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<p>(21) International Application Number: PCT/US96/11872</p> <p>(22) International Filing Date: 18 July 1996 (18.07.96)</p> <p>(30) Priority Data: 08/506,586 25 July 1995 (25.07.95) US</p> <p>(71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).</p> <p>(72) Inventor: WILLEY, Alan, David; 1071 Celestial Street, Cincinnati, OH 45202 (US).</p> <p>(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).</p>	<p>(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: LOW HUE PHOTOBLEACHES</p> <p>(57) Abstract</p> <p>Low hue photobleaching compositions comprising oragnosilicon (IV) phthalocyanine and naphthalocyanines having Q-band absorption maxima at wavelengths greater than 660 nm and increased triplet state yields whereby production of singlet oxygen is increased. Use of Si⁴⁺ phthalocyanine and naphthalocyanines compounds in photobleaching compositions allows for formulation of low hue laundry compositions, bleach compositions, and hard surface cleaners.</p>		

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LOW HUE PHOTOBLEACHES

FIELD OF THE INVENTION

5 The present invention relates to novel organosilicon photosensitizing compounds having a Q-band maximum absorption wavelength of 660 nanometers or greater and their use as photoactivators (photosensitizer) or singlet oxygen producers, in particular for low hue photobleaching for removing stains from textiles and hard surfaces. The present invention also relates to laundry compositions and
10 hard surface cleaners comprising the novel organosilicon photosensitizing compounds of the present invention. The present invention further relates to a method of delivering compositions comprising low hue photobleaches to soiled and stained fabrics and to hard surfaces.

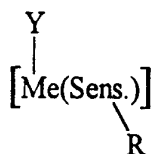
BACKGROUND OF THE INVENTION

15 It is known that various water-soluble phthalocyanine and naphthalocyanine compounds, in particular those having certain metals as the central atom, have a photosensitizing action and can therefore be used as photo-bleaching agents or anti-microbial active compounds.

20 Phthalocyanines and naphthalocyanines especially when combined with a suitable metal can undergo a series of photochemical reactions in conjunction with molecular oxygen to produce molecules of "singlet oxygen". The excited "singlet oxygen", formed in these photosensitizing reactions, is an oxidative species capable of reacting with stains to chemically bleach them to a colorless and usually water-soluble state, thereby resulting in what is called photochemical bleaching.

25 There are many examples of photobleaches comprising phthalocyanines and naphthalocyanines, the most common being the zinc and aluminum phthalocyanines. In the literature the term "photosensitizer" is often used instead of "photoactivator" and may therefore be considered as standing equally well for the latter term used throughout this specification

30 The prior art teaches phthalocyanine and naphthalocyanine compounds having the general structure



where Me is a transition or non-transition metal, (Sens.) is a phthalocyanine or naphthalocyanine ring which, when combined with a suitable Me unit, is capable of

undergoing photosensitization of oxygen molecules, R units are substituent groups which are bonded to the photosensitization ring units (Sens.) to enhance the solubility or photochemical properties of the molecule, and Y units are substituents associated with the metal atom, for example, anions to provide electronic neutrality. The
5 selection of a particular substituent R unit for substitution into the molecule has been the focus of many years of research and these units are typically chosen by the formulator to impart into the target molecule the desired level of water solubility without affecting the degree of photosensitizing properties.

A major limitation to the use of phthalocyanine and naphthalocyanine
10 compounds for fabric photobleaching is the fact that these molecules have a Q-band absorption maxima (λ_{\max}) in the range of visible light that is. Therefore they are highly colored materials. Phthalocyanines have Q-band absorption in the range of 600-700 nanometers, while naphthalocyanines have Q-band absorption in the 700-800 nanometer range. This is not surprising given the fact that these molecules are
15 structurally similar to dyestuffs.

A second limitation arises from the fact that the parent phthalocyanine and naphthalocyanine compounds when combined with a transition or non-transition metal are not inherently water soluble. This fact is especially true in the case of naphthalocyanines. It has therefore been the task of phthalocyanine and
20 naphthalocyanine photobleach formulators to select for R units moieties that are polar or hydrophilic, then attach these moieties to the (Sens.) unit in an attempt to increase the molecule's water solubility without adversely affecting the photochemical properties of the ring system.

A further task for the formulators of phthalocyanines and naphthalocyanines
25 has been the need to modify the properties of the (Sens.) unit of the molecule to increase the "photobleaching capacity" (photophysics) of the molecule, in other words, to increase the quantum efficiency. Again, selection of suitable R units to accomplish this task must not in turn adversely affect the water solubility. While balancing water solubility and enhanced photophysics, the formulator must insure
30 that the structural modifications do not shift the λ_{\max} of the Q-band to a wavelength that is now in the visible region. Maintaining the Q-band λ_{\max} to a wavelength above 660 nm, while not having the more desirable "low hue" properties of materials exhibiting a Q-band λ_{\max} of 700 nm or greater, it provides a molecule with photobleaching properties acceptable to consumers.

35 It is well known to formulators skilled in the art that an R unit which may produce a desired increase in one of these three properties may cause an equally large decrease in one or both of the other desirable properties. For example, a change

which increases solubility may reduce the quantum efficiency of the molecule and thereby render the final molecule without sufficient photobleaching properties.

Exacerbating this problem further is another factor; choice of a suitable Y group. Many phthalocyanine and naphthalocyanines comprise a metal or non-metal atom
5 that is hypervalent to the chelate ring system. Satisfying the valency requirement of these atoms or providing for the electronic neutrality of the molecule may cause the delicate balance of properties, once achieved, to collapse.

Surprisingly, it has been found that the compounds of the present invention allow the formulators to modify the levels of solubility, photoefficiency, Q-band
10 wavelength maxima and the electronic requirements of the central silicon atom separately without adversely affecting the other parameters of the molecule. This ability to delineate and selectively modify the key structural elements contributing to the target properties of the molecule allows the formulator to proceed without having to rely upon a "hit and miss" stratagem.

One key to this ability to control the molecular properties is found when
15 contrasting the structure of known photobleaches comprising phthalocyanines and naphthalocyanines with those of the present invention. The examples of photobleaches previously described in the art are generally flat molecules due to their planar ring structure. This inherently leads to molecular stacking, layering and other
20 forms of aggregation which tend to clump the molecules together. A photobleach molecule which is overlaid by other photobleach molecules will tend to quench each other thereby effectively stopping the generation of singlet oxygen.

The organosilicon photosensitizing compounds of the present invention comprise axial substituents that act to break up this ordering effect, hence providing
25 an efficiently formed mono-layer of photosensitizers evenly applied to a given substrate. Because each molecule of this mono-layer can now contribute to bleaching there is better cost efficiency to the formulator.

It has been surprisingly found that because of the separating out of physical
30 properties into "molecular sectors", e.g. R groups for solubility, new uses for the compounds of the present invention have been realized. Adducts which provide unique solubility profiles, but which detract from the photophysics, were once excluded from use in photobleaches. However, the inclusion of these moieties into the photobleaches of the present invention results in the ability to formulate photobleaches for use in non-classical applications, for example dry cleaning
35 applications. Solvent based or low aqueous solutions of the present invention are now obtainable for the very reason that control over solubility is manifest in the choice of the axial R substitutions.

The proper selection of axial R units attached to the compounds of the present invention allow the formulator to balance the changes in photoefficiency of the desired compound with the water solubility of the parent material. In addition, these axial R unit modifications provide the formulator with the ability to balance solubility, Q-band λ_{\max} , and quantum efficiency of the (Sens.) unit.

It is an object of the present invention to provide "substantive" and "non-substantive" organosilicon photosensitizers. The terms "substantive" and "non-substantive", as used in the present specification and as further defined hereinafter, describe the propensity of a compound to elicit a surface affinity or, in the alternative, the lack of a surface affinity, in other words a "substantive" organosilicon photosensitizer will be attracted to a surface and a "non-substantive" organosilicon photosensitizer will repel a surface.

It is a further object of the present invention to provide substantive and non-substantive photobleaching laundry compositions for natural, synthetic or blended fabrics.

It is a further object of the present invention to provide photobleaching compositions that comprise non-aqueous and low aqueous carriers, that is, photobleaching compositions having carriers wherein water constitutes less than half of the carrier liquid.

It is a further object of the present invention to provide photobleaching compositions and cleaning compositions comprising substantive materials for non-porous hard surfaces, *inter alia*, Formica[®], ceramic tile, glass, or for porous hard surfaces such as concrete or wood.

An object of the present invention is to provide a method for bleaching fabric with laundry compositions comprising organosilicon photosensitizing compounds of the present invention.

An object of the present invention is to provide a method for cleaning hard surfaces with compositions comprising organosilicon photosensitizing compounds of the present invention.

An object of the present invention is to provide for low hue organosilicon photosensitizing compounds having a Q-band maximum absorption wavelength of at least 660 nanometers.

BACKGROUND ART

Various patent documents relate to photochemical bleaching or to the use of phthalocyanine and naphthalocyanine compounds as well as their formulation and synthesis. See for example U.S. Pat. No. 3,094,536 issued June 18, 1963; U.S. Pat. No. 3,927,967 issued December 23, 1975; U.S. Pat. No. 4,033,718 issued July 5,

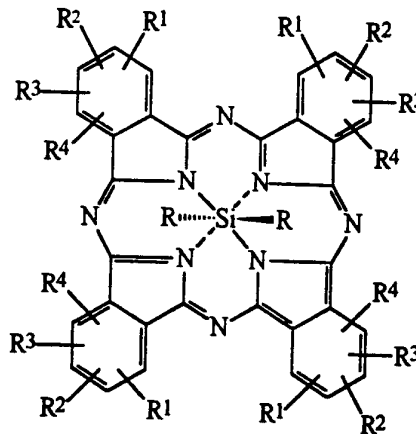
1977; U.S. Pat. No. 4,166,718 issued September 4, 1979; U.S. Pat. No. 4,240,920 issued December 23, 1980; U.S. Pat. No. 4,255,273 issued March 10, 1981; U.S. Pat. No. 4,256,597 issued March 17, 1981; U.S. Pat. No. 4,318,883 issued March 9, 1982; U.S. Pat. No. 4,368,053 issued January 11, 1983; U.S. Pat. No. 4,497,741
5 issued February 5, 1985; U.S. Pat. No. 4,648,992 issued March 10, 1987; and U.K. Pat. App. 1,372,035 published October 30, 1974; U.K. Pat. App. 1,408,144 published October 1, 1975; U.K. Pat App. 2,159,516 published December 4, 1985; E.P. 484,027 A1 published May 6, 1992; WO 91/18006 published November 28, 1991 and Japanese Kokai 06-73397 Derwent Abst. No. (94-128933) published March 15,
10 1994.

In addition to the above cited patent publications, other references describing the synthesis, preparation and properties of phthalocyanines and naphthalocyanines, in incorporated herein also by reference; *Phthalocyanines: Properties and Applications*, Leznoff, C. C. and Lever A. B. P. (Eds), VCH, 1989; *Infrared Absorbing Dyes*, Matsuoka, M. (Ed), Plenum, 1990; *Inorg. Chem.*, Lowery, M. J. et al., 4, pg. 128, (1965); *Inorg. Chem.* Joyner R. D. et al., 1, pg. 236, (1962); *Inorg. Chem.*, Kroenke, W. E. et al., 3, 696, 1964; *Inorg. Chem.* Esposito, J. N. et al., 5, pg. 1979, (1966); *J. Am. Chem. Soc.* Wheeler, B. L. et al., 106, pg. 7404, (1984); *Inorg. Chem.* Ford, W. E, et al., 31, pg. 3371, (1992); *Material Science*, Witkiewicz, Z. et al., 11, pg. 39, (1978); *J. Chem. Soc. Perkin Trans. I*, Cook, M. J., et al., pg. 2453, (1988).
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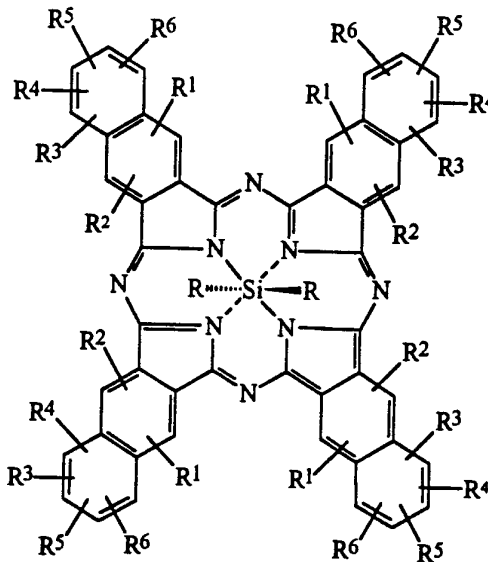
SUMMARY OF THE INVENTION

The present invention relates to laundry and other cleaning compositions comprising:

- 25 a) at least about 0.01% of a cationic, anionic, nonionic, ampholytic, or zwitterionic surfactant;
- b) an organosilicon photosensitizing compound having a Q-band maximum absorption wavelength of 660 nanometers or greater wherein said organosilicon(IV) photosensitizing compound is a
30 phthalocyanine having the formula



or a naphthalocyanine having the formula:

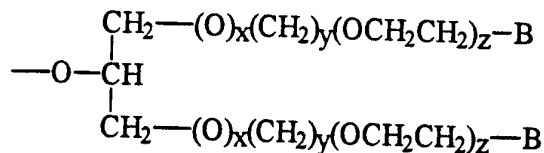


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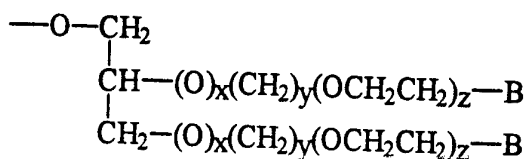
wherein R¹, R², R³, R⁴, R⁵, and R⁶ units are each independently selected from the group consisting of:

- a) hydrogen;
- b) halogen;
- c) hydroxyl;
- 10 d) cyano;
- e) nitrilo;
- f) oximino;
- g) C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;
- 15 h) halogen substituted C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;
- i) polyhydroxyl substituted C₃-C₂₂ alkyl;

- j) C₁-C₂₂ alkoxy;
 k) branched alkoxy having the formula



or



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wherein B is hydrogen, hydroxyl, C₁-C₃₀ alkyl, C₁-C₃₀ alkoxy, -CO₂H, -CH₂CO₂H, -SO₃⁻M⁺, -OSO₃⁻M⁺, -PO₃²⁻M, -OPO₃²⁻M, and mixtures thereof; M is a water soluble cation in sufficient amount to satisfy charge balance; x is 0 or 1, each y independently has the value from 0 to 6, each z independently has the value from 0 to 100;

10

- l) substituted and unsubstituted aryl;
 m) substituted and unsubstituted alkylenearyl;
 n) substituted and unsubstituted aryloxy;
 o) substituted and unsubstituted oxyalkylenearyl;
 p) substituted and unsubstituted alkyleneoxyaryl;
 q) C₁-C₂₂ thioalkyl, C₄-C₂₂ branched thioalkyl, and mixtures thereof;
 r) an ester of the formula -CO₂R¹⁰ wherein R¹⁰ comprises
- i) C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;
 ii) halogen substituted C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;
 iii) polyhydroxyl substituted C₃-C₂₂ alkyl;
 iv) C₃-C₂₂ glycol;
 v) C₁-C₂₂ alkoxy;
 vi) C₄-C₂₂ branched alkoxy;
 vii) substituted and unsubstituted aryl;
 viii) substituted and unsubstituted alkylaryl;

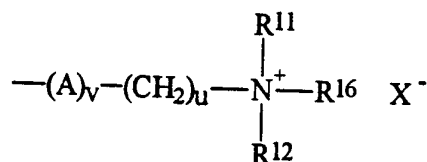
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- ix) substituted and unsubstituted aryloxy;
- x) substituted and unsubstituted alkoxyaryl;
- xi) substituted and unsubstituted alkyleneoxyaryl; and mixtures thereof;

5 s) an alkyleneamino unit of the formula



10 wherein R¹¹ and R¹² comprises C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;

R¹⁶ comprises:

- i) hydrogen;
 - ii) C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;
- 15

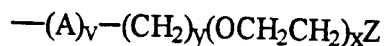
A units comprise nitrogen or oxygen; X comprises chlorine, bromine, iodine, or other water soluble anion, v is 0 or 1, u is from 0 to 22;

20 t) an amino unit of the formula



25 wherein R¹¹ and R¹² comprises C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;

u) an alkylethyleneoxy unit of the formula



wherein Z comprises:

- i) hydrogen;
 - ii) hydroxyl;
 - iii) -CO₂H;
 - iv) -SO₃^{-M+};
 - v) -OSO₃^{-M+};
- 30

- vi) C₁-C₆ alkoxy;
- vii) substituted and unsubstituted aryl;
- viii) substituted and unsubstituted aryloxy;
- ix) alkyleneamino; and mixtures thereof;

5

A units comprise nitrogen or oxygen, M is a water soluble cation, v is 0 or 1, x is from 0 to 100, y is from 0 to 12;

- v) substituted siloxy of the formula

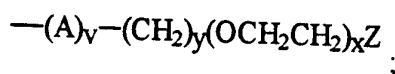


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wherein each R⁷, R⁸, and R⁹ is independently selected from the group consisting of:

- i) C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;
- ii) substituted and unsubstituted aryl;
- iii) substituted and unsubstituted aryloxy;
- iv) an alkylethyleneoxy unit of the formula

15



20

wherein Z comprises:

- a) hydrogen;
- b) C₁-C₃₀ alkyl;
- c) hydroxyl;
- d) -CO₂H;
- e) -SO₃⁻M⁺;
- f) -OSO₃⁻M⁺;
- g) C₁-C₆ alkoxy;
- h) substituted and unsubstituted aryl;
- i) substituted and unsubstituted aryloxy;
- j) alkyleneamino; and mixtures thereof;

25

A units comprise nitrogen or oxygen, M is a water soluble cation, v is 0 or 1, x is from 0 to 100, y is from 0 to 12; and mixtures thereof;

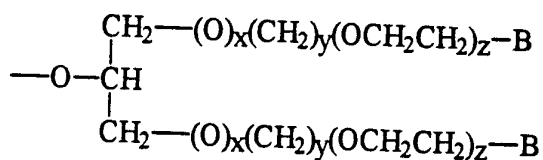
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axial R units wherein each R is independently selected from the group consisting of:

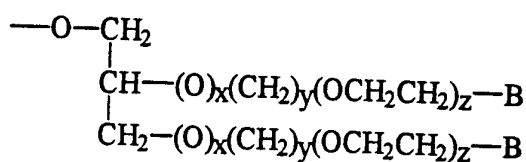
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- a) hydrogen;
- b) halogen;

- 5
- 10
- c) hydroxyl;
 - d) cyano;
 - e) nitrilo;
 - f) oximino;
 - g) C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;
 - h) halogen substituted C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;
 - i) polyhydroxyl substituted C₃-C₂₂ alkyl;
 - j) C₁-C₂₂ alkoxy;
 - k) branched alkoxy having the formula



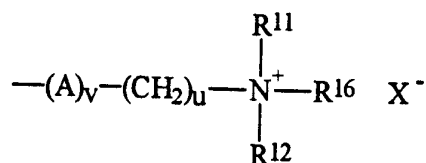
or



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wherein B is hydrogen, hydroxyl, C₁-C₃₀ alkyl, C₁-C₃₀ alkoxy, -CO₂H, -CH₂CO₂H, -SO₃^{-M+}, -OSO₃^{-M+}, -PO₃^{2-M}, -OPO₃^{2-M}, and mixtures thereof; M is a water soluble cation in sufficient amount to satisfy charge balance; x is 0 or 1, each y independently has the value from 0 to 6, each z independently has the value from 0 to 100;

