

**POLYHEDRAL OLIGOMERIC SILSESQUIOXANES AND METALLIZED
POLYHEDRAL OLIGOMERIC SILSESQUIOXANES
AS COATINGS, COMPOSITES AND ADDITIVES**

Cross-Reference to Related Applications

This application claims the benefit of U.S. Provisional Application Serial No. 60/531,458 filed on December 18, 2003.

Field of the Invention

This invention relates generally to methods for enhancing the properties of thermoplastic and thermoset polymers of man-made or natural origins and their compositions. More particularly, it relates to the incorporation of nanostructured chemicals into such polymers for radiation absorption, in situ glassification, gas and moisture barriers, and modification of surface and bulk properties.

The applications for such materials include use in coatings and molded articles that benefit from radiation resistance, stain resistance, printability, scratch resistance, low permeability, low surface roughness, and unique electronic and optical properties.

BACKGROUND OF THE INVENTION

The invention is related to use of polyhedral oligomeric silsesquioxane (POSS), silsesquioxane, polyhedral oligomeric silicate, silicates, silicones or metallized- polyhedral oligomeric silsesquioxane, silsesquioxane, polyhedral oligomeric silicate, silicates, and silicones as alloyable agents with polymeric materials. Polyhedral oligomeric silsesquioxane, silsesquioxane, polyhedral oligomeric silicate, silicates, silicones and metallized-polyhedral oligomeric

1 silsesquioxane, silsesquioxane, polyhedral oligomeric silicate, silicates, silicones are
2 here after referred to as Silicon Containing Agents.

3 Silicon Containing Agents have previously been utilized to complex metal
4 atom(s) as reported by Abbenhuis et. al in U.S. Patent No. 6,441,210. As discussed
5 by Lichtenhan et. al in U.S. Patent No. 6,716,919 and WO 01/72885 A1, such
6 Silicon Containing Agents are useful for dispersion and alloying of silicon and metal
7 atoms with polymer chains uniformly at the nanoscopic level. As discussed by
8 Lichtenhan et al. in U.S. Patent No. 6,767,930, Silicon Containing Agents can be
9 converted in the presence of atomic oxygen to form a glass like silica layer which is
10 useful in the protection of spacecraft from atomic oxygen.

11 It is now surprisingly discovered that such Silicon Containing Agents are also
12 useful for the formation of gas and liquid barriers and as additives for absorbing
13 radiation. In such capacity, the Silicon Containing Agents are themselves effective
14 when alloyed into a polymer but may also be preferably utilized for the in situ
15 formation of nanoscopically thin glass barriers. This process can be carried out in a
16 facile manner through exposure of polymers containing the Silicon Containing
17 Agents to oxygen plasma, ozone, or an oxidizing flame. The resulting nanoscopically
18 thin glass layers provide exceptional barrier and radiation absorption properties.
19 Upon exposure to such oxidants, the Silicon Containing Agents render surface glass
20 layers comprised of silica and metallized silica. Advantages of the method and
21 nanoscopically thin glass layer include: nondetectable by the human eye, toughness
22 and flexibility, suitability for storage on rolls and thin film packaging, impermeability
23 to moisture and gas, direct printability, stain resistance, scratch resistance, lower
24 cost and lighter weight than glass, excellent adhesion between polymer and glass
25 due to elimination of discreet compositional bondlines and replacement of them by

1 compositionally graded material interfaces. Finally, nanoscopically thin glass layers
2 containing metals absorb photon and particle radiation that could otherwise damage
3 polymer surfaces and substrates. In this same capacity, nanoscopically thin glass
4 layers containing mixtures of metals may also be utilized as phosphores and
5 luminescent materials, or in combination with existing phosphorescent and
6 luminescent materials. Prior art with nonmetalized POSS such as U.S. Patent No.
7 6,517,958 has shown it to enhance the brightness of semiconducting and
8 luminescent polymers but failed to recognize the potential for luminescent
9 contributions of metallized POSS.

10 As has been discussed in U.S. Patent Nos. 6,127,557 and 5,750,741, prior
11 art in metallized-polyhedral oligomeric silsesquioxane, silsesquioxane, polyhedral
12 oligomeric silicate, silicates, and silicones has focused on their utility in catalysis for
13 epoxidation of olefins and the addition polymerization of olefins. However,
14 metallized silicon agents had not been recognized as useful as polymer stabilizers
15 nor as radiation absorbers. Nor had the metallized POSS been described as useful
16 as a catalyst in condensation polymerizations. They have been found particularly
17 useful in the condensation polymerization of polyurethanes and epoxides and
18 bismaleimide and silicone materials.

