers. Such pH buffers include many materials which are known to the art and which are conventionally used in paint stripping formulations to adjust or maintain pH. By way of non-limiting example, pH adjusting agents can include phosphorus containing compounds, monovalent and polyvalent salts such as of silicates, carbonates, and borates, certain acids and bases, tartrates and certain acetates. Further exemplary pH adjusting agents include mineral acids, basic compositions, and organic acids, which are typically required in only minor amounts. By way of further non-limiting example pH buffering compositions include the alkali metal phosphates, polyphosphates, pyrophosphates, triphosphates, tetraphosphates, silicates, metasilicates, polysilicates, carbonates, hydroxides, and mixtures of the same. Certain salts, such as the alkaline earth phosphates, carbonates, hydroxides, can also function as buffers. It may also be suitable to use as buffers such materials as aluminosilicates (zeolites), borates, aluminates and certain organic materials such as gluconates, succinates, maleates, and their alkali metal salts. When present, the pH adjusting agent, and/or pH buffers are present in an amount effective in order to help maintain the pH of the inventive composition within a target pH range.

In embodiments of the invention, the paint stripper composition comprises: (a) from about 5 to about 50% by weight of an aromatic alcohol; (b) from about 0.5 to about 20% by weight malic acid; (c) from about 15 to about 60% by weight water; and (d) from about 0.3 to about 15% by weight, or about 0.5 to about 10% by weight, of a peroxide generating agent.

In embodiments of the invention, the paint stripper composition can include one or more of the following: an aromatic ether, an aromatic hydrocarbon co-solvent, a hydroxycarboxylic acid, coupling agents, chelating agents, corrosion inhibitors, rheology modifying agents, evaporation retardants, additional stabilizers and combinations thereof.

In one embodiment, the aromatic ether is benzyl ether. In embodiments of the invention, the paint stripper composition can include from about 1 to about 30% by weight of aromatic ether based upon 100% weight of total composition. In embodiments, the weight ratio of aromatic alcohol to aromatic ether can be from about 3:1 to about 1:1, or about 2.5:1.

In embodiments of the invention, the aromatic hydrocarbon co-solvent may be a mixture of one or more aromatic hydrocarbon solvents. In embodiments of the invention, the aromatic hydrocarbon co-solvent can be selected, e.g., to improve the stability of the composition, improve the rheological properties of the composition, alter the speed of penetration of the paint stripper composition into paints and coatings, or reduce the surface tension and evaporation rate of the composition. In one embodiment, the aromatic hydrocarbon co-solvent is a naphthalene depleted aromatic hydrocarbon. Examples of suitable aromatic hydrocarbon co-solvents, include, but are not limited to, Aromatic 200ND available from Exxon Chemicals of Houston, Tex.; Solvesso 200 available from Esso Corporation of Toronto, Canada; metaphenoxy benzyl alcohol; and combinations thereof. In embodiments of the invention, the paint stripper composition can include from about 0.5 to about 40% by weight, or from about 1 to about 30% by

weight, of the aromatic hydrocarbon co-solvent based upon 100% weight of total composition.

In embodiments of the invention, in addition to malic acid, the paint stripper composition may include one or more second hydroxycarboxylic acids. In one embodiment, the second hydroxycarboxylic acid is glycolic acid. In embodiments of the invention, the paint stripper composition contains from about 0.5 to about 10% by weight, or from about 0.5 to about 3.5% by weight, of the second hydroxycarboxylic acid based upon 100% weight of total composition.

Suitable coupling agents can include, but are not limited to, alkylene glycols, dimethylsulfoxide (DMSO), and combinations thereof. In one embodiment, the coupling agent is propylene glycol. In embodiments of the invention, the composition can contain from about 0.5 to about 5% by weight of coupling agent based upon 100% weight of total composition.

Suitable chelating agents include, but are not limited to, phosphonic acids, such as bis(hexamethylene)triamino penta(methylenic phosphonic) acid and phosphoric acid; citric acid; ethylenediaminetetraacetic acid (EDTA); and combinations thereof. In embodiments of the invention, the paint stripper composition can contain from about 0.5 to about 4% by weight of chelating agent based upon 100% weight of total composition.

Suitable corrosion inhibitors include, but are not limited to, benzotriazoles, such as 2-mercaptobenzothiazole, tolutriazole, benzotriazole, 2(3H)-benzothiazolethioine; borates; and combinations thereof. In embodiments of the invention, the paint stripper composition can contain from about 0.3 to about 3% by weight of corrosion inhibitor based upon 100% weight of total composition.

Suitable rheology modifying agents include, but are not limited to, hydroxypropyl cellulose, hydroxypropyl methyl cellulose, hydroxyethyl cellulose, fumed silica, precipitated silica, castor oil, and combinations thereof. In one embodiment, the

rheology modifying agent is hydroxypropyl cellulose. In embodiments of the invention, the paint stripper composition can contain from about 0.1 to about 3% by weight of rheology modifying agent based upon 100% weight of total composition.

Suitable evaporation retardants include, but are not limited to, silicone fluid, a water-based wax emulsion, paraffin oil, paraffin wax, and combinations thereof. In one embodiment, the evaporation retardant is paraffin wax. In embodiments, the paint stripper composition can contain from about 0.1 to about 3% by weight of evaporation retardant based upon 100% weight of total composition.

In embodiments of the invention, the formulation (or composition) containing the amphiphilic antioxidant component in accordance with the invention contains less than 0.05 wt%, or less than 0.025 wt%, or is free from an organic acid peroxide precursor.

In an aspect of the invention, the invention is directed to a method for removing paint or a coating from a substrate comprising applying a paint or coating removing effective amount of the paint stripper composition according to any of the embodiments described in herein.

In another aspect, the invention is directed to a process for preparing a paint stripper composition, the process comprising dispersing (i) a polar phase containing from about 0.5 to about 20 parts by weight of malic acid; from about 15 to about 60 parts by weight of deionized or distilled water; from about 0.5 to about 10% by weight of a peroxide generating agent into (ii) a non-polar phase containing from about 5 to about 50 parts by weight of benzyl alcohol to form said paint stripper composition, wherein an emulsifier component comprising an emulsifier and an amphiphilic antioxidant component comprising at least one amphiphilic antioxidant and at least one hydrophilic antioxidant booster, wherein the molar ratio of amphiphilic antioxidant:booster is at least 1:1, are included in either the polar or non-polar phase prior to or during the dispersing.

In yet another aspect, the invention is directed to use of an amphiphilic antioxidant component to improve the stability of a paint stripper composition that contains an emulsifier, an organic solvent and an oxidant; wherein the amphiphilic antioxidant component comprises at least one amphiphilic antioxidant and at least one hydrophilic antioxidant booster, wherein the molar ratio of amphiphilic antioxidant:booster is at least 1:1, and wherein the amphiphilic antioxidant component is present in an amount sufficient to improve the stability of at least one of the emulsifier or the organic solvent against oxidative attack against by said oxidant.

The examples set forth below are for the purpose of illustration and to describe embodiments of the best mode of the invention at the present time. The scope of the invention is not in any way limited by the examples set forth below.

EXAMPLES

The following examples have been carried out to illustrate preferred embodiments of the invention. These examples include the preparation of solutions and stability tests conducted on the test solutions.

All formulations have been made with deionized water at room temperature using a magnetic mixer and stir bars. The “% stability” is defined as the percentage of hydrogen peroxide remaining after the described stress test. Both 16 hours at 96°C and 24 hours at 94°C simulate the behavior that can be expected of these formulations after one year at room temperature. The test utilizing 7 days at 94°C is particularly harsh and indicative of the robustness of the invention.

Comparative Example 1:

A formulation was prepared as follows: A 250 ml beaker was charged with 84 grams of deionized water and 5 grams of a nonionic/cationic surfactant blend (Berol® 226SA) was added under constant mixing. To this mixture was added 10 grams of a stabilized hydrogen peroxide, stabilized with a phosphonate stabilizer (Peroxy-Blend® PB33), also under constant mixing. Caustic was added to bring the mixture to a pH of 7. A small amount of deionized water was added at the end to bring the total to 100 grams. The resulting aqueous formulation contained about 5 wt% surfactant blend, about 3.3 wt% hydrogen peroxide and about 0.05% to about 1% phosphonate stabilizer.

Comparative Example 2:

A second formulation was prepared in a similar manner to comparative example 1, except technical grade hydrogen peroxide (35 wt%) was used as the source of the hydrogen peroxide. The resulting aqueous formulation contained about 5 wt% surfactant blend and about 3.5 wt% hydrogen peroxide.

Example 1:

A formulation was prepared in a similar manner to comparative example 1, except an amphiphilic antioxidant and antioxidant booster blend, consisting of alpha tocopherol/lipoic acid in a ratio 1909:91 ppm, based on the total formulation, was added prior to adjusting to a pH of 7 (with caustic).

Example 2:

A formulation was prepared in a similar manner to comparative example 2, except an amphiphilic antioxidant and antioxidant booster blend, consisting of alpha tocopherol/lipoic acid in a ratio 1909:91 ppm, based on the total formulation, was added prior to adjusting to a pH of 7 (with caustic).

Example 3:

The formulations according to comparative examples 1 and 2, and examples 1 and 2, were each subjected to elevated temperature aging for 24 hours at 94°C and then measured for change in pH. The results are shown below in Table 1 and Figure 1.

Formulation	pH Change from 7
Comp. Ex. 2	-4.3
Ex. 2	-3.5
Comp. Ex. 1	-3.0
Ex. 1	-0.93

Table 1: Elevated temperature aging.

A review of table 1 and figure 1 reveals that adding the amphiphilic antioxidant and antioxidant booster blend reduces the pH drop. The presence of the phosphonate stabilizer also contributed to reducing the pH drop. The best result is seen from the synergistic combination of both the amphiphilic antioxidant/booster package and the phosphonate stabilizer.

