Title: PHOSPHATE ESTER COATED HOLLOW GLASS MICROSPHERES, RESIN COMPOSITIONS COMPRISING SUCH MICROSPHERES, AND LOW DENSITY SYNTACTIC FOAMS PREPARED THEREFROM

Abstract: Hollow glass microspheres having surfaces coated with a phosphate ester and optional surface tension reducer are provided. By virtue of the presence of the phosphate ester and optional surface tension reducer, unexpectedly high volumes of such coated hollow glass microspheres can be utilized in resin compositions. Low density resin compositions containing high volumes of such coated hollow glass microspheres are also provided. This invention further provides new, lower density syntactic foams derived from these compositions. Still further, this invention provides low density epoxy resin compositions that comprise hollow glass microspheres, resins, resin curing agents and/or catalysts, and certain phosphate esters. By virtue of the low density of such compositions, new, lower density syntactic foams derived from these compositions can be attained and are provided.
PHOSPHATE ESTER COATED HOLLOW GLASS MICROSPHERES, RESIN COMPOSITIONS COMPRISING SUCH MICROSPHERES, AND LOW DENSITY SYNTACTIC FOAMS PREPARE THEREFROM

10

TECHNICAL FIELD

This invention relates to hollow glass microspheres having surfaces coated with a phosphate ester and optional surface tension reducer, and to resin compositions containing high volumes of such glass microspheres. This invention further relates to new, lower density syntactic foams derived from these compositions. Still further, this invention relates to mixtures of resins, hollow glass microspheres and phosphate esters, as well as to new, lower density syntactic foams derived from these mixtures.

BACKGROUND OF THE INVENTION

Particulate and fiberous fillers are used extensively in coatings and molded articles to reduce costs associated with the resin and to achieve desired performance. It is well known that fillers can be coated with various materials to improve such performance properties as handling characteristics and interaction with resins and other liquids. For example, calcium carbonate is commercially available with coatings of stearic acid, zinc stearate, silicones, or wax, each coating providing some desirable attribute, such as easier dispersion into resins or increased hydrophobicity. Canadian Patent No. 2167881 describes calcium carbonate and certain other mineral fillers treated with phosphate esters of stearyl alcohol, providing stable and favorable viscosities when the treated fillers are suspended in polyols for making polyurethane foams. Silica, another widely used filler, is available with several surface treatments, including silanes for improved composite properties. Orthoester treatments for silicon or silica substrates for reduced wettability have been described in U.S. Patent No. 5,709,715. Glass beads have been modified with silanes for wettability as described in U.S. Patent No. 4,713,295. Cellular siliceous glass
spheres have been strengthened by polymerizing a thin coating of thermosetting monomer on the surface of the spheres as described in U.S. Patent No. 3,661,620. Hollow glass balloons have been coated with silane and titanate coupling agents and thermoplastic resin as described in Japanese Patent No. 3079644. U.S. Patent No. 4,629,751 describes glass micro-bubbles coated with a low molecular weight polyhydroxy compound in a gel-resistant composition.

When a high filler level is desired, the filler loading is often limited by the viscosity requirements imposed by the process used for molding or coating the mixture containing the filler. In the case of glass beads in a polyester resin, U.S. Patent No. 4,574,109 describes obtaining some relief from high viscosity problems by mixing the glass beads with a finely divided material such as hydrophobic silica. Modification of epoxide resins with glass microspheres is cited by J. Zelenka and I. Dobas in Polimery Tworzywa Weilkołoczasteckowe, 43 (11-12), 709-712 (1998). Zelenka and Dobas describe lower viscosity epoxy resin compositions by modification with aliphatic polyols, which after acid anhydride curing have improved mechanical properties. European Patent No. 0 091555 describes hollow microspheres with essentially siliceous shells having organo-silicon-silicate surfaces for lower surface energy, and for making the viscosity of a filled liquid system lower, while making a higher loading of microspheres possible. U.S. Patent Nos. 5,151,218 and 5,130,463 describe reduced viscosities resulting from addition of certain phosphoric acid esters to unsaturated polyester resin solutions with polystyrene or styrene–butadiene copolymer filled with aluminum hydroxide or calcium carbonate. Increased pigment content in certain pigment pastes is also exemplified in 5,151,218 and 5,130,463. However, increased content of such pigments and fillers produces a density increase in these solutions and pastes because of the high densities of these pigments and fillers relative to the densities of the resins in which they are incorporated. In addition, such phosphoric acid esters are available, for the most part, only as solutions in organic solvents, and in some applications, such as syntactic foam preparation, solvents cannot be tolerated.

Some low density composites containing low density fillers have been described. For example, U.S. Patent No. 5,019,605 describes a low density, self-extinguishing epoxide composition including a low density filler and an organic phosphorous-containing compound for flame-retardancy. European Patent Application No. 814121 describes
processable, low density, fire retardant one-part epoxy compositions, including a filler capable of reducing the density of the composition and phosphoric or phosphonic acid ester flame-retardant plasticizers. However, no densities below 0.688 gram/cc are described in 814121. A need, therefore continues for still lower density composites and the resulting performance benefits, especially in the area of composite mixtures of hollow glass microspheres in epoxy, urethane, and polyester compositions.

These problems of attaining lower densities and overcoming the limits imposed by the viscosity requirements of the processes for molding or coating filled compositions are of particular importance in achieving syntactic foams of high strength and very low density. International Publication No. WO 9420286 describes a method and apparatus for producing syntactic materials with microspheres of incompressible material. European Patent Application No. 630956 describes a fire resistant syntactic foam, expanded with hollow glass spheres, and made by curing a phenolic resin with a partial phosphate ester. Syntactic foams are essentially a resin matrix surrounding particles which themselves contain a sealed void. The resin used for the matrix is often chosen for its hydrolytic stability and structural toughness, and epoxide and polyepoxide, and urethane resins are a preferred resin type. By maximizing the sealed void volume in the foam, very low density is achieved, which in turn provides such properties as reduced thermal conductivity and added buoyancy. When combined with resistance to volume shrinkage under pressure, a requirement for buoyant supports used in deep water oil recovery, attainment of very low density becomes particularly desirable for sub-sea buoyancy applications.

**SUMMARY OF THE INVENTION**

A need, therefore, exists for still lower density syntactic foams for improved buoyance. Furthermore, higher filler loadings are especially desirable and needed in the case of composites containing hollow glass microspheres to attain still lower densities and reduced resin content compared with that achievable by known methods.

Accordingly, it would be highly beneficial to provide coated hollow glass microspheres useful, for example, in making still lower density syntactic foams. Further, it would be highly beneficial to provide uncured epoxy and urethane resin compositions useful, for example, in making still lower density syntactic foams. It would also be highly beneficial to provide a syntactic foam with increased loading levels of incompressible
hollow glass microspheres in epoxy and urethane matrices and having a still lower density than was heretofore possible. One of the greatest contributions that hollow glass microspheres make to high compressive strength syntactic foams is reduction of density. Hollow glass microspheres are uniquely suited for this application because, in addition to having excellent isotropic compressive strengths, they have the lowest density of any filler that would be useful in the manufacture of high compressive strength syntactic foam. The combination of high compressive strength and low density make hollow glass microspheres the filler of choice for deep-water syntactic foams. The principal purpose of underwater syntactic foam is to provide buoyancy to heavy underwater metal pipes, risers, ducting, platform floatation, and other equipment for the mining of oil and gas. Such buoyancy decreases the effective weight of underwater structures, and thereby enables use of longer and deeper lines from the drilling platform to the bore hole in the seabed. Therefore, any decrease in density (i.e., increase in buoyancy) of syntactic foams is of paramount importance for drilling oil or gas at greater underwater depths. Reduced thermal conductivity from any decrease in density would allow more efficient flow of fluids through underwater pipelines by preventing excessive temperature drops in cold sea-water. Additional benefit would be derived from increased loading levels of hollow glass microspheres if even low levels of solvent could be avoided, since the presence of any solvent in the preparation of syntactic foams causes compressible voids which detract from the compression resistance of the foam, and cause a reduction in buoyancy. All of these benefits are of particular utility in new exploration for oil. Established sources of oil are found on land and relatively shallow areas of the oceans. Deeper drilling will be needed to find and develop new sources of oil and gas. It is, therefore, a preferred embodiment of this invention to provide high compressive strength syntactic foams, particularly epoxy and urethane syntactic foams, with greater volumes of hollow glass microspheres, and having lower densities than was heretofore possible. The increased buoyancy and compression resistance of these syntactic foams will allow support and insulation of heavier, longer, and deeper sub-sea structures.

The present invention provides in one embodiment a coated glass microbubble composition comprising:

(a) glass microbubbles; and
(b) a coating on the glass microbubbles, wherein the coating comprises a phosphate ester.

The present invention provides in another embodiment a coated glass microbubble composition comprising:

(a) glass microbubbles; and
(b) a coating on the glass microbubbles, wherein the coating comprises a phosphate ester and a surface tension reducer.

The present invention provides in another embodiment a coated glass microbubble composition comprising:

(a) glass microbubbles; and
(b) a coating on the glass microbubbles, wherein the coating comprises a phosphate ester; and

wherein the coated glass microbubbles provide a density decrease of at least about 2% at constant viscosity according to at least one of Test Procedures I and II (described below).

In another embodiment the present invention provides a coated glass microbubble composition comprising:

(a) glass microbubbles; and
(b) a coating on the glass microbubbles, wherein the coating comprises a phosphate ester and a surface tension reducer; and

wherein the coated glass microbubbles provide a density decrease of at least about 2% at constant viscosity according to at least one of Test Procedures I and II.

With respect to the coated glass microbubble compositions, the coated glass microbubbles preferably provide a density decrease of at least about 3%, more preferably of at least about 5%, even more preferably at least about 7%, and most preferably at least about 9% at constant viscosity according to at least one of Test Procedures I and II.

Preferably the surface tension reducer useful according to the present invention is selected from the group consisting of surfactants, silicon-containing compounds and mixtures thereof. More preferably the surface tension reducer is selected from the group consisting of nonionic surfactants, anionic surfactants, silicon-containing compounds, acrylate copolymers and mixtures thereof.
According to the present invention preferably the weight ratio of surface tension reducer to phosphate ester ranges from about 1:50 to about 10:1, more preferably about 1:30 to about 4:1, and most preferably about 1:20 to about 1:1.

In a preferred embodiment the phosphate ester comprises a phosphorylated reaction product of a methoxy endcapped polyoxyethylene and caprolactone, the phosphate ester having a number average molecular weight of less than about 1200.

With respect to the coated glass microbubble compositions preferably the coating on the glass microbubbles is about 0.1 to about 30 percent by weight, more preferably about 0.2 to about 20 percent by weight, and most preferably about 0.3 to about 10 percent by weight based on the total weight of the coated glass microspheres.

With respect to the coated glass microbubble composition preferably the coated glass microbubbles provide at least about a 2 % density decrease at constant viscosity and at least about a 2 percent reduction in viscosity at constant volume loading according to at least one of Test Procedures I and II.

The present invention provides in another embodiment an uncured resin composition comprising:

(a) coated glass microbubbles comprising:

(i) glass microbubbles;

(ii) a coating on the glass microbubbles, wherein the coating comprises a phosphate ester and optional surface tension reducer;

(b) an uncured resin; and

(c) optional resin curing agent, catalyst, or initiator (selected as necessary to cause the resin to cure);

wherein the volume loading of coated glass microbubbles is at least about 40 percent based on the total volume of the uncured resin composition; wherein the coated microbubbles provide a density decrease of at least about 2 percent at constant viscosity according to Test Procedure II (described below).

With respect to the uncured resin composition, preferably the loading of microbubbles is at least about 40 percent by volume, more preferably at least about 50 percent by volume, and most preferably at least about 60 percent by volume based on the total volume of the uncured resin composition.
The present invention provides in another embodiment an uncured resin composition comprising:

(a) glass microbubbles;
(b) uncured resin;
(c) phosphate ester;
(d) optional surface tension reducer; and
(e) optional resin curing agent, catalyst, or initiator (selected as necessary to cause the resin to cure);

wherein the volume loading of glass microbubbles is at least about 40 percent based on the total volume of the uncured resin composition; wherein the phosphate ester and optional surface tension reducer in combination with the glass microbubbles provide a density decrease of at least about 2 percent at constant viscosity according to Test Procedure III; and wherein the uncured resin composition is formed by combining the glass microbubbles, uncured resin, phosphate ester, optional surface tension reducer, and optional resin curing agent, catalyst, or initiator in situ.

Note, as used herein, “uncured resin” refers to resin materials that are partially or completely uncured. Such resins are considered workable, i.e., typically liquid in form them can be mixed, shaped, molded, pumped, formed, etc. into desired dimensions and configurations.

Preferably the phosphate ester comprises a phosphorylated copolymer comprising a polyoxyethylene residue. More preferably the phosphate ester comprises a phosphorylated reaction product of a methoxy endcapped polyoxyethylene and caprolactone, the phosphate ester having a number average molecular weight of less than about 1200.

Preferably the uncured resin composition has a loading of microbubbles of at least about 40 percent by volume, more preferably at least about 50 percent by volume, and most preferably at least about 60 percent by volume based on the total volume of the uncured resin composition.

In another embodiment the present invention provides a cured syntactic foam composition comprising:

(a) glass microbubbles; and
(b) the reaction product of a composition comprising one or more uncured resins, a phosphate ester comprising a phosphorylated copolymer comprising a polyoxyethylene residue, an optional surface tension reducer, and a component selected from the group consisting of an resin curing agent and a catalyst;

wherein the loading of the glass microbubbles is at least about 50 percent by volume based on the total volume of the glass microbubbles, uncured resin, and the component.

Preferably the cured syntactic foam composition has a density of less than about 0.65 g/cc.

With respect to the cured syntactic foam composition preferably the loading of the glass microbubbles is at least about 50 percent by volume, more preferably at least about 55 percent by volume, and most preferably at least about 60 percent by volume based on the total volume of the glass microbubbles, uncured resin, and optional resin curing agent, catalyst, or initiator (selected as necessary to cause the resin to cure). Higher volume loadings, for example of at least about 70 percent, may also be possible.