19 The use of metals and organic metal complexes as polymer stabilizers are
20 well known items of commerce. However, such metals-based stabilizer additives are
21 not available in a form that allows them to be incorporated into a polymer and to
22 serve as a glass forming precursor.

23 The use of metals and metal particles such as boron and gadolinium is also
24 known to be of use in fast neutron tumor therapy, see U.S. Patent Nos. 5,630,786
25 and 6,248,916. A shortcoming of this prior art is that neutron trapping agents such

1 as carboranes lack high enough proton concentrations to effectively slow enough
2 fast neutrons to a capturable energy level. This causes patients to be subjected to
3 longer radiation exposures and higher dosages of the neutron capturing particle.
4 This deficiency can be mitigated by the incorporation of metals such as boron,
5 samurium, and gadolinium into nanoscopic POSS systems as the protons on the
6 organic arms of the cage thermalize fast neutrons.

7 The incorporation of metal particles into a polymeric binder and its application
8 as a conformal coating for the absorption of X-ray, electron radiation discussed in
9 U.S. Patent No. 6,583,432. However, this approach is deficient in that it does not
10 afford an optically transparent coating, it requires careful preparation and application
11 procedures to avoid becoming electrically conductive, and it does not afford
12 protection against thermal and fast neutron radiation. The sensitivity of commercial
13 electronic components to damage by thermal neutrons is well known as is the
14 absence of a low cost and neutron effective polymeric shielding material. Therefore,
15 the use of metallized Silicon Containing Agents for the specific absorption of neutron
16 radiation in a conformal coating or potting agent with or without a passivating glass
17 layer is a needed improvement over prior art coatings.

18 A number of prior art methods are known to produce glass coatings and
19 metallized glass coatings on polymers. Such methods include elevated temperature
20 sintering, sputtering, vapor deposition, sol-gel, and coating process which all require
21 additional manufacturing steps and are not amenable to high speed molding and
22 extrusion processing. These prior art methods also suffer from poor interfacial
23 bonding between the glass and polymer layers. The prior art is also deficient in its
24 ability to incorporate metal and nonmetal atoms into a well defined nanoscopic
25 structure within a single glass layer. Finally, the prior art is not able to produce

1 nanoscopically thin glass surfaces and consequently the methods are not amenable
2 to the high speed manufacture of flexible film packaging and especially bottling and
3 film manufacture.

4 The Silicon Containing Agents of the present invention are best exemplified
5 by those based on low cost silicones such as silsesquioxanes, polyhedral oligomeric
6 silsesquioxanes (POSS), and polyhedral oligomeric silicates. Figure 1 illustrates
7 some representative examples of Silicon Containing Agents containing siloxane,
8 silsesquioxane, and silicate examples. The R groups in such structures can range
9 from H to alkane, alkene, alkyne, aromatic and substituted organic systems including
10 ethers, acids, amines, thiols, phosphates, and halogenated R groups. The
11 structures and compositions are also intended to include metallized derivatives
12 where metals ranging from high to low Z can be incorporated into the structures as
13 shown in Figure 2.

14 The Silicon Containing Agents all share a common hybrid (i.e. organic-
15 inorganic) composition in which the internal framework is primarily comprised of
16 inorganic silicon-oxygen bonds. Upon mild and further oxidation these systems
17 readily form silica glasses. The exterior of a nanostructure is covered by both
18 reactive and nonreactive organic functionalities (R), which ensure compatibility and
19 tailorability of the nanostructure with organic polymers. These and other properties
20 of nanostructured chemicals are discussed in detail in U.S. Patent No. 5,412,053
21 and U.S. Patent No. 5,484,867 to Lichtenhan, both of which are incorporated herein
22 by reference. These nanostructured chemicals are of low density, and can range in
23 diameter from 0.5 nm to 5.0 nm and can be utilized in combination with micron sized
24 metal fillers.