Comparative Example 3:

A formulation was prepared as follows: A 250 ml beaker was charged with 30 grams of deionized water and 55 grams of a stabilized hydrogen peroxide, stabilized with a phosphonate stabilizer (Peroxy-Blend® PB31), was added under constant mixing. To this mixture was added 7 grams of a nonionic surfactant (Berol® 508) also under constant mixing. Caustic was added to bring the mixture to a pH of 4. A small amount of deionized water was added at the end to bring the total to 100 grams. This solution was then diluted 1:7 with deionized water and then caustic was added to bring the pH to 7. The resulting aqueous formulation contained about 1 wt% surfactant blend, about 2.5% hydrogen peroxide and about 0.05% to about 1% phosphonate stabilizer.

Comparative Example 4:

A formulation was prepared in a similar manner to comparative example 3, except that 400 ppm of BHT (Butylated Hydroxytoluene) was added based on the 1 in 7 diluted formulation prior to adjusting to a pH of 7.

Example 4:

A formulation was prepared in a similar manner to comparative example 3, except that an amphiphilic antioxidant and antioxidant booster blend, consisting of alpha tocopherol/caffeic acid in a ratio of 384:16 ppm, was added based on the 1 in 7 diluted formulation prior to adjusting to a pH of 7.

Comparative example 5:

A formulation was prepared as follows: : A 250 ml beaker was charged with 30 grams of deionized water and 55 grams of a stabilized hydrogen peroxide, stabilized with a phosphonate stabilizer (Peroxy-Blend® PB31), was added under constant mixing. To this mixture was added 7 grams of a nonionic surfactant (Berol® 508) and 3 grams of an anionic surfactant (NAS-8), also under constant mixing. Caustic was added to bring the mixture to a pH of 4. A small amount of deionized water was added at the end to bring the total to 100 grams. This solution was then diluted 1:7 with deionized water and then caustic was added to bring the pH to 7. The resulting aqueous formulation contained about 1 wt% nonionic surfactant, about 0.43% anionic surfactant, about 2.5% hydrogen peroxide and about 0.05% to about 1% phosphonate stabilizer.

Comparative Example 6:

A formulation was prepared in a similar manner to comparative example 5, except that 400 ppm of BHT (Butylated Hydroxytoluene) was added based on the 1 in 7 diluted formulation prior to adjusting to a pH of 7.

Example 5:

A formulation was prepared in a similar manner to comparative example 5, except that an amphiphilic antioxidant and antioxidant booster blend, consisting of alpha

tocopherol/caffeic acid in a ratio of 384:16 ppm, was added based on the 1 in 7 diluted formulation prior to adjusting to a pH of 7.

Example 6:

Various combinations of the above formulations with additives were measured for turbidity and hydrogen peroxide stability after being subjected to accelerated aging for 7 days at 94°C. The results for turbidity and stability are shown in Table 2. The results for stability are also shown graphically in Figure 2.

Formulation	Turbidity (FAU)	% Stability
Comp. Ex. 3	825	74.1
Comp. Ex. 4	45	83.2
Ex. 4	3	87.4
Comp. Ex. 5	772	77.6
Comp. Ex. 6	65	91
Ex. 5	4	92.5

Table 2: accelerated turbidity and stability testing.

A review of Table 2 and Figure 2 reveals that the formulations according to the invention out-perform the formulations with BHT added.

Comparative Example 7:

A formulation was prepared as follows: A 250 ml beaker was charged with 30 grams of deionized water and 55 grams of a stabilized hydrogen peroxide, stabilized with a phosphonate stabilizer (Peroxy-Blend® PB31), was added under constant mixing. To this mixture was added 7 grams of a nonionic surfactant (Berol® 508) also under constant mixing. Caustic was added to bring the mixture to a pH of 4. A small amount of deionized water was added at the end to bring the total to 100 grams. This solution was then diluted 1:7 with deionized water and then caustic was added to bring the pH to 7. The resulting aqueous formulation contained about 1 wt% surfactant blend, about 2.5% hydrogen peroxide and about 0.05% to about 1% phosphonate stabilizer.

Comparative Example 8:

A formulation was prepared in a similar manner to comparative example 7, except that 13 ppm of cinnamic acid was added based on the diluted solution containing 1% nonionic surfactant, about 2.5% hydrogen peroxide and about 0.05% to 1% phosphonate stabilizer.

Comparative Example 9:

A formulation was prepared in a similar manner to comparative example 7, except that 16 ppm of caffeic acid was added based on the diluted solution containing 1% nonionic surfactant, about 2.5% hydrogen peroxide and about 0.05% to 1% phosphonate stabilizer.

Example 7:

A formulation was prepared in a similar manner to comparative example 7, except that 400 ppm of alpha tocopherol was added based on the diluted solution containing 1% nonionic surfactant, about 2.5% hydrogen peroxide and about 0.05% to 1% phosphonate stabilizer.

Example 8:

A formulation was prepared in a similar manner to comparative example 7, except that an amphiphilic antioxidant and antioxidant booster blend, consisting of alpha tocopherol/cinnamic acid in a ratio of 387:13 ppm, was added based on the diluted solution containing 1% nonionic surfactant, about 2.5% hydrogen peroxide and about 0.05% to 1% phosphonate stabilizer.

Example 9:

A formulation was prepared in a similar manner to comparative example 7, except that an amphiphilic antioxidant and antioxidant booster blend, consisting of alpha tocopherol/caffeic acid in a ratio of 384:16 ppm, was added based on the diluted solution containing 1% nonionic surfactant, about 2.5% hydrogen peroxide and about 0.05% to 1% phosphonate stabilizer.

Example 10:

Various formulations above were measured for turbidity and hydrogen peroxide stability after being subjected to accelerated aging for 7 days at 94°C. The results are shown in Table 3, and Figures 3a and 3b.

Formulation	Turbidity (FAU)	% Stability
Comp. Ex. 7	99	65.6
Comp. Ex. 8	276	52.3
Comp. Ex. 9	482	61.5
Ex. 7	91	67.9
Ex. 8	13	73.3
Ex. 9	13	73.7

Table 3: accelerated turbidity and stability testing.

A review of table 3 and figures 3a and 3b reveals that there is a synergistic effect from combining the polyphenol antioxidants with the amphiphilic alpha tocopherol (vitamin E) antioxidant.

Comparative Example 10:

A formulation was prepared as follows: A 250 ml beaker was charged with 84 grams of deionized water and 5 grams of a nonionic/cationic surfactant blend (Berol® 226SA) was added under constant mixing. To this mixture was added 10 grams of a stabilized hydrogen peroxide, stabilized with a phosphonate stabilizer (Peroxy-Blend® PB33), also under constant mixing. Caustic was added to bring the mixture to a pH of 7. A small amount of deionized water was added at the end to bring the total to 100 grams. The resulting aqueous formulation contained about 5 wt% surfactant blend, about 3.3 wt% hydrogen peroxide, and about 0.05% to about 1% phosphonate stabilizer.

Example 11:

A formulation was prepared in a similar manner to comparative example 10, except an amphiphilic antioxidant and antioxidant booster blend, consisting of alpha tocopherol/cinnamic acid in a ratio 1966:34 ppm, based on the total formulation, was added prior to adjusting to a pH of 7 (with caustic).

Example 12:

A formulation was prepared in a similar manner to comparative example 10, except an amphiphilic antioxidant and antioxidant booster blend, consisting of alpha tocopherol/caffeic acid in a ratio 1959:41 ppm, based on the total formulation, was added prior to adjusting to a pH of 7 (with caustic).

Example 13:

The formulations according to comparative example 10, and examples 11 and 12, were each subjected to elevated temperature aging for 24 hours at 94°C and then measured for change in pH and hydrogen peroxide stability. The results are shown below in Table 4 and Figures 4a and 4b.

Formulation	pH Change from 7	% Stability
Comp. Ex. 10	-2.93	90.9
Ex. 11	-0.97	95.8
Ex. 12	-1.11	96.4

Table 4: pH change and stability testing.

A review of table 4 and Figures 4a and 4b reveals that the formulations according to the invention results in a very positive impact on both the change in pH (much less) and the hydrogen peroxide stability (more left after stress). In addition to being effective for both nonionic and nonionic/anionic surfactant systems, the invention is effective on nonionic/cationic systems as well.

Example 14:

Cleaning performance was evaluated for cleaning solutions by subjecting the solutions of the invention and a control solution to accelerated aging and testing for any change in cleaning performance. A starting solution for all test samples was prepared similar to comparative example 1 that contained 5% Berol® 226SA and 10% Peroxy-Blend® PB33, which was adjusted with caustic to a pH of 9.5.

The control was prepared by diluting the starting solution with water 1:5 giving a cleaning solution with 1% surfactant and then adjusting the pH to 7. A pH of 7 was chosen to provide a more aggressive challenge to the stability of the system.

Test samples were prepared by adding a 2000 ppm dose of a 10:1 mixture of alpha-tocopherol and picolinic acid to the starting solution (Test Sample 1) and by adding a 2000 ppm dose of a 1500:500:100 mixture of alpha-tocopherol, lecithin and picolinic acid to the starting solution (Test Sample 2). Both test solutions were diluted and the pH was adjusted to 7, similar to the control.

Cleaning performance was tested as follows: accelerated aging was for 24 hours at 94°C, the test solutions were diluted 1:5 (as discussed above) before and after accelerated aging to make pour-down solutions, the pour down solutions were poured over train-engine grease on white painted steel panels, and surface reflectivity was measured using a brightness meter. ASTM D-4488 definition of cleaning efficiency was applied to evaluate the performance.

The change in pH was measure before and after the accelerated aging. The results are shown in Figure 5. A review of Figure 5 reveals that the pH dropped much more for the control compared to Test Samples 1 and 2.