In another embodiment the present invention provides a coated glass microbubble composition comprising:

(a) glass microbubbles; and

(b) a coating on the glass microbubbles, wherein the coating comprises a phosphate ester; and

wherein the coated glass microbubbles provide at least about 2 % density decrease at constant viscosity and at least about a 5 percent reduction in viscosity at constant volume loading according to at least one of Test Procedures I and II.

With respect to the coated glass microbubble composition preferably the coated glass microbubbles provide at least about a 2 % density decrease at constant viscosity and at least about a 10 percent reduction in viscosity at constant volume loading, more preferably at least about a 2 % density decrease at constant viscosity and at least about a 20 percent reduction in viscosity at constant volume loading, and most preferably at least about a 2 % density decrease at constant viscosity and at least about a 30 percent reduction in viscosity at constant volume loading according to at least one of Test Procedures I and II.

In another embodiment the present invention provides an uncured resin composition comprising:
(a) coated glass microbubbles comprising:
   (i) glass microbubbles;
   (ii) a coating on the glass microbubbles, wherein the coating comprises phosphate ester and optional surface tension reducer;

(b) uncured resin; and

(c) optional resin curing agent, catalyst, or initiator;

wherein the volume loading of coated glass microbubbles is at least about 40 percent based on the total volume of the uncured resin composition; wherein the coated glass microbubbles provide at least about a 2% density decrease at constant viscosity and at least about a 2 percent reduction in viscosity at constant volume loading according to at least one of Test Procedures I and II (described below).

In another embodiment the present invention provides an uncured resin composition comprising:

(a) glass microbubbles;

(b) uncured resin;

(c) phosphate ester;

(d) optional surface tension reducer; and

(e) optional resin curing agent, catalyst, or initiator (selected as necessary to cause the resin to cure);

wherein the volume loading of glass microbubbles is at least about 40 percent based on the total volume of the uncured resin composition; wherein the phosphate ester and optional surface tension reducer in combination with the glass microbubbles provide at least about a 2% density decrease at constant viscosity and at least about a 2 percent reduction in viscosity at constant volume loading according to Test Procedure III; wherein the uncured resin composition is formed by combining the glass microbubbles, uncured resin, phosphate ester, optional surface tension reducer, and optional resin curing agent, catalyst, or initiator in situ.

With respect to the compositions of the invention preferably the uncured resin, phosphate ester, and optional surface tension reducer in combination with the glass microbubbles provide at least about a 2% density decrease at constant viscosity and at least about a 10 percent reduction in viscosity at constant volume loading, more preferably at least about a 2% density decrease at constant viscosity and at least about a 20 percent
reduction in viscosity at constant volume loading, and most preferably at least about a 2 % density decrease at constant viscosity and at least about a 30 percent reduction in viscosity at constant volume loading according to Test Procedure III (described below).

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS OF THE INVENTION

The coated glass microbubble composition of the invention is comprised of hollow glass microspheres and a coating on the hollow glass microspheres. Hollow glass microspheres useful according to the present invention preferably have a shell structure and a volume within the shell equal to at least about 90 percent of the volume of the microsphere. The volume within the shell is occupied by a gas. The diameter of the hollow glass microspheres useful in the present invention is preferably about 0.1 to 1000 microns, more preferably about 0.5 to 500 microns, and most preferably about 1.0 to 200 microns. Hollow glass microspheres of the present invention include, for example, glass microbubbles described in U.S. Patent No. 4,767,726, incorporated herein by reference. Hollow glass microspheres of the present invention also include hollow microspheres, the shells of which contain alkali metal silicate and a polyanion, and are described in European Patent Specification 0 091555. Hollow glass microspheres can vary in their hydrolytic stability, and it is preferred that in underwater applications more hydrolytically stable hollow glass microspheres be used. Microspheres made with shells of sodium silicate have been found to be hydrolytically unstable. Glass microbubbles such as those described in U.S. Patent No. 4,767,726 are known to be more hydrolytically stable and are preferred.

The coated glass microbubble composition of the invention preferably provides an increased volume loading at constant viscosity of at least about 1 percent, further preferably of at least about 5 percent, more preferably at least about 10 percent, even more preferably at least about 20 percent, and more preferably at least about 30 percent, according to Test Procedure I. The coated glass microbubble composition of the invention preferably provides a density decrease of at least about 2 percent at constant viscosity, further preferably of at least about 3 percent, more preferably at least about 5
percent, even more preferably at least about 7 percent, and more preferably at least about 9 percent, according to at least one of Test Procedures I and II.

The coating on the hollow glass microspheres is comprised of a phosphate ester and an optional surface tension reducer. Phosphate esters of the present invention are preferably chosen such that, when included in an uncured resin composition, the volume loading of hollow glass microspheres in the resin composition can be increased with an attendant density decrease at the same viscosity according to one of Test Procedures I-III. Alternately, preferred phosphate esters are chosen such that, when added to an uncured resin composition, the viscosity of the uncured resin composition containing hollow glass microspheres is decreased making possible a density decrease according to one of Test Procedures I-III. A preferred example is a phosphate ester obtained by phosphorylation of the co-polymer obtained by reaction of a methanol initiated poly(ethylene oxide) with caprolactone. In the course of the phosphorylation, the phosphoric acid may condense with one or two of these co-polymer molecules, resulting in the presence of both monophosphate and diphosphate esters, respectively. Some of the phosphoric acid may not condense with any of the co-polymer molecules, causing the presence of free phosphoric acid as well.

The phosphate ester may be added to an uncured resin composition as a coating on the hollow glass microspheres, or it may be added separately to the composition. When added separately to the uncured resin composition, the phosphate ester is considered to be added in situ. Preferably, the phosphate ester is added as a coating on the hollow glass microspheres. The phosphate ester may be coated on the hollow glass microspheres by a variety of means, such as solvent coating and spray coating. For example, solvent coating may be accomplished by combining the hollow glass microspheres with a solution of the phosphate ester and solvent and evaporating the solvent of the solution while agitating the mixture of solution and microspheres. Spray coating may be done by spraying the phosphate ester in a finely divided state, without or with carrier solvent, onto the hollow glass microspheres as the microspheres are transported separately or in close proximity to each other through the finely divided phosphate ester. Regardless of the method employed, it is preferable that intimate mixing take place between the phosphate ester and the hollow glass microspheres, and that the phosphate ester be uniformly distributed on the surface of the hollow glass microspheres. The coating on the hollow glass
microspheres is preferably about 0.1 to about 30 percent by weight, more preferably about 0.2 to about 20 percent by weight, and most preferably about 0.3 to about 10 percent by weight based on the total weight of the coated hollow glass microspheres.

The optional surface tension reducer is a component preferably chosen such that, when added to an uncured resin composition in combination with a phosphate ester, the viscosity of the uncured resin composition is decreased according to at least one of Test Procedures I-III to a greater extent than that found when the identical test procedure is conducted without the surface tension reducer component. Alternatively, the optional surface tension reducer is chosen such that, when added to an uncured resin composition in combination with a phosphate ester, the volume loading of hollow glass microspheres is increased, and the density of the composition is decreased according to one of Test Procedures I-III to a greater extent than when the identical test procedure is conducted without the surface tension reducer component.

The surface tension reducer component is preferably a surfactant or silicon-containing compound that is believed to reduce the interfacial tension between uncured resins and hollow glass microspheres, and may be added directly to the resin, or coated on the surface of the hollow glass microspheres which are then incorporated in an uncured resin. Some, but not all, of the surfactants useful herein are silicon-containing. Some, but not all, of the silicon-containing compounds useful herein are surfactants.

Silicon-containing compounds useful as surface tension reducers include, but are not limited to, methyltrimethoxysilane, octyltrimethoxysilane, decyltrimethoxysilane, octyltriethoxysilane, hexamethyldisilazane, N-2-(vinylbenzylamino)-ethyl-3-aminopropyltrimethoxysilane, aminoethylaminopropyltrimethoxysilane, 3-aminopropytriethoxysilane, 3-chloropropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, vinyltrimethoxysilane, methyl hydrogen polysiloxane, phenyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, and vinyltriacetoxyisilane. A preferred silicon-containing compound is a copolymer of octenyl methyl siloxane and poly(propylene oxide), a siloxane copolymer containing about an equal number of alkenyl and propylene oxide units, and having a number average molecular weight under 5500. Preferred surfactants are nonionic or anionic. Preferably, the surface tension reducer is added to an uncured resin composition as a coating on hollow glass microspheres, which have been coated with a phosphate ester and the surface
tension reducer simultaneously. Preferably, the phosphate ester and surface tension reducer are combined and applied as a mixture.

When phosphate esters and surface tension reducers are present together on the surface of hollow glass microspheres surprising reductions in viscosities are found in uncured resin compositions containing these coated hollow glass microspheres. This is surprising, because surface tension reducers coated alone on hollow glass microspheres have been found to cause an increase in viscosity. The presently discovered reductions in viscosities are particularly evident at relatively high volume loadings of these coated hollow glass microspheres, such as loadings of 40 volume % or higher. Because of the reductions in viscosities, the loadings of coated hollow glass microspheres can be increased until normal viscosities are reached, resulting in greater density decreases. Thus, the combined presence of phosphate esters and surface tension reducers produces greater density decreases in the uncured resin compositions than when phosphate esters are used alone. Furthermore, such density decreases are unique to low density fillers, such as hollow glass microspheres, since other fillers at increased loading levels would actually increase the density of the composition. If the density of the filler is less than the density of the resin, higher loadings of filler cause a decrease in density; correspondingly, if the density of the filler is greater than that of the resin, higher loadings of filler cause an increase in density. Hollow glass microspheres have densities ranging from about 0.1 g/cc to about 0.5 g/cc, and are much lower in density than most resins, for example, epoxy resins. Therefore, higher loadings of hollow glass microspheres produce a decrease in density. In contrast to hollow glass microspheres, other fillers, such as calcium carbonate and titanium dioxide have densities ranging from about 2 g/cc to over about 4 g/cc, and increased loadings of these materials cause increased densities.

Coated hollow glass microspheres of the present invention are an improvement over uncoated hollow glass microspheres. During handling and transferring from one container to another, the coated hollow glass microspheres are less dusty, and much fewer particles become airborne. In addition the coated hollow glass microspheres are more readily wetted by and mixed with uncured resins during the process of preparing syntactic foams.

Another embodiment of the present invention is an uncured resin composition comprising coated glass microbubbles described above, an uncured resin, and an optional
resin curing agent, catalyst, or initiator; wherein the volume loading of coated glass microbubbles is at least about 40 percent based on the total volume of the uncured resin composition; and wherein the coated microbubbles provide a density decrease of at least about 2 percent at constant viscosity according to at least one of Test Procedures I and II.

A suitable uncured resin can be readily selected by one skilled in the art, in accordance with the present invention. Uncured resins used herein are preferably epoxies, polyols, liquid isocyanates, urethanes, unsaturated polyesters, or mixtures thereof.

Epoxide resins useful in the present invention are organic epoxide compounds having oxirane rings polymerizable by ring opening. Such epoxides can be monomeric or polymeric epoxide compounds or combinations of these compounds, which can be aliphatic, cycloaliphatic, aromatic, or heterocyclic. These materials generally have at least one polymerizable epoxide group per molecule, preferably two or more epoxide groups per molecule and, in the polymeric type there may be many pendent epoxide groups. These epoxy-containing materials may vary from low molecular weight monomeric materials to high molecular weight polymers and may vary greatly in the nature of their backbone and substituent groups. For example, the backbone may be of any type, and substituent groups thereon can be any group not having a nucleophilic group or electrophilic group (such as an active hydrogen atom) which is reactive with an oxirane ring. Illustrative of substituent groups are halogens, ester groups, ethers, sulfonate groups, siloxane groups, nitro groups, substituted amide groups, nitrile groups, and phosphate groups. The molecular weight of the epoxy-containing materials may vary from 58 to about 100,000 or more. Mixtures of various epoxy-containing materials can also be used in the compositions of this invention.

Such epoxy-containing materials are well known and include epoxides such as epichlorohydrins (e.g. epichlorohydrin); alkyleneoxides (e.g., propylene oxide, styrene oxide); alkenyl oxides (e.g., butadiene oxide); glycidyl esters (e.g., ethyl glycidate); and glycidyl-type epoxide resins (e.g., the diglycidyl ethers of bisphenol A and of novolac resins, such as described in “Handbook of Epoxy Resins” by Lee and Neville, McGraw-Hill Book Co., New York (1967)). Other useful epoxy-containing materials which can be used in this invention are those which contain one or more cyclohexene oxide groups such as the epoxycyclohexanecarboxylates, typified by 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate; 2,4-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexanecarboxylate; and bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate. A
more detailed list of useful epoxides of this nature are described in U.S. Patent No. 3,117,099, incorporated herein by reference. Further epoxy-containing materials, which are particularly useful in the practice of this invention, include glycidyl ether monomers of the formula

\[ R(OCH_2CH-CH_2)_n \]

where R is alkyl or aryl and n is an integer of 1 to 6, preferably from 2 to 4. Examples are the glycidyl ethers of polyhydric phenols obtained by reacting a polyhydric phenol with an excess of chlorohydrin such as epichlorohydrin (e.g., the diglycidyl ether of 2,2-bis-(2,3-epoxy propoxyphenol)-propane). Further examples of epoxides of this type which can be used in the practice of this invention are described in U.S. Pat. No. 3,018,262.