- 20
- 25
- l) substituted and unsubstituted aryl;
 - m) substituted and unsubstituted alkylenearyl;
 - n) substituted and unsubstituted aryloxy;
 - o) substituted and unsubstituted oxyalkylenearyl;
 - p) substituted and unsubstituted alkyleneoxyaryl;
 - q) C₁-C₂₂ thioalkyl, C₄-C₂₂ branched thioalkyl, and mixtures thereof;
 - r) an alkyleneamino unit of the formula



wherein R¹¹ and R¹² comprises C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;

5

R¹⁶ comprises:

- i) hydrogen;
- ii) C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;

10

A units comprise nitrogen or oxygen; X comprises chlorine, bromine, iodine, or other water soluble anion, v is 0 or 1, u is from 0 to 22;

- s) an amino unit of the formula

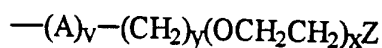
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wherein R¹¹ and R¹² comprises C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;

- t) an alkylethyleneoxy unit of the formula

20



wherein Z comprises:

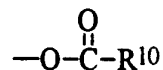
- i) hydrogen;
- ii) hydroxyl;
- iii) -CO₂H;
- iv) -SO₃⁻M⁺;
- v) -OSO₃⁻M⁺;
- vi) C₁-C₆ alkoxy;
- vii) substituted and unsubstituted aryl;
- viii) substituted and unsubstituted aryloxy;
- ix) alkyleneamino; and mixtures thereof;

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A comprises nitrogen or oxygen, M is a water soluble cation, v is 0 or 1, x is from 0 to 100, y is from 0 to 12;

u) carboxylate of the formula



wherein R¹⁰ comprises:

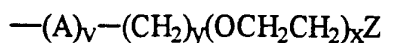
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- i) C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;
- 10
- ii) halogen substituted C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;
- iii) poly-hydroxyl substituted C₃-C₂₂ alkyl;
- iv) C₃-C₂₂ glycol;
- v) C₁-C₂₂ alkoxy;
- vi) C₄-C₂₂ branched alkoxy;
- 15
- vii) substituted and unsubstituted aryl;
- viii) substituted and unsubstituted alkylaryl;
- ix) substituted and unsubstituted aryloxy;
- x) substituted and unsubstituted alkoxyaryl;
- xi) substituted and unsubstituted alkyleneoxyaryl;
- 20
- xii) alkyleneamino; and mixtures thereof;

v) substituted siloxy of the formula



wherein each R⁷, R⁸, and R⁹ is independently selected from the group consisting of:

- 25
- i) C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;
- ii) substituted and unsubstituted aryl;
- iii) substituted and unsubstituted aryloxy;
- 30
- iv) an alkylethyleneoxy unit of the formula



wherein Z comprises:

- 35
- a) hydrogen;
- b) C₁-C₃₀ alkyl,

- 5
- c) hydroxyl;
 - d) $-\text{CO}_2\text{H}$;
 - e) $-\text{SO}_3^-\text{M}^+$;
 - f) $-\text{OSO}_3^-\text{M}^+$;
 - g) $\text{C}_1\text{-C}_6$ alkoxy;
 - h) substituted and unsubstituted aryl;
 - i) substituted and unsubstituted aryloxy;
 - j) alkyleneamino; and mixtures thereof;

10 A units comprise nitrogen or oxygen, M is a water soluble cation, v is 0 or 1, x is from 0 to 100, y is from 0 to 12; and mixtures thereof; and

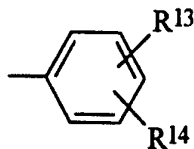
- c) the balance adjunct ingredients.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius ($^{\circ}\text{C}$) unless otherwise specified.

15 All documents cited are, in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

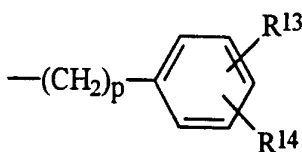
For the purposes of the present invention substituted aryl units are defined as moieties having essentially the formula:



20 wherein R^{13} and R^{14} are independently selected from the group consisting of hydrogen, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ alkenyl, $\text{C}_1\text{-C}_6$ alkoxy, $\text{C}_1\text{-C}_6$ branched alkoxy, halogen, morpholino, cyano, nitrilo, $-\text{CO}_2^-\text{M}^+$, $-\text{SO}_3^-\text{M}^+$, $-\text{OSO}_3^-\text{M}^+$, $-\text{N}(\text{R}^{15})_2$, and $-\text{N}^+(\text{R}^{15})_3\text{X}^-$ wherein each R^{15} is independently hydrogen or $\text{C}_1\text{-C}_4$ alkyl; and mixtures thereof; wherein M is a water soluble cation and X is chlorine, bromine, iodine, or other water soluble anion. Examples of other water soluble anions include organic species such as fumarate, tartrate, oxalate and the like, inorganic species include sulfate, hydrogen sulfate, phosphate and the like.

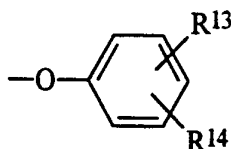
25 For the purposes of the present invention alkylenearyl units are defined as moieties having essentially the formula:

30



wherein R¹³ and R¹⁴ are the same as define above, p is from 1 to about 10.

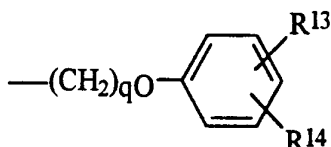
For the purposes of the present invention aryloxy units are defined as moieties having essentially the formula:



5

wherein R¹³ and R¹⁴ are the same as define above.

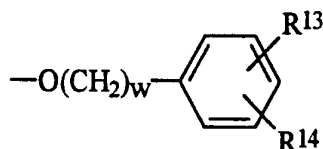
For the purposes of the present invention alkyleneoxyaryl units are defined as moieties having essentially the formula:



10

wherein R¹³ and R¹⁴ are the same as define above, q is from 0 to about 10.

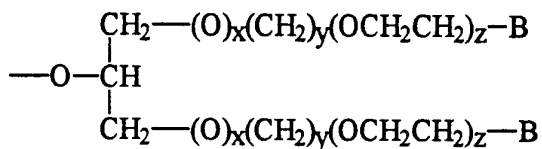
For the purposes of the present invention oxyalkylenearyl units are defined as moieties having essentially the formula:



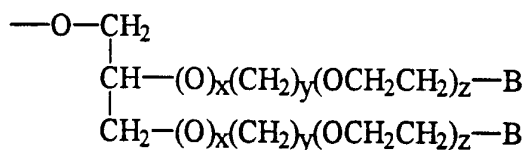
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wherein R¹³ and R¹⁴ are the same as define above, w is from 1 to about 10.

For the purposes of the present invention branched alkoxy units are defined as moieties having essentially the formula



or

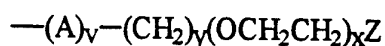


20

wherein B is hydrogen, hydroxyl, C₁-C₃₀ alkyl, C₁-C₃₀ alkoxy, -CO₂H, -CH₂CO₂H, -SO₃^{-M⁺}, -OSO₃^{-M⁺}, -PO₃^{2-M}, -OPO₃^{2-M}, and mixtures thereof; preferably C₁-C₁₈ alkyl, -CO₂H, -SO₃^{-M⁺}, -OSO₃^{-M⁺}, -PO₃^{2-M}, -OPO₃^{2-M}; M is a water soluble cation in sufficient amount to satisfy charge balance; x is 0 or 1, each y independently has the value from 0 to 6, each z independently has the value from 0 to 100;

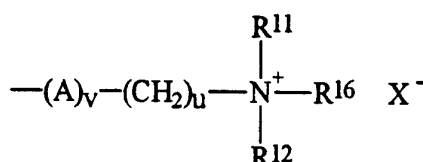
For the purposes of the present invention both substituted and un-substituted aryl, alkylenearyl, aryloxy, oxyalkylenearyl and alkyleneoxyaryl have the indices p, q, and w as defined herein above, and aryl can be any aromatic moiety substituted or unsubstituted, for example, phenyl, naphthyl, thienyl, pyridinyl, etc.

For the purposes of the present invention alkylethyleneoxy units are defined as moieties having essentially the formula:



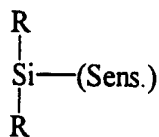
wherein A is the heteroatom nitrogen or oxygen, preferably A is oxygen, the index v is 0 when the heteroatom is absent, v is equal to 1 when the heteroatom is present, Z is hydrogen, C₁-C₆ alkoxy, aryl, substituted aryl, aryloxy, substituted aryloxy, alkyleneamino, -SO₃^{-M⁺}, -OSO₃^{-M⁺}, -CO₂H, and mixtures thereof; x is from 1 to 100 and y is from 1 to 12.

For the purposes of the present invention alkyleneamino units are defined as moieties having essentially the formula:



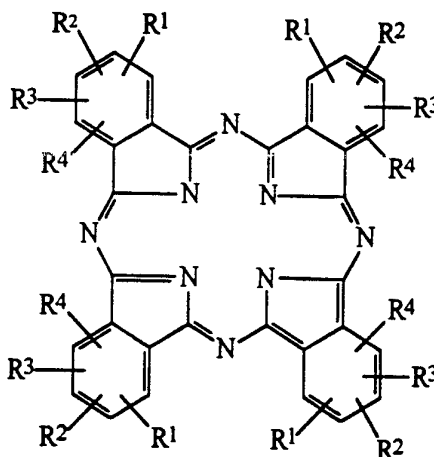
wherein R¹¹, and R¹² are each a C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, R¹⁶ is hydrogen, C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl and mixtures thereof, A is the heteroatom nitrogen or oxygen, preferably A is oxygen, the index v is 0 when the heteroatom is absent, v is equal to 1 when the heteroatom is present, X is chloride, bromide, iodide, or other water soluble anion, u is from 0 to 22. Examples of other water soluble anions include organic species such as fumarate, tartrate, oxalate and the like, inorganic species include sulfate, hydrogen sulfate, phosphate and the like.

The present invention provides for photobleaching compositions comprising Si⁴⁺ organosilicon photosensitizing compounds having a Q-band maximum absorption wavelength of 660 nanometers or greater essentially of the formula

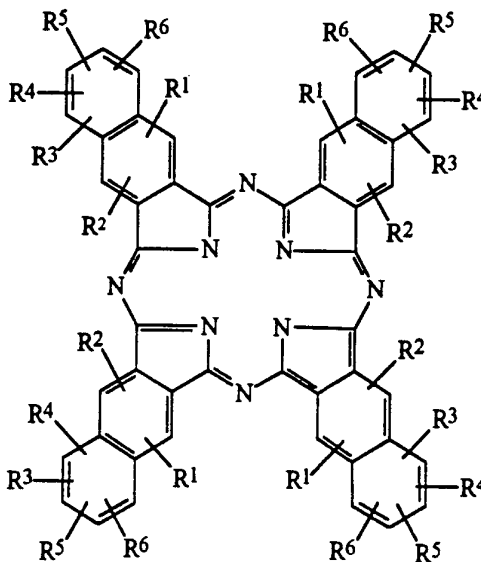


In the above formula the (Sens.) units are bi dentate photosensitizing units which form an essentially planar chelate around the central silicon atom, wherein these (Sens.) units are either phthalocyanines having the formula:

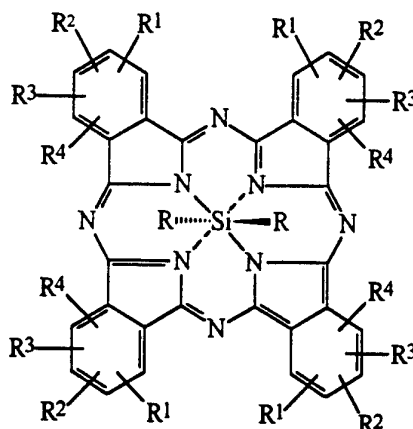
5



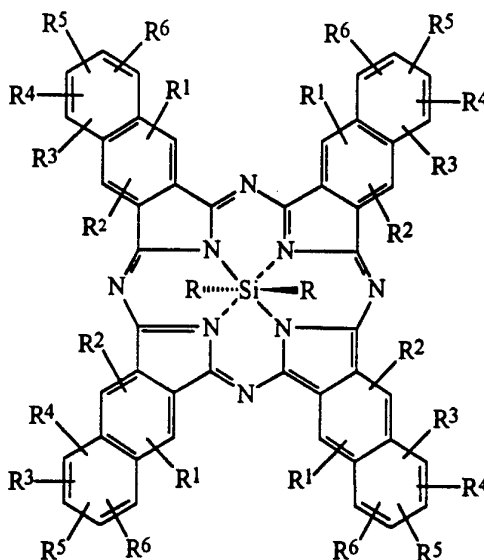
or naphthalocyanines having the formula



10 and when the Si^{4+} is combined with the the above described phthalocyanine or naphthalocyanine rings they form the organosilicon compounds having essentially the following formulas



and:

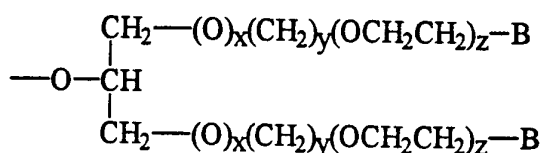


- 5 wherein each aromatic ring of the phthalocyanine ring system can be substituted with up to four units, for example, R¹, R², R³, and R⁴ units, for a maximum of sixteen substitutions per phthalocyanine molecule, and each aromatic ring system of the naphthalocyanine ring system can be substituted with up to six units, for example R¹, R², R³, R⁴, R⁵, and R⁶ units, for a maximum of twenty-four substitutions per
10 naphthalocyanine molecule.

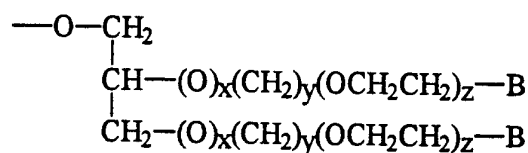
Phthalocyanine and naphthalocyanine ring units

- The hydrogen atoms of the phthalocyanine and naphthalocyanine bi-dentate chelant rings are substituted to effect the photochemical properties of the molecules. Phthalocyanines have R¹, R², R³, and R⁴ units which are capable of substitution and
15 naphthalocyanines have R¹, R², R³, R⁴, R⁵, and R⁶ units capable of substitution. These units are bonded to the phthalocyanine or naphthalocyanine rings and are independently selected from the group consisting of:

- 5 a) hydrogen;
 b) halogen;
 c) hydroxyl;
 d) cyano;
 e) nitrilo;
 f) oximino;
 g) C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl;
 10 h) halogen substituted C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl;
 i) polyhydroxyl substituted C₃-C₂₂ alkyl;
 j) C₁-C₂₂ alkoxy, preferably C₁-C₄ alkoxy, more preferred methoxy;
 k) branched alkoxy having the formula



or

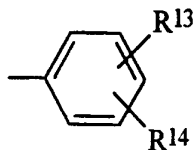


15

20

wherein B is hydrogen, hydroxyl, C₁-C₃₀ alkyl, C₁-C₃₀ alkoxy, -CO₂H, -CH₂CO₂H, -SO₃⁻M⁺, -OSO₃⁻M⁺, -PO₃²⁻M, -OPO₃²⁻M, and mixtures thereof; M is a water soluble cation in sufficient amount to satisfy charge balance; x is 0 or 1, each y independently has the value from 0 to 6, preferably from 0 to 6; each z independently has the value from 0 to 100, preferably from 0 to about 10, more preferably from 0 to about 3;

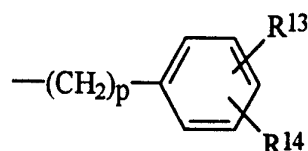
- l) aryl, and substituted aryl having essentially the formula:



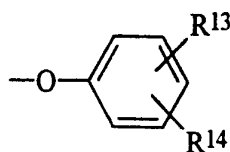
25

wherein R¹³ and R¹⁴ are independently selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₁-C₆ alkenyl, C₁-C₆ alkoxy, C₁-C₆ branched alkoxy, halogen, morpholino, cyano, nitrilo, -CO₂⁻

- 5 M^+ , $-SO_3^- M^+$, $-OSO_3^- M^+$, $-N(R^{15})_2$, and $-N^+(R^{15})_3 X^-$ wherein each R^{15} is independently hydrogen or C_1 - C_4 alkyl; and mixtures thereof; preferably hydrogen C_1 - C_6 alkyl, $-CO_2^- M^+$, $-SO_3^- M^+$, $-OSO_3^- M^+$, and mixtures thereof, more preferably C^{13} or C^{14} is hydrogen and the other moiety is C_1 - C_6 ; wherein M is a water soluble cation and X is chlorine, bromine, iodine, or other water soluble anion. Examples of other water soluble anions include organic species such as fumarate, tartrate, oxalate and the like, inorganic species include sulfate, hydrogen sulfate, phosphate and the like;
- 10 m) alkylenearyl and substituted alkylenearyl having essentially the formula:

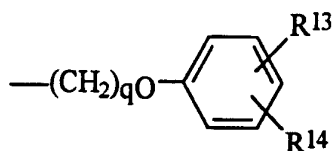


- 15 wherein R^{13} and R^{14} are independently selected from the group consisting of hydrogen, C_1 - C_6 alkyl, C_1 - C_6 alkenyl, C_1 - C_6 alkoxy, C_1 - C_6 branched alkoxy, halogen, morpholino, cyano, nitrilo, $-CO_2^- M^+$, $-SO_3^- M^+$, $-OSO_3^- M^+$, $-N(R^{15})_2$, and $-N^+(R^{15})_3 X^-$ wherein each R^{15} is independently hydrogen or C_1 - C_4 alkyl; and mixtures thereof; preferably hydrogen C_1 - C_6 alkyl, $-CO_2^- M^+$, $-SO_3^- M^+$, $-OSO_3^- M^+$, and mixtures thereof, more preferably C^{13} or C^{14} is hydrogen and the other moiety is C_1 - C_6 ; wherein M is a water soluble cation and X is chlorine, bromine, iodine, or other water soluble anion. Examples of other water soluble anions include organic species such as fumarate, tartrate, oxalate and the like, inorganic species include sulfate, hydrogen sulfate, phosphate and the like; p is from 1 to about 10, preferably from 1 to about 3;
- 20
- 25 n) aryloxy and substituted aryloxy having essentially the formula:

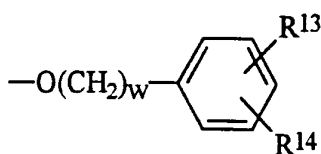


- 30 wherein R^{13} and R^{14} are independently selected from the group consisting of hydrogen, C_1 - C_6 alkyl, C_1 - C_6 alkenyl, C_1 - C_6 alkoxy,

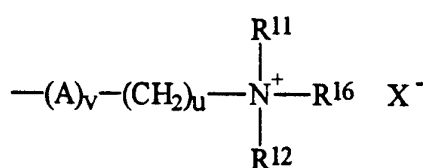
- 5 C₁-C₆ branched alkoxy, halogen, morpholino, cyano, nitrilo, -CO₂⁻M⁺, -SO₃⁻M⁺, -OSO₃⁻M⁺, -N(R¹⁵)₂, and -N⁺(R¹⁵)₃X⁻ wherein each R¹⁵ is independently hydrogen or C₁-C₄ alkyl; and mixtures thereof; preferably hydrogen C₁-C₆ alkyl, -CO₂⁻M⁺, -SO₃⁻M⁺, -OSO₃⁻M⁺, and mixtures thereof, more preferably C¹³ or C¹⁴ is hydrogen and the other moiety is C₁-C₆; wherein M is a water soluble cation and X is chlorine, bromine, iodine, or other water soluble anion. Examples of other water soluble anions include organic species such as fumarate, tartrate, oxalate and the like, inorganic species
- 10 include sulfate, hydrogen sulfate, phosphate and the like;
- o) alkyleneoxyaryl and substituted alkyleneoxyarylalkyleneoxyaryl units are defined as moieties having essentially the formula:



- 15 wherein R¹³ and R¹⁴ are independently selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₁-C₆ alkenyl, C₁-C₆ alkoxy, C₁-C₆ branched alkoxy, halogen, morpholino, cyano, nitrilo, -CO₂⁻M⁺, -SO₃⁻M⁺, -OSO₃⁻M⁺, -N(R¹⁵)₂, and -N⁺(R¹⁵)₃X⁻ wherein each R¹⁵ is independently hydrogen or C₁-C₄ alkyl; and mixtures thereof; preferably hydrogen C₁-C₆ alkyl, -CO₂⁻M⁺, -SO₃⁻M⁺, -OSO₃⁻M⁺, and mixtures thereof, more preferably C¹³ or C¹⁴ is hydrogen and the other moiety is C₁-C₆; wherein M is a water soluble cation and X is chlorine, bromine, iodine, or other water soluble anion. Examples of other water soluble anions include organic species such as fumarate, tartrate, oxalate and the like, inorganic species
- 20 include sulfate, hydrogen sulfate, phosphate and the like; q is from 0 to about 10 preferably from about 1 to about 3;
- 25 p) oxyalkylenearyl and substituted oxyalkylenearyl having essentially the formula:



- wherein R¹³ and R¹⁴ are independently selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₁-C₆ alkenyl, C₁-C₆ alkoxy, C₁-C₆ branched alkoxy, halogen, morpholino, cyano, nitrilo, -CO₂⁻ M⁺, -SO₃⁻ M⁺, -OSO₃⁻ M⁺, -N(R¹⁵)₂, and -N⁺(R¹⁵)₃X⁻ wherein each R¹⁵ is independently hydrogen or C₁-C₄ alkyl; and mixtures thereof; preferably hydrogen C₁-C₆ alkyl, -CO₂⁻ M⁺, -SO₃⁻ M⁺, -OSO₃⁻ M⁺, and mixtures thereof, more preferably C¹³ or C¹⁴ is hydrogen and the other moiety is C₁-C₆; wherein M is a water soluble cation and X is chlorine, bromine, iodine, or other water soluble anion. Examples of other water soluble anions include organic species such as fumarate, tartrate, oxalate and the like, inorganic species include sulfate, hydrogen sulfate, phosphate and the like; w is from 1 to about 10, preferably from about 1 to about 3;
- q) C₁-C₂₂ thioalkyl, C₄-C₂₂ substituted thioalkyl, and mixtures thereof;
- r) ester units of the formula -CO₂R¹⁰ wherein R¹⁰ is C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, all of which can be substituted with halogen; poly-hydroxyl substituted C₃-C₂₂ alkyl, C₃-C₂₂ glycol; C₁-C₂₂ alkoxy, C₄-C₂₂ branched alkoxy; aryl, substituted aryl, alkylenearyl, aryloxy, alkyleneoxyaryl, alkyleneoxyaryl; preferably C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, and mixtures thereof;
- s) alkyleneamino units having essentially the formula:



- wherein R¹¹, and R¹² are each a C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, R¹⁶ is hydrogen, C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl and mixtures thereof, A is the heteroatom nitrogen or oxygen, preferably A is oxygen, the index v is 0 when the heteroatom is absent, v is equal to 1 when the heteroatom is present, preferably v is equal to 0; X is chloride, bromide, iodide, or other water soluble anion, u is from 0 to 22, preferably u is from 3 to about 10. Examples of other water soluble anions include organic species

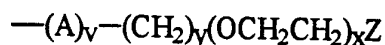
such as fumarate, tartrate, oxalate and the like, inorganic species include sulfate, hydrogen sulfate, phosphate and the like;

t) an amino unit of the formula



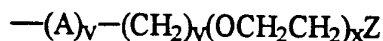
wherein R^{11} and R^{12} comprises C_1 - C_{22} alkyl, C_4 - C_{22} branched alkyl, C_1 - C_{22} alkenyl, C_4 - C_{22} branched alkenyl, and mixtures thereof;

u) alkylethyleneoxy units having essentially the formula:



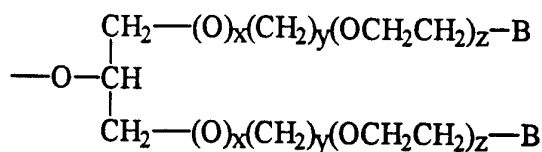
wherein A is the heteroatom nitrogen or oxygen, preferably A is oxygen, the index v is 0 when the heteroatom is absent, v is equal to 1 when the heteroatom is present, Z is hydrogen, C_1 - C_6 alkoxy, aryl, substituted aryl, aryloxy, substituted aryloxy, alkyleneamino, $-SO_3^-M^+$, $-OSO_3^-M^+$, $-CO_2H$, and mixtures thereof, preferably hydrogen or C_1 - C_6 alkoxy, more preferably methoxy; x is from 1 to 100, preferably from 0 to about 20, more preferably from 3 to about 10; and y is from 1 to 12, preferably from about 1 to about 5;

v) siloxy and substituted siloxy of the formula $-OSiR^7R^8R^9$ wherein each R^7 , R^8 , and R^9 is independently selected from the group consisting of C_1 - C_8 alkyl, C_4 - C_8 branched alkyl, C_1 - C_8 alkenyl, C_4 - C_8 branched alkenyl, substituted alkyl, aryl, alkylethyleneoxy units of the formula

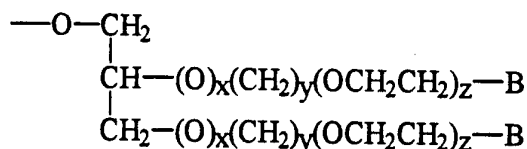


wherein Z is hydrogen, C_1 - C_{30} alkyl, hydroxyl, $-CO_2H$, $-SO_3^-M^+$, $-OSO_3^-M^+$, C_1 - C_6 alkoxy, aryl, substituted aryl, aryloxy, substituted aryloxy alkyleneamino; and mixtures thereof; A units comprise nitrogen or oxygen, M is a water soluble cation, v is 0 or 1, x is from 0 to 100, y is from 0 to 12; and mixtures thereof; and, alkyleneamino units and mixtures thereof.

Preferred R^1 , R^2 , R^3 , R^4 , R^5 , and R^6 units are C_1 - C_{22} alkoxy, branched alkoxy having the formula



or

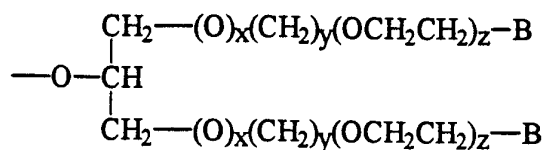


wherein B is hydrogen, hydroxyl, C₁-C₃₀ alkyl, C₁-C₃₀ alkoxy, -CO₂H, -CH₂CO₂H, -SO₃⁻M⁺, -OSO₃⁻M⁺, -PO₃²⁻M, -OPO₃²⁻M, and mixtures thereof; preferably C₁-C₁₈ alkyl, -CO₂H, -SO₃⁻M⁺, -OSO₃⁻M⁺, -PO₃²⁻M, -OPO₃²⁻M; M is a water soluble cation in sufficient amount to satisfy charge balance; x is 0 or 1, each y independently has the value from 0 to 6, preferably from 0 to 6; each z independently has the value from 0 to 100, preferably from 0 to about 10, more preferably from 0 to about 3; and halogen, more preferred R¹, R², R³, R⁴, R⁵, and R⁶ units are methoxy, branched alkoxy and halogen. When the (Sens.) unit is phthalocyanine most preferred R¹, R², R³, and R⁴ units are methoxy and branched alkoxy. When the (Sens.) unit is naphthalocyanine most preferred R¹, R², R³, R⁴, R⁵, and R⁶ units are chlorine, bromine or iodine.

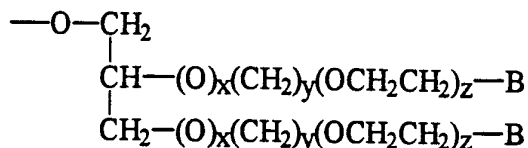
Axial R units

The compounds useful for the present invention also comprise axial R units bonded directly to the central silicon atom, wherein R is independently selected from the group consisting of:

- a) hydrogen;
- b) halogen;
- 20 c) hydroxyl;
- d) cyano;
- e) nitrilo;
- f) oximino;
- g) C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl;
- 25 h) halogen substituted C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl;
- i) polyhydroxyl substituted C₃-C₂₂ alkyl;
- j) C₁-C₂₂ alkoxy, preferably C₁-C₄ alkoxy, more preferred methoxy;
- 30 k) branched alkoxy having the formula

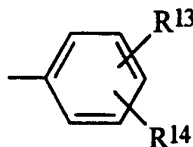


or



wherein B is hydrogen, hydroxyl, C₁-C₃₀ alkyl, C₁-C₃₀ alkoxy, -CO₂H, -CH₂CO₂H, -SO₃⁻M⁺, -OSO₃⁻M⁺, -PO₃²⁻M, -OPO₃²⁻M, and mixtures thereof; M is a water soluble cation in sufficient amount to satisfy charge balance; x is 0 or 1, each y independently has the value from 0 to 6, preferably from 0 to 6; each z independently has the value from 0 to 100, preferably from 0 to about 10, more preferably from 0 to about 3;

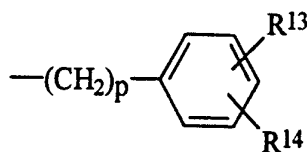
10 l) aryl, and substituted aryl having essentially the formula:



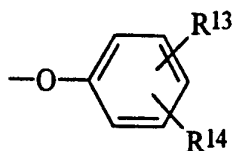
wherein R¹³ and R¹⁴ are independently selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₁-C₆ alkenyl, C₁-C₆ alkoxy, C₁-C₆ branched alkoxy, halogen, morpholino, cyano, nitrilo, -CO₂⁻M⁺, -SO₃⁻M⁺, -OSO₃⁻M⁺, -N(R¹⁵)₂, and -N⁺(R¹⁵)₃X⁻ wherein each R¹⁵ is independently hydrogen or C₁-C₄ alkyl; and mixtures thereof; preferably hydrogen C₁-C₆ alkyl, -CO₂⁻M⁺, -SO₃⁻M⁺, -OSO₃⁻M⁺, and mixtures thereof, more preferably C¹³ or C¹⁴ is hydrogen and the other moiety is C₁-C₆; wherein M is a water soluble cation and X is chlorine, bromine, iodine, or other water soluble anion. Examples of other water soluble anions include organic species such as fumarate, tartrate, oxalate and the like, inorganic species include sulfate, hydrogen sulfate, phosphate and the like;

20 m) alkylenearyl and substituted alkylenearyl having essentially the formula:

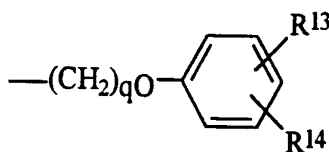
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- wherein R^{13} and R^{14} are independently selected from the group consisting of hydrogen, C_1 - C_6 alkyl, C_1 - C_6 alkenyl, C_1 - C_6 alkoxy, C_1 - C_6 branched alkoxy, halogen, morpholino, cyano, nitrilo, $-\text{CO}_2^- \text{M}^+$, $-\text{SO}_3^- \text{M}^+$, $-\text{OSO}_3^- \text{M}^+$, $-\text{N}(\text{R}^{15})_2$, and $-\text{N}^+(\text{R}^{15})_3 \text{X}^-$ wherein each R^{15} is independently hydrogen or C_1 - C_4 alkyl; and mixtures thereof; preferably hydrogen C_1 - C_6 alkyl, $-\text{CO}_2^- \text{M}^+$, $-\text{SO}_3^- \text{M}^+$, $-\text{OSO}_3^- \text{M}^+$, and mixtures thereof, more preferably C^{13} or C^{14} is hydrogen and the other moiety is C_1 - C_6 ; wherein M is a water soluble cation and X is chlorine, bromine, iodine, or other water soluble anion. Examples of other water soluble anions include organic species such as fumarate, tartrate, oxalate and the like, inorganic species include sulfate, hydrogen sulfate, phosphate and the like; p is from 1 to about 10, preferably from 1 to about 3;
- 15 n) aryloxy and substituted aryloxy having essentially the formula:

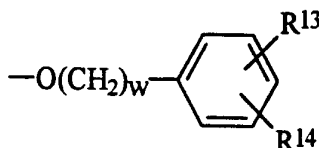


- wherein R^{13} and R^{14} are independently selected from the group consisting of hydrogen, C_1 - C_6 alkyl, C_1 - C_6 alkenyl, C_1 - C_6 alkoxy, C_1 - C_6 branched alkoxy, halogen, morpholino, cyano, nitrilo, $-\text{CO}_2^- \text{M}^+$, $-\text{SO}_3^- \text{M}^+$, $-\text{OSO}_3^- \text{M}^+$, $-\text{N}(\text{R}^{15})_2$, and $-\text{N}^+(\text{R}^{15})_3 \text{X}^-$ wherein each R^{15} is independently hydrogen or C_1 - C_4 alkyl; and mixtures thereof; preferably hydrogen C_1 - C_6 alkyl, $-\text{CO}_2^- \text{M}^+$, $-\text{SO}_3^- \text{M}^+$, $-\text{OSO}_3^- \text{M}^+$, and mixtures thereof, more preferably C^{13} or C^{14} is hydrogen and the other moiety is C_1 - C_6 ; wherein M is a water soluble cation and X is chlorine, bromine, iodine, or other water soluble anion. Examples of other water soluble anions include organic species such as fumarate, tartrate, oxalate and the like, inorganic species include sulfate, hydrogen sulfate, phosphate and the like;
- 20
- 25
- 30 o) alkyleneoxyaryl and substituted alkyleneoxyarylalkyleneoxyaryl units are defined as moieties having essentially the formula:



5 wherein R¹³ and R¹⁴ are independently selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₁-C₆ alkenyl, C₁-C₆ alkoxy, C₁-C₆ branched alkoxy, halogen, morpholino, cyano, nitrilo, -CO₂⁻M⁺, -SO₃⁻M⁺, -OSO₃⁻M⁺, -N(R¹⁵)₂, and -N⁺(R¹⁵)₃X⁻ wherein each R¹⁵ is independently hydrogen or C₁-C₄ alkyl; and mixtures thereof; preferably hydrogen C₁-C₆ alkyl, -CO₂⁻M⁺, -SO₃⁻M⁺, -OSO₃⁻M⁺, and mixtures thereof, more preferably C¹³ or C¹⁴ is hydrogen and the other moiety is C₁-C₆; wherein M is a water soluble cation and X is chlorine, bromine, iodine, or other water soluble anion. Examples of other water soluble anions include organic species such as fumarate, tartrate, oxalate and the like, inorganic species include sulfate, hydrogen sulfate, phosphate and the like; q is from 0 to about 10 preferably from about 1 to about 3;

15 p) oxyalkylenearyl and substituted oxyalkylenearyl having essentially the formula:



20 wherein R¹³ and R¹⁴ are independently selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₁-C₆ alkenyl, C₁-C₆ alkoxy, C₁-C₆ branched alkoxy, halogen, morpholino, cyano, nitrilo, -CO₂⁻M⁺, -SO₃⁻M⁺, -OSO₃⁻M⁺, -N(R¹⁵)₂, and -N⁺(R¹⁵)₃X⁻ wherein each R¹⁵ is independently hydrogen or C₁-C₄ alkyl; and mixtures thereof; preferably hydrogen C₁-C₆ alkyl, -CO₂⁻M⁺, -SO₃⁻M⁺, -OSO₃⁻M⁺, and mixtures thereof, more preferably C¹³ or C¹⁴ is hydrogen and the other moiety is C₁-C₆; wherein M is a water soluble cation and X is chlorine, bromine, iodine, or other water soluble anion. Examples of other water soluble anions include organic species such as fumarate, tartrate, oxalate and the like, inorganic species

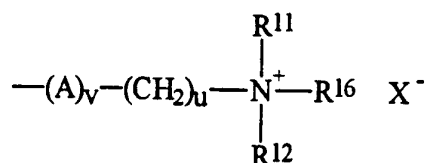
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include sulfate, hydrogen sulfate, phosphate and the like; w is from 1 to about 10, preferably from about 1 to about 3;

- q) C₁-C₂₂ thioalkyl, C₄-C₂₂ substituted thioalkyl, and mixtures thereof;
 r) alkyleneamino units having essentially the formula:

5



wherein R¹¹, and R¹² are each a C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, R¹⁶ is hydrogen, C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl and mixtures thereof, A is the heteroatom nitrogen or oxygen, preferably A is oxygen, the index v is 0 when the heteroatom is absent, v is equal to 1 when the heteroatom is present, preferably v is equal to 0; X is chloride, bromide, iodide, or other water soluble anion, u is from 0 to 22, preferably u is from 3 to about 10. Examples of other water soluble anions include organic species such as fumarate, tartrate, oxalate and the like, inorganic species include sulfate, hydrogen sulfate, phosphate and the like;

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- s) an amino unit of the formula

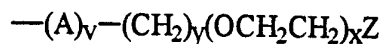
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wherein R¹¹ and R¹² comprises C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, and mixtures thereof;

- t) alkylethyleneoxy units having essentially the formula:

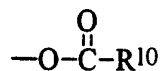
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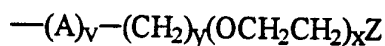
wherein A is the heteroatom nitrogen or oxygen, preferably A is oxygen, the index v is 0 when the heteroatom is absent, v is equal to 1 when the heteroatom is present, Z is hydrogen, C₁-C₆ alkoxy, aryl, substituted aryl, aryloxy, substituted aryloxy, alkyleneamino, -SO₃⁻M⁺, -OSO₃⁻M⁺, -CO₂H, and mixtures thereof, preferably hydrogen or C₁-C₆ alkoxy, more preferably methoxy; x is from 1 to 100, preferably from 0 to about 20, more preferably from 3 to about 10; and y is from 1 to 12, preferably from about 1 to about 5;

u) carboxylate units of the formula



5 wherein R¹⁰ is C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, C₁-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, all of which can be substituted with halogen; poly-hydroxyl substituted C₃-C₂₂ alkyl, C₃-C₂₂ glycol; C₁-C₂₂ alkoxy, C₄-C₂₂ branched alkoxy; substituted and unsubstituted aryl, substituted and unsubstituted alkylenearyl, substituted and
10 unsubstituted aryloxy, substituted and unsubstituted alkyleneoxyaryl, substituted and unsubstituted alkyleneoxyaryl; preferably C₁-C₂₂ alkyl, C₄-C₂₂ branched alkyl, and mixtures thereof;

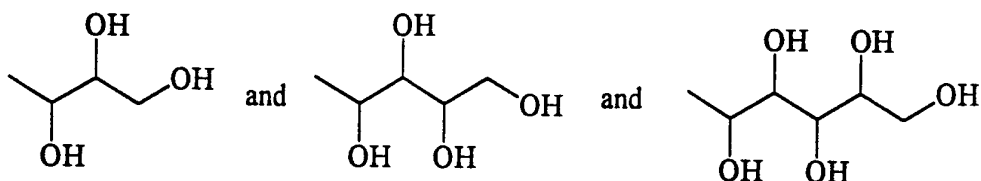
v) siloxy and substituted siloxy of the formula -OSiR⁷R⁸R⁹ wherein
15 each R⁷, R⁸, and R⁹ is independently selected from the group consisting of C₁-C₈ alkyl, C₄-C₈ branched alkyl, C₁-C₈ alkenyl, C₄-C₈ branched alkenyl, substituted alkyl, aryl, alkylethyleneoxy units of the formula



20 wherein Z is hydrogen, C₁-C₃₀ alkyl, hydroxyl, -CO₂H, -SO₃^{-M⁺}, -OSO₃^{-M⁺}, C₁-C₆ alkoxy, aryl, substituted aryl, aryloxy, substituted aryloxy alkyleneamino; and mixtures thereof; A units comprise nitrogen or oxygen, M is a water soluble cation, v is 0 or 1, x is from 0 to 100, y is from 0 to 12; and mixtures thereof; and, alkyleneamino
25 units and mixtures thereof.