SUMMARY OF THE INVENTION

The present invention describes a new series of polymer additives and their utility in the absorption of radiation, gas and liquid barrier formation, catalysis of condensation polymerization, and in situ formation of nanoscopic glass layers. The metallized POSS are wholly useful by themselves or in combination with polymers, or metals, or composites or in combination with macroscopic reinforcements such as fiber, clay, glass, metal, mineral, and other particulate fillers.

The metallized POSS are particularly useful as polymeric compositions with special radiation absorption, emissive, and refractive characteristics, and in packaging for enhanced printability, stain resistance, gas and liquid barrier properties. The metallized POSS are also useful in catalyzing the condensation polymerization of reactive monomers. Finally, the metallized and nonmetallized POSS are useful for in situ formation of nanoscopically thin glass layers.

The preferred compositions presented herein contain three primary material combinations: (1) Silicon Containing Agents including nanostructured chemicals, nanostructured oligomers, or nanostructured polymers from the chemical classes of silicones, polyhedral oligomeric silsesquioxanes (POSS), polysilsesquioxanes, polyhedral oligomeric silicates, polysilicates, polyoxometallates, carboranes, boranes; (2) metal atoms including alkali, alkaline earth, transition metals, lanthanide and actinide metals; and (3) manmade polymer systems such as polystyrene, polyamides, polyolefins, polyurethanes, polyesters, polycarbonates, polyethers, epoxy, cyanate esters, maleimides, phenolics, polyimides, fluoropolymers, rubber, and natural polymers including cellulose, sugars, starches, proteins, chitins, and all semicrystalline, crystalline, glassy, elastomeric polymers and copolymers thereof.

1 The preferred method of incorporating the Silicon Containing Agents into
2 thermoplastics is accomplished via melt mixing into the molten polymers. The
3 incorporation of the Silicon Containing Agents into thermosets can be accomplished
4 through melt blending, milling or solvent assisted methods or by dissolving into
5 compatibilizing monomers. All types and techniques of blending, including melt
6 blending, dry blending, solution blending, reactive and nonreactive blending are
7 effective.

8 In addition, the selective incorporation and maximum loading levels of a
9 Silicon Containing Agent into a specific polymer can be accomplished through use of
10 a Silicon Containing Agent with a chemical potential (miscibility) compatible with the
11 chemical potential of the region within the polymer in which it is to be alloyed.
12 Because of their chemical nature, Silicon Containing Agents can be tailored to show
13 compatibility or incompatibility with selected sequences and segments within
14 polymer chains and coils. Their physical size in combination with their tailorable
15 compatibility enables Silicon Containing Agents based on nanostructured chemicals
16 to be selectively incorporated into polymers and to control the dynamics of coils,
17 blocks, domains, and segments, and subsequently favorably impact a multitude of
18 physical properties. A picture illustrating attainment of a 1 – 3 nm level of dispersion
19 is shown in Figure 3.

20 The process of forming in situ glass glazings on articles molded from or
21 coated by polymers alloyed with Silicon Containing Agents is carried out by
22 exposure of the articles to oxygen plasma, ozone, or other highly oxidizing mediums.
23 These chemical oxidation methods are desirable as they are current industrial
24 processes and they do not necessarily result in heating of the polymer surface.

1 There are no topological constraints on the molded articles. Both thin films and thick
2 parts derived from the alloyed polymers can be processed to contain nanometer
3 thick surface glass layers. The most efficient and thereby preferred oxidation
4 method is oxygen plasma. However for alloys where the R on the Silicon Containing
5 Agents is H, methyl or vinyl, they can be converted to glass upon exposure to ozone,
6 peroxide, or even hot steam. A reliable alternate to the above methods is the use of
7 an oxidizing flame or laser operating in an oxidizing atmosphere. The choice of
8 method is dependent upon the chemical agent, polymer alloy system, loading level
9 of the silicon containing chemical agent, surface segregation of agent, the thickness
10 of the silica surface desired, and manufacturing considerations. A schematic view of
11 the alloyed and in situ glassified materials is shown in Figure 4.

12 Upon exposure of the surface to the oxidation source, a nanoscopically thin
13 layer of glass from 1 – 500 nm will result. If the Silicon Containing Agent contained
14 a metal, then the metal will also be incorporated into the glass layer as shown in
15 Figure 5. Advantages derived from the formation of a nanoscopic glass surface
16 layer include a smoother surface as shown in Figure 6, barrier properties for gases
17 and liquids, improved oxidative stability, flammability reduction, improved electrical
18 properties, improved printability, improved stain and scratch resistance, and
19 improved radiation resistance.