There are a host of commercially available epoxy-containing materials which can be used in this invention. In particular, epoxides which are readily available include propylene oxide, epichlorohydrin, styrene oxide, vinyl cyclohexene oxide, glycidol, glycidylmethacrylate, diglycidyl ether of bisphenol A (e.g., those available under the trade designations "Epon 828" and "Epon 8132" from Shell Chemical Co., "DER 324", "DER 331", "DER 332", and "DER 334", from Dow Chemical Co.), vinylcyclohexane dioxide (e.g., "ERL-4206" from Union Carbide Corp.), 3,4-epoxy cyclohexylmethyl-3,4-epoxycyclohexane carboxylate (e.g., "ERL-4221" from Union Carbide Corp.), 3,4-epoxy-6-methyl cyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate (e.g., "ERL-4201" from Union Carbide Corp.), bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate (e.g., "ERL-4289" from Union Carbide Corp.), bis(2,3-epoxy cyclopentyl)ether (e.g., "ERL-0400" from Union Carbide Corp.), aliphatic epoxy modified with polypropylene glycol (e.g., "ERL-4050" and "ERL-4052" from Union Carbide Corp.), dipentene dioxide (e.g., "ERL-4269" from Union Carbide Corp.), epoxidized polybutadiene (e.g., "Oxiran 2001" from FMC Corp.), fluorinated epoxy resins (e.g., "Epon 1379" from Shell Chemical Company), silicone resins containing epoxy functionality, flame retardant epoxy resins (e.g., "DER-580", a brominated bisphenol type epoxy resin available from Dow Chemical Co.), 1,4-butandiol diglycidyl ether (e.g., "Araldite GY-506" and "Araldite RD-2" from Ciba-Geigy), polyglycidyl ether of phenolformaldehyde novolacs (e.g., "DEN-431" and "DEN-438" from Dow Chemical Co.), difunctional polyglycol glycidyl ethers (e.g., "PEP 6756 from Pacific Epoxy Polymers, Inc.", and resorcinol diglycidyl ethers (e.g., "Kopoxite" from Koppers Company, Inc.).
Still other useful epoxy-containing materials are copolymers of acrylic acid esters of glycidol such as glycidylacrylate and glycidylmethacrylate with one or more copolymerizable vinyl compounds. Examples of such copolymers are 1:1 styrene-glycidylmethacrylate, 1:1 methylmethacrylate-glycidylacrylate and a 62.5:24:13.5 methylmethacrylate-ethyl acrylate-glycidylmethacrylate.

Still other useful epoxy-containing materials are the polyurethane polyepoxides which are obtained by reacting an organic polyisocyanate with a triol or a mixture of a triol and diol to form an isocyanate terminated polyurethane prepolymer and reacting the prepolymer with a hydroxy aliphatic epoxide compound. Further examples of epoxy-containing material of this type, which can be used in the practice of this invention, are described in U.S. Pat. No. 3,445,436.

Typically the epoxy resin is present at a level of from about 20 to 80 weight percent of the composition. Preferably the composition comprises from 20 to 60 percent by weight of the epoxy resin.

Epoxisy resin curing agents and catalysts useful in the invention are materials which react with the oxirane ring of the organic epoxide causing substantial increases in molecular weights, and polymer formation. Epoxy resin curing agents are co-reactants that react with the epoxides to form higher molecular weight polymers, and are usually employed at a weight ratio of about 0.5:1 to 2:1 with respect to the weight of epoxide (curing agent/epoxide ratio). Epoxy resin curing agents, capable of reacting with two oxirane rings, become part of the polymer chain within the formed polymer and may be considered to be epoxy chain extension agents. Epoxy resin curing agents as used herein are also known in the art as hardeners, epoxy curatives, and curatives.

Catalysts contain at least one nucleophilic or electrophilic group (such as an active hydrogen atom) which initiates the polymerization of the epoxide. Catalysts accelerate the rate of reaction, and are usually present at low concentrations (less than 5 % by weight). Epoxy catalysts useful in the invention include those conventionally used for curing epoxy resin compositions and forming polymer networks. Such catalysts include, for example, aliphatic and aromatic tertiary amines such as dimethylaminopropylamine and pyridine, and, further, boron trifluoride complexes such as BF₃–monoethanolamine.

Other compounds which may act as catalysts or curing agents may include aliphatic and aromatic primary amines, for example: di-(4-aminophenyl)sulfone; di-(4-
aminophenyl)ethers; and 2,2-bis(4-aminophenyl)propane; imidazoles such as 2-ethyl-4-methylimidazole; guanidines such as tetramethyl guanidine; substituted ureas such as toluene diisocyanate urea; dicyandiamide; polyamines; mercaptans; and phenols. Preferred curing agents are acid anhydrides such as dodecenylsuccinic anhydride, methyltetrahydrophthalic anhydride, 4-methyltetrahydrophthalic acid anhydride; 3-methyltetrahydrophthalic acid anhydride; and methylnorbornene phthalic acid anhydride.

The choice of epoxy resin curing agent has some influence upon the viscosity of the uncured composition. For example, the use of amine based curing agents generally results in a very viscous, paste-like product. As a result, such curing agents are generally used only when a two-part composition is to be provided. On the other hand, some acid anhydride curing agents provide a more fluid, low viscosity product. As a result, this type of curing agent is very useful when a one-part product is desired.

The amount of curing agent needed in the composition will vary from curing agent to curing agent and from epoxide to epoxide. However, the curing agent is provided in such an amount as to be effective in causing substantially complete hardening or curing of the composition. The weight ratio of epoxy resin to curing agent preferably is in the range of from about 1/2 to 2/1.

Urethane resins useful in the present invention are reaction mixtures which comprise one or more organic polyfunctional isocyanates, and one or more poly(alkyl hydrogen) compounds. These reaction mixtures are ordinarily provided as two-part compositions, "Part A" normally comprising the poly(alkyl hydrogen) compound such as a polyol, catalyst, and hollow glass microspheres, with "Part B" normally comprising the polyfunctional isocyanate. The coated hollow glass microspheres of this invention may also be combined with "Part B", the polyfunctional isocyanate portion of the two-part system to provide urethanes with even greater loadings of hollow glass microspheres.

Polyfunctional isocyanate compounds useful in the present invention comprise isocyanate radicals attached to a multivalent organic group, which can comprise a multivalent aliphatic, alicyclic, araliphatic, or aromatic moiety; or multivalent aliphatic, alicyclic, araliphatic, or aromatic moieties attached to a biuret, an isocyanurate, a uretdione, or mixtures thereof. Preferred polyfunctional isocyanate compounds contain two or three -NCO radicals. Compounds containing two -NCO radicals are comprised of
divalent aliphatic, alicyclic, araliphatic, or aromatic moieties to which the –NCO radicals are attached.

Representative examples of suitable polyfunctional isocyanate compounds include isocyanate functional derivatives of the polyfunctional isocyanate compounds as defined herein. Examples of derivatives include, but are not limited to, those selected from the group consisting of ureas, biurets, allophanates, dimers and trimers (such as uretdiones and isocyanurates) of isocyanate compounds, and mixtures thereof. Any suitable organic polyisocyanate, such as an aliphatic, alicyclic, araliphatic, or aromatic polyisocyanate, may be used either singly or in mixtures of two or more. The aliphatic polyfunctional isocyanate compounds generally provide better light stability than the aromatic compounds. Aromatic polyfunctional isocyanate compounds, on the other hand, are generally more economical and reactive toward polyols and other poly(active hydrogen) compounds than are aliphatic polyfunctional isocyanate compounds. Suitable aromatic polyfunctional isocyanate compounds include, but are not limited to, those selected from the group consisting of 2,4-toluene diisocyanate (TDI), 2,6-toluene diisocyanate, an adduct of TDI with trimethylolpropane (available as Desmodur™ CB from Bayer Corporation, Pittsburgh, PA), the isocyanurate trimer of TDI (available as Desmodur™ IL from Bayer Corporation, Pittsburgh, PA), diphenylmethane 4,4'-diisocyanate (MDI), diphenylmethane 2,4'-diisocyanate, 1,5-diisocyanato-naphthalene, 1,4-phenylene diisocyanate, 1,3-phenylene diisocyanate, 1-methoxy-2,4-phenylene diisocyanate, 1-chlorophenyl-2,4-diisocyanate, 3,3'-dimethyl-4,4'-diphenylene diisocyanate, 3,3'-dimethoxy-4,4'-bisphenylene diisocyanate, 3,3'-diphenyl-4,4'-biphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dichloro-4,4'-biphenylene diisocyanate, and mixtures thereof.

Examples of useful alicyclic polyfunctional isocyanate compounds include, but are not limited to, those selected from the group consisting of dicyclohexylmethane diisocyanate (H₁₂MDI, commercially available as Desmodur™ W, available from Bayer Corporation, Pittsburgh, PA), 4,4'-isopropyl-bis(cyclohexylisocyanate), isophorone diisocyanate (IPDI), cyclobutane-1,3-diisocyanate, cyclohexane 1,3-diisocyanate, cyclohexane 1,4-diisocyanate (CHDI), 1,4-cyclohexanebis(methylene isocyanate) (BDI), 1,3-bis(isocyanatomethyl)cyclohexane (H₂XDI), 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, and mixtures thereof.
Examples of useful aliphatic polyfunctional isocyanate compounds include, but are not limited to, those selected from the group consisting of 1,4-tetramethylene diisocyanate, hexamethylene 1,4-diisocyanate, hexamethylene 1,6-diisocyanate (HDI) (available as Desmodur™ N-100 and N-3200 from Bayer Corporation, Pittsburgh, PA), 1,12-dodecane diisocyanate, 2,2,4-trimethyl-hexamethylene diisocyanate (TMDI), 2,4,4-trimethyl-hexamethylene diisocyanate (TMDI), 2-methyl-1,5-pentamethylene diisocyanate, dimer diisocyanate, the urea of hexamethylene diisocyanate, the biuret of hexamethylene 1,6-diisocyanate (HDI) (Desmodur™ N-100 and N-3200), the isocyanurate of HDI (available as Demodur™ N-3300 and Desmodur™ N-3600 from Bayer Corporation, Pittsburgh, PA), a blend of the isocyanurate of HDI and the uretdione of HDI (available as Desmodure™ N-3400 available from Bayer Corporation, Pittsburgh, PA), and mixtures thereof.

Examples of useful aroaliphatic polyisocyanates include, but are not limited to, those selected from the group consisting of m-tetramethyl xylene diisocyanate (m-TMXDI), p-tetramethyl xylene diisocyanate (p-TMXDI), 1,4-xyylene diisocyanate (XDI), 1,3-xyylene diisocyanate, p-(1-isocyanatoethyl)-phenyl isocyanate, m-(3-isocyanatobutyl)-phenyl isocyanate, 4-(2-isocyanatocyclohexyl-methyl)-phenyl isocyanate, and mixtures thereof.

Suitable organic poly(active hydrogen) compounds include hydroxy, thiol, and amine (primary and secondary) terminated polymers having a molecular weight of about 200 to about 5000. The poly(active hydrogen) compounds or polymers may be used singly or as mixtures of poly(active hydrogen) compounds and/or polymers. Polymers include certain polyethers, polyepihalohydrins, polythioethers, polysulfides, polyalkadienes, and polyesters. Illustrative polyethers are the following: poly(propylene glycol), poly(propylene glycol)-poly(ethylene glycol) copolymers wherein the poly(ethylene glycol) is present at less than about 10% by weight of the copolymer, and poly(tetramethylene glycol). Polyethers can be prepared by reaction of a 1,2-alkylene oxide with a simple di- or polyhydroxy compound, such as ethylene glycol, propylene glycol, butylene glycol, hexane diol, glycerine, hexane triol, trimethylolpropane, diethylene glycol, pentaerythritol, or sorbitol.

Thiol terminated poly(alkylene glycol) polymers are usually prepared by the acid catalyzed condensation of thiodiethyleneglycol with itself (i.e., homopolymers of
thiodiethyleneglycol) or at elevated temperatures with formaldehyde, paraformaldehyde, etc., or with polyols such as 1,4-butandiol. Polymers of this type with molecular weights of at least 750 are described in U.S. Pat. No. 2,900,368.

Hydroxy-terminated polysulfides such as are disclosed in U.S. Pat. No. 3,168,119, may also be employed in the practice of this invention. Other suitable polysulfides are the liquid mercaptoterminated polysulfides such as are disclosed in Patrick et al, U.S. Pat. No. 2,466,963.

Exemplary hydroxy terminated polyesters are polycaprolactones, polyethylene-propylene adipate, polyethylene adipate, polyethylene adipate (70)-phthalate (30), and polynopentyl sebacate.

Useful commercially available polymeric polyols include Carbowax™ poly(ethylene oxide) materials in the number average molecular weight (Mn) range of from about 200 to about 2000 (available from Union Carbide Corp.); poly(propylene oxide) materials such as PPG-425 (available from Lyondell Chemicals); block copolymers of poly(ethylene oxide) and poly(propylene oxide) such as Pluronic™ L31 (available from BASF Corporation); branched polyether-based polyols such as Lupranol™ Polyls (from Elastrogran GmbH, Lemfoerde, Germany); Bisphenol A ethoxylate, Bisphenol A propyloxylate, and Bisphenol A propoxylate/ethoxylate (available from Sigma-Aldrich); polytetramethylene ether glycols such as Polymeg™ 650 and 1000 (available from Quaker Oats Company) and the Terathane™ polyols (available from DuPont); hydroxyl-terminated polybutadiene resins such as the Poly bd™ materials (available from Elf Atochem); the "PeP" series (available from Wyandotte Chemicals Corporation) of polyoxyalkylene tetrals having secondary hydroxyl groups, for example, "PeP" 450, 550, and 650; polycaprolactone polyols with Mn in the range of about 200 to about 2000 such as Tone™ 0201, 0210, 0301, and 0310 (available from Union Carbide); "Paraplex™ U-148" (available from Rohm and Haas), an aliphatic polyester diol; polyester polyols such as the Multron™ poly(ethylenedipropylene)polyols (available from Mobay Chemical Co.); polycarbonate diols such as Duracarb™ 120, a hexanediol carbonate with Mn = 900 (available from PPG Industries Inc.); and the like; and mixtures thereof.