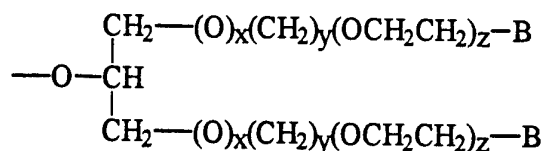
Preferred R units are the polyhydroxyl substituted C₃-C₂₂ alkylene moieties that are essentially polyglycols of the formula -(CHOH)_nCH₂OH, wherein the value of n is from 2 to 21; preferred polyhydroxy substituted alkenes are those polyhydroxy glycols essentially of the formula

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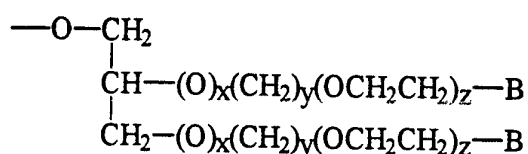


wherein the stereochemical configuration of these polyhydroxyl moieties are equivalent for the purposes of the present invention.

Most preferred axial R units are branched alkoxy having the formula



or

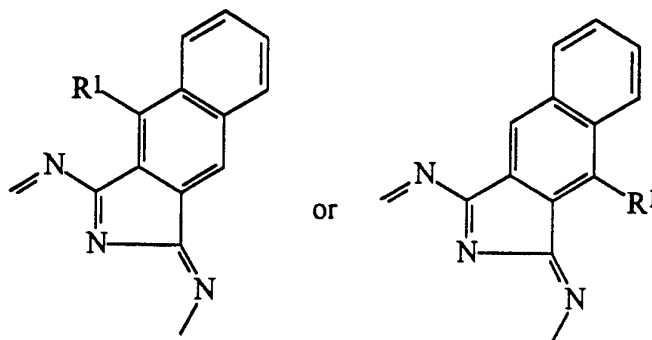


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wherein B is hydrogen, hydroxyl, C₁-C₃₀ alkyl, C₁-C₃₀ alkoxy, -CO₂H, -CH₂CO₂H, -SO₃⁻M⁺, -OSO₃⁻M⁺, -PO₃²⁻M, -OPO₃²⁻M, and mixtures thereof; M is a water soluble cation in sufficient amount to satisfy charge balance; x is 0 or 1, each y independently has the value from 0 to 6, preferably from 0 to 6; each z independently has the value from 0 to 100, preferably from 0 to about 10, more preferably from 0 to about 3.

When compounds of the present invention have present one or more substituent R¹, R², R³, and R⁴ units, as in the case of phthalocyanine, or R¹, R², R³, R⁴, R⁵, and R⁶ units, as in the case of naphthalocyanines, the exact orientation of the substituents may not be exactly known. However, for the purposes of the compounds of the present invention, certain equivalencies of substitution exist. For example, the two units of the following formula

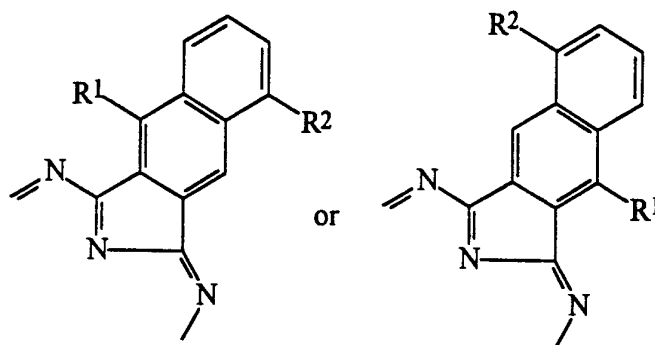
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which contain the same R¹ substitution, are equivalent for the purposes of the present invention and the selection of either one structure over the other will not effect the desired properties of the molecule described herein.

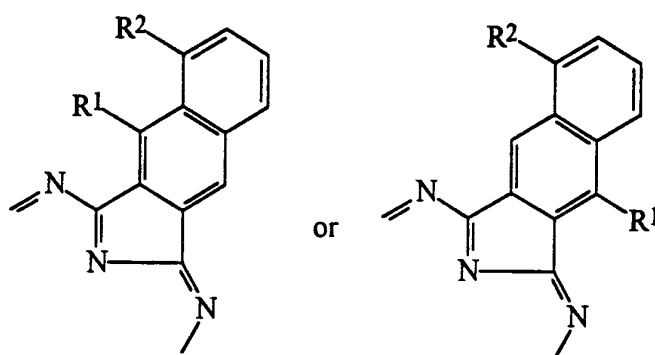
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In addition, compounds containing the substitution represented by the following formulas



which contain the same R^1 and R^2 unit substitutions, are also equivalent for the purposes of the present invention and the selection of either one structure over the other will not effect the desired properties of the molecule described herein. The above examples, however, are only representative of the total number of equivalent structure examples that will be recognized by those skilled in the art.

Compounds useful for the present invention having substituted one or more R^1 , R^2 , R^3 , and R^4 unit, as in the case of phthalocyanine, or R^1 , R^2 , R^3 , R^4 , R^5 , and R^6 unit, as in the case of naphthalocyanines, which have their substitutions oriented in a manner described essentially by the following formula



are not equivalent for the purposes of the present invention and would each constitute separate compounds regardless of the fact that the R^1 and R^2 units are equivalent. The above example does not exhaust the number of non-equivalent structures that are possible using any combination of R^1 , R^2 , R^3 , R^4 , R^5 , and R^6 units recognized by those skilled in the art.

Solublizing axial R units, are bonded directly to the central silicon atom, which for the purposes of the present invention is a Si^{4+} atom, and occupy a position axial to the essentially planar (Sens.) unit. The utility of each R unit is primarily directed to the solubility properties of the compounds of the present invention and each R unit can be chosen independently of the other. The selection of an R unit can be made, in addition to, or in lieu of, solubility requirements, and be totally directed

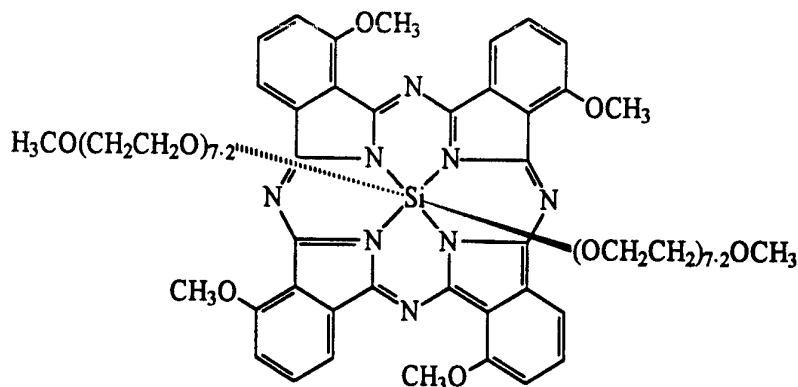
instead to the "substantivity" or "non-substantivity" of the compound. R units are essentially nonionic, cationic, or anionic units.

Below is an example of a preferred "substantive" embodiment (has an affinity for surfaces, e.g. fabric) of the present invention comprising a phthalocyanine ring system wherein at least one of the R¹, R², R³, and R⁴ units of each aromatic moiety is methoxy, each R group comprises an ethyleneoxy unit of essentially the formula



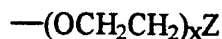
wherein for each R unit Z is methoxy and x is 7.2 thereby giving the moiety an average ethoxylation value of 7.2.

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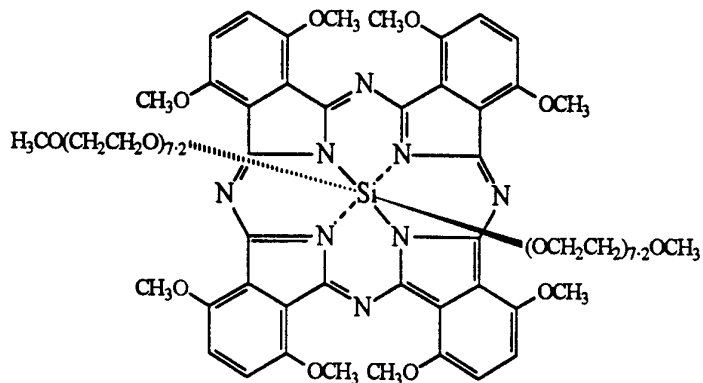
Below is an example of a more preferred "substantive" embodiment (has an affinity for surfaces, e.g. fabric) of the present invention comprising a phthalocyanine ring system wherein at least two of the R¹, R², R³, and R⁴ units of each aromatic moiety is methoxy, each R group comprises an ethyleneoxy unit of essentially the formula

15



wherein for each R unit Z is methoxy and x is 7.2 thereby giving the moiety an average ethoxylation value of 7.2.

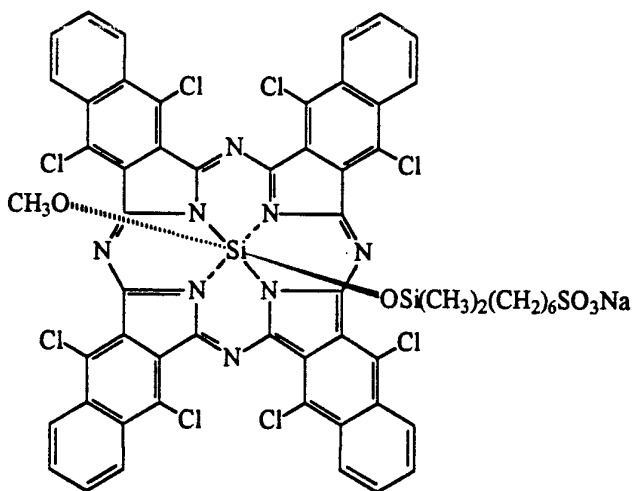
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Below is an example of a "non-substantive" embodiment (charged R units reduces the affinity for surfaces, e.g. fabric) of the present invention comprising a naphthalocyanine ring system wherein at least two of the R¹, R², R³, R⁴, R⁵, and R⁶ units of each aromatic moiety are chlorine, one R group comprises an siloxy unit essentially the formula -OSiR⁷R⁸R⁹ wherein R⁷ and R⁸ units are methyl and R⁹ is essentially of the formula



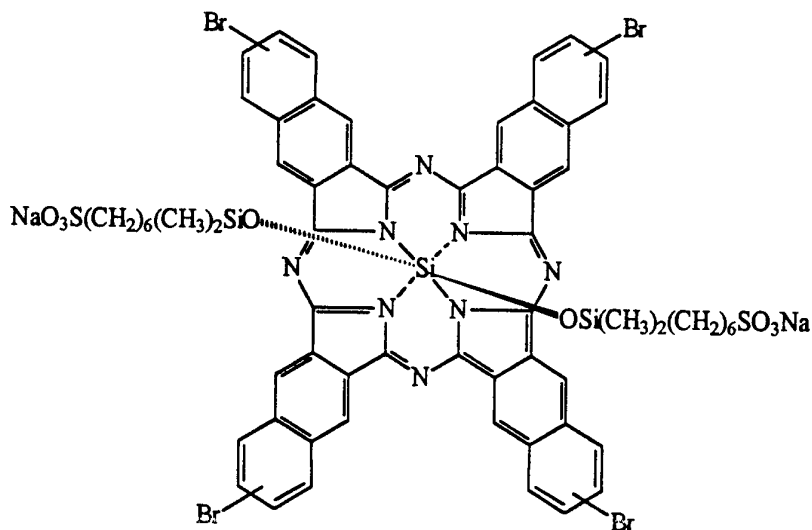
wherein Z is -SO₃-M⁺, M is sodium and y is equal to six; the second axial R unit is methoxy.



Below is an example of a preferred "non-substantive" embodiment (charged R units reduces the affinity for surfaces, e.g. fabric) of the present invention comprising a naphthalocyanine ring system wherein at least one of the R¹, R², R³, R⁴, R⁵, and R⁶ units of each aromatic moiety is bromine, and the R groups comprise an siloxy unit essentially the formula -OSiR⁷R⁸R⁹ wherein R⁷ and R⁸ units are methyl and R⁹ is essentially of the formula



wherein Z is -SO₃-M⁺, M is sodium and y is equal to six.



The compounds of the present invention can be modified to have a wide range of surface affinities. Molecules can be made "substantive" or "non-substantive" by the choice of axial R units. The term "substantivity" as defined herein is the property which allows the photobleaching agent to successfully contact a particular targeted surface. For example, the axial groups R, hereinafter defined in the specification, may be selected to provide compatibility of the photobleaching compound with a synthetic fabric, a durable surface such as ceramic tile, or in general any fabric, article of manufacture or situs that is to be a target of photobleaching.

For example, the R unit is matched to the structural properties of either the targeted material (i.e. fabric) or to the targeted substrate (i.e. stain). The option to tailor the properties of the R unit to the material such as a disposable paper article of manufacture, is due to the ability to select R units independently of effecting the phthalocyanine or naphthalocyanine ring thereby leaving the photophysics unaffected.

An additional benefit of the photobleaching system of the present invention is that they are generally more fabric and color safe than conventional bleaches (i.e. hypochlorite). Without being limited by theory it is believed that the improved fabric and color safety is due to quenching of singlet oxygen by dyestuffs used in the manufacture of colored articles.

"Non-substantive" molecules are desirable for applications where the photosensitizing compound must remain in the liquor rather than becoming attracted to a particular surface, i.e. when used as a steeping agent. While not wishing to be limited by way of example, the substitution of a charged moiety in the R unit will act to make the compound repel any surface that is similarly charged.

The term "low hue" as used herein and throughout the specification refers to photobleaches that have a λ_{\max} of their Q-band above about 700 nm and are

therefore only slightly perceptible to the human eye. The term "low hue" photo
disinfectant in the context of the present invention describes a material that even
when present in concentrations greater than the operable range described herein, are
not perceptible by most people. Those additional materials of the present invention
5 having Q-band maximum wavelengths in the "visible" range, (i.e. 660-700
nanometers) are photodisinfectating materials that are most suitable when the
perception of a colored material is not a factor in deterring utility. Also "hue" is
relative to the surface, for example, a material that would appear slightly colored on a
white cotton fabric would generally appear colorless in other applications, most
10 notably when used as a glass cleaner where more inherent color can be tolerated.

The term "low hue", as used in the present specification and as further defined
hereinafter, is a point of reference and refers to the visible perception created when
organosilicon compounds of the present invention are applied to a solid white
background, as compared to other conventional materials or standard surfaces.
15 Compounds that elicit a measurable "hueing" or "perceived color" in a standard
spectrophotometric measurement or "white background" test, will in many instances
be imperceptible to the un-trained eye. However, some "low hue" organosilicon
photosensitizing compounds of the present invention will appear more visible than
other embodiments depending on the type of surface on which they are applied.
20 Those skilled in the art of color perception recognize that even colorless surfaces will
appear "hued" due to light scattering and other surface effects rather than due to
inherent color. Also the amount or color perceived by the user of the compounds of
the present invention may be effected by the presence of adjunct ingredients such as
fluorescent whitening agents, dyes, colorants or by the wavelength range of the light
25 that is present.

While not wishing to be limited by theory, the mechanism by which
photobleaching occurs is a diffusion controlled process and therefore the compounds
of the present invention by their unique structural qualities are well suited for high
efficiency singlet oxygen production. Effective photobleaching is predicated on the
30 production of a molecule of singlet oxygen, a theory which has been extensively
studied and is well understood by those skilled in the art of photobleaching. Because
the singlet oxygen species is short-lived and its photo-energy transfer is diffusion
controlled, that is, singlet oxygen rapidly reacts with receptor molecules in the
surrounding molecular milieu, having the photosensitizing molecule in proximity to
35 the situs of the microbe or similar object to be "attacked" is of primary advantage.

The molecules of the present invention because of the ability of the
formulator to achieve a rational degree of "substantivity" can direct the molecules of

the present invention to any desired surface. The additional ability to prevent layering and stacking of photosensitizing molecules due to the axial nature of the R units, provides for an efficient mono-layer to be applied to the "situs of action". For example, an embodiment of the present invention for removing stains from a fabric will have the requirements that the organosilicon photosensitizing compound have an affinity for the fabric surface (substantivity for the surface), that the photobleaching compound be close to the desired site of action (achieved by manipulation of one or more R units) for "high molecular efficiency". Clearly it would be advantageous given these requirements to deposit a "monolayer" of the photobleach, this requires that the Q-band be sufficiently above 700 nm to prevent the eye detecting the photobleach.

The present invention also relates to a process for carrying out a photosensitized reaction or a reaction catalyzed by singlet oxygen, wherein one or more phthalocyanine or naphthylcyanine compounds in the presence of oxygen, are brought into contact with the medium in which or on which the said reaction is to take place, or are incorporated in this medium, and are irradiated with light.

While not wishing to be limited by theory, the photobleaches of the present invention are more "adjustable" with regard to the efficiency of photophysics. The formulator, now unburdened in the choice of substituent on the phthalocyanine or naphthalocyanine ring system because solubility considerations are a pervue of the axial R moieties, can fully concentrate on optimizing the photophysics of the compound.

It has long been known that certain large conjugated adducts, such as phthalocyanine and naphthalocyanine rings, can absorb light quanta and form electronically excited species (singlet and triplet) and that these species can be quenched by oxygen to yield 'excited oxygen species'. A particularly preferred 'excited oxygen species' is singlet oxygen which is most reliably formed by the quenching of the triplet state of a photosensitizer, such as a phthalocyanine, by molecular oxygen. It is therefore an aim of the photobleach formulator to produce compounds that favor the formation of the triplet state.

When a photosensitizer is irradiated with light, the singlet energy state that results undergoes a variety of processes i.e. re-emission of light (fluorescence). The most important process with regard to photobleaching via singlet oxygen is intersystem crossing (ISC). This is the mechanism by which the singlet state is converted to the triplet state within a molecule. In general, the efficiency of this process is discussed in terms of quantum yield, i.e. the number of photons absorbed that lead to the desired triplet excited state. The present invention provides for increased

photobleaching by modifying the efficiency of inter system crossing from the singlet state to the triplet state. The molecules of the present invention, can be modified by the formulator to increase the quantum efficiency by which the triplet state is formed. Surprisingly, the formulator can manipulate the substituents according to the present invention to increase the contribution certain substituents have on the "heavy atom effect", a term familiar to those skilled in the art. The selection of a moiety for its "heavy atom effect" can be made independently of other factors, for example, without undue concern for solubility factors. This is because the choice of axial R groups for solubility will have no bearing on the changes made to the phthalocyanine or naphthalocyanine ring system.

The Q-band, as well understood by those skilled in the art, is the low energy absorption band that is associated with excitation of an electron to its first singlet state. For example, in the case of the phthalocyanines and naphthalocyanines of the present invention, the wavelength associated with this absorption is typically from 600 to 800 nanometers. This range encompasses wavelengths of both the visible and the near infrared spectrum. A weaker absorption band relative to the Q-band for the compounds of the present invention can be found at shorter wavelengths that comprise the UV and visible spectrum. This second absorption band is known as the B-band. Unlike the Q-band, the B-band represents the excitement of an electron to its second singlet state. The present invention concerns the stronger Q-band absorption which is associated with the strong color of phthalocyanines, naphthalocyanines and the like.