The results of the pour down testing is shown in Figures 6a-6c. The test before aging is shown on the left and after aging on the right for each of the figures. A review of the figures reveals that the control did not effectively remove the grease after accelerated aging. In contrast, both Test Samples 1 and 2 were still effective after accelerated aging.

The quantified cleaning test results according to ASTM D-4488 are shown in Figure 7. A review of Figure 7 reveals that the control significantly reduced in cleaning ability, while Test Samples 1 and 2 maintained cleaning ability after accelerated aging.

Example 15:

A formulation having a nonionic/cationic surfactant blend was prepared in a similar manner to comparative example 1, except that it was not diluted. The formulation contained 5% Berol® 226SA and 10% Peroxy-Blend® PB33, which was adjusted with caustic to a pH of 7 (PB 33 formulation). Four additional test formulations were prepared, similar to above, except different blends of alpha tocopherol and different hydrophilic antioxidants (at a 20:1 molar ratio of alpha tocopherol:hydrophilic antioxidant) were added in each test formulation prior to adjusting to a pH of 7. The added blends were as follows: 1) alpha tocopherol:lipoic acid in a ratio 293:7 ppm; 2) alpha tocopherol:ascorbic acid in a ratio 294:6 ppm; 3) alpha tocopherol:cinnamic acid in a ratio 295:5 ppm; and 4) alpha tocopherol:caffeic acid in a ratio 294:6 ppm; all based on the total formulation.

The formulations were each subjected to elevated temperature aging for 24 hours at 94°C and for 1 year at ambient temperature (an average temperature of approximately 20°C) and then measured for change in pH. The results are shown below in Figure 8.

A review of Figure 8 reveals that adding the alpha tocopherol and antioxidant booster blend according to the invention significantly reduces the pH drop for real time aging.

Example 16:

A formulation having a nonionic surfactant was prepared in a similar manner to comparative example 1, except that the formulation contained 7% Berol® 508 and 54% Peroxy-Blend® PB31, which was adjusted with caustic to a pH of 7 and then diluted with water 1:7 to have a final surfactant concentration of about 1% (PBX formulation). Five additional test formulations were prepared, similar to above, except different antioxidants and blends of antioxidants were added in each test formulation prior to adjusting to a pH of 7 and dilution with water. The added alpha tocopherol:booster blends were as follows: 1) 400 ppm alpha tocopherol; 2) alpha tocopherol:cinnamic acid in a ratio 387:13 ppm; 3) alpha tocopherol:caffeic acid in a ratio 384:16 ppm; and 4) 13 ppm cinnamic acid; and 5) 16 ppm caffeic acid; all based on the total formulation.

The formulations were each subjected to elevated temperature aging for 24 hours at 94°C and for 1 year at ambient temperature (an average temperature of approximately 20°C) and then measured for change in pH. The results are shown below in Figure 9.

A review of Figure 9 reveals that adding the alpha tocopherol and antioxidant booster blend according to the invention (i.e., blends 2) and 3) described above) showed synergistic improvement in preventing pH drop.

Example 17:

A formulation having a nonionic/anionic surfactant blend was prepared in a similar manner to example 16, except that the formulation contained 7% Berol® 508, 3% NAS-8 and 54% Peroxy-Blend® PB31, which was adjusted with caustic to a pH of 7 and then diluted with water 1:7 to have a final surfactant concentration of about 1.4% (PBX formulation). Three additional test formulations were prepared, similar to above, except different blends of alpha tocopherol and antioxidant boosters were added in each test formulation prior to adjusting to a pH of 7 and dilution with water. The added blends were as follows: 1) alpha tocopherol:lipoic acid in a ratio 382:18 ppm; 2) alpha tocopherol:cinnamic acid in a ratio 387:13 ppm; and 3) alpha tocopherol:caffeic acid in a ratio 384:16 ppm; all based on the total formulation. Another test formulation was prepared as above for the PBX formulation, except technical grade hydrogen peroxide was used instead of the Peroxy-Blend® PB31.

The formulations were each subjected to elevated temperature aging for 7 days at 94°C, 28 days at 55°C, and for 1 year at ambient temperature (an average temperature of approximately 20°C) and then measured for change in pH. The results are shown below in Figure 10.

A review of Figure 10 reveals that adding the alpha tocopherol and antioxidant booster blend according to the invention (i.e., blends 1-3 described above) showed significant

improvement in preventing pH drop and technical grade peroxide resulted in much a greater pH drift than the PB31 peroxide.

Example 18:

Paint stripper compositions are mainly in the form of emulsions with the water phase dispersed into the oil phase. Given the structure of emulsions and that hydrogen peroxide solubility is high in the water phase and virtually nil in the oil phase, the damaging attack of hydrogen peroxide on the emulsifier and benzyl alcohol is likely taking place in the dispersed aqueous phase. Consequently, the effect of the peroxide can be simulated in a single, aqueous phase with emulsifier and alcohol dissolved in it.

Thus, to simulate an aqueous paint stripper composition, a aqueous solution containing emulsifier (Polysorbate 80) at 0.85% by weight, and benzyl alcohol at 3.5% by weight (which is near its solubility limit in water) were combined under constant agitation. To this was added Peroxy-Blend® PB33 to a concentration of about 3.5% by weight as hydrogen peroxide, and then the pH was adjusted with caustic soda to neutral pH (~7). The sample was split and a blend of alpha-tocopherol acetate (AT) and picolinic acid (PA) (in a molar ratio of AT:PA of 5:1) at 0.194% by weight was added (to the candidate half) in accordance with the invention, and then the samples were heated to 94°C for 24 hours. Weight % was based on the total solution.

After 24 hours at 94°C the control solution with benzyl alcohol, Polysorbate 80, hydrogen peroxide and diphosphonic acid, all starting at a pH of 7.28, had a pH of 4.98. This indicates a drop of 2.3 units of pH or the theoretical generation of 1.04×10^{-5} moles of acid. In the case of the candidate composition with the invention, the pH started at 7.1 and only dropped to 5.3 for a drop 1.8 units of pH. This represents about 5.05×10^{-6} moles of acid generated, or less than half (~48%) the acid developed in the control. The results are shown in Figure 11.

A review of figure 11 reveals that adding the amphiphilic antioxidant and antioxidant booster blend reduces the pH drop.

Example 19:

The amount of hydrogen peroxide retained in each sample, i.e., the control and candidate, was determined for the samples from Example 18. The results are shown in figure 12. A review of figure 12 reveals that the candidate according to the invention retained about 92% of the hydrogen peroxide after accelerated aging, while the control only retained about 87% of the hydrogen peroxide.

Example 20:

The samples, i.e., the control and candidate, from Example 18 were analyzed in an HPLC before and after controlled aging to analyze changes in the composition. The HPLC graph is shown in figure 13.

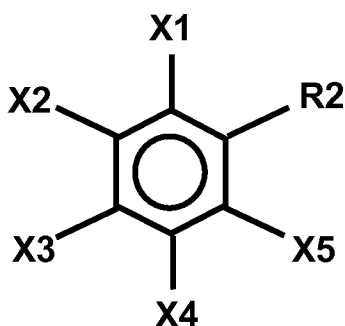
A review of figure 13 reveals that there was by-product formation in the aged control sample, but not in the aged candidate sample. This first occurs at the elution time of 1.19 minutes and is circled in red. The fresh control does not have any indication at this location on the graph. The aged control shows the appearance of a by-product. The candidate scan at the bottom shows no such indication, suggesting the impeding of a reaction pathway otherwise left unchecked in the control. The red circles to the right of this pair at time value of 1.3 minutes indicates another by-product formation that has been reduce by about $1/3^{\text{rd}}$ as compared to the control.

Thus, while there has been disclosed what is presently believed to be the preferred embodiments of the invention, those skilled in the art will appreciate that other and further changes and modifications can be made without departing from the scope or spirit of the invention, and it is intended that all such other changes and modifications are included within the scope of the invention.

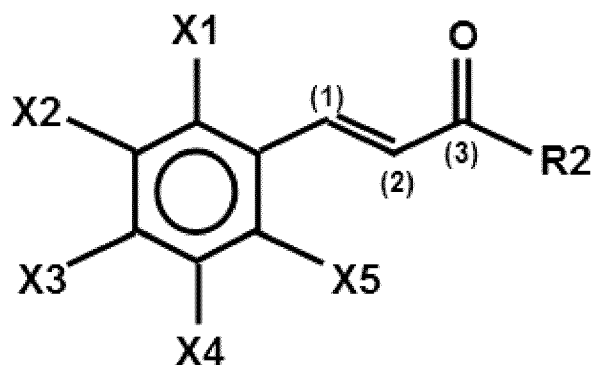
CLAIMS

What is claimed is:

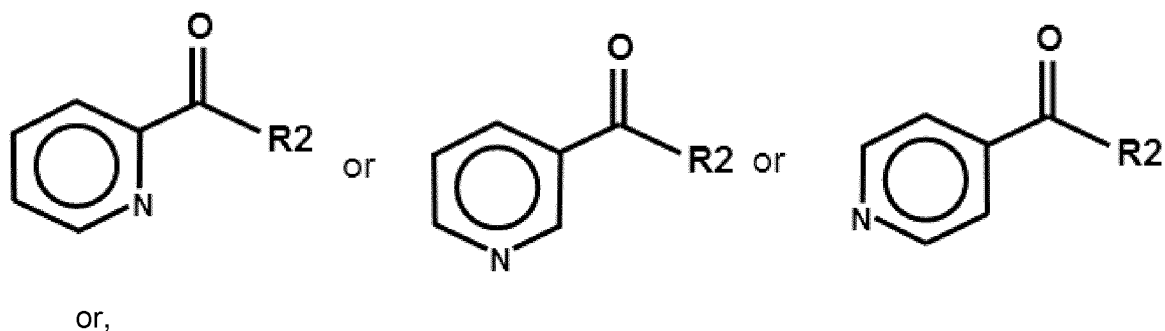
1. A paint stripper composition comprising:
 - a) an oxidant component,
 - b) water,
 - c) an emulsifier component, and
 - d) an amphiphilic antioxidant component,wherein the oxidant component comprises an oxidant,
wherein the emulsifier component comprises an emulsifier,
wherein the amphiphilic antioxidant component comprises at least one amphiphilic antioxidant and at least one hydrophilic antioxidant booster, wherein the ratio of amphiphilic antioxidant:booster is at least 1:1, and
wherein the amphiphilic antioxidant component is present in an amount sufficient to improve the stability of the emulsifier against oxidative attack.
2. The composition according to claim 1, wherein said oxidant component comprises a peroxide and a phosphonic acid based sequestering agent.
3. The composition according to claims 1 or 2, wherein the amphiphilic antioxidant is a compound having the formula: R1-R2;
Wherein R1 is a functional group chosen from the following:



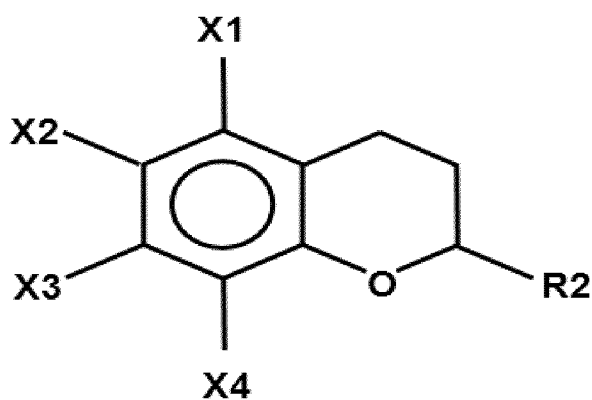
wherein X1 through X5 can be H, OH, CH₃ or any combination thereof, or optionally, can be O that joins a CH₃ group to the resonant ring structure; or,



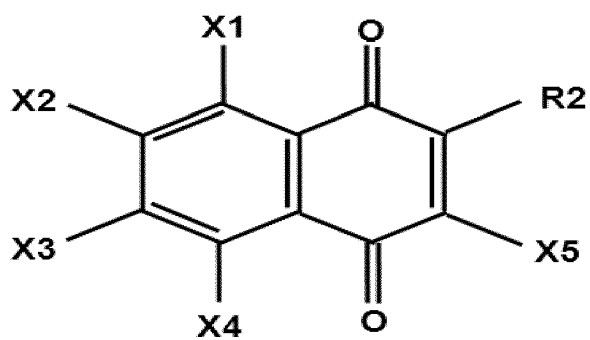
Wherein R1 contains either a double bond between carbons (1) and (2), or a pendant oxygen attached to carbon (3), or a combination of both; and wherein X1 through X5 are as described above; or,



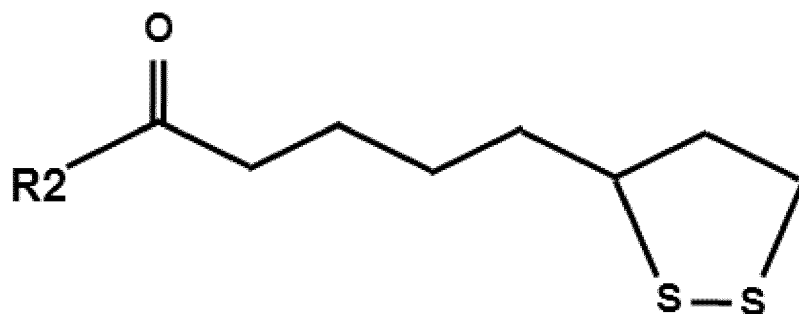
or,



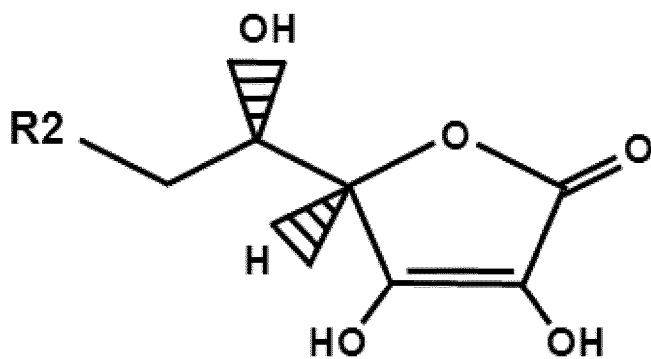
wherein X1, X2, X3, and X4 can be H, OH, or CH₃ or any combination of thereof;
or,



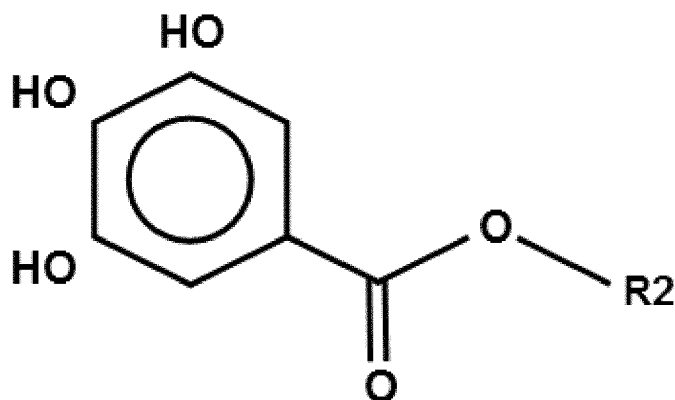
wherein X1, X2, X3, X4 and X5 can be H, O, CH₃, or a combination thereof; or,



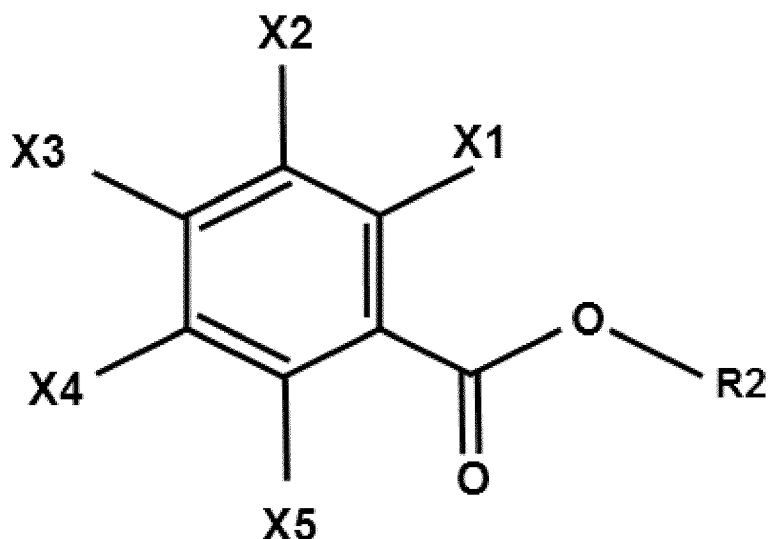
or,



or,



or,



wherein X1, X2, X3, X4 and X5 can be H, O, CH₃ or a combination thereof; and
wherein R2 is a straight or branched carbon chain hydrophobic structure having a number of carbon atoms in the range of from C4 to C20.

4. The composition according to claim 3, wherein compounds having R1 formulas containing X1-X5 have OH groups at each of the X1, X3, and X5 positions.

5. The composition according to any one of claims 1-4, wherein the antioxidant booster is at least one hydrophilic compound having the formula: R3-R4;

wherein R₃ is a 5 or 6 member ring; wherein the members of the 6 member ring are all C or optionally where one ring member is N, and wherein one C has -R₄ as a substituent and the other carbon ring members can have a substituent group selected

from -H, -OH, -OCH₃; and wherein the members of the 5 member ring are all C or optionally where up to 2 ring members are S, and wherein one C has -R₄ as a substituent and the other ring members only have -H as a substituent; and

wherein R₄ is a carbon chain having a length from C1 to C5 and at least one carboxylic acid functional group.

6. The composition according to claim 5, wherein R₄ has one carboxylic acid functional group that is a terminal group on the chain.

7. The composition according to claim 6, wherein the antioxidant booster is selected from the group consisting of lipoic acid, caffeic acid, cinnamic acid, nicotinic acid, picolinic acid, ferulic acid, coumaric acid, derivatives thereof, and combinations thereof.

8. The composition according to any one of claims 1-7, wherein the amphiphilic antioxidant component comprises alpha-tocopherol and picolinic acid, wherein the alpha-tocopherol and picolinic acid are each present in an amount from about 1 to about 10 wt%, based on the amount of emulsifier.

9. The composition according to any one of claims 2-8, wherein the peroxide is hydrogen peroxide.

10. The composition according to claim 9, wherein oxidant component further comprises at least one diphosphonic acid stabilizer.

11. The composition according to claim 10, wherein the oxidant component comprises: (1) hydrogen peroxide in an amount of 0.1 to about 8 wt%, based on the total composition, and (2) HEDP, its salts or degradation products thereof in an amount from about 10 to about 60 wt%, based on the amount of hydrogen peroxide; wherein the emulsifier is present in an amount of 0.1 to about 5 wt%, based on the total composition; and wherein the at least one amphiphilic antioxidant compound is alpha-tocopherol and is present in an amount from about 0.5 to about 20 wt%, based on the amount of emulsifier.

12. The composition according to claim 11, wherein the alpha-tocopherol is present in an amount from about 1.5 to about 6 wt% based on the emulsifier.

13. The composition according to any one of claims 1-12, wherein the emulsifier component comprises one or more polyethoxylated sorbitan esters.

14. The composition according to any one of claims 1-13, further comprising an organic solvent.

15. The composition according to claims 14, wherein the organic solvent is an aromatic alcohol.

16. The composition according to any one of claims 1-15, wherein the paint stripper composition further comprises one or more additional components chosen from an aromatic ether, a hydroxycarboxylic acid, an aromatic hydrocarbon co-solvent, a coupling agent, chelating agent, corrosion inhibitor, rheology modifying agent, evaporation retardant, and any combination of any of the foregoing.