Suitable catalysts for curing the urethane resin include but are not limited to tertiary amine and tin compounds. Examples of useful tin compounds include tin II and tin IV salts such as stanous octoate, dibutyltin dilaurate, dibutyltin diacetate, dibutyltin di-
2-ethylhexanoate, and dibutyltin oxide. Examples of useful tertiary amine compounds include triethyl amine, tributylamine, triethylenediamine, tripropylamine, bis(dimethylaminoethyl) ether, morpholine compounds such as ethyl morpholine, and 2,2’-dimorpholinodiethyl ether, 1,4-diazabicyclo[2,2,2]octane (DABCO, Aldrich Chemical Co., Milwaukee, Wis.), and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU, Aldrich Chemical Co., Milwaukee, Wis.). Depending on reaction conditions (e.g., reaction temperature and/or polyfunctional isocyanate used), a catalyst level of up to about 0.5 percent by weight of the polyfunctional isocyanate/polyol mixture may be used, but typically about 0.00005 to about 0.5 percent by weight is required.

Unsaturated (thermosettable, or crosslinkable) polyester resins useful in this invention as well as co-monomers, accelerators, and initiators used therewith are well known and are generally described in U.S. Pat. No. 3,328,231. The polyester resins are characterized by a large number of repeating units of the formula

--OCO--A¹--COO--A²--

and preferably at least some units are of the formula

--OCO--A³--COO--A⁴--

wherein A¹ is the residue of a diacid of the formula

A¹(COOH)₂ containing at least one carbon-to-carbon double bond, e.g., fumaric and/or maleic acid or the like; A² and A⁴ are the residue of glycols such as ethylene glycol, propylene glycol, diethylene glycol, and/or dipropylene glycol, or the like; and A³ is the residue of a saturated diacid such as phthalic, adipic, and/or glutaric acid or the like. The condensation product of these diacids and glycols is usually formulated to be flexible after crosslinking with one of the following monomers or mixtures of monomers: an aromatic vinyl such as styrene (preferred), vinyl toluene, etc., acrylonitrile; an acrylate such as methylmethacrylate; diallyl phthalate, and the like. Preferably the monomer is an organic liquid having low volatility and capable of dissolving the polyester. Initiators such as dibenzoyl peroxide or methyl ethyl ketone peroxide in conjunction with tertiary amines and organo metallic accelerators can be used for "curing" at room temperature. Heat can, if desired, be used to accelerate the reaction; if heat alone is used, initiators such as dicumyl peroxide, azobisisobutyryl nitrile and the like are used in catalytic amounts without accelerators. The final cured polyester is preferably a flexible, infusible, hardened mass.

Another embodiment of the present invention is a cured syntactic foam composition comprising glass microbubbles, and the reaction product of a composition
comprising an uncured resin, a phosphate ester comprising a phosphorylated copolymer comprising a polyoxyethylene residue, an optional surface tension reducer, and a component selected from the group consisting of resin curing agents, initiators, and catalysts, and wherein the loading of the glass microbubbles is preferably at least about 50 percent by volume, more preferably at least about 55 percent by volume, and most preferably at least about 60 percent by volume, based on the total volume of the glass microbubbles and the reaction product of the uncured resin and the component. Higher volume loadings, for example at least about 70 percent, may also be possible.

Syntactic foams of the present invention are essentially a resin matrix surrounding particles which themselves contain a sealed void. The compressive strength required of a syntactic foam used in underwater applications is dictated by the depth of water at which it will be employed: at shallow depths, the compressive strength of syntactic foams does not have to be high, but at very great depths under the sea, the hydrostatic pressure exerted on the foam becomes enormous, and the foam is required to have very high resistance to compression (high compressive strengths). Only closed-cell foams can be used. Gas voids and other unsupported hollow cells produced in the resin by blowing agents and solvents collapse at high compression, severely decreasing the buoyancy of the foam; therefore, such foams are not suited for deep water applications. Hollow glass microspheres, because of their spherical form, provide resistance to compression equally from all directions (isotropic compressive strength), and are ideally suited for this application, in contrast to other shaped fillers such as fibers, plate-like fillers, or any nonspherical materials.

For underwater applications, syntactic foams must be hydrolytically stable, and the choice of resin type is important. Preferred resins exhibit excellent hydrolytic stability, and in addition, offer outstanding compressive strengths. Strong resins and strong low density hollow glass microspheres can be advantageously used to meet the stringent requirements of deep water syntactic foams. For these reasons, epoxy and urethane resins are most preferred.

The cured syntactic foam composition of the invention preferably has a density of less than about 0.65 g/cc, more preferably less than about 0.62 g/cc, even more preferably less than about 0.60 g/cc, and more preferably less than about 0.55 g/cc. Some buoyancy and insulation materials are comprised of a syntactic foam matrix with hollow
macrospheres encased therein. Macrospheres are included to further reduce the density of the foam. The macrospheres are typically several millimeters to several centimeters in diameter and are usually comprised of a thermoset composition. Macrosphere densities typically range from about 0.1 g/cc to about 0.7 g/cc. The shell of the macrospheres may be reinforced with glass fiber, carbon fiber, or other reinforcing additives. Thermoplastic macrospheres can also be used in certain applications. Uncured syntactic foam compositions of uncured resin, curing agent, and glass bubbles are typically cast around macrospheres pre-placed in a mold and then cured to form a solid material. Syntactic foam materials containing macrospheres are sometimes referred to as "macrosphere syntactic foam" and foams containing only microspheres are sometimes referred to as "solid syntactic foam".

In addition to underwater applications, it is foreseen that the syntactic foams of the invention have numerous other uses, including but not limited to coring materials, void fillers, tooling boards, and other light weight composites.

It is also foreseen that the functionality and utility of these syntactic foam materials may be further enhanced by the inclusion of one or more adjuvants including but not limited to those selected from the group consisting of metal powders, perfumes, fragrances, dyes, pigments, anti-fouling agents, x-ray detectable hollow glass bubbles, electrically conductive materials, plate-type, waxes, oils, reinforcing materials, and combinations thereof.

GLOSSARY

Glass Bubbles:

The terms “glass bubbles”, “glass microbubbles”, “hollow glass microspheres”, and HGM are used interchangeably herein.

K1 Glass Bubbles - Glass bubbles having a size range of about 10 microns to 135 microns, and a true density of around 0.125 g/cc, available from Minnesota Mining and Manufacturing Company, St. Paul, MN 55144-1000.
K25 Glass Bubbles - Glass bubbles having a size range of about 10 microns to 110 microns, and a true density of around 0.250 g/cc, available from Minnesota Mining and Manufacturing Company, St. Paul, MN 55144-1000.

PQ 5019 - Silane-treated, water-soluble, hollow microbubbles based on spray-dried sodium silicate. They have a size range of about 5-150 microns, a true density of about 0.20 g/cc, and are available from PQ Corp., P.O. Box 840, Valley Forge, PA 19482-0840.

S32 Glass Bubbles – Hollow glass microspheres having a density of about 0.32g/cc, and are available from the Specialty Additives Group of the 3M Performance Materials Division, Saint Paul, MN 55144.

Phosphate Esters:

BYK™-W 995 – About a 50% solution of a phosphate ester in organic solvents, in which the phosphate ester is a saturated polyester with acidic groups having a number average molecular weight of about 1010 as determined by gel permeation chromatography (GPC), and available from BYK-Chemie USA, Wallingford, CT.

BYK™-W 9010 – Similar to BYK-W 995 but has a number average molecular weight of about 765 found by GPC, and is available as a solvent-free phosphate ester from BYK-Chemie USA, Wallingford, CT.

BYK™ L-6012 – A phosphate ester similar to BYK W-995, but without solvent; L-6012 is 100% active and available from BYK-Chemie USA, 524 South Cherry Street, Wallingford, CT.

Surface Tension Reducers:

BYK™-A 525 – About a 50% solution of a polyether modified methyl alkyl polysiloxane copolymer having a number average molecular weight under 5500, and available from BYK-Chemie USA, Wallingford, CT.
BYK™ 361 – An acrylate copolymer containing about 2% naphtha, petroleum, and other light aromatic solvents. It is available from BYK-Chemie USA, 524 Spouth Cherry Street, Wallingford, CT.

FC 430 - A fluorochemical surfactant containing fluoroaliphatic polymeric esters and available from 3M Specialty Materials Division, St. Paul, MN 55144.

A-137 Silane - Octyltriethoxysilane. This compound is available as A-137 from Witco-OSI Corporation, One American Lane, Greenwich, CT 06831-2559.

I-6341 Silane - Octyltriethoxysilane. This compound is available from Dow Corning Corporation, Midland, MI 48686-0994.

A-1630 Silane - Methyltrimethoxysilane. This compound is available as A-1630 from Witco-OSI Corporation, One American Lane, Greenwich, CT 06831-2559.

Z-6070 Silane - Methyltrimethoxysilane. This compound is available from Dow Corning Corporation, Midland, MI 48686-0994.

DC-1107 Silane - Methyl hydrogen polysiloxane manufactured by Dow Corning Corporation, Midland, MI 48686-0994.

Span™ 80 - Sorbitan monooleate available from ICI Americas Inc., Wilmington, DE 19897.

Surfynol™420 and Surfynol™104S – Surfactants which are ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7-diol, and 2,4,7,9-tetramethyl-5-decyne-4,7-diol respectively, and are available from Air Products, 7201 Hamilton Boulevard, Allentown, PA 18195-1501.
Triton™X-100 - Surfactant which is a mixture of octylphenoxypolyethoxy-ethanol and polyethylene glycol available form Union Carbide Chemicals And Plastics Company Inc., 39 Old Ridgebury Road, Danbury, CT 06817-0001.

FC-171 - A Fluorad™ fluorochemical surfactant, containing > 90% by weight C₈F₁₇SO₂N(C₂H₅)(CH₂CH₂O)₇.₅CH₃ and < 10% by weight C₈F₁₇SO₂N(C₂H₅)H, available from 3M Specialty Materials Division, St. Paul, MN 55144.

Dawn™ Detergent - A dishwashing product available from Procter & Gamble, Cincinnati, OH 45202.

Polystep B-29 - A sodium octyl sulfate surface active agent available from Stepan Co., Northfield, IL 69089.


Alkaterge™-E - 2-heptadecenyl-4-ethyl-2-oxazoline-4-methanol, and is sold as a surface active agent by Angus Chemical Company, 2211 Sanders Road, Northbrook, IL 60062.

FC-129, FC-120, and FC-809 - Fluorochemical surfactants available from 3M, St. Paul, MN 55144.

Witconate 7093 - A sodium alkyl ether sulfate with the generalized structure, R₈₋₁₀O(C₂H₄O)ₓSO₃⁻, and available from Witco Organic Division, Witco Corp., 520 Madison Ave., N.Y. 10022.

Witconate AOS - An alpha-olefin sulfonate with the generalized structure, R₁₂₋₁₄SO₃⁻Na⁺, and available from Witco Organic Division, Witco Corp., 520 Madison Ave., N.Y. 10022.

Resins:
Epon™ 8132 - A bisphenol A – epichlorohydrin based epoxy resin, containing about 20 weight percent C12-C13 alkyl glycidyl ether as a reactive diluent. It has an epoxy equivalent weight of 195–215 as determined by ASTM D1652, and a Ubbelohde viscosity of 5–7 Poise (ASTM D445), and is available from Shell Chemical Co., P.O. Box 4320, Houston, TX 77210.

Araldite™GY-506 - A bisphenol A based epoxy resin with an epoxy equivalent weight of 172-185, containing butyl glycidyl ether as a reactive diluent, and available from Ciba Specialty Chemicals Corp., Brewster, NY.

DER™ 324 - A bisphenol A based epoxy resin with an epoxy equivalent weight of 197-206, containing a C12,14 alkyl glycidyl ether as a reactive diluent, and available from Dow Chemical Co., Midland, MI.

Lupranol™ Polyl Mixture – A mixture of two branched polyether-based polyols, only partially soluble in water, and having a specific gravity of 1.02 g/cc. One polyol is believed to have a hydroxy functionality of about 3 and a molecular weight of about 3000, and one polyol has a hydroxy functionality of about 5 and a molecular weight of about 600. It was obtained from Elastogran GmbH, Lemfoerde, Germany.

PEP™ 6756 - A difunctional polyglycol glycidyl ether (not based on bisphenol A) with an epoxy equivalent weight of 175-205 and a Brookfield viscosity of 30-60 cps at 25° C. PEP™ 6756 is available from Pacific Epoxy Polymers, Inc., 8905 Wollard, Richmond, MO 64085.

Reichold Polyester Resin 32367-00 - an unsaturated polyester resin, containing about 32-36% styrene monomer as a reactive diluent, and is available from Reichold Chemical Co., Research Triangle Park, NC 27709.

Styrene Monomer – vinylbenzene, used as a reactive diluent, and available from Chemcentral/Minnesota, 21675 Hamburg Ave., Lakeville, MN 55044.
Resin Curing Agents:

**DDSA** - Dodecenylsuccinic anhydride, available from Lonza Inc., Fairlawn, NJ 07410.

**Lindride 12** - Methyltetrahydrophthalic anhydride (MTHPA), used as a curing agent for epoxy resins. Lindride 12 is a special, low VOC (volatile organic compounds) version of MTHPA, and is available from Lindau Chemicals, Inc., 731 Rosewood Dr., Columbia, South Carolina 29201.

Fillers/Pigments/Rheological Agents:

**Haltex™ 100** - Aluminum trihydrate, a common filler used as a fire retardant. It has a size range of 1 to 40 microns, and is available from Hitox Corporation Of America, 722 Burleson Street, Corpus Christi, TX 78402.

**Micro-White™ 15** - Ultrafine ground calcium carbonate having a particle size ranging from submicron to 35 microns, with a mean particle size of 2.0 microns. It has a density of 2.71 g/cc, is a common filler used in coatings, and in rubber and plastic compounds, and is available from ECC International, 5775 Peachtree-Dunwoody Road, Atlanta, GA 30342.

**Kemera™ 6001** - Rutile titanium dioxide with a crystal size of about 0.2 microns. It is a common filler used as a pigment, and is available from Kemira Pigments Inc., Savannah, Georgia 31402.

**Kronos™ 2073** - Rutile titanium dioxide with an aluminum hydroxide/silica surface treatment. It is a common filler used as a pigment, and is available from Kronos Inc., Houston TX 77205.