20 21 **BRIEF DESCRIPTION OF THE DRAWINGS**

22 FIG. 1 shows representative structural examples of nonmetallized Silicon
23 Containing Agents.

FIG. 2 shows representative structural examples of metallized Silicon Containing Agents.

FIG. 3 illustrates the ability to uniformly disperse nanostructured silicon agents at the 1 – 3 nm level at the surface and the bulk of a polymer.

FIG. 4 illustrates the conceptual comparison of an alloyed and nanoscopically surface glassified material.

FIG. 5 illustrates the chemical process of oxidative conversion of the silicon agents into a fused nanoscopically thin glass layer.

FIG. 6 illustrates the roughness of an alloyed surface and an in situ glassified surface.

FIG. 7 illustrates the ability to conformally coat an integrated circuit.

FIG. 8 illustrates the ability to attenuate neutron radiation.

FIG. 9 illustrates the effective shielding level for natural abundance Gd POSS loaded at 50% in a conformal coating.

FIG. 10 illustrates the effective shielding level for ¹⁵⁷ isotopically enriched Gd POSS loaded at 50% in a conformal coating.

FIG. 11 illustrates the ability to form a nanoscopically thin barrier layers inside and outside a molded plastic article.

FIG. 12 illustrates the UV absorption ranges for metallized POSS.

1 DEFINITION OF FORMULA REPRESENTATIONS FOR NANOSTRUCTURES

2 For the purposes of understanding this invention's chemical compositions, the
 3 following definition for formula representations of Silicon Containing Agents and in
 4 particular Polyhedral Oligomeric Silsesquioxane (POSS) and Polyhedral Oligomeric
 5 Silicate (POS) nanostructures is made.

6 Polysilsesquioxanes are materials represented by the formula $[R\text{SiO}_{1.5}]_{\infty}$
 7 where ∞ represents molar degree of polymerization and R = represents organic
 8 substituent (H, siloxy, cyclic or linear aliphatic or aromatic groups that may
 9 additionally contain reactive functionalities such as alcohols, thiols, esters, amines,
 10 aldehydes, acids, ketones, esters, olefins, ethers or which may contain halogens).
 11 Polysilsesquioxanes may be either homoleptic or heteroleptic. Homoleptic systems
 12 contain only one type of R group while heteroleptic systems contain more than one
 13 type of R group.

14 A subset of Silicon Containing Agents are classified as POSS and POS
 15 nanostructure compositions are represented by the formula:

16 $[(R\text{SiO}_{1.5})_n]_{\Sigma\#}$ for homoleptic compositions

17 $[(R\text{SiO}_{1.5})_n(R'\text{SiO}_{1.5})_m]_{\Sigma\#}$ for heteroleptic compositions (where $R \neq R'$)

18 $[(R\text{SiO}_{1.5})_n(R\text{SiO}_{1.0})_m(M)_j]_{\Sigma\#}$ for heterofunctionalized heteroleptic compositions

19 $[(R\text{SiO}_{1.5})_n(RX\text{SiO}_{1.0})_m]_{\Sigma\#}$ for functionalized heteroleptic compositions (where R
 20 groups can be equivalent or inequivalent)

1 In all of the above R is the same as defined above and X includes but is not
2 limited to OH, Cl, Br, I, alkoxide (OR), acetate (OOCR), peroxide (OOR), amine
3 (NR_2) isocyanate (NCO), and R. The symbols m, n and j refer to the stoichiometry of
4 the composition. The symbol Σ indicates that the composition forms a
5 nanostructure and the symbol # refers to the number of silicon atoms contained
6 within the nanostructure. The value for # is usually the sum of m+n, where n ranges
7 typically from 1 to 24 and m ranges typically from 1 to 12. It should be noted that $\Sigma\#$
8 is not to be confused as a multiplier for determining stoichiometry, as it merely
9 describes the overall nanostructural characteristics of the system (aka cage size).
10 The symbol M refers to metallic elements within the composition that include high
11 and low Z metals and in particular Al, B, Ga, Gd, Ce, W, Ni, Er, Y, Zn, Mn, Os, Ir, Ta,
12 Cd, Cu, Ag, V, As, Tb, In, Ba, Ti, Sm, Sr, Pb, Lu, Cs, Tl, Te.