17. The composition according to claim 16, wherein the paint stripper composition comprises: (a) from about 5 to about 50% by weight of an aromatic alcohol; and (b) a hydroxycarboxylic acid that is malic acid.

18. The composition according to any one of claims 1-17, wherein the pH of the paint stripper composition is in the range of 4 to about 12.

19. A process for preparing a paint stripper composition, said process comprising: 1) preparing a stabilized emulsifier composition by combining an emulsifier component with an amphiphilic antioxidant component; and 2) combining the stabilized emulsifier composition with a peroxide composition,

wherein the emulsifier component comprises an emulsifier and the amphiphilic antioxidant component comprises at least one amphiphilic antioxidant and at least one hydrophilic antioxidant booster, wherein the molar ratio of amphiphilic antioxidant:booster is at least 1:1, and

wherein the peroxide composition comprises a peroxide, a phosphonic acid based sequestering agent, and water.

20. Use of an amphiphilic antioxidant component to improve the stability of a paint stripper composition that contains an emulsifier and an oxidant;

wherein the amphiphilic antioxidant component comprises at least one amphiphilic antioxidant and at least one hydrophilic antioxidant booster, wherein the molar ratio of amphiphilic antioxidant:booster is at least 1:1, and

wherein the amphiphilic antioxidant component is present in an amount sufficient to improve the stability of the emulsifier against oxidative attack by said oxidant.

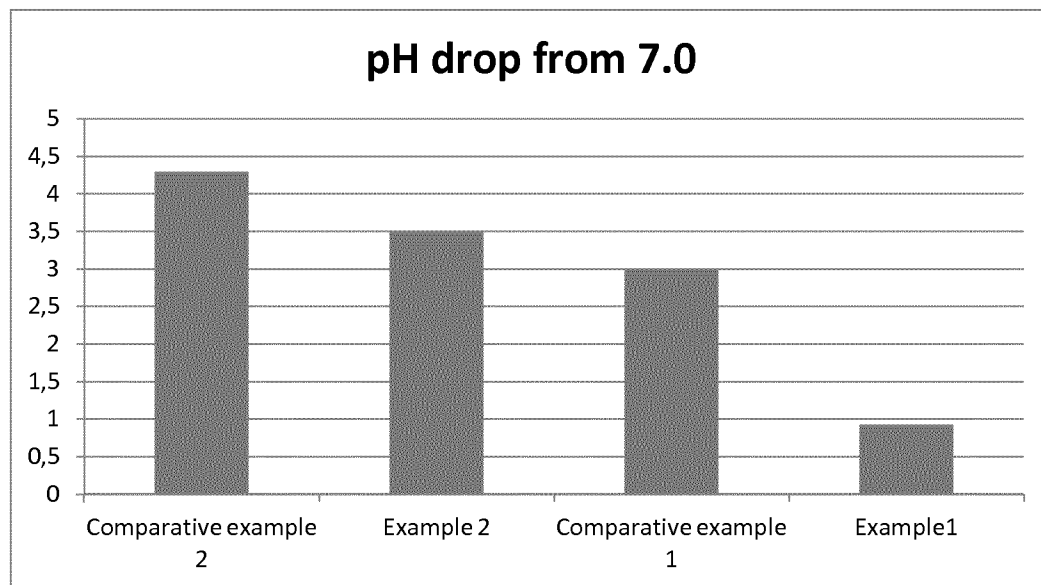
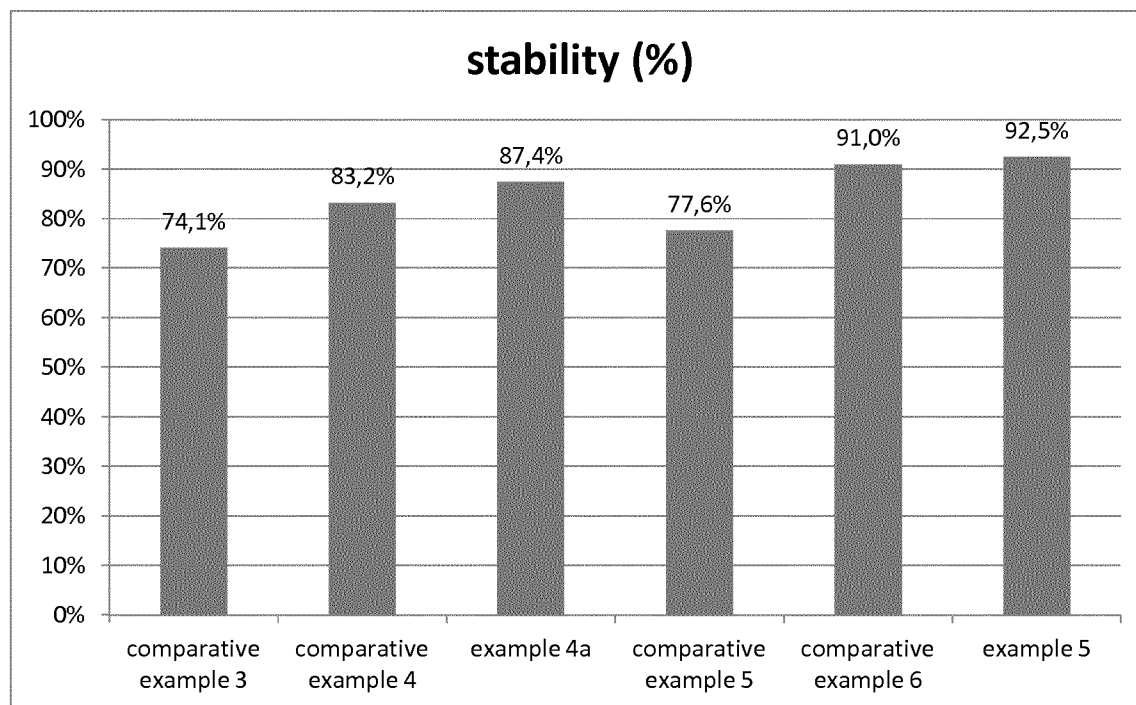
FIGURE 1FIGURE 2