**Luzenac America Talc** - a fine grade talc, used as a filler, and is available from Luzenac America, Englewood, CO 80112.
Pulpro White 8 Calcium Carbonate - a filler available from Omaya, Saint-Armand, Quebec, Canada.

Zeothix 95 Silica - an amorphous silica used as a flattening and rheological agent, and is available from J.M. Huber Corp., Chemical Division, 907 Revolution Street, Havre de Grace, MD 21078.

TEST METHODS

Test Procedure I: Viscosity Difference, Increased Volume Loading, And Density Difference With Coated Hollow Glass Microspheres In An Epon™ 8132 Epoxy Resin Composition

This test measures the Percent Viscosity Difference, Percent Increased Volume Loading (Percent IVL), and Percent Density Difference achieved with coated hollow glass microspheres in an Epon™ 8132/DDSA resin blend. Percent IVL is the percent increase in volume loading of coated hollow glass microspheres in an Epon™ 8132/DDSA blend compared to a similar composition prepared with uncoated hollow glass microspheres (HGM) at the same viscosity. The test is conducted at an HGM volume selected from the range of 50-52.5 %. Control viscosity is the viscosity of uncoated hollow glass microspheres mixed in this resin blend at the same volume % loading, all viscosities being measured at the same temperature. The temperature used is in the range of 20-25°C.

This test is conducted as follows. A resin blend is made by mixing Epon™ 8132 (100 g) with an epoxy resin curing agent, dodecenylocyninic anhydride (DDSA), (145 g) in a one liter polyethylene beaker. Enough uncoated hollow glass microspheres are added to the resin blend in the beaker to make a control composition containing 50-52.5 volume % HGM. To calculate the weight of HGM needed for this, the following equation may be used:

\[
\text{Wt. of HGM} = \frac{\text{Volume} \% \text{ HGM} \times \text{density (g/cc) of HGM} \times \text{weight of resin blend (g)}}{100-\text{Volume} \% \text{ HGM}}
\]
density (g/cc) of resin blend

The volume percent of HGM is based on the total volume of the composition. If the resin blend has a density of 1.0496 g/cc, and if the density of the HGM is 0.125 g/cc, and if the volume % of HGM is 52.5, then the weight of HGM to add to 245g of resin blend is:

Weight of HGM = 1.1053 x 0.125 x 245/1.0496 = 32.26 g.

The uncoated hollow glass microspheres are stirred into the resin blend by hand with a spatula until a uniform, smooth composition is obtained. The control composition is then de-aerated in a bell jar under vacuum cycling by applying a vacuum until the control composition rises to the top of the beaker, and then releasing the vacuum. After three vacuum cycles the control composition is gently re-stirred to make uniform again. The control viscosity is then measured with a Brookfield Viscometer, Model DV-II+ (Brookfield Engineering Laboratories, Inc., Stoughton, MA) at 0.5 rpm.

Using the above equation to calculate the weight of coated HGM to add, a similar composition, containing the same volume % coated HGM as that used for uncoated HGM in the control, is prepared, followed by de-aeration, and viscosity measurement as above at the same temperature. This is the initial composition. The Viscosity Difference is calculated as follows:

Percent Viscosity Difference =

\[
\frac{\text{viscosity of initial coated HGM composition} - \text{control viscosity}}{\text{control viscosity}} \times 100
\]

A negative viscosity difference indicates a viscosity decrease and a positive viscosity difference indicates a viscosity increase.

When a negative viscosity difference is found, additional coated HGM are then incrementally added to the initial composition with mixing followed by de-aeration and viscosity measurement as above, until the control viscosity is reached. This is the final composition. The weight of all the coated HGM increments is totaled, and its percentage relative to the weight of coated HGM in the initial composition calculated. This is the Percent IVL.

\[
\text{Percent IVL} = 100 \times \frac{\text{total weight of added coated HGM increments}}{\text{weight of coated HGM in initial composition}}
\]
For example, when a total of 4.0 g additional coated HGM are required to be added to the initial composition beyond the coated HGM present in the initial composition to arrive at the control viscosity, and 33.1 g of coated HGM are used to make the initial composition, the Percent IVL of the coated glass bubbles is: Percent IVL = 100 x (4.0/33.1) = 12.08%

The density difference resulting from the increased volume loading is calculated according to the following equation:

\[
\text{Percent Density Difference} = \frac{\text{density (g/cc) final composition} - \text{density (g/cc) control composition}}{\text{density (g/cc) of control composition}} \times 100
\]

A negative density difference indicates a decrease in density, and a positive density difference indicates an increase in density. The density of the control composition is calculated by dividing the sum of the weights of all the components by the sum of the volumes of all the components. The volume of each component is calculated by dividing the weight of the component by its density. For example, if the control composition consists of 245g of resin blend, and 32.26g of K1 HGM, the calculation looks like this:

<table>
<thead>
<tr>
<th>Wt. of Components</th>
<th>Density (g/cc)</th>
<th>Volume of Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>245.00 g Resin blend</td>
<td>1.049</td>
<td>245/1.049 = 233.56 cc</td>
</tr>
<tr>
<td>32.26 g K1 HGM</td>
<td>0.125</td>
<td>32.26/0.125 = 258.08 cc</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td><strong>277.26 g</strong></td>
<td><strong>491.64 cc</strong></td>
</tr>
</tbody>
</table>

Density of control composition = 277.26 g/491.64 cc = 0.5639 g/cc

Similarly, the density of the final composition, resulting from the addition of coated K1 HGM to the initial composition bringing the total weight of coated K1 HGM to 37.10 g, is calculated as follows:

<table>
<thead>
<tr>
<th>Wt. of Components</th>
<th>Density (g/cc)</th>
<th>Volume of Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>245.00 g Resin blend</td>
<td>1.049</td>
<td>245/1.049 = 233.56 cc</td>
</tr>
<tr>
<td>37.10 g coated K1 HGM</td>
<td>0.130</td>
<td>37.10/0.130 = 285.38 cc</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td><strong>282.10 g</strong></td>
<td><strong>518.94 cc</strong></td>
</tr>
</tbody>
</table>
Density of final composition = 282.10 g/518.94 cc = 0.5436 g/cc

Percent Density Difference = \( \frac{(0.5436 - 0.5639) \times 100}{0.5639} \) = -3.6%

Test Procedure II: Viscosity Difference, Increased Volume Loading And Density Difference With Coated Hollow Glass Microspheres In An Uncured Resin Composition

This test measures the Percent Viscosity Difference, Percent Increased Volume Loading (Percent IVL), and Percent Density Difference obtained with coated hollow glass microspheres in an uncured resin composition of choice when compared with uncoated hollow glass microspheres in an otherwise identical composition. Percent IVL is the percent increase in volume loading over a known volume loading of at least 40%, achieved with coated HGM in an uncured resin composition at the control viscosity. The control viscosity is the viscosity of the uncured resin composition containing uncoated HGM present at the above known volume % loading, all viscosities being measured at the same temperature. The temperature used is in the range of 20-25°C.

This test is conducted as follows. The uncured resin of choice is blended with a resin curing agent as needed, and with any other desired components (excluding the phosphate ester and surface tension reducer), and the density of the blend measured. Uncoated HGM are added to make a control composition containing a desired known volume % of uncoated HGM. The weight of uncoated HGM used is noted. The uncoated HGM are stirred into the resin blend by hand with a spatula until a uniform, smooth composition is obtained. The composition is then de-aerated and the viscosity is measured as in Test Procedure I. This is the control viscosity.

An otherwise identical composition, containing the same known volume % of coated HGM as uncoated HGM present in the control composition, is provided, followed by de-aeration, and viscosity measurement as above at the same temperature. This is the initial composition. The percent viscosity difference between the control and initial composition is calculated as follows:

\[
\text{Percent Viscosity Difference} = \left( \frac{\text{viscosity of initial coated HGM composition} - \text{control viscosity}}{\text{control viscosity}} \right) \times 100
\]
A negative viscosity difference indicates a viscosity decrease and a positive viscosity difference indicates a viscosity increase.

When a negative viscosity difference is found, additional coated HGM are then incrementally added to the initial composition and mixed in, followed by de-aeration and viscosity measurement as above, until the control viscosity is reached. This is the final composition. The weight of all the coated HGM increments is totaled, and its percentage relative to the weight of coated HGM in the initial composition calculated. This is the Percent IVL.

\[
\text{Percent IVL} = 100 \times \frac{\text{total weight of added coated HGM increments}}{\text{weight of coated HGM in initial coated HGM composition}}
\]

The percent density difference resulting from the increased volume loading is calculated as in Test Procedure I according to the following equation:

\[
\text{Percent Density Difference} = \left( \frac{\text{density (g/cc) final composition} - \text{density (g/cc) control composition}}{\text{density (g/cc) of control composition}} \right) \times 100
\]

A negative density difference indicates a decrease in density, and a positive density difference indicates an increase in density.

**Test Procedure III: Viscosity Difference, Increased Volume Loading, And Density Difference With In Situ Addition of Phosphate Ester In An Epoxy Resin Composition Containing Hollow Glass Microspheres**

This test measures the Percent Viscosity Difference, Percent Increased Volume Loading (Percent IVL), and Percent Density Difference of hollow glass microspheres in an epoxy resin composition containing a phosphate ester and optional surface tension reducer added in situ. Percent IVL is the percent increase in volume of HGM in an epoxy resin composition containing phosphate ester and optional surface tension reducer over the volume of HGM in an otherwise identical epoxy resin composition at the same viscosity, but not containing phosphate ester and surface tension reducer. A volume % of HGM of
at least 40% is used, and all viscosities are measured at the same temperature. The temperature used is in the range of 20-25°C.

A control composition is made as follows. The epoxy resin of choice is blended with an optional epoxy resin curing agent, and with any other desired components (excluding the phosphate ester and any surface tension reducer). HGM are added to make a control composition containing a desired known initial volume % HGM of at least 40%, and the weight of HGM used is noted. The HGM are stirred into the resin blend by hand with a spatula until a uniform, smooth control composition is obtained. The control composition is then de-aerated and the viscosity is measured as in Test Procedure I. This is the control viscosity.

An initial composition is provided which is similar in composition to the control composition except that the initial composition further comprises a phosphate ester and optional surface tension reducer. Following de-aeration of the initial composition, the viscosity is measured as above. The % Viscosity Difference is calculated as follows:

\[
\text{Percent Viscosity Difference} = \frac{(\text{viscosity of initial composition} - \text{control viscosity}) \times 100}{\text{control viscosity}}
\]

A negative viscosity difference indicates a viscosity decrease and a positive viscosity difference indicates a viscosity increase.

When a negative viscosity difference is found additional HGM are then incrementally added to the initial composition with mixing, followed by de-aeration and viscosity measurement as above, until the control viscosity is reached. This is the final composition. The weight of all the HGM increments is totaled, and its percentage relative to the weight of HGM in the initial composition calculated. This is the Percent IVL.

\[
\text{Percent IVL} = 100 \times \frac{\text{(total weight of added HGM increments)}}{\text{(weight of HGM in initial composition)}}
\]

The density difference resulting from the increased volume loading is calculated as in Test Procedure I according to the following equation:

\[
\text{Percent Density Difference} =
\]
(density (g/cc) final composition – density (g/cc) control composition) x 100 
density (g/cc) of control composition

A negative density difference indicates a decrease in density, and a positive density
difference indicates an increase in density.

EXAMPLES

The present invention is further illustrated by the following non-limiting examples.

Example 1

Preparation of Coated Hollow Glass Microspheres. K1 HGM (100 g) were placed
in a 4 liter, wide mouth glass jar. Separately, a solution, consisting of 400 ml acetone, 250
ml heptane, 2.0 g BYK™-A 525 (surface tension reducer), and 8.0 g BYK™-W-995
(phosphate ester), was prepared, and added to the jar containing the glass microbubbles.
The mixture was stirred with a large spatula so that all the glass microbubbles became
wetted by the solution. The jar was then placed in a vented oven at 100°C, allowing the
solvents to evaporate. The mixture was stirred every 15 minutes to keep the microbubbles
and the coating ingredients uniformly dispersed until complete removal of the solvents.
The dried, coated HGM thus obtained were then passed through an 80 mesh screen to
remove any lumps.

An epoxy resin blend made by combining 100 grams Epon™ 8132 and 145 grams
DDSA was mixed with 33.86 grams of the above K1 hollow glass microspheres coated
with 2 weight % BYK™-A 525 and 8 weight % BYK™-W 995, based on the weight of
the hollow glass microspheres to make a composition containing 52.5% by volume of the
coated HGM.

This epoxy resin composition containing the coated HGM was then evaluated for
Percent Density Difference, Percent Increased Volume Loading (Percent IVL) and Percent
Viscosity Difference with Test Procedure I, using a 52.5 volume % loading of uncoated
K1 HGM for determining the control viscosity. The control viscosity of the epoxy resin
composition with uncoated K1 HGM was 57,600 cps, and the calculated density of the
control composition was 0.565 g/cc. The viscosity of the initial epoxy resin composition
with 52.5 volume % loading of the coated K1 HGM was 32,000 cps. It was found that
when an additional 8.0 grams of the coated K1 HGM were added to the initial coated
HGM epoxy resin composition, a viscosity of 57,600 cps was obtained, and the calculated density of the resulting final composition was 0.520 g/cc. Using Test Procedure I, a Percent Density Difference of −8.2 %, a Percent IVL of 23.6 %, and a Percent Viscosity Difference of −44% were found. These results demonstrate a very significant decrease in density, a large reduction in viscosity, and a large increase in the volume loading made possible by the presence of a phosphate ester in combination with a surface tension reducer as a coating on hollow glass microspheres.