14 DETAILED DESCRIPTION OF THE INVENTION

15 The present invention teaches the use of Silicon Containing Agents as
16 alloying agents for the absorption of radiation, formation of gas and liquid barrier
17 properties, for the catalysis of condensation polymers, for the control of refractive
18 index, for control of emissive properties, laser marking, in situ formation of glass
19 layers in polymeric materials and for the reinforcement of polymer coils, domains,
20 chains, and segments at the molecular level.

21 The keys that enable Silicon Containing Agents such as nanostructured
22 chemicals to function in this capacity include: (1) their unique size with respect to
23 polymer chain dimensions, (2) their ability to be compatibilized and uniformly

1 dispersed at the nanoscopic level with polymer systems to overcome repulsive
2 forces that promote incompatibility and expulsion of the nanoreinforcing agent by the
3 polymer chains, (3) their hybrid composition and its ability glassify upon exposure to
4 selective oxidants, and (4) the ability to chemically incorporate metals into the Silicon
5 Containing Agents and into the corresponding glass rendered therefrom. Therefore,
6 the factors to effect selection of a Silicon Containing Agent for radiation absorption
7 include the specific wavelength and type of radiation, the loading level of the Silicon
8 Containing Agent, and the optical, electronic, and physical properties of the
9 polymers. The factors to effect selection of a Silicon Containing Agent for emissive
10 and refractive index properties include the specific wavelength desired, the
11 sensitivity desired, the loading level of the Silicon Containing Agent, and the optical,
12 electronic, and physical properties of the polymers. The factors to effect selection of
13 a Silicon Containing Agent for catalysis of condensation polymers include the type of
14 polymerization, the rate of polymerization desired, and the type of metal necessary.
15 The factors to effect selection of a Silicon Containing Agent for permeability control
16 and glassification include the nanosizes of nanostructured chemicals, distributions of
17 nanosizes, and compatibilities and disparities between the nanostructured chemical
18 and the polymer system, the loading level of the Silicon Containing Agent, the
19 thickness of the silica layer desired, and the optical, electronic, and physical
20 properties of the polymer.

21 Silicon Containing Agents, such as the polyhedral oligomeric silsesquioxanes
22 illustrated in Figures 1 and 2, are available as solids and oils and with or without
23 metals. Both forms dissolve in molten polymers or in solvents, or can be reacted
24 directly into polymers or can themselves be utilized as a binder material. For POSS,
25 dispersion appears to be thermodynamically governed by the free energy of mixing

equation ($\Delta G = \Delta H - T\Delta S$). The nature of the R group and ability of the reactive groups on the POSS cage to react or interact with polymers and surfaces greatly contributes to a favorable enthalpic (ΔH) term while the entropic term (ΔS) is highly favorable because of the monoscopic cage size and distribution of 1.0.

The above thermodynamic forces driving dispersion are also contributed to by kinetic mixing forces such as occur during high shear mixing, solvent blending or alloying. The kinetic dispersion is also aided by the ability of some Silicon Containing Agents to melt at or near the processing temperatures of most polymers.

By controlling the chemical and processing parameters, nanoreinforcement and the alloying of polymers at the 1.5 nm level can be achieved for virtually any polymer system, as illustrated in Figure 3. Silicon Containing Agents can also be utilized in combination with macroscopic fillers to render similar desirable benefits relative to enhancements of physical properties, barrier, stain resistance and radiation absorption. Thus, metallized or halogenated Silicon Containing Agents can be used in combination with tungsten or boron particles to provide highly neutron absorbing effective coatings with resistance toward other types of ionizing and non-ionizing radiation. In such instances, metallized Silicon Containing Agents containing isotopically enriched isotopes of boron, samarium, and gadolinium are of particular utility. Such coatings are of high value for terrestrial and space based electronics, mirrors, portals, structures, and vehicles, and for terrestrial and space based, sensors, microelectromechanical machines (MEMS), and food packaging.

The present invention shows that property enhancements can be realized by the direct blending of Silicon Containing Agents, and preferably nanostructured chemicals, into polymers.