The determination of the value of the Q-band wavelength and whether a shift occurs in this wavelength when a particular moiety (R^1 , R^2 , R^3 , R^4 , R^5 or R^6 unit) replaces a hydrogen atom on the phthalocyanine or naphthalocyanine ring is straightforward. Typically, a solution having a concentration of approximately 1×10^{-6} M of the phthalocyanine or naphthalocyanine to be measured is prepared using a suitable solvent (e.g. dimethylformamide) which contains 1 wt % triton X-100. A UV/visible spectrum is then obtained and the Q-band λ_{\max} is recorded. This value is the "substrate $\lambda_{s-\max}$ ". A spectrum for the material prior to introduction of the substituent group is obtained in the same manner. This value is the "reference $\lambda_{r-\max}$ ". The two spectra are compared and the resulting measured values are placed into the following equation

$$\text{wavelength red shift} = \Delta \lambda_{\max} = \lambda_{s-\max} - \lambda_{r-\max}$$

wherein if the number obtained is greater than or equal to 1, then the substituent group has produced a positive red shift of at least one nanometer and is a material suitable for use in the embodiments of the present invention. Those skilled in the art of photochemistry will recognize that the term $\Delta \lambda_{\max}$ is a dimensionless number and for the purposes of the present invention when the Q-band of the modified photobleach is measured in nanometers and compared to the un-modified photobleach, the Q-band of the modified photobleach will have an increase in wavelength of at least one nanometer. If the material of interest is not soluble in dimethylformamide another suitable solvent may be used. Aggregation of the phthalocyanine or naphthalocyanine compounds, leading to a false value for the Q-band wavelength, can be avoided by the addition of triton X-100.

Quantum yields and excited state energies are well known to those skilled in the art and the procedures for the determination of triplet quantum yield and like photophysical parameters are thoroughly described in the following references
Bonnet, R.; McGarvey, D. J.; Harriman, A.; Land, E. J.; Truscott, T. G.; Winfield, U.-J. *Photochem. Photobiol.* 1988, 48 (3), pg. 271-6; Davila, J., Harriman, A., Gulliya, K. S., *Photochem. Photobiol.*, 1991, 53 (1), pg. 1-11; Davila, J., Harriman, A., *Photochem. Photobiol.*, 1989, 50 (1), pg. 29-35; Charlesworth, P., Truscott, T. G., Brooks, R. C., Wilson, B. C., *J. Photochem. Photobiol.*, part B 1994, 26 (3), pg. 277-82; Zhang, X., Xu, H., *J. Chem. Soc., Faraday Trans.*, 1993, 89 (18), pg. 3347-51; Simpson, M. S. C., Beeby, A., Bishop, S. M., MacRobert, A. J., Parker, A. W., Phillips, D., *Proc. SPIE-int. Soc. Opt. Eng.*, 1992, 1640, pg. 520-9; Phillips, D., *Pure Appl. Chem.*, 1995, 67 (1), pg. 117-26; Wilkinson, F., Helman, W. P., Ross, A. B., *J. Phys. Chem. Ref. Data*, 1993, 22 (1), pg. 113-262; Lever, A. P. B., Licoccia, S., Magnell, K., Minor, P. C., Ramaswamy, B. S., *Adv. Chem. Ser.*, 1982, 201, pg. 237-52; West, M. A., *Creat. Detect. Excited State*, 1976, 4, pg. 217-307; Ford, W. E., Rihter, B. D., Kenney, M. E., Rodgers, M. A. J., *Photochem. Photobiol.*, 1989, 50 (3), pg. 277-282; Firey, P. A., Ford, W. E., Sounik, J. R., Kenney, M. E., Rodgers, A. J. R., *J. Am. Chem. Soc.*, 1988, 110, pg. 7626-7630; Firey, P. A., Rodgers, M. A. J., *Photochem. Photobiol.*, 1987, 45 (4), pg. 535-8; all of which are incorporated by reference in their entirety.

For the purposes of the present invention the delta triplet yield is determined according to the following equation

$$\text{triplet state yield increase} = \Delta \Phi_{\text{trip}} = \Phi_{\text{trip-substrate}} - \Phi_{\text{trip-reference}}$$

wherein the values for $\Phi_{\text{trip-substrate}} - \Phi_{\text{trip-reference}}$ can be obtained by any of the methods described in the references cited herein above. When the value for $\Delta \Phi_{\text{trip}}$ is a number greater than or equal to 1, the substitution made therein for a hydrogen atom on the (Sens.) unit of the photosensitizer is suitable for use in the embodiments of the present invention.

In addition, modifications to "hueing", that is the inherent color or lack of color, can be manipulated without regard to the properties brought to bear by the choice of axial R group.

In particular, the present invention relates to process for bleaching or removing spots from textiles and removing stains in or on organic or inorganic substrates or for protecting the latter against attack by microorganisms, wherein the textiles or the substrates to be freed from or protected against micro-organisms, are treated with phthalocyanines or naphthalocyanines of the present invention, in the presence of water and while being irradiated by light.

Another advantage of the present invention is the fact that each R unit may be directed toward a separate desired property and the molecules of the present invention can therefore be thought of as being "sided". For example, one axial R unit may be direct toward increased solubility while the other axial R group may be chosen for its ability to provide increase substantivity with respect to a given surface.

The ability to provide "substantivity" to a molecule of the present invention is matched by the desire and ability of the formulator to provide "non-substantivity" to examples of photodisinfectants of the present invention. The use of a substantive embodiment of the present invention would be applicable when using a method of the present invention for the purpose of cleaning or disinfecting a toilet bowl with a photo disinfectant of the present invention. A substantive material would bind or adhere to the sides of the bowl and have more effect than a non-substantive material that would remain evenly dispersed in solution.

The irradiation can be effected by means of an artificial source of light or by means of sunlight. A good effect is achieved for example, by means of light within the range between about 300 and 2500 nm, but preferably in the range of from 600 to about 1500 nm. Thus irradiation can be carried out, for example, using a commercially available incandescent lamp. The intensity of the illumination can vary within wide limits, and it depends both on the concentration of active substrate as well as the nature of the light source as to the photobleaching efficiency of any particular compound of the present invention. A further parameter which can be varied is the exposure time, i.e. for the same effect exposure must be longer at a

lower light intensity than at a higher intensity. In general, depending on the field of use, exposure time of a few minutes up to a few hours is possible.

If the process is carried out in an aqueous medium (for example the sterilization of textiles), the irradiation with light can either be carried out directly in the treatment medium, by means of an artificial source of light mounted inside or outside
5 the medium, or the articles, in a moist state, can subsequently either be irradiated, again by means of an artificial source of light, or can be exposed to sunlight. Good antimicrobial effects can be achieved even with very low concentrations of active substance, for example at 0.001 ppm. Depending on the field of use and on the
10 phthalocyanine or naphthylcyanine derivative employed, a concentration between 0.005 and 2000, preferably 0.01 and 1000 ppm is preferable.

The methods of the present invention can also be accomplished in solvent based carriers or in low aqueous solutions. For the purpose of the present invention the term low aqueous means that water is added to a carrier system to modify the
15 properties of the carrier and not solely for the purpose of solubilizing the substrate. For example, solvents that are capable of holding solubilized oxygen as well as forming a miscible system with water are preferred. Non-limiting examples of these solvents are butoxy propoxy propanol (BPP), which is available in commercial quantities as a mixture of isomers in about equal amounts, methoxy propoxy
20 propanol (MPP), ethoxy propoxy propanol (EPP), and propoxy propoxy propanol (PPP). Embodiments of the present invention which comprise these non-classical aqueous compositions are most useful when the photobleach must be applied to a woven fabric or surface that contains agents which repel water and moisture.

The sterilization of textiles of synthetic or natural origin may be mentioned
25 as an important application. Thus, material to be washed in the household or in industry can be disinfected by means of the methods of the present invention. The material to be washed can be treated for this purpose in the manner mentioned above with aqueous solutions of the phthalocyanines or naphthylcyanines of the present invention while being irradiated with light. The phthalocyanine and naphthyl-
30 cyanines can advantageously be present in the treatment medium in a concentration of from 0.01 to about 2000 mg per liter, preferably from 0.1 to 1000, more preferably from 1 to 500. The sterilization can be carried out advantageously together with the washing process. For this purpose, the material to be washed is treated with a wash medium containing customary detergent substances, one or more
35 phthalocyanines or naphthylcyanines according to the present invention and, if desired, inorganic salts and/or other adjunct materials having antimicrobial properties. The washing process can be carried out manually, for example in a tub,

or can be carried out in a washing machine. The necessary exposure to light can be effected during the washing process by means of suitable light sources, or the moist material being washed can also, subsequently, for example during drying, either be exposed to a suitable artificial source of light or simply exposed to sunlight, for example line drying.

Surface bleaching can be achieved, for example by applying (for example by spraying) to the appropriate surface, an aqueous solution of the phthalocyanine or naphthalocyanine compound according to the present invention, this solution preferably comprising from about 0.001 to about 10 %, by weight of active substance. The solution can also comprise, in addition, other customary additives, for example wetting agents, dispersing agents or emulsifiers, detergent substances and, if desired inorganic salts. After this solution has been applied, the surface is simply exposed to sunlight or, if required, it can in addition be irradiated by means of an artificial source of light, for example and incandescent lamp. It is advisable to keep the surface moist during the exposure to light.

The laundry compositions of the present invention optionally comprise deterative surfactants, examples of which are, anionic, cationic, nonionic, amphoteric and zwitterionic, however the formulator is not limited to these examples or combinations thereof. The surfactants are present from about 0% to about 95%, preferably from about 5% to about 30%, by weight of the composition.

The cleaning compositions of the present invention optionally comprise deterative surfactants, examples of which are, anionic, cationic, nonionic, amphoteric and zwitterionic, however the formulator is not limited to these examples or combinations thereof. The surfactants are present from about 0% to about 50%, preferably from about 5% to about 30%, by weight of the composition.

The laundry compositions of the present invention optionally contains builders, examples of which are, silicates, carbonates, and zeolites, however the user is not limited to these examples or combinations thereof. The builders are present from about 0% to about 50%, preferably from about 5% to about 30%, by weight of the composition.

The cleaning compositions of the present invention optionally contains builders, examples of which are, silicates, carbonates, and zeolites, however the user is not limited to these examples or combinations thereof. The builders are present from about 0% to about 50%, preferably from about 5% to about 30%, by weight of the composition.

The hard surface cleaner of the present invention optionally contains builders, examples of which are, silicates, carbonates, and zeolites, however the user is not

limited to these examples or combinations thereof. The builders are present from about 0% to about 50%, preferably from about 5% to about 30%, by weight of the composition.

5 The hard surface cleaner of the present invention optionally contains abrasives from about 0.5% to about 85%, preferably from about 10% to about 85%, by weight of the composition. Suitable abrasives are silicates, carbonates, perlite, clay, and pulverized ceramic clay, however, the user is not restricted to these examples or combinations thereof.

10 The present invention also relates to a process for carrying out a photosensitized reaction or a reaction catalyzed by singlet oxygen, wherein one or more phthalocyanine or naphthylcyanine compounds in the presence of oxygen, are brought into contact with the medium in which or on which the said reaction is to take place, or are incorporated in this medium, and are irradiated with light.

15 If the method is carried out in an aqueous medium (for example the sterilization of textiles), the irradiation with light can either be carried out directly in the treatment medium by means of an artificial source of light mounted inside or outside the medium or the substrates, in a moist state, can subsequently either be irradiated, again by means of an artificial source of light, or can be exposed to sunlight. Good antimicrobial effects of the present compounds can be achieved even with very low concentrations of active substance, for example at 0.001 ppm. Depending on the field of use and on the phthalocyanine or naphthylcyanine derivative employed, a concentration between 0.005 and 100, preferably 0.01 and 50 ppm is preferable.

20 Substances which increase the action can also be added in the process according to the invention, *inter alia* electrolytes, for example inorganic salts, for instance sodium chloride, potassium chloride, sodium sulfate, potassium sulfate, sodium acetate ammonium acetate, alkali metal phosphates and alkali metal tri-
25 polyphosphates, especially sodium chloride and sodium sulfate. These salts can be added to the agents according to the invention or can be added directly in the application method, so that they are present in the application solution in a concentration of, preferably 0.1 to 10%, by weight.

30 What is meant by the term aqueous solution is a solution that is essentially water, however the formulator may include adjunct materials as well as a surfactant to aid in removal of the "treated" micro organisms during rinsing or subsequent cleaning. The presence of an aqueous solution facilitates the production of singlet
35 oxygen due to the higher concentration of oxygen in water than in air.

Surfactant - The instant cleaning compositions contain from about 0.1 % to about 60% by weight of a surfactant selected from the group consisting of anionic,

nonionic, ampholytic and zwitterinonic surface active agents. For liquid systems, surfactant is preferably present to the extent of from about 0.1 % to 20% by weight of the composition. For solid (i.e. granular) and viscous semi-solid (i.e. gelatinous, pastes, etc.) systems, surfactant is preferably present to the extent of from about
5 1.5% to 30 % by weight of the composition.

Nonlimiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula
10 $\text{CH}_3(\text{CH}_2)_x(\text{CHOSO}_3^- \text{M}^+) \text{CH}_3$ and $\text{CH}_3(\text{CH}_2)_y(\text{CHOSO}_3^- \text{M}^+) \text{CH}_2\text{CH}_3$ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5
15 ethoxycarboxylates), the C₁₀-18 glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine
20 oxides, and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-
25 (3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are described further herein and are listed in standard texts.

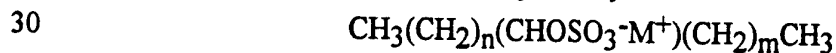
30 Anionic surfactants can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. (Included in the term alkyl is the alkyl portion of higher acyl
35 radicals.) Important examples of the anionic synthetic detergents which can form the surfactant component of the compositions of the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols

(C8-18 carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, (the alkyl radical can be a straight or branched aliphatic chain); sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid ester of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut alcohols) and about 1 to about 10 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to 12 carbon atoms; the reaction products of fatty acids are derived from coconut oil sodium or potassium salts of fatty acid amides of a methyl tauride in which the fatty acids, for example, are derived from coconut oil and sodium or potassium beta-acetoxy- or beta-acetamido-alkanesulfonates where the alkane has from 8 to 22 carbon atoms.

Additionally, secondary alkyl sulfates may be used by the formulator exclusively or in conjunction with other surfactant materials and the following identifies and illustrates the differences between sulfated surfactants and otherwise conventional alkyl sulfate surfactants. Non-limiting examples of such ingredients are as follows.

Conventional primary alkyl sulfates (LAS), such as those illustrated above, have the general formula $ROSO_3-M^+$ wherein R is typically a linear C8-22 hydrocarbyl group and M is a water solublizing cation, for example sodium LAS. Branched chain primary alkyl sulfate surfactants (i.e., branched-chain "PAS") having 8-20 carbon atoms are also know; see, for example, Eur. Pat. Appl. 439,316, Smith et al., filed January 21, 1991.

Conventional secondary alkyl sulfate surfactants are those materials which have the sulfate moiety distributed randomly along the hydrocarbyl "backbone" of the molecule. Such materials may be depicted by the structure



wherein m and n are integers of 2 or greater and the sum of m + n is typically about 9 to 17, and M is a water-solublizing cation.

The aforementioned secondary alkyl sulfates are those prepared by the addition of H_2SO_4 to olefins. A typical synthesis using alpha olefins and sulfuric acid is disclosed in U.S. Pat. No. 3,234,258, Morris, issued February 8, 1966 or in U.S. Pat. No. 5,075,041, Lutz, issued December 24, 1991. The synthesis conducted in solvents which afford the secondary (2,3) alkyl sulfates on cooling, yields products

which, when purified to remove the unreacted materials, randomly sulfated materials, unsulfated by-products such as C10 and higher alcohols, secondary olefin sulfonates, and the like, are typically 90 + % pure mixtures of 2- and 3- sulfated materials (some sodium sulfate may be present) and are white, non tacky, apparently crystalline, solids. Some 2,3-disulfates may also be present, but generally comprise no more than 5 % of the mixture of secondary (2,3) alkyl mono-sulfates. Such materials are available as under the name "DAN", e.g., "DAN 200" from Shell Oil Company.

Bleaching Agents and Bleach Activators - The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches other than the hypohalite (e.g. hypochlorite) bleaches. Perborate (e.g., mono- or tetra-hydrate sodium salts) and percarbonate bleaches can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxypropionic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

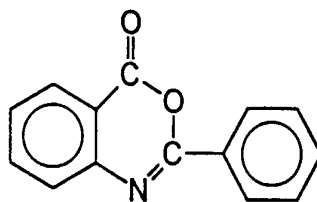
Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

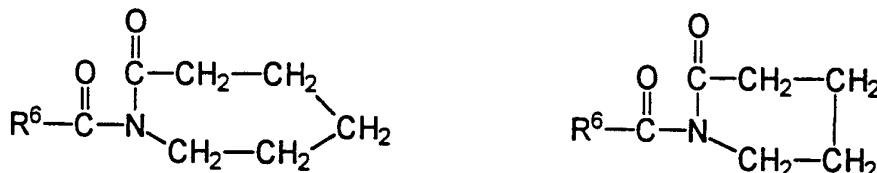
Highly preferred amido-derived bleach activators are those of the formulae:
 $R^1N(R^5)C(O)R^2C(O)L$ or $R^1C(O)N(R^5)R^2C(O)L$
wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R⁶ is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

Buffers - Buffers can be included in the formulations herein for a variety of purposes. One such purpose is to adjust the cleaning surface pH to optimize the hard surface cleaner composition effectiveness relative to a particular type of soil or stain. Buffers may be included to stabilize the adjunct ingredients with respect to extended shelf life or for the purpose of maintaining compatibility between various aesthetic ingredients. The hard surface cleaner of the present invention optionally contains buffers to adjust the pH in a range from about 7 to about 13, preferably from about 8 to about 13, more preferably from about 10 to about 11. Non-limiting examples of such suitable buffers are potassium carbonate, sodium carbonate, and sodium bicarbonate, however, the formulator is not restricted to these examples or combinations thereof.

ADJUNCT MATERIALS

The compositions herein can optionally include one or more other detergent adjunct materials or other materials for assisting or enhancing cleaning performance, treatment of the surface to be cleaned, or to modify the aesthetics of the composition (e.g., perfumes, colorants, dyes, etc.). The following are illustrative examples of such adjunct materials but are not meant to be exclusive or limiting in scope.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions

Inert Salts. The inert salts (filler salts) used in the compositions of the present invention can be any water-soluble inorganic or organic salt or mixtures of such salts which do not destabilize the surfactant. For the purposes of the present invention, "water-soluble" means having a solubility in water of at least 1 gram per 100 grams of water at 20° C. Examples of suitable salts include various alkali metal and/or alkali earth metal sulfate, chlorides, borates, bromides, fluorides, phosphates, carbonates, bicarbonates, citrates, acetates, lactates, etc.

Specific examples of suitable salts include sodium sulfate, sodium chloride, potassium chloride, sodium carbonate, potassium sulfate, lithium chloride, lithium sulfate, tripotassium phosphate, sodium borate, potassium bromide, potassium fluoride, sodium bicarbonate, magnesium sulfate, magnesium chloride, sodium citrate, sodium acetate, magnesium lactate, sodium fluoride. The preferred salts are inorganic salts preferably the alkali metal sulfates and chlorides. Particularly preferred salts, because of their low cost are sodium sulfate and sodium chloride. The salts are present in the compositions at levels of from 0% to 40%, preferably 10% to 20%.

Abrasives. An essential component of many solid or viscous semi-solid hard surface cleaning compositions is the abrasive material added to facilitate the action of scouring. Abrasive scouring cleansers provide a convenient and useful means for carrying out the sanitizing of porcelain and tile surfaces, especially tubs, showers and toilet bowls. The particulate abrasive material within such compositions serves to abrade and loosen soil adhering to hard surfaces and further serves to create more intimate contact between hard surface stain and the surfactant and/or bleaching agents also present in the cleansing compositions.

Abrasive cleaners have traditionally contained water-insoluble, relatively hard, particulate mineral material as the abrasive agent. The most common such abrasive agent is finely divided silica sand having particle size varying between about 1 and 300 microns and specific gravity of about 2.1 or higher. While such material is generally very effective in scouring soil and stains from the surfaces being treated, abrasive material of this type tends to be difficult to rinse away from the toilet bowl, shower or bathtub surface.

In the case where moderate or highly water soluble abrasive material is required (i.e. sodium carbonate) imidodisulfate can be used as the sole abrasive or otherwise added in part.