FIGURE 3a

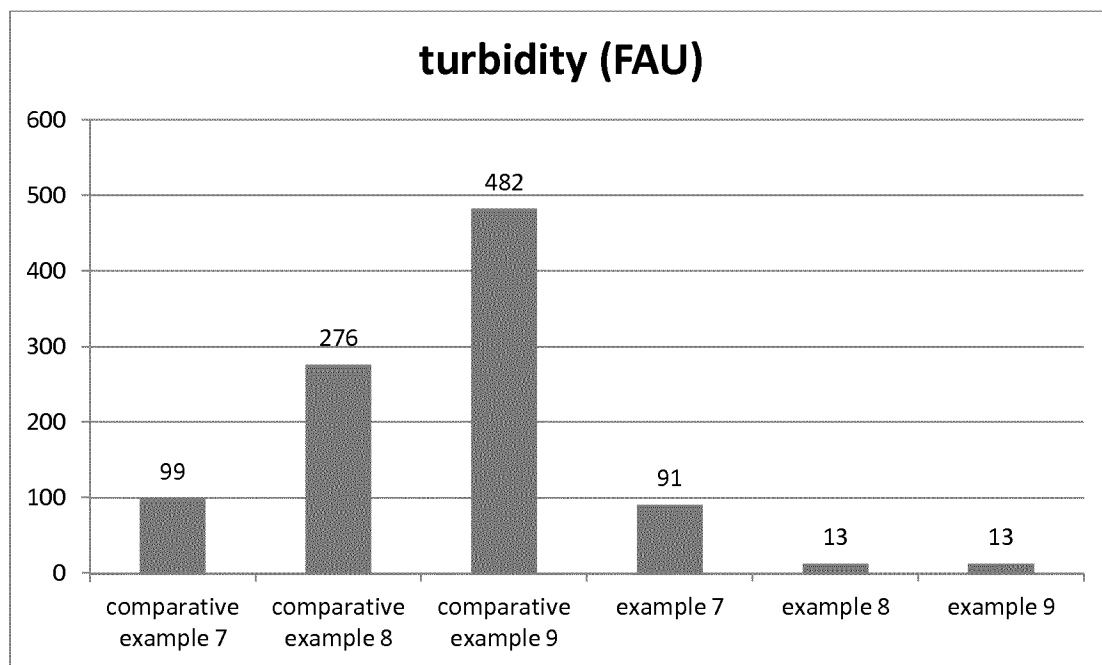


FIGURE 3b

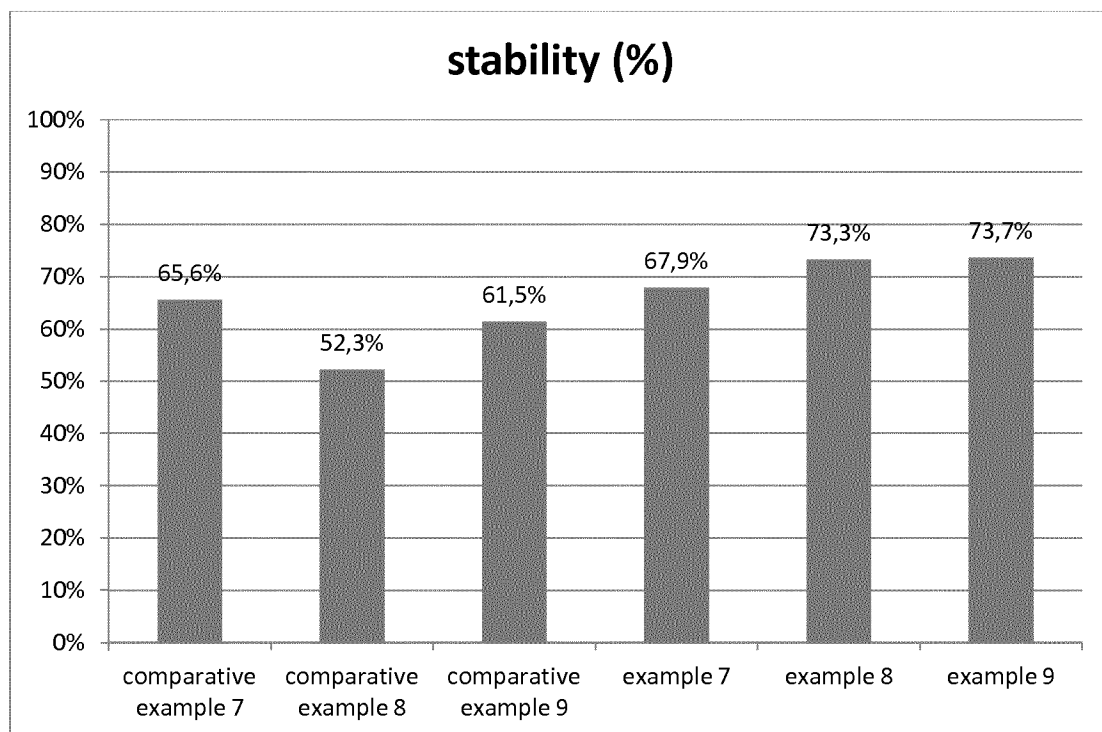


FIGURE 4a

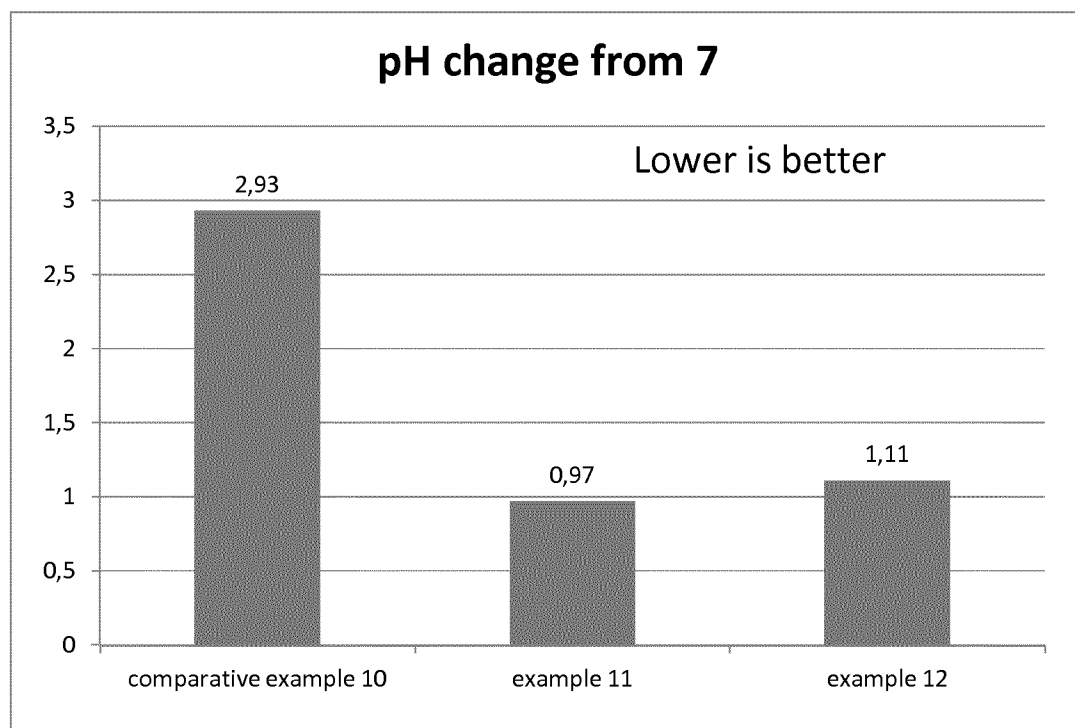


FIGURE 4b

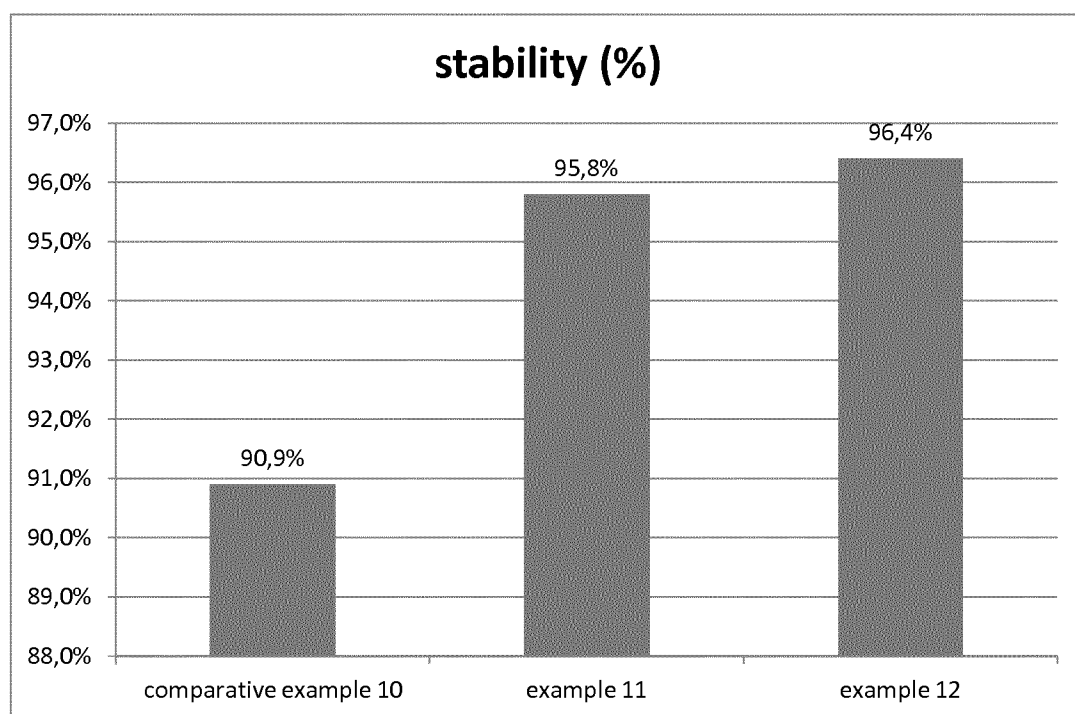


FIGURE 5

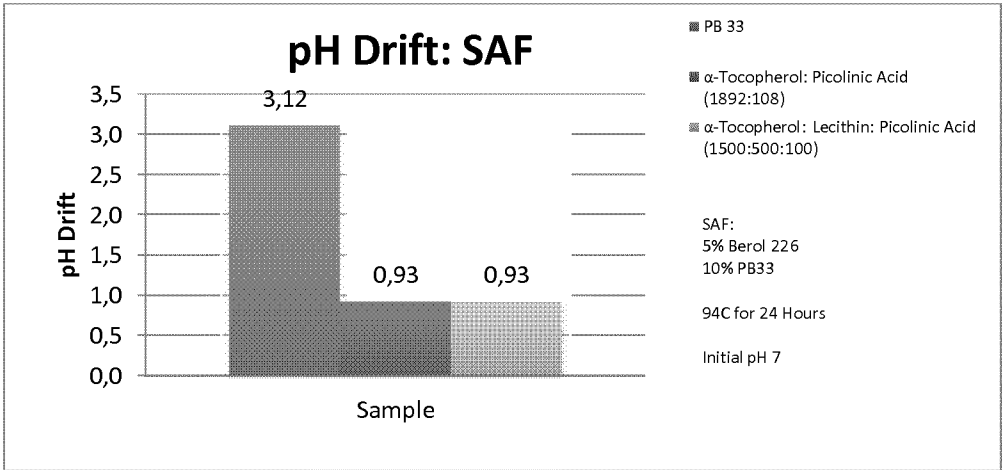
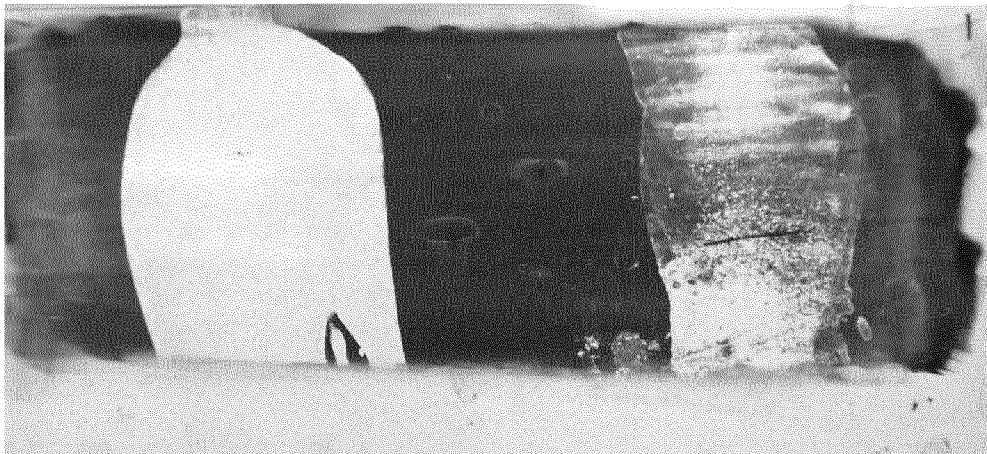