1 Because Silicon Containing Agents like nanostructured chemicals possess
2 spherical shapes (per single crystal X-ray diffraction studies), like molecular spheres,
3 and because they dissolve, they are also effective at reducing the viscosity of
4 polymer systems. This benefits the processing, molding, or coating of articles using
5 such nano-alloyed polymers, yet with the added benefits of reinforcement of the
6 individual polymer chains due to the nanoscopic nature of the chemicals.
7 Subsequent exposure of the nano-alloyed polymers to oxidizing agents results in the
8 in situ formation of nanoscopic glass on the exposed surfaces. Figures 4 and 6
9 illustrate the oxidation of silicones such as silsesquioxanes to glass. Upon exposure
10 of the nano-alloyed polymer to an oxidizing source the silicon – R bonds are broken
11 and the R group is lost as a volatile reaction byproduct. The valency to the silicon is
12 maintained through the fusing of cages together by bridging oxygen atoms, thus
13 rendering the equivalent of fused glass Figures 5. Thus, ease of in situ formation of
14 this glass surface layer is obtained through the use of nanostructured Silicon
15 Containing Agents while the prior art requires the use a secondary coating or
16 deposition method that results in formation of a micron thick layer of glass on the
17 surface. The nanoscopically dispersed nature of the Silicon Containing Agents within
18 and throughout the polymer affords the formation of the glass layer on the inside and
19 outside of molded articles (Figure 11). This is of tremendous advantage for articles
20 such as bottles and pouches, as it allows for an in situ formed glass barrier inside
21 and out, while the oxidizing source also provides sterilization. Such glass layers are
22 also advantageous as they provide a more desirable surface for printing product
23 information directly on the package.

24 Additional benefit from the use of such nano-alloyed polymers is the ability of
25 such materials to self-heal in the event of a loss of the surface glass layer. In such

an event, the nanoscopic Silicon Containing Agents present underneath the original glass surface are available to undergo in situ conversion to a new and healing glass surface layer upon exposure to an oxidant. Such control over compatibility, dispersability, size, and manufacturability is unprecedented for traditional fillers and coating technologies. Loading levels of the Silicon Containing Agents can range from 0.1% - 99% by weight, with a preferred range from 1% - 30% by weight.

EXAMPLES

General Process Variables Applicable To All Processes

As is typical with chemical processes, there are a number of variables that can be used to control the purity, selectivity, rate and mechanism of any process. Variables influencing the process for the incorporation of Silicon Containing Agents into plastics include the size and polydispersity, and composition of the nanoscopic agent. Similarly the molecular weight, polydispersity and composition of the polymer system must also be matched between that of the Silicon Containing Agent and polymer. Finally, the kinetics, thermodynamics, processing aids, and fillers used during the compounding or mixing process are also tools of the trade that can impact the loading level and degree of enhancement resulting from incorporation. Blending processes such as melt blending, dry blending and solution mixing blending are all effective at mixing and alloying nanoscopic Silicon Containing Agents into plastics.

Alternate Method: Solvent Assisted Formulation. Silicon Containing Agents can be added to a vessel containing the desired polymer, prepolymer or monomers and dissolved in a sufficient amount of an organic solvent (e.g. hexane, toluene,

dichloromethane, etc.) or fluorinated solvent to effect the formation of one homogeneous phase. The mixture is then stirred under high shear at sufficient temperature to ensure adequate mixing for 30 minutes and the volatile solvent is then removed and recovered under vacuum or using a similar type of process including distillation. Note that supercritical fluids such as CO₂ can also be utilized as a replacement for the flammable hydrocarbon solvents. The resulting formulation may then be used directly or for subsequent processing.

The examples provided below should not be construed as limiting toward specific material combinations or conditions.

Example 1. Moisture and Gas Barrier

A Silicon Containing Agent was incorporated into the polymer by melt compounding using a twin screw mixer and was processed into film followed by permeation measurements made on Mocon[®] equipment for nonglassified (Figure 4a) and glassified (Figure 4b) (oxidized) films.

Typical oxygen plasma treatments range from 1 seconds to 5 minutes under 100% power. Typical ozonolysis treatments range from 1 second to 5 minutes with ozone being administered through a CH₂Cl₂ solution with 0.03 equivalents O₃ per vinyl group. Typical steam treatments range from 1 second to 5 minutes. Typical oxidizing flame treatments range from 1 second to 5 minutes. Similar oxidation may be obtained through laser marking techniques via use of a laser operating in an oxidizing medium.