It has been discovered that abrasive compositions of this desired type can be realized by utilizing a particular type of expanded perlite abrasive in combination with the surfactants, filler material, and other optional scouring material ingredients listed herein. The abrasive materials suitable to the present invention are those contained in U.S. Pat. No. 4,051,056, Hartman, issued September 27, 1977 and included herein by reference.

Perfumes. Perfumes are an important ingredient especially for the liquid composition embodiment. Perfume is usually used at levels of from 0% to 5%. In U.S. Pat. No. 4,246,129, Kacher, issued January 20, 1981 (incorporated herein by reference), certain perfume materials are disclosed which perform the added function

reducing the solubility of anionic sulfonate and sulfate surfactants.

Dyes. Dyes may be include at levels of from about 0.5% to 12%, preferably 1.5% to 5%. Solids and viscous semi-solids can be made with 1.5% dye and no perfume. Examples of suitable dyes are Alizarine Light Blue B (C.I. 63010), Carta Blue VP (C.I. 24401), Acid Green 2G (C.I. 42085), Astrogen Green D (C.I. 42040),
5 Supranol Cyanine 7B (C.I. 42675, Maxilon Blue 3RL (C.I. Basic Blue 80),
Drimarine Blue Z-RL (C.I. Reactive Blue 18), Alizarine Light Blue H-RL (C.I. Acid Blue 182), FD&C Blue No. 1 and FD&C Green No. 3. (See the patents of Kitko, U.S. Pat. No. 4,248,827 issued February 3, 1981 and U. S. Pat. No. 4,200,606,
10 issued April 29, 1980, both incorporated herein by reference.) C.I. refers to Color Index.

Optional Adjuncts Ingredients. As a preferred embodiment, the conventional adjunct ingredients employed herein can be selected from typical components such as enzymes (compatible with the applicable with other adjunct ingredients), especially
15 proteases, lipases, cellulases, color speckles, suds boosters, suds suppressors, anti-tarnish and/or anti-corrosion agents, soil-suspending agents, germicides, alkalinity sources, hydrotropes, anti-oxidants, enzyme stabilizing agents, solvents, clay soil chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents
20 will comprise from about 0.1% to about 3.0% by weight of such composition removal/anti-redeposition agents, polymeric dispersing agents, dye transfer inhibiting agents, including polyamine N-oxides such as polyvinylpyrrolidone and copolymers of N-vinyl imidazole and N-vinyl pyrrolidone, etc.

Example 1

25 Preparation of 1,4-Dimethoxy-2,3-dicyanobenzene

Dimethyl sulfate (15 mL, 0.16 mol) and anhydrous potassium carbonate (24 g, 0.17 mol) are added to a solution of 2,3-dicyanohydroquinone (3.0 g, 0.019 mol) in 100 mL 2-butanone. The reaction mixture is refluxed for 18 hr. under a stream of argon, cooled to room temperature and the resulting solid is collected by filtration.
30 The residue is added to water (100 mL) to dissolve the potassium carbonate and the resulting insoluble material is collected by filtration and dried under vacuum to yield 3.10 g (88%), m.p. 276-280 °C, ¹H NMR (DMSO-d₆) in ppm, δ = 7.63 (s, 2 H), 3.93 (s, 6 H).

Example 2

35 Preparation of octamethoxy phthalocyanine di-lithium salt

Lithium methoxide (6.05 g, 0.16 mol) is added to a solution of 1,4-dimethoxy-2,3-dicyanobenzene (10 g, 0.05 mol) in 100 mL anhydrous methanol.

The reaction mixture is pressurized to approximately 2000-2400 psi with nitrogen gas, heated to 120 °C for 6 hr., cooled to room temperature and vented to atmospheric pressure. The resulting gray/green solid is collected by filtration and dried under vacuum to yield 7.08 g (70%). Q-band λ_{\max} at 714 nm (DMF).

5

Example 3

Preparation of octamethoxy phthalocyanine

p-Toluene sulfonic acid (15.73 g, 91 mmol) is added to a solution of octamethoxy phthalocyanine di-lithium salt (7.0 g, 9.1 mmol) in 100 mL anhydrous DMF at 50 °C. The reaction mixture is stirred at 50 °C 8 hr. under a stream of argon, cooled to approximately 10 °C for 2 hr. and the resulting purple solid is collected by filtration and dried under vacuum to yield 4.91g (71%). Q-band λ_{\max} at 764 nm (DMF).

10

Example 4

Preparation of silicon (IV) octamethoxyphthalocyanine dichloride

Silicon tetrachloride (8 mL, 31.8 mmol) is added to a frozen mixture of octamethoxy phthalocyanine (1.0 g, 0.66 mmol) in 60 mL anhydrous pyridine. The reaction mixture is pressurized to ~2000-2400 psi with nitrogen gas, heated to 180 °C for 24 hr., cooled to room temperature and vented to atmospheric pressure. The product is precipitated by the addition of water and the resulting solid is collected by filtration. The filtrate is dissolved in methanol, precipitated by the addition of 1N hydrochloric acid and collected by filtration. The product is purified by silica gel chromatography using methylene chloride as the elutant. Yield of green product is 0.55 g (49%). Q-band λ_{\max} at 730 nm (DMF).

15

20

Example 5

Preparation of phthalocyanine di-lithium salt

Phthalonitrile (6.4 g, 0.05 mol) is added to 100 mL of refluxing anhydrous butanol containing lithium metal (1.11 g, 0.16 mol). The reaction mixture is refluxed 2 hr. under a stream of argon, cooled to room temperature and the resulting solid is collected by filtration. The blue solid is dried under vacuum to yield 4.26g (65%).

25

30

Example 6

Preparation of phthalocyanine

p-Toluene sulfonic acid (13.14 g 76 mmol) was added to a solution of phthalocyanine di-lithium salt (4.0 g, 7.6 mmol) in 100 mL anhydrous DMF at 50 °C. The reaction mixture is stirred at 50 °C for 8 hr. under stream of argon, cooled to approximately 10 °C and held at that temperature for 2 hr. The resulting blue solid is collect by filtration and dried to yield 2.96 g (76%). Q-band λ_{\max} at 659 and 690 nm (DMF).

35

Example 7Preparation of silicon (IV) phthalocyanine dichloride

Silicon tetrachloride (8 mL, 31.8 mmol) is added to a frozen mixture of phthalocyanine (0.68 g, 1.32 mmol) in 60 mL anhydrous pyridine. The reaction mixture is pressurized to approximately 2000-2400 psi with nitrogen gas, heated to 180 °C for 24 hr., cooled to room temperature and vented to atmospheric pressure. The reaction product is precipitated by the addition of water and collected by filtration. The filtrate is dissolved in methanol, re-precipitated by the addition of 1N hydrochloric acid and collected by filtration. The product is purified by silica gel chromatography using methylene chloride as the elutant. Yield of blue colored product is 0.44 g (55%). Q-band λ_{\max} at 670 nm (DMF).

Example 8Preparation of tetrabromonaphthalocyanine di-lithium salt

Lithium methoxide (6.05 g, 0.16 mol) is added to a solution of 6-bromonaphthalene-2,3-dicarbonitrile (1 g, 4 mmol) in 100 mL anhydrous methanol. The reaction mixture is pressurized with nitrogen gas to approximately 2000-2400 psi, heated to 120 °C for 6 hr., then cooled to room temperature. The precipitate is collected by filtration and dried under vacuum to yield approximately 0.4g (39 %).

Example 9Preparation of tetrabromonaphthalocyanine

p-Toluene sulfonic acid (15.73 g, 91 mmol) is added to a solution of tetrabromonaphthalocyanine di-lithium salt (0.3 g, 0.3 mmol) in 100 mL of anhydrous DMF at 50 °C. The reaction mixture is stirred at 50 °C of 8 hr. under a stream of argon, cooled to approximately at 10 °C and held for 2 hr. after which the precipitated solid is collected by filtration. The solid is dried under vacuum to yield 0.25g (83%). Q-band λ_{\max} at 782 nm (DMF).

Example 10Preparation of tetra-t-butylphthalocyanine di-lithium salt

Lithium methoxide (6.05 g, 0.16 mol) is added to a solution of 4-t-butylphthalonitrile (1 g, 5.4 mmol) in 100 mL of anhydrous methanol. The reaction mixture is pressurized with nitrogen gas to approximately 2000-2400 psi, heated to 120 °C for 6 hr., then cooled to room temperature. The resulting precipitate is collected by filtration and dried under vacuum to yield 0.8 g (79 %).

Example 11Preparation of tetra-t-butylphthalocyanine

p-Toluene sulfonic acid (15.73 g, 91 mmol) is added to a solution of tetra-t-butylphthalocyanine di-lithium salt (0.5 g, 0.6 mmol) in 100 mL of anhydrous DMF

at 50 °C. The reaction mixture is stirred at 50 °C 8 hr. under a stream of argon, cooled to approximately at 10 °C and held for 2 hr. after which the precipitated solid is collected by filtration. The solid is dried under vacuum to yield 0.35g (70%). Q-band λ_{max} at 680 nm (DMF).

5

Example 12

Preparation of 1,4-Dipropoxy-2,3-dicyanobenzene

Propyl iodide (15 mL, 0.16 mol) and anhydrous potassium carbonate (24 g, 0.17 mol) are combined with to a solution of 2,3-dicyanohydroquinone (3.0 g, 0.019 mol) in 100 mL of 2-butanone. The reaction mixture is refluxed for 18 hr. under a stream of argon, cooled to room temperature and the solid collected by filtration. The residue is then added to water (100 mL) to dissolve the potassium carbonate and the resulting solid is collected by filtration and dried under vacuum to yield 3.4 g (74%).

10

Example 13

Preparation of tetrapropoxyphthalocyanine di lithium salt

Tetrapropoxyphthalocyanine di lithium salt is prepared in the manner described above in Example 2 where 1,4-dipropoxy-2,3-dicyanobenzene is substituted for 1,4-dimethoxy-2,3-dicyanobenzene as the starting material. A yield 52% is typically obtained.

15

20

Example 14

Preparation of tetrapropoxyphthalocyanine.

Tetrapropoxyphthalocyanine was prepared in the manner described above in Example 3 where tetrapropoxyphthalocyanine di lithium salt is substituted for tetramethoxyphthalocyanine as the starting material. A yield of 73 % is typically obtained. Q-band λ_{max} at 760 nm.

25

Example 15

Preparation of silicon (IV) phthalocyanine di-(PEG 350 mono-methyl ether)

Silicon (IV) phthalocyanine dichloride (2 g of an 85% sample, 2.78 mmol) is added to a refluxing solution of 40 g of PEG 350 mono-methyl ether in 100 mL of anhydrous DMF. Refluxing is continued for 48 hr. under argon blanketing, then the reaction mixture is cooled to room temperature and the DMF removed under reduced pressure. The resulting 44.21g of blue oil comprised 7.78% of the desired material. Q-band λ_{max} at 682 nm (water).

30

35

Example 16

Preparation of silicon(IV) phthalocyanine di-propoxide

Silicon (IV) phthalocyanine dichloride (0.20 g of 85% active, 0.278 mmol) is added to refluxing anhydrous n-propanol (25 mL). Refluxing is continued for an additional 48 hr. under argon blanketing, the reaction mixture is then cooled to room temperature and the solvent removed to afford 0.25 g of a blue solid. Q-band λ_{\max} at 672 nm (DMF).

Example 17

Preparation of silicon (IV) phthalocyanine

di-(p-phenol sulfonate, sodium salt)

Silicon (IV) phthalocyanine dichloride (0.02 g of 85% active, 0.278 mmol) is added to a refluxing solution of anhydrous di-sodium phenol sulfonate (0.12 g, 0.56 mmol) in 100 mL of anhydrous DMF. Refluxing is continued for an additional 96 hr. under argon blanketing, then the reaction is cooled to room temperature and the DMF is removed under reduced pressure. Yield of blue solid is 0.31 g. Q-band λ_{\max} at 674 nm (DMF).

15

Example 18

Preparation of silicon (IV) octanemethoxyphthalocyanine

di-(PEG 350 mono-methyl ether)

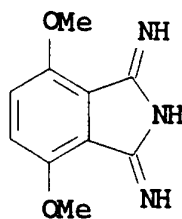
The procedure as described in Example 15 is used with 2.0 gm of silicon (IV) octamethoxyphthalocyanine dichloride as the starting material. The resultant green oil comprised 6% of the desired product. Q-band λ_{\max} at 736 nm (DMF).

20

Example 19

Preparation of 1,3-di-methoxy-3,6-di-iminoisoindoline

from 1,4-di-methoxy-2,3-di-cyanobenzene



25

Anhydrous ammonia is bubbled into a solution comprising 1,4-di-methoxy-2,3-di-cyanobenzene (10 g, 53.2 mmol), sodium methoxide (85 mg, 1.6 mmol) and 25 mL of anhydrous methanol for 30 minutes at room temperature. The reaction mixture is then brought to reflux for 3.5 hr. with the continued addition of ammonia then cooled to room temperature and the product collected by filtration. Yield is 4.68 g (43%).

30

Example 20

Preparation of octamethoxy silicon (IV) phthalocyanine dichloride
from 1,3-di-methoxy-3,6-di-iminoisoindoline

Silicon tetrachloride (3.59 g, 21.1 mmol) is added to a solution of 1,3-di-methoxy-3,6-diiminoisoindoline (3 g, 14.6 mmol) in 25 mL of anhydrous quinoline at room temperature. The reaction mixture is then slowly brought to reflux over a period of 1.5 hr. then maintained at reflux another half hour. The reaction mixture is subsequently cooled to 100 °C and the crude product removed by filtration. The product is purified by silica gel chromatography with methylene chloride as elutant. Yield of green solid is 1.71 g (55%).

10

Example 21

Preparation of octamethoxy silicon (IV) phthalocyanine dichloride
from octamethoxy phthalocyanine di-lithium salt

Silicon tetrachloride (2.22 g, 13.0 mmol) is added to a solution of octamethoxy phthalocyanine di-lithium salt (1 g, 1.3 mmol) in 50 mL of anhydrous nitrobenzene. The reaction mixture is pressurized with nitrogen gas to approximately 2000-2400 psi, heated to 120 °C for 24 hr. The crude product is precipitated by the addition of 400 mL of anhydrous diethyl ether and the resulting solid is collected by filtration. Purification by silica gel chromatography using methylene chloride as elutant affords 0.57 g of a green solid (51%).

15

20

Example 22

Preparation of silicon (IV) tetra-t-butylphthalocyanine dichloride

The procedure as described in Example 20 is used with 0.5 g of tetra-t-butylphthalocyanine di-lithium salt (as prepared in example 10) as the starting material. A 50% yield of the desired product is obtained. Q-band λ_{\max} at 700 nm (DMF).

25

Example 23

Preparation of silicon (IV) tetra-t-butylphthalocyanine dipropoxide

The procedure as described in Example 16 is used with 0.2 g of silicon (IV) tetra-t-butylphthalocyanine (as in Example 22) as starting material. An 80% yield of the desired product is obtained. Q-band λ_{\max} at 690 nm (propanol).

30

Example 24

Preparation of 1,2-di-cyano-4,5-di-chloro-3,6-hydroquinone
from 1,2-di-cyano-4,5-di-chloro-3,6-benzenequinone

Sodium bisulfite (34.4 g, 0.33 mol) is added to a solution of 1,2-di-cyano-4,5-di-chloro-3,6-benzenquinone (25 g, 0.11 mol) in 300 mL of water. The reaction mixture is stirred at room temperature for 3 hr. The product is collected by filtration and dried to yield 23.01 g (91.3%).

35

Example 25Preparation of 1,2-di-cyano-4,5-di-chloro-3,6-di-methoxybenzene
from 1,2-di-cyano-4,5-di-chloro-3,6-hydroquinone

The procedure as described in example 1 above is used to provide a yield of
5 85% of the desired material.

Example 26Preparation of Octachloro-octamethoxyphthalocyanine di lithium salt
from 1,2-di-cyano-4,5-di-chloro-3,6-di-methoxybenzene

1,2-dicyano-4,5-dichloro-3,6-dimethoxybenzene (6.0g , 23.3 mmol) is added
10 to a refluxing solution of lithium metal (0.65 g, 93.4 mmol) in 75 mL of anhydrous
methanol. The reaction mixture is refluxed for 24 hr under argon blanketing and
cooled to room temperature. The resulting green solid is collected by filtration to
afford 3.98 g (66%). Q-band λ_{\max} at 692 (DMF).

Example 27

15 Preparation of silicon (IV) octachloro-octamethoxy
phthalocyanine dichloride

The procedure as described in Example 20 is used with 1 g of octachloro-
octamethoxyphthalocyanine di lithium salt as the starting material. A yield of 63% of
the desired product is obtained. Q-band λ_{\max} at 730 nm (DMF).

20

Example 28Bromination of silicon (IV) naphthalocyanine dichloride

N-bromosuccinimide (0.559 g, 3.1 mmol) is added in 3 equal portions over 8
hour intervals to a solution of silicon (IV) naphthalocyanine dichloride (0.25 g, 0.26
mmol) in 100 mL of anhydrous DMF at 70 °C. The reaction mixture is then stirred
25 at 70 °C for 48 hr. under a stream of argon, cooled to room temperature and the
solvent removed under reduced pressure. The residue that is obtained is stirred in
100 mL of anhydrous methanol for 18 hr. at room temperature. The product is
collected by filtration and dried to yield 0.189 g (77%). Elemental analysis confirms
the addition of 1.2 equivalents of bromine.

30

Example 29Preparation of silicon (IV) bromonaphthalocyanine
di-(PEG 2000 monomethyl ether)

The procedure as described in Example 15 is used with 0.1 g of the
brominated silicon (IV) naphthalocyanine dichloride (as in example 27) as starting
35 material and PEG 2000 mono methyl ether. The resultant green solid comprised
approximately 0.03% of the desired material. Q-band λ_{\max} at 780 nm (DMF).

Example 30

Preparation of silicon (IV) tetrabromonaphthalocyanine dichloride

The procedure as described in Example 20 is used with 0.2 g of tetrabromonaphthalocyanine di lithium salt as starting material. A 40% yield is obtained of the desired product. Q-band λ_{\max} at 790 nm (DMF).

5

Example 31

Preparation of silicon (IV) tetrabromonaphthalocyanine di-(PEG 2000 monomethyl ether)

The procedure as described in Example 15 is used with 0.1 g of silicon (IV) tetrabromonaphthalocyanine dichloride (as in Example 28) and PEG 2000 monomethyl ether in place of PEG 350 as in the earlier examples. The resultant green solid contained approximately 0.03% of the desired material. Q-band λ_{\max} at 780 nm (DMF).

10

Example 32

Preparation of octamethoxy silicon (IV) phthalocyanine dihydroxide

Octamethoxy silicon (IV) phthalocyanine dichloride (0.2 g, 0.26 μmol) is added to a refluxing solution of sodium methoxide (0.8 g, 0.15 μmole) in 15 mL of 95:5 ethanol/water. The reaction mixture is refluxed for 4 hours and cooled to room temperature. The resulting blue green precipitate is collected by filtration to afford 0.174 g (92%). Q-band λ_{\max} at 734 nm (DMF).

15

20

Example 33

Preparation of Glycerol-di-(Triethylene glycol methyl ether)

To a suspension of sodium hydride (20.4 g, 0.85 moles) in anhydrous dioxane (500mL) at cooled to about 10° C under stream of argon is added triethylene glycol mono-methyl ether (131.4 g, 0.80 moles) over a period of about 1 hour. The mixture is allowed to warm to room temperature and is subsequently refluxed for 1 hour. After warming to room temperature epichlorohydrin (37.0 g, 0.40 moles) is added. The solution is heated over a period of 2 hours until reflux temperature and then refluxing is continued for an additional 48 hours. After cooling, the solvent is removed *in vacuo*. The resulting solid is slurried in ether (500 mL), cooled to about 10° C and then 10% HCl (75 mL) is added over about 0.5 hour. The aqueous layer is decanted and the organic phase extracted with two additional portions of acid. The three aqueous extracts are combined, saturated with NaCl and extracted x 4 with 50 mL portions of chloroform. The combined chloroform extracts are dried (MgSO₄) and concentrated to yield 97.17 g of a brown oil. The product is used without further purification.