Comparative Examples C1-C14

To prepare Comparative Examples C1-C14, fourteen separate 100 gram quantities of K1 hollow glass microspheres were coated as in Example 1 with the following exceptions. A non-ionic or anionic surfactant was used in place of the BYK™-A 525 and BYK™-W 995 combination. In addition, for certain Comparative Examples the following solvent systems were used rather than the particular acetone/heptane combination in Example 1. When Dawn™ detergent was coated on the K1, 400 ml of acetone was used as the solvent. With Surlynol™ 420, Surlynol™ 104S, or Triton™ X-100, 200 ml acetone with 200 ml heptane was used as the solvent. When the anionic surfactants were coated, 300 ml acetone with 50 ml water was used as the solvent. The amount of surfactant coated on the K1 hollow glass microspheres was 1 % by weight based on the total weight of the uncoated K1.

Each separate quantity of coated K1 was evaluated for its effect on the viscosity of an epoxy composition made with 142.7 grams Epon™ 8132, and 15.2 grams of the coated K1; this mixture contained 50% by volume of the coated K1. The Percent Viscosity Difference was determined using Test Procedure II with an RV-2 spindle for viscosity measurements.
Table 1. Percent Viscosity Difference In Epon™ 8132 Of K1 Coated With 1% By Weight Of Various Non-ionic And Anionic Surfactants.

<table>
<thead>
<tr>
<th>Comparative Example</th>
<th>Surfactant</th>
<th>Type of Surfactant</th>
<th>Percent Viscosity Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>FC 430</td>
<td>Non-ionic</td>
<td>+121 %</td>
</tr>
<tr>
<td>C2</td>
<td>Dawn detergent</td>
<td>Non-ionic</td>
<td>+212 %</td>
</tr>
<tr>
<td>C3</td>
<td>Surlynol 420</td>
<td>Non-ionic</td>
<td>+8.3 %</td>
</tr>
<tr>
<td>C4</td>
<td>Surlynol 104S</td>
<td>Non-ionic</td>
<td>+2.1 %</td>
</tr>
<tr>
<td>C5</td>
<td>Triton X-100</td>
<td>Non-ionic</td>
<td>0</td>
</tr>
<tr>
<td>C6</td>
<td>BYK A-525</td>
<td>Non-ionic</td>
<td>-4.17%</td>
</tr>
<tr>
<td>C7</td>
<td>FC-129</td>
<td>Anionic</td>
<td>+1060 %</td>
</tr>
<tr>
<td>C8</td>
<td>FC-120</td>
<td>Anionic</td>
<td>+313 %</td>
</tr>
<tr>
<td>C9</td>
<td>FC-809</td>
<td>Anionic</td>
<td>+1221 %</td>
</tr>
<tr>
<td>C10</td>
<td>Wiconate 7093</td>
<td>Anionic</td>
<td>+331%</td>
</tr>
<tr>
<td>C11</td>
<td>Wiconate AOS</td>
<td>Anionic</td>
<td>+543%</td>
</tr>
<tr>
<td>C12</td>
<td>Polystep B-29</td>
<td>Anionic</td>
<td>+205 %</td>
</tr>
<tr>
<td>C13</td>
<td>AOF</td>
<td>Anionic</td>
<td>+103 %</td>
</tr>
<tr>
<td>C14</td>
<td>Phosphoric acid</td>
<td>Anionic</td>
<td>+105 %</td>
</tr>
</tbody>
</table>

The results in Table 1 show that most of the tested surfactants significantly increased viscosity when coated alone on HGM. The others (Triton X-100 and BYK W-525) produced little or no viscosity difference. The Comparative Examples demonstrate that hollow glass microspheres coated with surface tension reducers (surfactants) without a phosphate ester do not provide the benefit of substantially reduced viscosities which can be achieved with certain coated hollow glass microspheres of the invention.

Examples 2-26

To prepare Examples 2-26 twenty-five separate 100 gram quantities of K1 hollow glass microspheres were coated as in Example 1 with the following exceptions. Various combinations and amounts of BYK™-W 995, BYK™-W 9010 phosphate esters, and BYK™-A 525, and a variety of other surface tension reducers were used as shown in
Table 2, where all weight percents of phosphate esters and surface tension reducers are based on the weight of uncoated K1. In addition, for certain Comparative Examples the following solvent systems were used rather than the particular acetone/heptane combination in Example 1. When BYK™-W 995, and BYK™-W 9010 were coated alone or with Dawn™ detergent on the K1, 400 ml of acetone was used as the solvent. When BYK™-W 995 was coated along with Span™ 80, Polystep B-29, AOF, or Alkaterge™-E, 300 ml acetone with 50 ml water was used as the solvent. With Surfynol™ 420, Surfynol™ 104S, or Triton™ X-100, 200 ml acetone with 200 ml heptane was used as the solvent. With FC-171, 300 ml acetone with 100 ml heptane was used.

Each separate quantity of coated K1 was evaluated for its effect on the viscosity of an epoxy composition made with 100 grams Epon™ 8132, 145 grams DDSA, and an amount of the coated K1 equal to 52.5 volume % of the entire composition. Percent Viscosity Difference was determined using Test Procedure I. Results are shown in Table 2. Where Span™ 80 (Example 18) and Dawn™ detergent (Example 23) were used as the surface tension reducers, Percent IVL and Percent Density Difference were also determined according to Test Procedure I. Example 18: For the K1 coated with 1 weight % Span™ 80 + 4 weight % BYK™-W 995, it was found that an additional 2.0 g of coated K1 could be added to the initial composition containing 31.8 g coated K1 before reaching the same viscosity as the control composition. Percent IVL and Percent Density Difference calculations are as follows:

**Percent IVL = 100 \times (2.0/31.8) = 6.3\%**.

The density of the final composition was calculated as follows:

\[
\begin{align*}
245 \text{ g resin blend} & \quad \text{density} = 1.048 \quad \text{volume} = 233.78 \text{ cc} \\
33.8 \text{ g coated K1} & \quad \text{density} = 0.123 \quad \text{volume} = 274.80 \text{ cc} \\
\text{Totals: 278.8 g} & \quad \text{density} = 278.8 \text{ g}/508.58 \text{ cc} = 0.5482 \text{ g/cc}
\end{align*}
\]

The density of the control composition was similarly calculated:

\[
\begin{align*}
245 \text{ g resin blend} & \quad \text{density} = 1.048 \quad \text{volume} = 233.78 \text{ cc} \\
31.8 \text{ g K1} & \quad \text{density} = 0.123 \quad \text{volume} = 258.54 \text{ cc} \\
\text{Totals: 276.8 g} & \quad \text{density} = 276.8 \text{ g}/492.32 \text{ cc} = 0.5622 \text{ g/cc}
\end{align*}
\]

**Percent Density Difference = (0.5482-0.5622) \times 100 = -2.5\%**

\[
\frac{0.5622}{0.5622}
\]
Example 23: For the composition containing the K1 microspheres coated with Dawn™
detergent and BYK™-W 995, it was found that 4.0 g of additional coated K1
microspheres could be added to the initial composition containing 31.5 g coated K1 before
reaching the same viscosity as the control.

\[
\text{Percent IVL} = 100 \times \left( \frac{4.0}{31.5} \right) = 12.7\% 
\]

The density of the final composition containing the coated hollow glass
microspheres was calculated as follows:

\[
\begin{align*}
245 \text{ g resin blend} & \quad \text{density} = 1.048 \text{ g/cc} \quad \text{volume} = 233.78 \text{ cc} \\
35.5 \text{ g coated K1} & \quad \text{density} = 0.122 \text{ g/cc} \quad \text{volume} = 290.98 \text{ cc} \\
280.5 \text{ g} & \quad \text{density} = 280.5 \text{ g/524.76 cc} = 0.5345 \text{ g/cc}
\end{align*}
\]

The density of the control composition was similarly calculated:

\[
\begin{align*}
245 \text{ g resin blend} & \quad \text{density} = 1.048 \quad \text{volume} = 233.78 \text{ cc} \\
31.8 \text{ g K1} & \quad \text{density} = 0.123 \quad \text{volume} = 258.54 \text{ cc} \\
\text{Totals:} 276.8 \text{ g} & \quad \text{density} = 276.8 \text{ g/492.32 cc} = 0.5622 \text{ g/cc}
\end{align*}
\]

\[
\text{Percent Density Difference} = \left( \frac{0.5345 - 0.5622}{0.5622} \right) \times 100 = -4.9\% 
\]

The details of the compositions of Examples 6-30 and their Percent Viscosity Differences
are presented in Table 2.
Table 2. Percent Viscosity Difference In Epon™ 8132/DDSA Of K1 Coated With Various Combinations And Amounts Of Surface Tension Reducers And Phosphate Esters.

<table>
<thead>
<tr>
<th>Example</th>
<th>Weight % Surface Tension Reducer (STR)</th>
<th>Weight % Phosphate Ester (PE)</th>
<th>STR:PE Weight Ratio</th>
<th>% Viscosity Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>none</td>
<td>2% BYK-W 9010</td>
<td>-----</td>
<td>-11 %</td>
</tr>
<tr>
<td>3</td>
<td>1% BYK-A 525</td>
<td>2% BYK-W 995</td>
<td>1:2</td>
<td>-28 %</td>
</tr>
<tr>
<td>4</td>
<td>4% BYK-A 525</td>
<td>2% BYK-W 995</td>
<td>2:1</td>
<td>-44 %</td>
</tr>
<tr>
<td>5</td>
<td>none</td>
<td>4% BYK-W 995</td>
<td>-----</td>
<td>0 to -6 %</td>
</tr>
<tr>
<td>6</td>
<td>0.5% BYK-A 525</td>
<td>4% BYK-W 995</td>
<td>1:8</td>
<td>-25 %</td>
</tr>
<tr>
<td>7</td>
<td>1% BYK-A 525</td>
<td>4% BYK-W 995</td>
<td>1:4</td>
<td>-44 to -50 %</td>
</tr>
<tr>
<td>8</td>
<td>2% BYK-A 525</td>
<td>4% BYK-W 995</td>
<td>1:2</td>
<td>-33 %</td>
</tr>
<tr>
<td>9</td>
<td>1% A-137</td>
<td>4% BYK-W 995</td>
<td>1:2</td>
<td>-20 %</td>
</tr>
<tr>
<td>10</td>
<td>1% A-1630</td>
<td>4% BYK-W 995</td>
<td>1:2</td>
<td>-20 %</td>
</tr>
<tr>
<td>11</td>
<td>2% DC-1107</td>
<td>4% BYK-W 995</td>
<td>1:1</td>
<td>-20 %</td>
</tr>
<tr>
<td>12</td>
<td>0.5% FC STR-A</td>
<td>4% BYK-W 995</td>
<td>1:4</td>
<td>-20 %</td>
</tr>
<tr>
<td>13</td>
<td>1% FC STR-A</td>
<td>4% BYK-W 995</td>
<td>1:2</td>
<td>-40 %</td>
</tr>
<tr>
<td>14</td>
<td>1% Span 80</td>
<td>4% BYK-W 995</td>
<td>1:2</td>
<td>-30 %</td>
</tr>
<tr>
<td>15</td>
<td>1% Surlynol 420</td>
<td>4% BYK-W 995</td>
<td>1:2</td>
<td>-30 %</td>
</tr>
<tr>
<td>16</td>
<td>1% Surlynol 104S</td>
<td>4% BYK-W 995</td>
<td>1:2</td>
<td>-20 %</td>
</tr>
<tr>
<td>17</td>
<td>1% Triton X-100</td>
<td>4% BYK-W 995</td>
<td>1:2</td>
<td>-30 %</td>
</tr>
<tr>
<td>18</td>
<td>1% FC-171</td>
<td>4% BYK-W 995</td>
<td>1:2</td>
<td>-30 %</td>
</tr>
<tr>
<td>19</td>
<td>1% Dawn</td>
<td>4% BYK-W 995</td>
<td>1:2</td>
<td>-40 %</td>
</tr>
<tr>
<td>20</td>
<td>1% Polystep B-29</td>
<td>4% BYK-W 995</td>
<td>1:2</td>
<td>+10 %</td>
</tr>
<tr>
<td>21</td>
<td>1% AOF</td>
<td>4% BYK-W 995</td>
<td>1:2</td>
<td>+40 %</td>
</tr>
<tr>
<td>22</td>
<td>1% Alkaterge-E</td>
<td>4% BYK-W 995</td>
<td>1:2</td>
<td>+40 %</td>
</tr>
<tr>
<td>23</td>
<td>none</td>
<td>8% BYK-W 995</td>
<td>-----</td>
<td>-33 %</td>
</tr>
<tr>
<td>24</td>
<td>1% BYK-A 525</td>
<td>8% BYK-W 995</td>
<td>1:8</td>
<td>-25 to -44 %</td>
</tr>
<tr>
<td>25</td>
<td>2% BYK-A 525</td>
<td>8% BYK-W 995</td>
<td>1:4</td>
<td>-44 to -50 %</td>
</tr>
<tr>
<td>26</td>
<td>1% BYK-A 525</td>
<td>22% BYK-W 995</td>
<td>1:22</td>
<td>-12.5 %</td>
</tr>
</tbody>
</table>

BYK™-W 995 and BYK™-A 525 are about 50 weight % solids.

The results in Table 2 along with those in Table 1 show a surprisingly and significantly greater viscosity reduction when certain surface tension reducers are used in combination with a phosphate ester as a coating on K1 hollow glass microspheres. This is surprising since the surface tension reducers of Examples 3, 4, 6–8, 12, 13, 15–17, 19, and 24–26 alone without phosphate ester, as shown in Table 1, produced a significant viscosity increase or had essentially no effect. This “combination effect” is especially demonstrated by comparing Examples 5, 6, 7, and 23 and 25 in Table 2 above. The combination of surface tension reducer and phosphate ester produces greater viscosity...
differences than phosphate ester alone. Further, the results show that a preferred combination is a 1:4 weight ratio of BYK™-A 525 to BYK™-W 995.

Example 27-29

K1 hollow glass microspheres were coated using the method described in Example 1 except that a combination of BYK™-W 9010 and BYK™-A 525 was used in place of the BYK™ W-995 and BYK™-A 525 combination of Example 1. The weight percents of BYK™-W 9010 and BYK™-A 525 listed in Table 3 are based on the weight of the uncoated K1. Epon™ 8132 epoxy resin (100 grams) was mixed with the coated K1 at 50 volume %. Coating levels based on the weight of K1, and the Viscosity Differences determined using Test Procedure II are shown in Table 3.