FIGURE 6a



Control

FIGURE 6b



Test Sample 1

FIGURE 6c



Test Sample 2

FIGURE 7

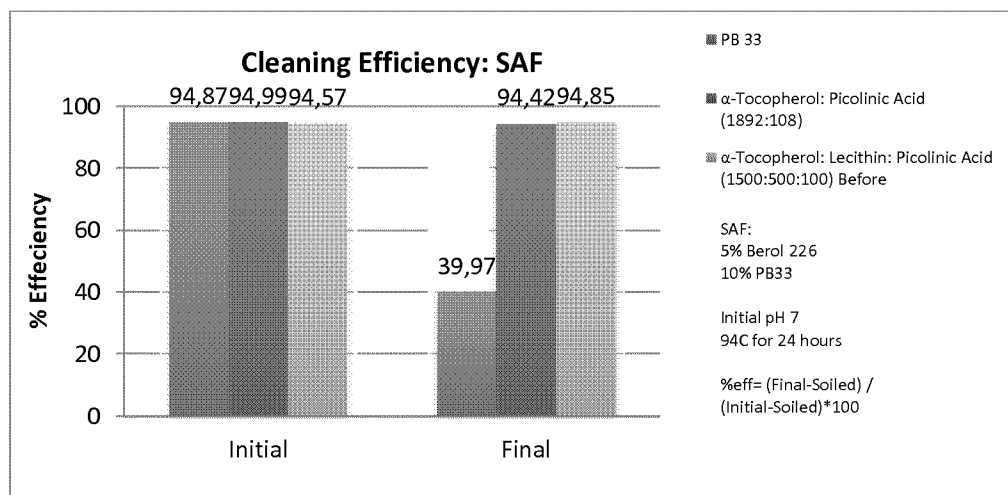


FIGURE 8

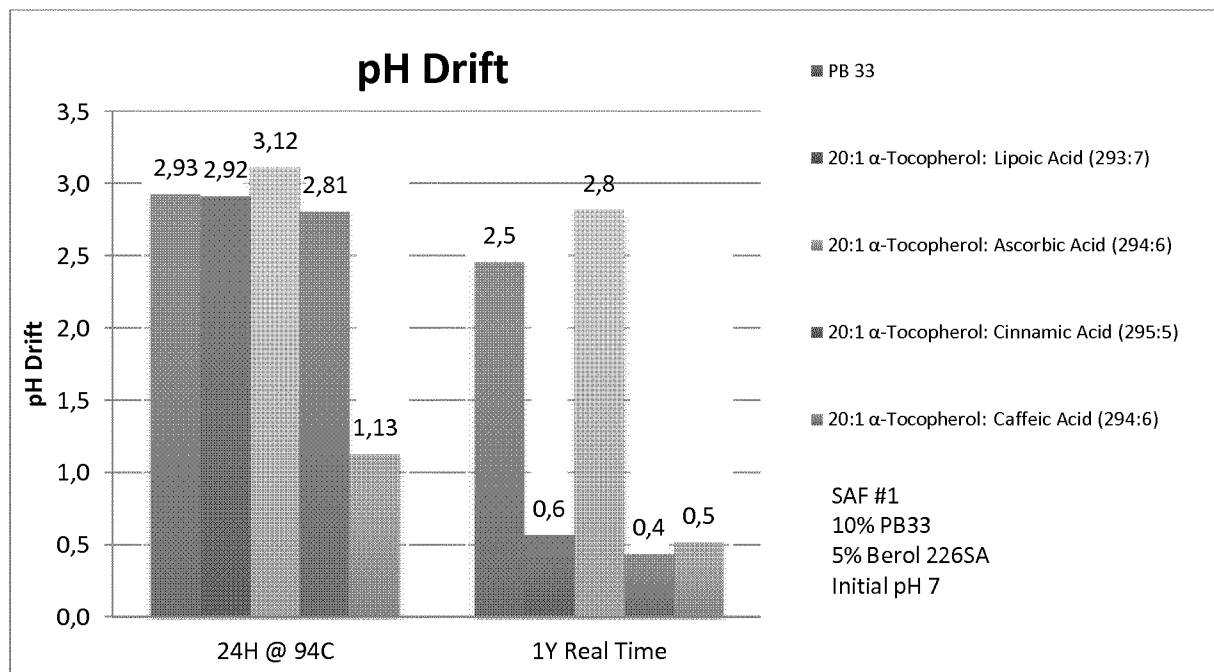


FIGURE 9

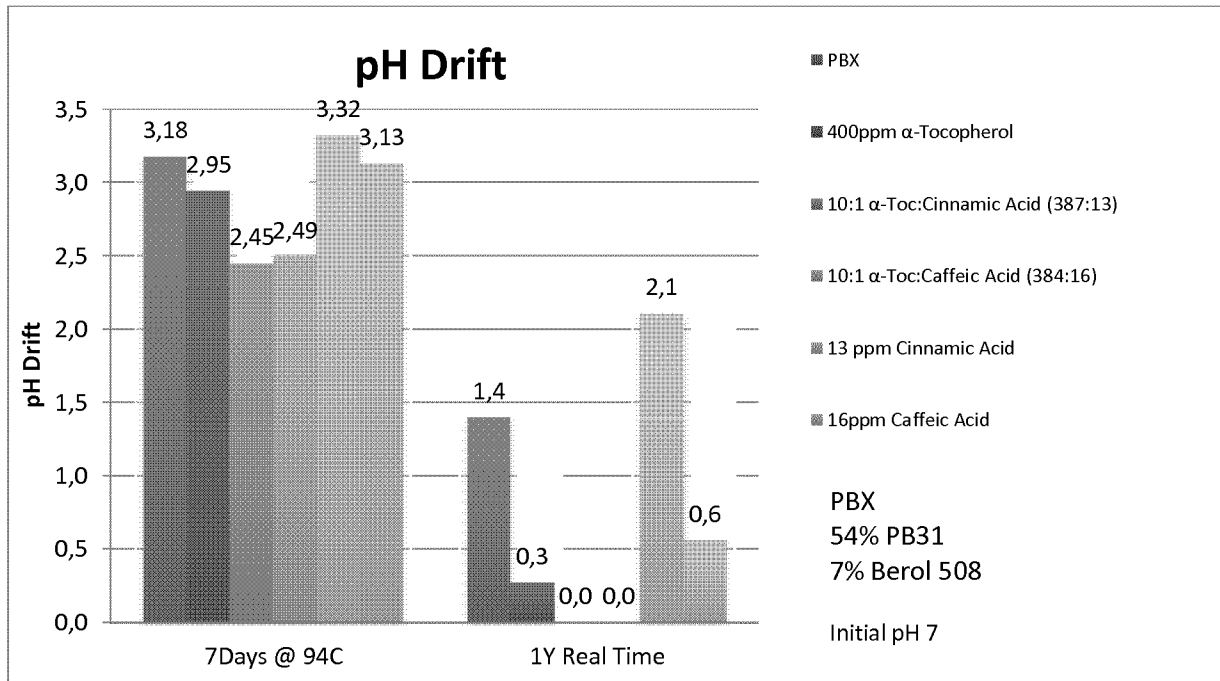


FIGURE 10

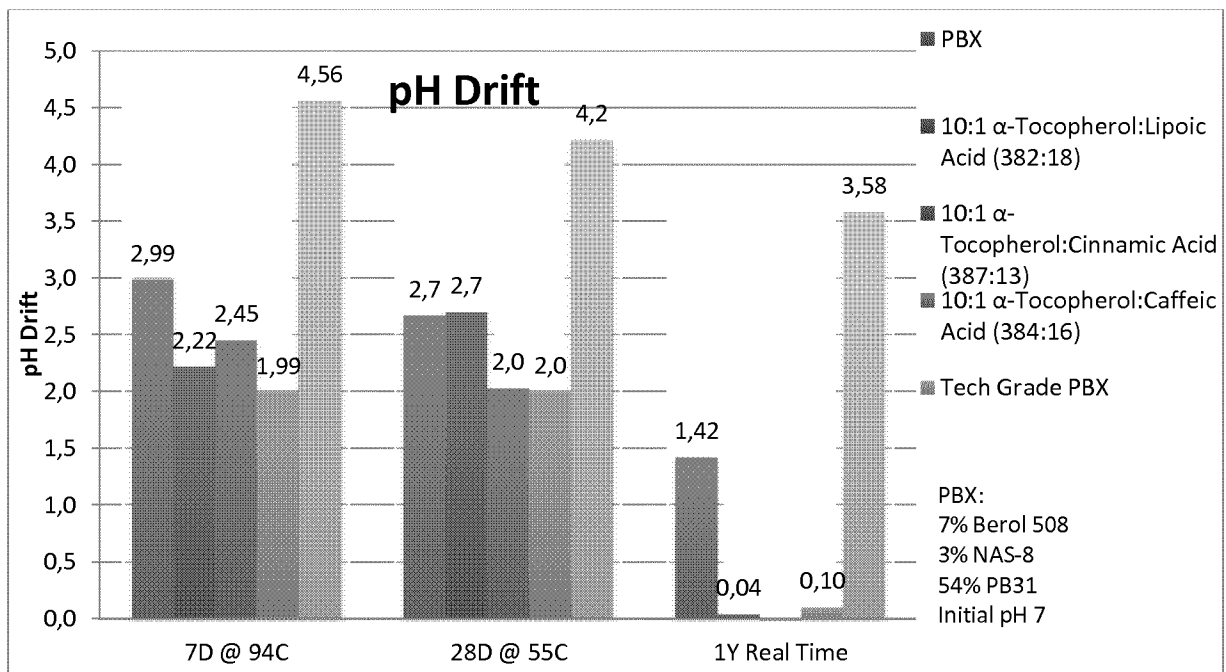


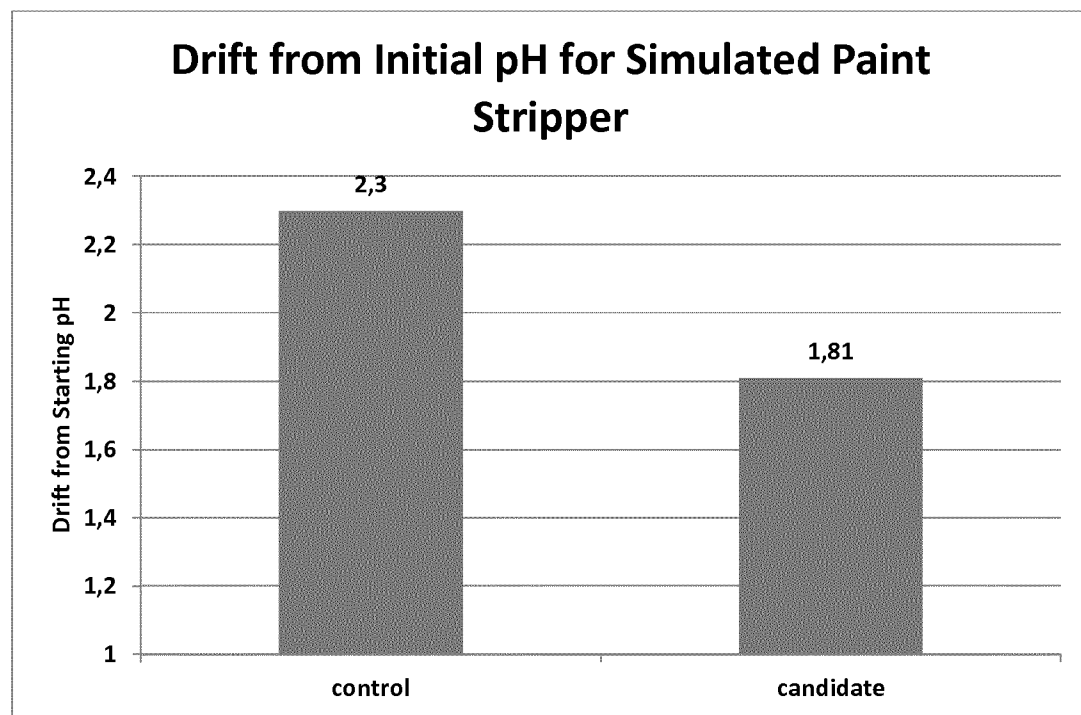
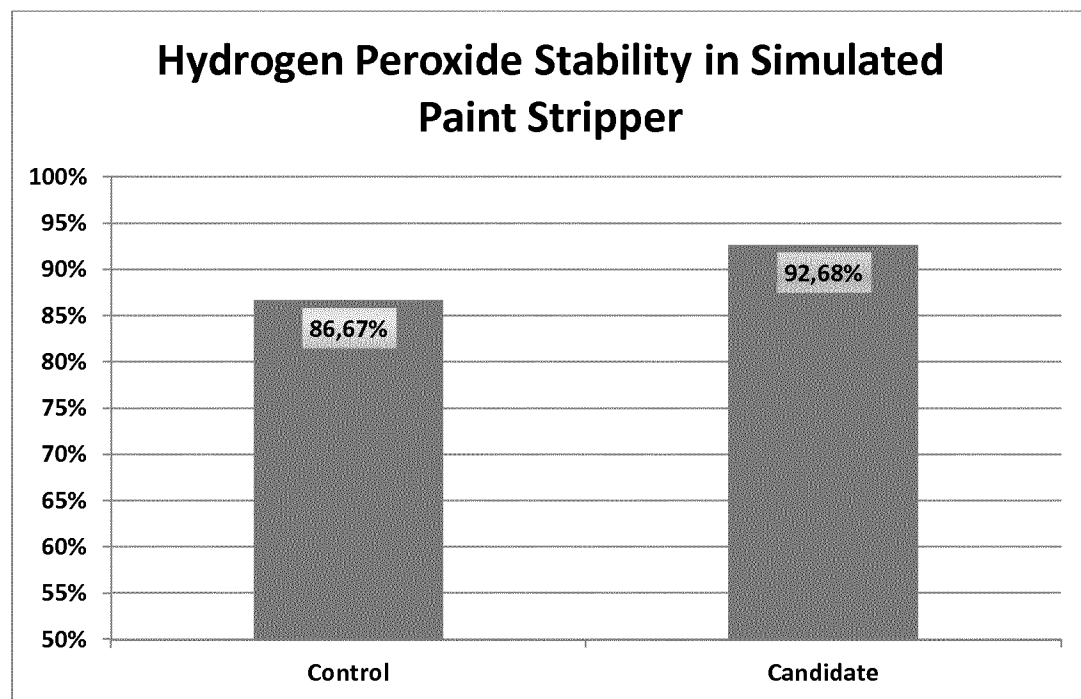
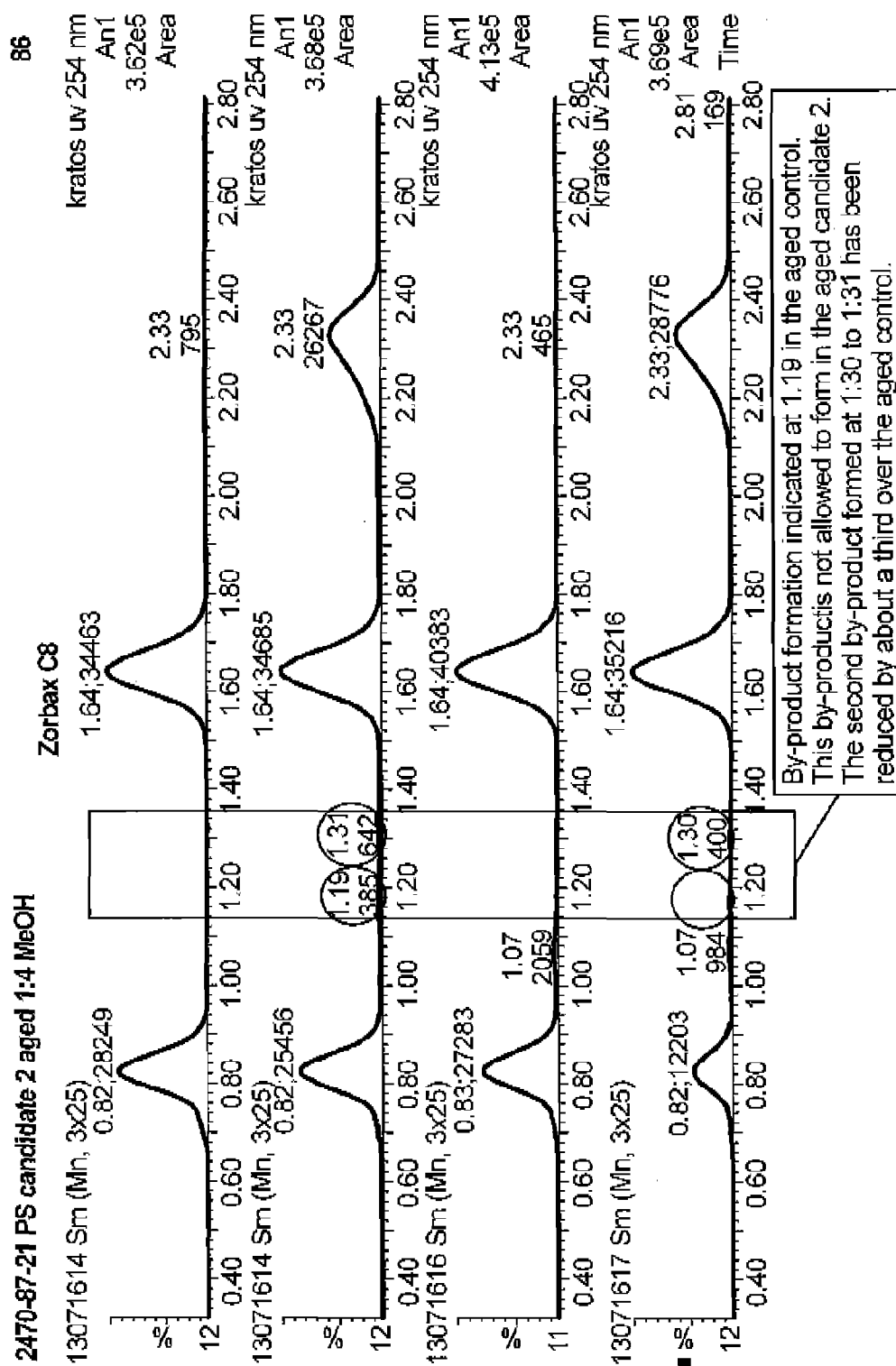
FIGURE 11FIGURE 12

FIGURE 13



INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/068780

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09D9/00

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/05898 A1 (NAPIER INTERNAT TECHNOLOGIES I [CA]; VITOMIR SERGIO [CA]) 25 January 2001 (2001-01-25) cited in the application page 1, line 27 - page 2, line 11 page 3, line 8 - page 5, line 24 page 6, line 25 - page 8, line 10 abstract; claims 1-3, 9-17, 19-23; examples 1-9; tables 1-5 -----	1-20
X	WO 2012/068001 A1 (ISP INVESTMENTS INC [US]; MUSA OSAMA M [US]; NARAYANAN KOLAZI S [US]) 24 May 2012 (2012-05-24) paragraphs [0032], [0033] paragraph [0052] - paragraph [0065] paragraph [0076] - paragraph [0088] abstract; claims 1-11, 14-21, 25-27; examples 16, 22; table 7 ----- -/-	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

7 January 2014

Date of mailing of the international search report

14/01/2014

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Fax: (+31-70) 340-3016

Authorized officer

Glomm, Bernhard

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/068780

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/109047 A2 (STEPAN CO [US]; BROWN AARON MICHAEL; DONG XUE MIN) 9 September 2011 (2011-09-09) paragraph [0005] - paragraph [0015] paragraph [0031] - paragraph [0038] paragraph [0041] - paragraph [0050] abstract; claims 1, 9-24; figure 2; examples 10-14; tables 2, 3 -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/068780

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