25

30

35

Example 34

Preparation of Glycerol-di-(Diethylene glycol methyl ether)

To a suspension of sodium hydride (20.4 g, 0.85 moles) in anhydrous dioxane (500mL) at cooled to about 10° C under stream of argon is added diethylene glycol mono-methyl ether (96.12 g, 0.80 moles) over a period of about 1 hour. The mixture is allowed to warm to room temperature and is subsequently refluxed for 1 hour.

5 After warming to room temperature epichlorohydrin (37.0 g, 0.40 moles) is added. The solution is heated over a period of 2 hours until reflux temperature and then refluxing is continued for an additional 48 hours. After cooling, the solvent is removed *in vacuo*. The resulting solid is slurried in ether (500 mL), cooled to about 10° C and then 10% HCl (75 mL) is added over about 0.5 hour. The aqueous layer

10 is decanted and the organic phase extracted with two additional portions of acid. The three aqueous extracts are combined, saturated with NaCl and extracted x 4 with 50 mL portions of chloroform. The combined chloroform extracts are dried (MgSO₄) and concentrated to yield 79.79g of a brown oil. The product is used without further purification.

15

Example 35

Preparation of Glycerol-di-(Ethylene glycol methyl ether)

To a suspension of sodium hydride (20.4 g, 0.85 moles) in anhydrous dioxane (500mL) at cooled to about 10° C under stream of argon is added ethylene glycol mono-methyl ether (60.92 g, 0.80 moles) over a period of about 1 hour. The mixture

20 is allowed to warm to room temperature and is subsequently refluxed for 1 hour. After warming to room temperature epichlorohydrin (37.0 g, 0.40 moles) is added. The solution is heated over a period of 2 hours until reflux temperature and then refluxing is continued for an additional 48 hours. After cooling, the solvent is removed *in vacuo*. The resulting solid is slurried in ether (500 mL), cooled to about

25 10° C and then 10% HCl (75 mL) is added over about 0.5 hour. The aqueous layer is decanted and the organic phase extracted with two additional portions of acid. The three aqueous extracts are combined, saturated with NaCl and extracted x 4 with 50 mL portions of chloroform. The combined chloroform extracts are dried (MgSO₄) and concentrated to yield 59.90 g of a brown oil. The product is used

30 without further purification.

Example 36

Preparation of Silicon(VI)phthalocyanine-di-IsoPEG 384

A mixture of silicon(VI)phthalocyanine di-hydroxide (1 g, 1.73 mmoles), glycerol-di-(triethylene glycol methyl ether) (20g, 52mmoles) (prepared in

35 accordance with Example 33) and xylenes (175ml) is slowly heated to reflux over a period of two hours. Once refluxing temperature is achieved, the solution is refluxed an additional 48 hours under a blanket of argon to azeotropically remove the water

formed. The solution is cooled to room temperature and the solvent removed under reduced pressure to yield 21.15 g of a blue oil resulted. Q-band λ_{\max} at 674 nm (water).

Example 37

5 Preparation of Silicon(VI)naphthalocyanine-di-IsoPEG 384

A mixture of silicon(VI)naphthalocyanine di-hydroxide (1 g, 1.29 mmoles), glycerol-di-(triethylene glycol methyl ether) (15 g, 38.72 mmoles) (prepared in accordance with Example 33) and xylenes (175ml) is slowly heated to reflux over a period of two hours. Once refluxing temperature is achieved, the solution is refluxed
10 an additional 48 hours under a blanket of argon to azeotropically remove the water formed. The solution is cooled to room temperature and the solvent removed under reduced pressure to yield 16.07 g of a green oil resulted. Q-band λ_{\max} at 788 nm (water, 1% Triton X-100).

The cleaning compositions provided in accordance with this invention may be
15 in the form of granules, liquids, bars, and the like, and typically are formulated to provide an in-use pH in the range of 9 to 11, however in the case of non-aqueous or low aqueous compositions the pH ranges may vary outside this range. Various carriers such as sodium sulfate, water, water-ethanol, BPP, MPP, EPP, PPP, sodium carbonate, and the like, may be used routinely to formulate the finished products.
20 Granules may be produced by spray-drying or by agglomeration, using known techniques, to provide products in the density range of 350-950 g/l. Bars may be formulated using conventional extrusion techniques. The photobleach-chelant may be pre-formed, if desired. The compositions may also contain conventional perfumes, bactericides, hydrotropes and the like. In the case of non-aqueous or low
25 aqueous compositions, the cleaning compositions may be applied to an article which is used to deliver the compositions of the present invention to a fabric or to a hard surface. Non-limiting examples of compositions according to this invention are as follows:

Ingredients	weight %			
	38	39	40	41
Sodium LAS	15	30	20	25
NEODOL	1	1	1	1
Alkyl Dimethyl				
Ammonium Chloride	0.5	1	0.5	0.7
Sodium Tripolyphosphate	15	35	22	28
Sodium Carbonate	10	10	15	15
SOKALAN	2	2	2	2
Carboxymethyl Cellulose	1	1	1	1
Tinopal CBS-X	0.1	0.1	0.1	0.1
Soil Release Agent ¹	0.2	0.2	0.3	0.3
Savinase 6.0T	0.3	0.6	0.5	0.6
BAN 300T	0.2	0.5	0.5	0.6
Lipolase 100T	0.1	0.2	0.2	0.3
CAREZYME 5T	0.1	0.2	0.2	0.3
Sodium Perborate	--	--	3.0	5.0
NOBS	--	--	2.0	3.0
Photobleach ²	0.005	0.01	--	--
Photobleach ³	--	--	0.008	0.01
Moisture+Sodium Sulfate+Perfume + Miscellaneous	Balance	Balance	Balance	Balance

1. Soil Release Agent according to U.S. Patent 5,415,807 Gosselinck et al., issued May 16, 1995.

- 5 2. Photobleach according to Example 36.
3. Photobleach according to Example 37.

Granular laundry detergents

Ingredients	Weight %		
	42	43	44
Zeolite	38	35	30
Silicate 2.0R	6	4	7
Carbonate (sodium)	9	10	4
Ethylene diamine tetramethylenphosphonate	0.2	0.1	0.3

Brightener 47	0.1	0.15	0.1
Brightener 49	0.05	-	0.05
Percarbonate	8	5	10
NOBS	--	--	3
TAED	7	-	-
Savinase (4.0 KNPU/g)	2	1.5	2
Lipolase (100 000 LU/g)	0.2	0.5	0.5
C12-C14 alkyl Sulphate	6	6	8
C12-C14 AE4.2 nonionic	11	12	10
Soap	1	-	-
Photobleach ¹	0.01	-	-
Photobleach ²	-	0.1	-
Photobleach ³	-	-	0.1
Miscellaneous/Moisture			
Balance	100	100	100

1. Photobleach according to Example 15.
2. Photobleach according to Example 36.
3. Photobleach according to Example 31.

5

Example 45Granular Laundry Detergent

<u>Ingredients</u>	<u>Weight %</u>
Anionic alkyl sulfate	7
Nonionic surfactant	5
Zeolite	10
Trisodium citrate	2
SKS-6 silicate builder	10
Acrylate/maleate copolymer	4
Sodium percarbonate	25
Sodium carbonate	5
Ethylenediamine disuccinate	0.4
Suds suppressor	2
Enzymes	1.5
Photobleach ¹	0.01
Miscellaneous/Moisture	
Balance	100

1. Photobleach according to Example 31.

The above embodiment may be allowed to fully dry prior to exposure. After exposure, reactivation with a solution produces more desirable properties.

Example 46

5

Laundry bar composition

<u>Ingredients</u>	<u>Weight %</u>
C ₁₂ Linear alkyl benzene sulphonate	30
Phosphate (as sodium tripolyphosphate)	7
Sodium carbonate	15
Sodium pyrophosphate	7
Coconut monoethanolamide	2
Zeolite A	5
Carboxymethylcellulose	0.2
Polyacrylate (m.w. 1400)	0.2
Sodium percarbonate	15
Protease	0.3
CaSO ₄	1
MgSO ₄	1
Photobleach ¹	0.01
Miscellaneous/Moisture	
Balance	100

1. Photobleach according to Example 36.

EXAMPLE 47

Low aqueous cleaning composition

<u>Ingredients</u>	<u>% (wt.) Formula Range</u>
Photobleach ¹	0.005-1.5
BPP ²	5-25
1,2-octanediol	0.1-7.0
MgAE ₁ S	0.01- 0.8
MgAE _{6,5} S	0.01-0.8
C ₁₂ Dimethyl Amine Oxide	0.01-0.8
PEMULEN ³	0.05-0.20
perfume	0.01-1.5
water	balance

pH range from about 6 to about 8

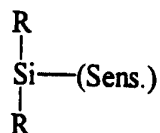
- 10 1. Photobleach according to Example 36.

2. Other co-solvents which can be used herein together with the BPP, MPP, EPP and PPP primary solvents include various glycol ethers, including materials marketed under trademarks such as Carbitol, methyl Carbitol, butyl Carbitol, propyl Carbitol, hexyl Cellosolve, and the like. If desired, and having due regard
5 for safety and odor for in-home use, various conventional chlorinated and hydrocarbon dry cleaning solvents may also be used. Included among these are 1,2-dichloroethane, trichloroethylene, isoparaffins, and mixtures thereof.
3. As disclosed in U.S. Patents 4,758,641 and 5,004,557, such polyacrylates include
10 homopolymers which may be crosslinked to varying degrees, as well as non-crosslinked. Preferred herein are homopolymers having a molecular weight in the range of from about 100,000 to about 10,000,000, preferably 2000,000 to 5,000,000.

15 Fabrics are laundered using the foregoing compositions, typically at usage concentrations of from about 10 ppm to about 10,000 ppm. The fabrics are dried in the presence of light, preferably natural sunlight, to achieve improved photobleaching benefits.

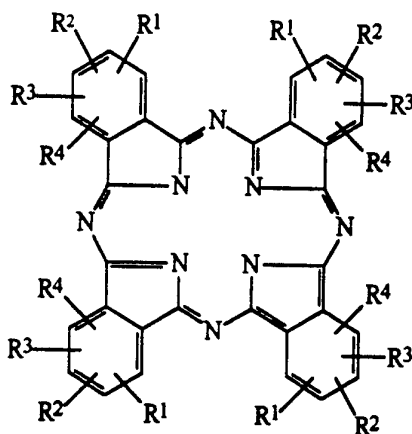
63

1. An organosilicon(IV) photosensitizing compound having a Q-band maximum absorption wavelength of 660 nanometers or greater of the formula

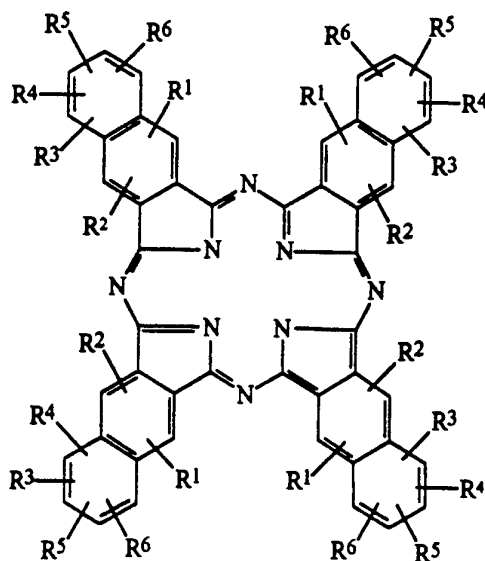


said compound comprising:

- a) photosensitizing (Sens.) units comprising:
phthalocyanines of the formula



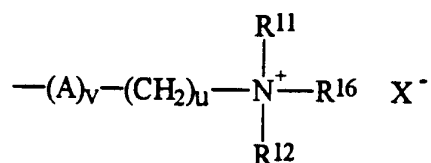
and naphthalocyanines of the formula



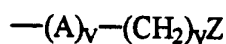
wherein R¹, R², R³, R⁴, R⁵, and R⁶ units are each independently selected from the group consisting of hydrogen, C₁-C₂₂ alkoxy,

chlorine, bromine, iodine, and mixtures thereof; preferably for phthalocyanin R¹, R², R³, and R⁴ units are methoxy, preferably for naphthalocyanin R¹, R², R³, R⁴, R⁵, and R⁶ units are chlorine, bromine, iodine, and mixtures thereof; and

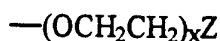
- b) axial R units wherein each R is independently selected from the group consisting of hydrogen, halogen, hydroxy, cyano, nitrilo, oximino, C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, all of which can be substituted with halogen; polyhydroxyl substituted C₃-C₂₂ alkylene, C₃-C₂₂ glycol, C₁-C₂₂ alkoxy, C₄-C₂₂ branched alkoxy, arylene, substituted arylene, alkylarylene, aryloxy, alkoxyarylene, aryloxyalkylene, C₁-C₂₂ thioalkyl, C₄-C₂₂ branched thioalkyl, an alkyleneamino unit of the formula



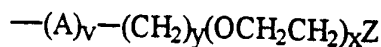
wherein R¹¹, and R¹² are each a C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, R¹⁶ is hydrogen, C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene and mixtures thereof, A is nitrogen or oxygen, X is chloride, bromide, iodide, or other water soluble anion, v is 0 or 1, u is from 0 to 22; -NR¹¹R¹² wherein R¹¹ and R¹² units are the same as defined above, and mixtures thereof; substituted alkylene of the formula



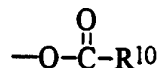
wherein Z is hydrogen, hydroxyl, -CO₂H, -SO₃⁻M⁺, -OSO₃⁻M⁺, C₁-C₆ alkoxy, arylene, substituted arylene, aryloxy, substituted aryloxy, alkyleneamino; A is nitrogen or oxygen, v is 1 or 0, y is from 0 to 22, M is a water soluble cation; an ethyleneoxy unit of the formula



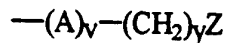
wherein Z is the same as above, x is from 1 to 100; an alkylethyleneoxy unit of the formula



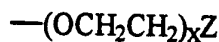
wherein A, Z and v are the same as above, x is from 1 to 100 and y is from 0 to 12; carboxylate of the formula



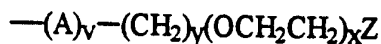
wherein R¹⁰ is C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, all of which can be substituted with halogen; poly-hydroxyl substituted C₃-C₂₂ alkylene, C₃-C₂₂ glycol, C₁-C₂₂ alkoxy, C₄-C₂₂ branched alkoxy, arylene, substituted arylene, alkylarylene, aryloxy, alkoxyarylene, aryloxyalkylene, an alkyleneamino, and mixtures thereof; substituted siloxy of the formula -OSiR⁷R⁸R⁹ wherein each R⁷, R⁸, and R⁹ is independently selected from the group consisting of C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, arylene, substituted arylene, aryloxy, substituted aryloxy, substituted alkylene of the formula



an ethyleneoxy unit of the formula

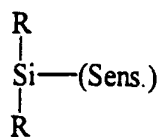


and an alkylethyleneoxy unit of the formula



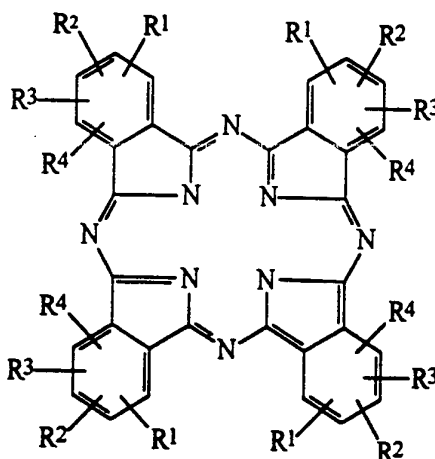
and mixtures thereof, wherein A, v, x, y and Z are the same as above.

2. A laundry or cleaning composition comprising:
 - a) at least about 0.01% of detergent surfactant;
 - b) at least 0.001 ppm of an organosilicon(IV) photosensitizing compound having a Q-band maximum absorption wavelength of 660 nanometers or greater of the formula

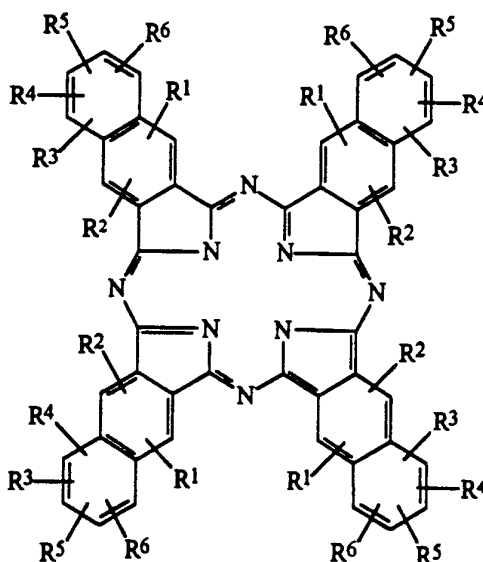


said compound comprising:

- i) photosensitizing (Sens.) units selected from the group consisting of phthalocyanines of the formula:

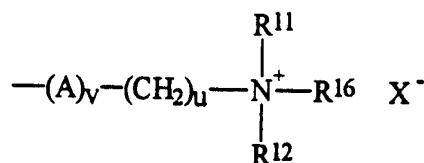


and naphthalocyanines of the formula:

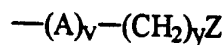


wherein R^1 , R^2 , R^3 , R^4 , R^5 , and R^6 units are each independently selected from the group consisting of hydrogen, halogen, hydroxy, cyano, nitrilo, oximino, C_1 - C_{22} alkylene, C_4 - C_{22} branched alkylene, C_1 - C_{22} alkenylene, C_4 - C_{22} branched alkenylene, all of which can be substituted with

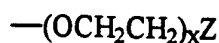
halogen; polyhydroxyl substituted C₃-C₂₂ alkylene, C₁-C₂₂ alkoxy, C₄-C₂₂ branched alkoxy, arylene, substituted arylene, alkylarylene, aryloxy, alkoxyarylene, aryloxyalkylene, C₁-C₂₂ thioalkyl, C₄-C₂₂ branched thioalkyl; an ester of the formula -CO₂R¹⁰ wherein R¹⁰ is C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, all of which can be substituted with halogen, poly-hydroxyl substituted C₃-C₂₂ alkylene, C₃-C₂₂ glycol, C₁-C₂₂ alkoxy, C₄-C₂₂ branched alkoxy, arylene, substituted arylene, alkylarylene, aryloxy, alkoxyarylene, aryloxyalkylene; an alkyleneamino unit of the formula



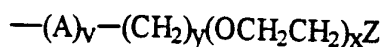
wherein R¹¹, and R¹² are each a C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, R¹⁶ is hydrogen, C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene and mixtures thereof, A is nitrogen or oxygen, X is chloride, bromide, iodide, or other water soluble anion, v is 0 or 1, u is from 0 to 22; -NR¹¹R¹² wherein R¹¹ and R¹² units are the same as defined above, and mixtures thereof; substituted alkylene of the formula



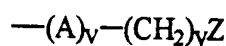
wherein Z is hydrogen, hydroxyl, -CO₂H, -SO₃⁻M⁺, -OSO₃⁻M⁺, C₁-C₆ alkoxy, arylene, substituted arylene, aryloxy, substituted aryloxy, alkyleneamino, and mixtures thereof; A is nitrogen or oxygen, v is 0 or 1, y is from 0 to 22; an ethyleneoxy unit of the formula



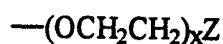
wherein Z is the same as above, x is from 1 to 100; an alkylethyleneoxy unit of the formula