Table 3. Percent Viscosity Difference Found In Epon™ 8132 Epoxy Resin With 50 Volume % Hollow Glass Microspheres Coated At Low Levels With BYK™-A 525 Combined With BYK™-W 9010.

<table>
<thead>
<tr>
<th>Example</th>
<th>Surface Tension Reducer</th>
<th>Phosphate Ester</th>
<th>STR:PE Weight Ratio</th>
<th>Percent Viscosity Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>0.4 % BYK-A 525</td>
<td>0.2 % BYK-W 9010</td>
<td>2:1</td>
<td>-61 %</td>
</tr>
<tr>
<td>28</td>
<td>0.3 % BYK-A 525</td>
<td>0.3 % BYK-W 9010</td>
<td>1:1</td>
<td>-44 %</td>
</tr>
<tr>
<td>29</td>
<td>0.2 % BYK-A 525</td>
<td>0.4 % BYK-W 9010</td>
<td>1:2</td>
<td>-62 %</td>
</tr>
</tbody>
</table>

The results in Table 3 show that the combination of phosphate ester and surface tension reducer coated on hollow glass microspheres is very effective in reducing viscosity even at low coating weights and over a range of surface tension reducer/phosphate ester ratios. Because of this, a lower density and an increased volume loading are achievable.

Examples 30

An epoxy resin composition, approximating that used for making syntactic foams, was prepared by blending Epon™ 8132 epoxy resin (100 parts by weight) with DDSA (145 parts by weight) and then adding K1 hollow glass microspheres (32.25 parts by
weight) to make a composition containing 52.5 volume % HGM. The viscosity difference from the in situ addition of BYK™-W 995 at 4 weight %, based on the weight of the hollow glass microspheres present, was measured using Test Procedure III. Results are shown in Table 4.

Examples 31

An epoxy resin composition, approximating that used for making syntactic foams, was prepared by blending Epon™ 8132 epoxy resin (100 parts by weight) with DDSA (145 parts by weight) and then adding K1 hollow glass microspheres (32.25 parts by weight) to make a composition containing 52.5 volume % HGM. The viscosity difference from the in situ addition of BYK™-W 9010 at 2 weight %, based on the weight of the hollow glass microspheres present, was measured using Test Procedure III. Results are shown in Table 4.

Table 4. Percent Viscosity Difference From In Situ Addition Of BYK™-W 995, And BYK™-W 9010 To An Epon™ 8132/DDSA/K1 Composition.

<table>
<thead>
<tr>
<th>Example</th>
<th>Phosphate Ester Added In Situ</th>
<th>% Viscosity Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>4% BYK-W 995</td>
<td>-39 %</td>
</tr>
<tr>
<td>31</td>
<td>2% BYK-W 9010</td>
<td>-26 % to -30%</td>
</tr>
</tbody>
</table>

It should be noted that BYK™-W 995 contains about 50% by weight solvents, but BYK™-W 9010 does not. These results in Table 4 show that the in situ addition of phosphate esters to epoxy compositions containing hollow glass microspheres produces a large reduction in viscosity, making possible a density decrease by increasing the volume loading.

Example 32

An epoxy resin blend, made by combining 100 part by weight of Epon™ 8132 and 80 parts by weight of Lindride 12 epoxy resin curing agent, was mixed with K1 hollow glass microspheres (21.4 grams) to make a composition containing 52.5 volume % K1. After measuring the viscosity of the resulting composition, 0.55 gram of BYK™-W 995 (0.27 % by weight of the composition) was added in situ, and the Percent Viscosity
Difference determined according to Test Procedure III, using a T-B spindle for viscosity measurement. Using Test Procedure III, the Percent Increased Volume Loading and Percent Density Difference were also determined. A Percent Viscosity Difference of ~60 %, and Percent Increased Volume Loading of 17 %, and a Percent Density Difference of ~4.9 % were found, thus indicating a high level of effectiveness of the in situ addition of phosphate ester in this resin system.

Example 33

An epoxy resin blend, made by combining Epon™ 8132 (100 grams) and DDSA (145 grams), was mixed with K1 hollow glass microspheres (32.2 grams) to make a composition containing 52.5 volume % K1. After measuring the viscosity of the composition, 0.97 gram of BYK™-W 995 (0.35 % by weight of the composition) was added in situ, and the Percent Viscosity Difference was determined according to Test Procedure III, using a T-B spindle for measuring viscosity. No viscosity reduction was found. When compared to the results found in Example 32, this indicates that the effectiveness of the in situ addition of phosphate ester can be dependent upon the resin system used.

Comparative Example 34

Epon™ 8132 epoxy resin (100 grams) was mixed with K1 hollow glass microspheres (4.76 grams) to make a composition containing 30 volume % K1. After measuring the viscosity of the composition, 0.4 gram BYK™-W 995 was added in situ, and the Percent Viscosity Difference was determined according to Test Procedure III (except that a 30 volume % loading was used), using an RV-2 spindle for viscosity measurement. Results are shown in Table 5. The viscosity of the Epon 8132 resin and mineral fillers mixtures were very high, and the compositions had to be limited to 30 volume percent filler in order to be able to measure the viscosities with our Viscometer (Brookfield Viscometer, Model DV-III+, T-A spindle @ 0.5 rpm). Even though higher loadings of hollow glass microspheres could be accommodated, they were held at 30 volume percent loading in order to better compare their viscosity with the mineral fillers.

Comparative Examples C15-C17
Example 34 was repeated, using several common fillers to make 30% by volume mixtures in Epon™ 8132 resin. BYK™-W 995 (0.4 g) was added in situ to each mixture, and the Percent Viscosity Difference determined. Results are shown in Table 5.

Table 5. Percent Viscosity Difference Found With In Situ Addition Of BYK™-W 995 To Epon™ 8132 Compositions With Various Fillers.

<table>
<thead>
<tr>
<th>Example</th>
<th>Filler</th>
<th>Volume % Filler</th>
<th>% Viscosity Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C34</td>
<td>4.76 g K1</td>
<td>30%</td>
<td>-37 %</td>
</tr>
<tr>
<td>C15</td>
<td>93.3 g HalteX 100 ATH</td>
<td>30%</td>
<td>+943 %</td>
</tr>
<tr>
<td>C16</td>
<td>104.1 g Micro-White 15 CaCO₃</td>
<td>30%</td>
<td>+56 %</td>
</tr>
<tr>
<td>C17</td>
<td>163 g Kimera 600i TiO₂</td>
<td>20% *</td>
<td>+40 %</td>
</tr>
</tbody>
</table>

* This was the maximum volume % measurable with the viscometer.

The results in Table 5 demonstrate the unique and unexpected viscosity reducing behavior of the phosphate ester when added in situ to epoxy resin containing hollow glass microspheres. This is surprising, because in situ addition of the same amount of phosphate ester to epoxy resin containing some common fillers caused the viscosity to increase.

Comparative Example 35

K1 hollow glass microspheres were coated with an amount of BYK™-W 995 in place of the amounts of BYK™-A 525 and BYK™-W 995 in Example 1, using the method described in Example 1 to yield coated K1 hollow glass microspheres wherein the weight % of BYK™-W 995 was 4% based on the total weight of uncoated K1. Epon™ 8132 epoxy resin (100 grams) was mixed with the 4.76 g coated K1 to make a composition containing 30 volume % coated K1. As illustrated in previous examples, higher volume loadings of coated hollow glass microspheres are easily achievable in the Epon 8132 resin. However, in this case, the volume loading of coated K1 hollow glass microspheres was kept at 30% in order to be directly comparable with the coated mineral filler compositions. The volume loading of the coated mineral fillers was limited to 30%
due to the upper limit of viscosity that could be measured by the Viscometer (Brookfield Viscometer, Model DV-II+, T-A spindle @ 0.5 rpm). The Percent Viscosity Difference was determined using Test Procedure II (except that a volume loading of 30 % was used), and the result is shown in Table 6.

Comparative Examples C18-C21

Example 35 was repeated, substituting each of several common fillers coated with 0.19 gram BYK™-W 995, using the method described in Example 1. The Percent Viscosity Differences were determined using Test Procedure II, substituting the filler and coated filler for hollow glass microspheres and coated hollow glass microspheres, respectively. The results are shown in Table 6.

Table 6. Percent Viscosity Difference Found In Epon™ 8132 Epoxy Resin With 30 Volume Percent Hollow Glass Microspheres And With The Same Volume Percent Of Other Fillers, All Coated With 0.19 Gram BYK™-W 995.

<table>
<thead>
<tr>
<th>Example</th>
<th>Filler Coated with 0.19 g Phosphate Ester</th>
<th>Volume % Filler</th>
<th>% Viscosity Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C35</td>
<td>4.76 g K1</td>
<td>30 %</td>
<td>-16.6 %</td>
</tr>
<tr>
<td>C18</td>
<td>93.3 g Haltex 100 ATH</td>
<td>30 %</td>
<td>+33 %</td>
</tr>
<tr>
<td>C19</td>
<td>104.1 g Micro-White 15 CaCO₃</td>
<td>30 %</td>
<td>-50 %</td>
</tr>
<tr>
<td>C20</td>
<td>103.4 g Min-U-Sil 15 silica</td>
<td>30 %</td>
<td>+133 %</td>
</tr>
<tr>
<td>C21</td>
<td>163 g Kronos 2073 TiO₂</td>
<td>30 %</td>
<td>-27 %</td>
</tr>
</tbody>
</table>

The results in Table 6, when compared to those in Table 5, demonstrate that the effect of the phosphate ester depends on whether it is added in situ, or is coated on the filler.

Example 36

An epoxy resin blend, made by combining Epon™ 8132 (100 grams) and DDSA (145 grams), was mixed with K25 hollow glass microspheres coated with both BYK™-A 525 at 1 weight % and BYK™-W 995 at 4 weight %, based on the weight of the hollow glass microspheres, using the coating procedure in Example 1. The dried coated K25
(62.2 g), which had a true density of 0.241 g/cc and a final dried coating weight of 2.5 % were present in the epoxy composition at 52.5 volume %. The control viscosity was determined with an otherwise identical epoxy composition, containing uncoated K25 (62.6 g), which had a true density of 0.243 g/cc. Percent Viscosity Difference, Percent Increased Volume Loading and Percent Density Difference were determined using Test Procedure I. The results are shown in Table 7.

Example 37
An epoxy resin blend made by combining Epon™ 8132 (100 grams) and DDSA (145 grams) was mixed with K25 hollow glass microspheres coated with both BYK™-A 525 at 0.5 weight % and BYK™-W 995 at 2.0 weight %, based on the weight of the hollow glass microspheres using the coating procedure in Example 1. The dried coated K25 (61.9 g), which had a true density of 0.240 g/cc and a final dried coating weight of 1.25 % were present in the epoxy composition at 52.5 volume %. The control viscosity was determined with an otherwise identical epoxy composition, containing uncoated K25 (62.6 g), which had a true density of 0.243 g/cc. Percent Viscosity Difference, Percent Density Difference, and Percent Increased Volume Loading were determined using Test Procedures I. The results are shown in Table 7.

Table 7. Percent Viscosity Difference, Percent Density Difference, And Percent Increased Volume Loading With K25 Coated With BYK™-A 525 And BYK™-W 995.

<table>
<thead>
<tr>
<th>Example</th>
<th>Weight % Surface Tension Reducer</th>
<th>Weight % Phosphate Ester</th>
<th>% Viscosity Difference</th>
<th>% Increased Volume Loading</th>
<th>% Density Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>1 % BYK-A 525</td>
<td>4 % BYK-W 995</td>
<td>-59 %</td>
<td>35.4 %</td>
<td>-9.8 %</td>
</tr>
<tr>
<td>37</td>
<td>0.5 % BYK-A 525</td>
<td>2 % BYK-W 995</td>
<td>-59 %</td>
<td>22.6 %</td>
<td>-6.8 %</td>
</tr>
</tbody>
</table>

The results in Table 7 show that the combination of phosphate ester and surface tension reducer coated on a higher density hollow glass microsphere produces large reductions in viscosity and density, and large increases in volume loading. It also demonstrates that two different coating weights can produce similar reductions in viscosity, but enable a different IVL and Density Difference.
Example 38

PQ 5019 sodium silicate based hollow glass microspheres were coated with 1% BYK™-W 995, based on weight of the uncoated hollow glass microspheres, in place of the BYK™-A 525 and BYK™ W-995 combination of Example 1, using the coating procedure in Example 1 with 400 ml of acetone but with no heptane as the solvent. An epoxy resin composition containing 50 volume % hollow silicate microspheres was made by mixing 142.7 grams Epon™8132 with 25.54 grams of the coated PQ 5019 silicate microspheres. Percent Viscosity Difference was determined according to Test Procedure II using a 50 volume % loading of uncoated PQ 5019 silicate microspheres in the control composition. An RV-2 spindle was used to measure viscosity. The control viscosity was found to be 38,400 cps. Percent Viscosity Difference is shown in Table 8 as Example 38.

Example 39

PQ 5019 sodium silicate based hollow glass microspheres were coated with BYK™-W 9010 at 1% by weight, based on weight of the uncoated hollow glass microspheres, in place of the BYK™-A 525 and BYK™ W-995 combination of Example 1, using the coating procedure in Example 1 with 400 ml of acetone but with no heptane as the solvent. An epoxy resin composition containing 50 volume % hollow silicate microspheres was made by mixing 142.7 grams Epon™8132 with 25.54 grams of the coated PQ 5019 silicate microspheres. Percent Viscosity Difference was determined according to Test Procedure II using a 50 volume % loading of uncoated PQ 5019 silicate microspheres in the control composition. Viscosity was measured using an RV-2 spindle. The control viscosity was found to be 38,400 cps. Percent Viscosity Difference is shown in Table 8 as Example 39.