Polymer	POSS	% POSS Loading	Oxidation Method	*P W/O POSS	*P W POSS	*Perm post oxidation
PMMA	MA0702	5	Plasma	0.1 (O ₂)	0.07 (O ₂)	0.03 (O ₂)

Nylon 6	MS0825	1	Plasma	180 (O ₂)	97 (O ₂)
				130 (H ₂ O)	1.56 (H ₂ O)
Nylon 6	MS0830	1	Plasma	4-25 (O ₂)	0.14 (O ₂)
				130 (H ₂ O)	1.52 (H ₂ O)

2- P (Permeability): cc cm m⁻² day⁻¹ atm⁻¹ (gm cm m⁻² day⁻¹ for H₂O)

The findings show that incorporation of small percentage loadings of POSS into the polymers resulted in reduced permeability to oxygen and water. The barrier to transport was further reduced by oxidation to form a surface glass.

Example 2. Neutron Radiation Barrier

Optically clear samples containing various loading levels of Gd POSS were formulated into the FireQuench[®] 1287 resin system. A foil of Au was sandwiched between the Gd POSS[®] FireQuench[®] alloy. The samples were then exposed to a nuclear reactor that provides a watt fission neutron spectrum (energy range: 1-20 MeV, Ave. :~ 1 MeV). Only thermal (0.0253 eV) and epithermal (>0.5 eV) neutron flux were measured. The total neutron flux was measured using high purity gold foil. The reaction involved is Au-197(n,γ) Au-198. A cadmium cover was used to determine the thermal component of the total neutron flux. The absolute flux was determined from the measured induced activity in the gold foils. Gamma spectroscopy is performed on an energy and efficiency calibrated high purity germanium detector (HPGe). The measured neutron flux distribution at 950 kW is 3.57E+07 n/cm²-sec thermal and 1.27E+07 n/cm²-sec epithermal. The calculated error in flux measurement is 0.75%. The reduction in neutron flux scaled linearly with the wt% of Gd POSS loaded into the resin (Figure 8). It was calculated that for a 2/3 reduction in thermal neutrons a 1 mm thick conformal coating containing 50% by weight natural abundance Gd POSS would be required (Figure 9) while only a 0.1

1 mm thick coating of isotopically enriched ^{157}Gd would provide the sample level of
2 protection (Figure 10). Similar results were obtained for boron and samarium POSS
3 systems. Thus, protection of electronic components from thermal neutron damage
4 can be achieved using conformal coatings containing B, Sm, or Gd POSS additives.
5 These additives can also be incorporated into composite resins to render structural
6 composites which also aid as neutron shields. The large number of hydrogen atoms
7 per POSS cage further aids in thermalizing fast neutrons, thus enabling their capture
8 by the B, Sm or Gd atoms. The use of B, Sm and Gd POSS systems to thermalize
9 fast neutrons and capture them also enables them to serve as more effective
10 neutron capture agents in fast neutron tumor therapy.

12 **Example 3. UV, VUV, Visible Radiation Barriers and Emissive Additives**

13 Samples of various metallized POSS were exposed to UV through visible
14 radiation and their absorption characteristics are shown in Figure 12. It is clear that
15 the absorption characteristics can be tuned through adjustment of the metal
16 contained in the system. For example, Ce and Ti based POSS are particularly good
17 absorbers for a broader spectrum of UV radiation than a narrowly absorbing Al
18 POSS. Further, it has been shown these systems can be incorporated into optically
19 clear polymers and composites and subsequently converted into nanoscopically thin
20 glass surface layers which may offer an additional advantage as radiation absorbing
21 top coats. These coatings will find utility in a variety of polymers including silicones
22 which are degraded at 150 nm and in polycarbonate which is degraded at 243 nm.

23 Additionally useful are the emissive characteristics of several metallized
24 POSS systems. For example, Tb POSS is a strong green emitter upon exposure to
25 black light while Er POSS is an emitter upon excitation by X-ray. Such systems

alloyed into polymers or incorporated into nanoscopically controlled glasses have utility in optical displays, signs, and as protective coatings on solar cells in which they could absorb damaging or unuseful radiation and reemit it in a range useful for electricity generation by the solar cell.