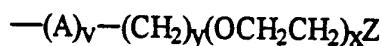
wherein A, Z and v are the same as above, x is from 1 to 100, y is from 1 to 12; substituted siloxy of the formula $-OSiR^7R^8R^9$ wherein each R^7 , R^8 , and R^9 is independently selected from the group consisting of C_1 - C_{22} alkylene, C_4 - C_{22} branched alkylene, C_1 - C_{22} alkenylene, C_4 - C_{22} branched alkenylene, arylene, substituted arylene, aryloxy, substituted aryloxy; substituted alkylene unit of the formula



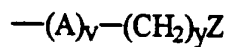
and an ethyleneoxy unit of the formula



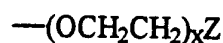
an alkylethyleneoxy unit of the formula



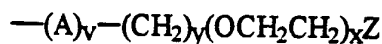
and mixtures thereof; wherein A, v, x, y and Z are the same as above; preferably R^1 , R^2 , R^3 , R^4 , R^5 , and R^6 units independently selected from the group consisting of hydrogen, hydroxyl, halogen, C_1 - C_{22} thioalkyl, C_4 - C_{22} branched thioalkyl, C_1 - C_{22} alkoxy, C_1 - C_{22} branched alkoxy, aryloxy, substituted alkylene of the formula



and ethyleneoxy of the formula

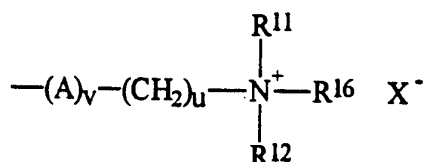


an alkylethyleneoxy unit of the formula

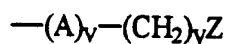


and mixtures thereof; wherein A, v, x, y and Z are the same as above; more preferably halogen or C_1 - C_6 alkoxy, most preferably for phthalocyanins R^1 , R^2 , R^3 , and R^4 units are methoxy, most preferably for naphthyloxy R^1 , R^2 , R^3 ,

- R⁴, R⁵, and R⁶ units are chlorine, bromine, iodine and mixtures thereof; and
- ii) axial R units wherein each R is independently selected from the group consisting of hydrogen, halogen, hydroxy, cyano, nitrilo, oximino, C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, all of which can be substituted with halogen; polyhydroxyl substituted C₃-C₂₂ alkylene, C₃-C₂₂ glycol, C₁-C₂₂ alkoxy, C₄-C₂₂ branched alkoxy, arylene, substituted arylene, alkylarylene, aryloxy, alkoxyarylene, aryloxyalkylene, C₁-C₂₂ thioalkyl, C₄-C₂₂ branched thioalkyl, an alkyleneamino unit of the formula



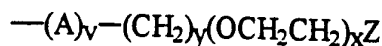
wherein R¹¹, and R¹² are each a C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, R¹⁶ is hydrogen, C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene and mixtures thereof, A is nitrogen or oxygen, X is chloride, bromide, iodide, or other water soluble anion, v is 0 or 1, u is from 0 to 22; -NR¹¹R¹² wherein R¹¹ and R¹² units are the same as defined above, and mixtures thereof; substituted alkylene of the formula



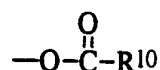
wherein Z is hydrogen, hydroxyl, -CO₂H, -SO₃⁻M⁺, -OSO₃⁻M⁺, C₁-C₆ alkoxy, arylene, substituted arylene, aryloxy, substituted aryloxy, alkyleneamino; A is nitrogen or oxygen, v is 0 or 1, y is from 0 to 22, M is a water soluble cation; an ethyleneoxy unit of the formula



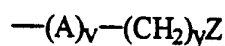
wherein Z is the same as above, x is from 1 to 100; an alkylethyleneoxy unit of the formula



wherein A, v and Z are the same as above, x is from 1 to 100 and y is from 0 to 12; carboxylate of the formula



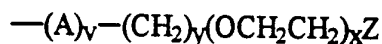
wherein R¹⁰ is C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, all of which can be substituted with halogen; poly-hydroxyl substituted C₃-C₂₂ alkylene, C₃-C₂₂ glycol, C₁-C₂₂ alkoxy, C₄-C₂₂ branched alkoxy, arylene, substituted arylene, alkylarylene, aryloxy, alkoxyarylene, aryloxyalkylene, an alkyleneamino, and mixtures thereof; substituted siloxy of the formula -OSiR⁷R⁸R⁹ wherein each R⁷, R⁸, and R⁹ is independently selected from the group consisting of C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, arylene, substituted arylene, aryloxy, substituted aryloxy, substituted alkylene of the formula



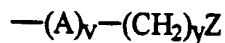
an ethyleneoxy unit of the formula



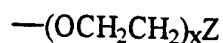
and an alkylethyleneoxy unit of the formula



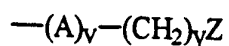
and mixtures thereof; wherein A, v, x, y and Z are the same as above; preferably R units are substituted alkylene of the formula



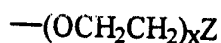
ethyleneoxy of the formula



substituted siloxy of the formula $-\text{OSiR}^7\text{R}^8\text{R}^9$ wherein each R^7 , R^8 , and R^9 is independently selected from the group consisting of C_1 - C_{22} alkylene, C_4 - C_{22} branched alkylene, arylene, substituted arylene, aryloxy, substituted aryloxy, substituted alkylene of the formula



ethyleneoxy of the formula

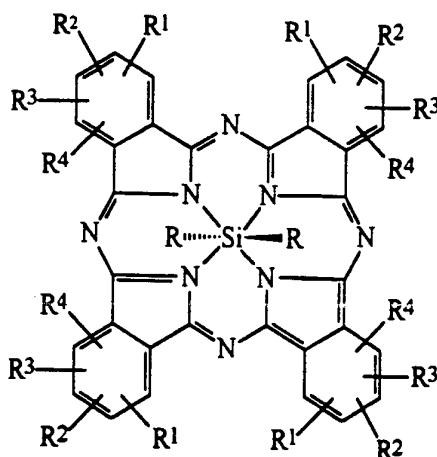


and mixtures thereof. and

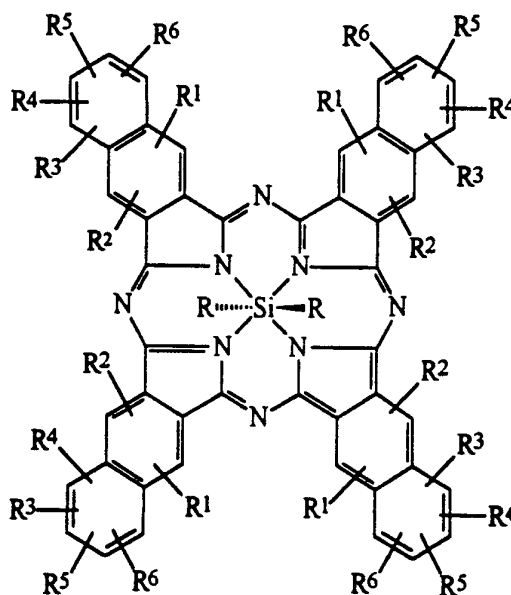
- c) the balance adjunct ingredients.
3. A composition according to Claim 2 wherein the deterative surfactant is a member selected from the group consisting of anionic, cationic, nonionic, ampholytic, and zwitterionic surfactants, and mixtures thereof.
 4. A composition according to Claims 2 and 3 wherein the deterative surfactant is a member selected from the group consisting of anionic, cationic, nonionic, ampholytic, and zwitterionic surfactants, and mixtures thereof.
 5. A composition according to Claims 2 - 4 wherein the adjunct ingredients are members selected from the group consisting of buffers, builders, chelants, filler salts, soil release agents, dispersants, enzymes, enzyme boosters, perfumes, thickeners, abrasives, solvents, clays, bleaches, and mixtures thereof.
 6. A composition according to Claims 2 - 5 comprising from 0.005 to 2000 ppm, preferably from 0.1 to 1000 ppm organosilicon photo-sensitizing compound.
 7. A composition according to Claims 2 - 6 comprising from 0.1 to 95 % by weight, preferably from 0.1 to 30 % by weight, deterative surfactant.

8. A silicon(IV) phthalocyanine or silicon(IV) naphthalocyanine photobleaching composition comprising:

a) a silicon(IV) phthalocyanine of the formula

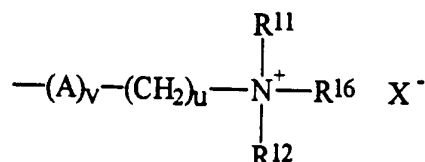


or a silicon(IV) naphthalocyanine of the formula

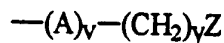


wherein R^1 , R^2 , R^3 , R^4 , R^5 , and R^6 units are moieties that provide a positive red shift value of at least 1, preferably at least 10, more preferably at least 30, when said moieties are substituted for hydrogen; axial R units wherein each R is independently selected from the group consisting of hydrogen, halogen, hydroxy, cyano, nitrilo, oximino, C_1 - C_{22} alkylene, C_4 - C_{22} branched alkylene, C_1 - C_{22} alkenylene, C_4 - C_{22} branched alkenylene, all of which can be substituted with halogen; polyhydroxyl substituted C_3 - C_{22} alkylene,

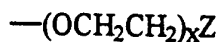
C₃-C₂₂ glycol, C₁-C₂₂ alkoxy, C₄-C₂₂ branched alkoxy, arylene, substituted arylene, alkylarylene, aryloxy, alkoxyarylene, aryloxyalkylene, C₁-C₂₂ thioalkyl, C₄-C₂₂ branched thioalkyl, an alkyleneamino unit of the formula



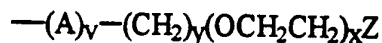
wherein R¹¹, and R¹² are each a C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, R¹⁶ is hydrogen, C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene and mixtures thereof, A is nitrogen or oxygen, X is chloride, bromide, iodide, or other water soluble anion, v is 0 or 1, u is from 0 to 22; -NR¹¹R¹² wherein R¹¹ and R¹² units are the same as defined above, and mixtures thereof, substituted alkylene of the formula



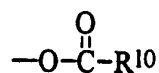
wherein Z is hydrogen, hydroxyl, -CO₂H, -SO₃^{-M+}, -OSO₃^{-M+}, C₁-C₆ alkoxy, arylene, substituted arylene, aryloxy, substituted aryloxy, alkyleneamino; A is nitrogen or oxygen, v is 0 or 1, y is from 0 to 22, M is a water soluble cation; an ethyleneoxy unit of the formula



wherein Z is the same as above, x is from 1 to 100; an alkylethyleneoxy unit of the formula

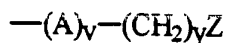


wherein A, v and Z are the same as above, x is from 1 to 100 and y is from 0 to 12; carboxylate of the formula



wherein R¹⁰ is C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, all of which can be

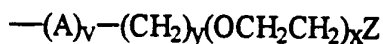
substituted with halogen; poly-hydroxyl substituted C₃-C₂₂ alkylene, C₃-C₂₂ glycol, C₁-C₂₂ alkoxy, C₄-C₂₂ branched alkoxy, arylene, substituted arylene, alkylarylene, aryloxy, alkoxyarylene, aryloxyalkylene, an alkyleneamino, and mixtures thereof; substituted siloxy of the formula $-\text{OSiR}^7\text{R}^8\text{R}^9$ wherein each R⁷, R⁸, and R⁹ is independently selected from the group consisting of C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, arylene, substituted arylene, aryloxy, substituted aryloxy, substituted alkylene of the formula



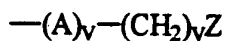
an ethyleneoxy unit of the formula



and an alkylethyleneoxy unit of the formula



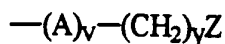
and mixtures thereof; wherein A, v, x, y and Z are the same as above; preferably R units are substituted alkylene of the formula



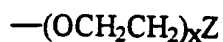
ethyleneoxy of the formula



substituted siloxy of the formula $-\text{OSiR}^7\text{R}^8\text{R}^9$ wherein each R⁷, R⁸, and R⁹ is independently selected from the group consisting of C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, arylene, substituted arylene, aryloxy, substituted aryloxy, substituted alkylene of the formula



ethyleneoxy of the formula

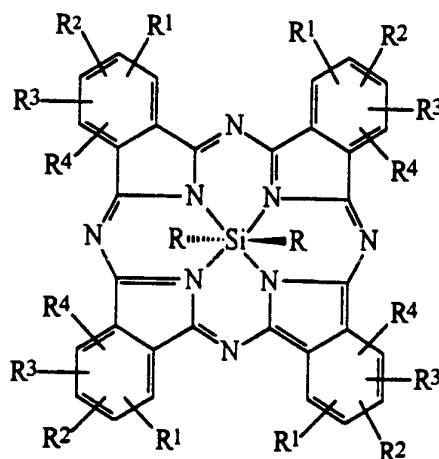


and mixtures thereof; and

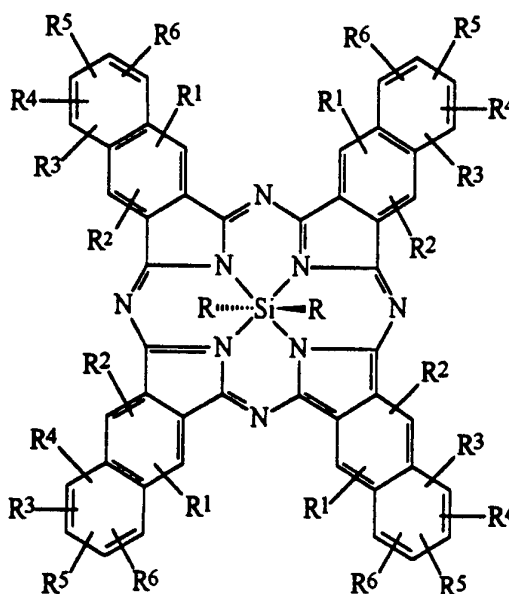
b) the balance adjunct ingredients.

9. A silicon phthalocyanine or silicon naphthalocyanine photobleaching composition comprising:

a) a silicon(IV)phthalocyanine of the formula

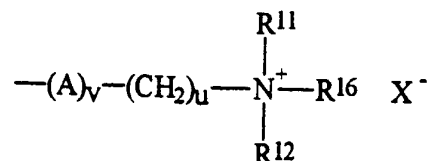


or a silicon(IV)naphthalocyanine of the formula

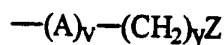


wherein wherein R^1 , R^2 , R^3 , R^4 , R^5 , and R^6 units are moieties that provide a positive Δ_{triplet} yield when said moiety replaces hydrogen; preferably a positive Δ_{triplet} yield of at least 10, more preferably a Δ_{triplet} yield of at least 30; axial R units wherein each R is independently selected from the group consisting of hydrogen, halogen, hydroxy, cyano, nitrido, oximino, C_1 - C_{22} alkylene, C_4 - C_{22} branched alkylene, C_1 - C_{22} alkenylene, C_4 - C_{22} branched alkenylene,

all of which can be substituted with halogen; polyhydroxyl substituted C₃-C₂₂ alkylene, C₃-C₂₂ glycol, C₁-C₂₂ alkoxy, C₄-C₂₂ branched alkoxy, arylene, substituted arylene, alkylarylene, aryloxy, alkoxyarylene, aryloxyalkylene, C₁-C₂₂ thioalkyl, C₄-C₂₂ branched thioalkyl, an alkyleneamino unit of the formula



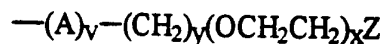
wherein R¹¹, and R¹² are each a C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, R¹⁶ is hydrogen, C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene and mixtures thereof, A is nitrogen or oxygen, X is chloride, bromide, iodide, or other water soluble anion, v is 0 or 1, u is from 0 to 22; -NR¹¹R¹² wherein R¹¹ and R¹² units are the same as defined above, and mixtures thereof; substituted alkylene of the formula



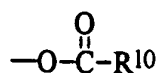
wherein Z is hydrogen, hydroxyl, -CO₂H, -SO₃-M⁺, -OSO₃-M⁺, C₁-C₆ alkoxy, arylene, substituted arylene, aryloxy, substituted aryloxy, alkyleneamino; A is nitrogen or oxygen, v is 0 or 1, y is from 0 to 22, M is a water soluble cation; an ethyleneoxy unit of the formula



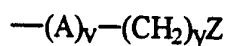
wherein Z is the same as above, x is from 1 to 100; an alkylethyleneoxy unit of the formula



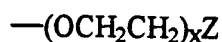
wherein A, v and Z are the same as above, x is from 1 to 100 and y is from 0 to 12; carboxylate of the formula



wherein R¹⁰ is C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, all of which can be substituted with halogen; poly-hydroxyl substituted C₃-C₂₂ alkylene, C₃-C₂₂ glycol, C₁-C₂₂ alkoxy, C₄-C₂₂ branched alkoxy, arylene, substituted arylene, alkylarylene, aryloxy, alkoxyarylene, aryloxyalkylene, an alkyleneamino, and mixtures thereof; substituted siloxy of the formula -OSiR⁷R⁸R⁹ wherein each R⁷, R⁸, and R⁹ is independently selected from the group consisting of C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, arylene, substituted arylene, aryloxy, substituted aryloxy, substituted alkylene of the formula



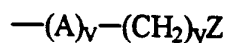
an ethyleneoxy unit of the formula



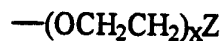
and an alkylethyleneoxy unit of the formula



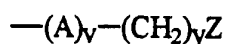
and mixtures thereof; wherein A, v, x, y and Z are the same as above; preferably R units are substituted alkylene of the formula



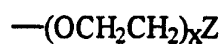
ethyleneoxy of the formula



substituted siloxy of the formula -OSiR⁷R⁸R⁹ wherein each R⁷, R⁸, and R⁹ is independently selected from the group consisting of C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, arylene, substituted arylene, aryloxy, substituted aryloxy, substituted alkylene of the formula



ethyleneoxy of the formula



- and mixtures thereof; and
- b) the balance adjunct ingredients.
10. A composition according to Claims 8 or 9 wherein the adjunct ingredients selected from the group consisting of deterative surfactants, preferably nonionic, cationic, anionic, zwitterionic, and ampholytic surfactants, and mixtures thereof; bleaches, bleach boosters, buffers, builders, chelants, filler salts, soil release agents, dispersants, enzymes, enzyme boosters, perfumes, thickeners, clays, bleaches, solvents, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/11872

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09B47/04 C09B47/08 C09B47/10 C09B47/18 C11D3/00
C11D3/16 C07D487/22

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)
IPC 6 C09B C11D C07D

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 153 278 A (CIBA GEIGY AG) 28 August 1985 see abstract & US 4 648 992 A cited in the application ---	1-10
Y	US 3 094 536 A (M.E. KENNEY) 18 June 1963 cited in the application see the whole document ---	1-10
Y	WO 91 18007 A (DIATRON CORP) 28 November 1991 see examples 1-10 ---	1-10
A	EP 0 484 027 A (ICI PLC) 6 May 1992 cited in the application see the whole document ---	1-10
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Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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"&" document member of the same patent family

Date of the actual completion of the international search: 26 November 1996

Date of mailing of the international search report: 04. 12. 96

Name and mailing address of the ISA: European Patent Office, P.B. 5818 Patentlaan 2, NL - 2280 HV Rijswijk, Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016

Authorized officer: Dauksch, H

INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/US 96/11872

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 191 970 A (CELANESE CORP ;UNIV CASE WESTERN RESERVE (US)) 27 August 1986 see page 7, last paragraph - page 9, line 26 ---	1
A	EP 0 597 389 A (HITACHI CHEMICAL CO LTD) 18 May 1994 see abstract see page 33, line 1 - line 49 ---	1
A	EP 0 296 876 A (HITACHI CHEMICAL CO LTD ;HITACHI LTD (JP)) 28 December 1988 see page 98, line 43 - page 99, line 40 ---	1
A	WO 95 08772 A (BIOSITE DIAGNOSTICS INC) 30 March 1995 see the whole document -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/11872

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