Example 4. Refractive Index layer

Optically clear samples containing various metalized POSS were formulated into the FireQuench® 1287 resin system. The refractive index values were measured using a refractometer at different incident wavelengths. The series shows an ability to fine tune the refractive index both narrowly through changes in the metal or radically through changes in the functionality (e.g. thiol). The more polarizable electrons on the metal or the R group on the POSS cage leads to a larger the shift in refractive index.

Sample	<u>RI@589nm</u>	<u>RI@414nm</u>
PM1287	1.4553	1.48660
Er-POSS	1.4582	1.48590
Tb-POSS	1.4586	1.48680
Gd-POSS	1.4585	1.49460
Sm-POSS	1.4591	1.48750
P-POSS	1.4548	1.49060
Y-POSS	1.4580	1.48660
Sn-POSS	1.4607	
Octathiol POSS	1.5470	

Example 5. Condensation Polymerization Catalyst

Optically clear samples of two part polyurethane, epoxide, and siloxane were obtained through catalysis with various metalized POSS. For example, Ti POSS loaded in the 1 ppm level and higher was found to promote the rapid condensation polymerization of polyurethane while Sn POSS was found to be advantageous in the cure of silanol and silane formulated silicones. In each case, cure was accelerated

1 through increase of temperature and catalyst loading. A particular advantage of
2 these metallized catalysts are their low flammability and migrations due to their large
3 atomic mass. A further advantage is their ability to be converted into glasses and to
4 serve as fillers to reduce shrinkage and improve the oxidation of permeation
5 properties of the resulting polymer.

6 What is claimed is:

CLAIMS

- 1 1. A method for formation of a glass layer on a polymer surface comprising the
2 steps of:
 - 3 (a) incorporating at least one nanoscopically dispersed and sized Silicon
4 Containing Agent into a polymer; and
 - 5 (b) oxidizing the surface to form a glass layer.
- 1 2. The method of claim 1, wherein the glass layer provides a barrier to attenuate
2 a member of the group consisting of water, oxygen, neutrons, ultraviolet
3 radiation, and visible radiation.
- 1 3. The method of claim 1, wherein the refractive index of the polymer is
2 controlled through selection of the Silicon Containing Agent.
- 1 4. The method of claim 1, wherein the emissive properties of the polymer are
2 controlled through selection of the Silicon Containing Agent.
- 1 5. The method of claim 1, further comprising laser marking the polymer after
2 formation of the glass layer.

- 1 6. The method of claim 1, wherein a plurality of Silicon Containing Agents is
2 incorporated into the polymer.
- 1 7. The method of claim 1, wherein the polymer is in a physical state selected
2 from the group consisting of oils, amorphous, semicrystalline, crystalline,
3 elastomeric, and rubber.
- 1 8. The method of claim 1, wherein the polymer is a polymer coil, a polymer
2 domain, a polymer chain, a polymer segment, or a mixture thereof.
- 1 9. The method of claim 1, wherein the Silicon Containing Agent reinforces the
2 polymer at a molecular level.
- 1 10. The method of claim 1, wherein the incorporation is nonreactive.
- 1 11. The method of claim 1, wherein the incorporation is reactive.
- 1 12. The method of claim 1, wherein a physical property of the polymer is
2 improved.

- 1 13. The method of claim 12, wherein the physical property is selected from the
2 group consisting of adhesion, water repellency, fire retardancy, density, low
3 dielectric constant, thermal conductivity, glass transition, viscosity, melt
4 transition, storage modulus, relaxation, stress transfer, abrasion resistance,
5 fire resistance, biological compatibility, gas permeability, porosity, radiation
6 absorption, radiation emission, refractive index, and optical quality.
- 1 14. The method of claim 1, wherein the incorporation is accomplished in
2 combination with at least one other filler or additive that is macroscopic or
3 nanoscopic.
- 1 15. A method of condensation polymerization catalysis of monomers comprising
2 the method of claim 1 wherein the Silicon Containing Agent is metallized, and
3 further comprising the step of polymerizing the monomers before the surface
4 oxidation step.
- 1 16. A method for formation of a neutron radiation barrier comprising the step of
2 incorporating a metal selected from the group consisting of B, Gd, and Sm
3 into a POSS cage.
- 1 17. The method of claim 17, wherein the barrier is used as a therapeutic chemical
2 in fast neutron therapy.