Table 8. Percent Viscosity Difference In Epon™ 8132 With 1% BYK™-W 995 And 9010 Coated Silicate Based Hollow Glass Microspheres

<table>
<thead>
<tr>
<th>Example</th>
<th>Coating on PQ 5019</th>
<th>Percent Viscosity Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>1 weight % BYK-W 995</td>
<td>-28 %</td>
</tr>
<tr>
<td>39</td>
<td>1 weight % BYK-W 9010</td>
<td>-39 %</td>
</tr>
</tbody>
</table>
It should be noted that BYK™-W 995 is only about 50% active solids, while BYK™-W 9010 is essentially 100% active solids. The above data in Table 8 demonstrate that PQ 5019 bubbles coated with a phosphate ester produce a large reduction in the viscosities of epoxy resin compositions containing PQ 5019 microspheres, making possible an increase in the volume loading and a density decrease.

Examples 40-43

Four epoxy resin blends were made by combining 100 grams of a selected epoxy resin and 145 grams of DDSA. Each blend was mixed with K1 hollow glass microspheres coated with both BYK™-A 525 at 2 weight % and BYK™-W 995 at 8 weight %, using the coating procedure in Example 1. All of the resulting compositions as well as the corresponding control compositions contained 52.5 volume % HGM based on the total volume of the epoxy composition. Percent Viscosity Difference for each composition was determined using Test Procedure II. Results according to the selected epoxy resin are tabulated in Table 9.

Table 9. Percent Viscosity Difference With K1 Coated With 2% BYK™-A 525 And 8% BYK™-W 995 In Various Epoxy Resins.

<table>
<thead>
<tr>
<th>Example</th>
<th>Epoxy Resin Blend</th>
<th>Percent Viscosity Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>Epon 8132/DDSA</td>
<td>-50 %</td>
</tr>
<tr>
<td>41</td>
<td>Araldite GY 506/DDSA</td>
<td>-46 %</td>
</tr>
<tr>
<td>42</td>
<td>D.E.R 324/DDSA</td>
<td>-58 %</td>
</tr>
<tr>
<td>43</td>
<td>PEP 6756/DDSA</td>
<td>-33 %</td>
</tr>
</tbody>
</table>

The results in Table 9 demonstrate that hollow glass microspheres coated with a combination of surface tension reducer and phosphate ester provide very significant viscosity reductions in a variety of epoxy resins. This makes possible compositions with a wide variety of resins having higher volume loadings and significantly lower densities.
Example 44

A masterbatch of an autobody filler comprising an unsaturated polyester resin was prepared by blending together the following components and corresponding amounts:

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Component Name</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Reichold Polyester Resin 32367-00</td>
<td>2744.6 g</td>
</tr>
<tr>
<td></td>
<td>Styrene Monomer</td>
<td>51.6 g</td>
</tr>
<tr>
<td></td>
<td>Glycerol</td>
<td>14.6 g</td>
</tr>
<tr>
<td></td>
<td>Zeothix 95 Silica</td>
<td>90.5 g</td>
</tr>
<tr>
<td></td>
<td>Kemera 6001 Titanium Dioxide</td>
<td>247.6 g</td>
</tr>
<tr>
<td>10</td>
<td>Luzenac America Tate</td>
<td>1855.2 g</td>
</tr>
<tr>
<td></td>
<td>Pulpro White 8 Calcium Carbonate</td>
<td>636.2 g</td>
</tr>
</tbody>
</table>

To 1000 g of the above unsaturated polyester masterbatch was added 26.12 g of K1 glass bubbles to make the control composition. The viscosity of the resulting control composition (control viscosity) was determined as in Test Procedure II and found to be 745,600 cps. Coated (2 % BYK™-A 525 and 8 % BYK™-W 995) K1 glass bubbles (27.43 g) prepared as described in Example 1 were blended with 1000 g of the above masterbatch, and the viscosity of the resulting initial coated HGM composition was measured and found to be 518,400 cps. Viscosities were measured using a T-A spindle at 0.5 rpm. The Percent Viscosity Difference calculated according to Test Procedure II was −30 %. Additional coated K1 glass bubbles were then incrementally added to the initial coated HGM composition until the control viscosity was reached, and the Percent IVL calculated according to Test Procedure II was 36%, based on a total weight of added coated HGM increments of 10 g.

The results of Example 44 show that the phosphate ester and surface tension reducer coated on the glass bubbles greatly reduced the viscosity of the unsaturated polyester resin/glass bubble blend compared to the same blend without the coating on the glass bubbles. The results also show that with the coating a much higher loading of glass bubbles was achieved than without the coating.

Examples 45-52 and Comparative Example C36

Example 44 was essentially repeated, evaluating K1 glass bubbles coated with 1 % BYK™-A 525, 4 % BYK™-W 995, 8 % BYK™-W 995, 2 % BYK™-W 9010, 1 %
BYK™-A 525 and 4% BYK™-W 995, 1% BYK™-A 525 and 8% BYK™-W 995, 1% BYK™-A 525 and 2% BYK™-W 9010, and 1% BYK™-A 525 and 4% BYK™-W 9010. The resulting Viscosity Difference Values are shown in Table 10.

Table 10. Percent Viscosity Difference Values Of Coated K1 Glass Bubbles In Unsaturated Polyester Resin Formulation.

<table>
<thead>
<tr>
<th>Example</th>
<th>Coating on K1 (weight %)</th>
<th>Viscosity (cps)</th>
<th>Percent Viscosity Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>None</td>
<td>752,000</td>
<td>NA</td>
</tr>
<tr>
<td>C36</td>
<td>1% BYK-A 525</td>
<td>804,640</td>
<td>+7%</td>
</tr>
<tr>
<td>45</td>
<td>4% BYK-W 995</td>
<td>676,800</td>
<td>-10%</td>
</tr>
<tr>
<td>46</td>
<td>8% BYK-W 995</td>
<td>579,200</td>
<td>-23%</td>
</tr>
<tr>
<td>47</td>
<td>1% BYK-A 525 + 4% BYK-W 995</td>
<td>654,240</td>
<td>-13%</td>
</tr>
<tr>
<td>48</td>
<td>1% BYK-A 525 + 8% BYK-W 995</td>
<td>524,800</td>
<td>-30%</td>
</tr>
<tr>
<td>49</td>
<td>1% BYK-A 525 + 22% BYK-W 995</td>
<td>-34%</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>2% BYK-W 9010</td>
<td>661,760</td>
<td>-12%</td>
</tr>
<tr>
<td>51</td>
<td>1% BYK-A 525 + 2% BYK-W 9010</td>
<td>635,440</td>
<td>-15.5%</td>
</tr>
<tr>
<td>52</td>
<td>1% BYK-A 525 + 2% BYK-W 9010</td>
<td>480,000</td>
<td>-36%</td>
</tr>
</tbody>
</table>

The results in Table 10 show that the combinations of BYK™-A 525 surface tension reducer with BYK™-W 995 and 9010 phosphate esters produced surprising synergistic reductions in the viscosities of the unsaturated polyester resin formulation/K1 glass bubble blend (Examples 47, 48, 49, 51, and 52). These reductions were in addition to the viscosity reductions observed when the phosphate esters were used alone (Examples 45, 46, and 50), and are particularly surprising, because the surface tension reducer alone was found to increase viscosity (Comparative Example C36).
Example 53

Using the procedure described in Example 1, S32 glass bubbles were coated with 3 % by weight of a mixture consisting of 96 % by weight BYK L-6012 and 4 % by weight BYK 361. A Lupranol™ polyl mixture (200 g), Germany), used for reacting with polyfunctional isocyanates to form polyurethanes, was blended with 87.9 g S32 glass bubbles, forming a blend containing 55 % by volume glass bubbles. A second blend containing the Lupranol™ polyl mixture 200 g) and 55 % by volume coated S32 bubbles (91.0 g) was also prepared. The viscosity of each blend was measured at 24 °C using a Brookfield Viscometer, Model DV-II+, with a T-A spindle at 1.0 rpm. The results are tabulated in Table 11.

Table 11. Viscosities Of Coated And Uncoated S32 Glass Bubbles In Lupranol™ Polyl Mixture For Polyurethane Formation.

<table>
<thead>
<tr>
<th>Example</th>
<th>Coating on S32 (weight %)</th>
<th>Bubble Density (g/cc)</th>
<th>Viscosity (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>None</td>
<td>0.374</td>
<td>1,326,000</td>
</tr>
<tr>
<td>53</td>
<td>2.88 % BYK L-6012 + 0.12 % BYK 361</td>
<td>0.387</td>
<td>265,600</td>
</tr>
</tbody>
</table>

The results in Table 11 show that a polyl blended with S32 glass bubbles coated with BYK™ L-6012 phosphate ester in combination with BYK 361 surface tension reducer had a much lower viscosity than a similar blend with no coating on the S32 glass bubbles present at the same volume percent. This means that greater amounts of coated glass bubbles can be incorporated into the polyl before the same viscosity as that of the control is reached. As a result, when such polyl/glass bubble blends are mixed with polyfunctional isocyanates, polyurethanes containing higher volume loadings of glass bubbles are possible. These polyurethanes will then have both lower densities and lower thermal conductivity.

Example 54

Example 53 was essentially repeated except that MDI was used in place of the polyl and 74.2 g of S32 glass bubbles were used to form the first blend (control), and
76.8 g of coated S32 glass bubbles were used to form the second blend. The viscosity of each blend was measured at 22 °C using a Brookfield Viscometer, Model DV-II+, with a T-A spindle at 1.0 rpm. The results are shown in Table 12.

Table 12. Viscosities of Coated and Uncoated S32 Glass Bubbles In MDI For Polyurethane Formation.

<table>
<thead>
<tr>
<th>Example</th>
<th>Coating on S32 (weight %)</th>
<th>Viscosity (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>None</td>
<td>24,000</td>
</tr>
<tr>
<td>54</td>
<td>2.88 % BYK L-6012 + 0.12% BYK 361</td>
<td>14,400</td>
</tr>
</tbody>
</table>

The results in Table 12 show that an MDI blend with S32 glass bubbles coated with BYK™ L-6012 phosphate in combination with BYK™ 361 surface tension reducer had a much lower viscosity (i.e., about 40 % lower) than a similar blend with no coating on the S32 glass bubbles present at the same volume percent. This means that higher loadings of glass bubbles can be incorporated into the polyfunctional isocyanate component before the same viscosity as that of the control is reached. As a result when such polyfunctional isocyanate/glass bubble blends are mixed with polyols or other active hydrogen containing compounds, polyurethanes containing higher volume loadings of glass bubbles are possible. These polyurethanes will then have both lower densities and lower thermal conductivity.

While this invention has been described in connection with specific embodiments, it should be understood that it is capable of further modification. The claims herein are intended to cover those variations which one skilled in the art would recognize as the equivalent of what has been described herein.
What is Claimed:

1. A coated glass microbubble composition comprising:
   (a) glass microbubbles; and
   (b) a coating on the glass microbubbles, wherein the coating comprises a
       phosphate ester.

2. The composition of claim 1 wherein the coated glass microbubbles provide a density
decrease of at least about 2% at constant viscosity according to at least one of Test
   Procedures I or II.

3. The composition of claim 2 wherein the coated glass microbubbles provide at least
   about a 5 percent reduction in viscosity at constant volume loading according to at least
   one of Test Procedures I or II.

4. The composition of claim 3 wherein the coated glass microbubbles provide at least
   about a 10 percent reduction in viscosity at constant volume loading according to at least
   one of Test Procedures I or II.

5. The composition of claim 3 wherein the coated glass microbubbles provide at least
   about a 20 percent reduction in viscosity at constant volume loading according to at least
   one of Test Procedures I or II.

6. The composition of 3 wherein the coated glass microbubbles provide at least about a
   30 percent in viscosity at constant volume loading according to at least one of Test
   Procedures I or II.

7. The composition of claim 2 wherein the coated glass microbubbles provide a density
decrease of at least about 3 % at constant viscosity according to at least one of Test
   Procedures I and II.
8. The composition of claim 2 wherein the coated glass microbubbles provide a density decrease of at least about 5% at constant viscosity according to at least one of Test Procedures I and II.

9. The composition of claim 2 wherein the coated glass microbubbles provide a density decrease of at least about 7% at constant viscosity according to at least one of Test Procedures I and II.

10. The composition of claim 2 wherein the coated glass microbubbles provide a density decrease of at least about 9% at constant viscosity according to at least one of Test Procedures I and II.

11. The composition of claim 2 wherein the coating on the glass microbubbles is about 0.1 to about 30 percent by weight based on the total weight of the coated glass microspheres.

12. The composition of claim 2 wherein the coating on the glass microbubbles is about 0.2 to about 20 percent by weight based on the total weight of the coated glass microspheres.

13. The composition of claim 2 wherein the coating on the glass microbubbles is about 0.3 to about 10 percent by weight based on the total weight of the coated glass microspheres.

14. The composition of any one of claims 2-13 wherein the coating further comprises a surface tension reducer.

15. The composition of claim 13 wherein the surface tension reducer is selected from the group consisting of surfactants, silicon-containing compounds and mixtures thereof.

16. The composition of claim 14 wherein the surface tension reducer is selected from the group consisting of nonionic surfactants, anionic surfactants, silicon-containing compounds and mixtures thereof.
17. The composition of claim 13 wherein the weight ratio of surface tension reducer to phosphate ester ranges from about 1:50 to about 10:1.

18. The composition of claim 13 wherein the weight ratio of surface tension reducer to phosphate ester ranges from about 1:30 to about 4:1.

19. The composition of claim 13 wherein the weight ratio of surface tension reducer to phosphate ester ranges from about 1:20 to about 1:1.

20. The composition of claim 2 wherein the phosphate ester comprises a phosphorylated reaction product of a methoxy endcapped polyoxyethylene and caprolactone, the phosphate ester having a number average molecular weight of less than about 1200.

21. The composition of claim 2 wherein the coated glass microbubbles provide at least about a 2 percent reduction in viscosity at constant volume loading according to Test Procedure I.

22. An uncured resin composition comprising:
   (a) coated glass microbubbles comprising:
      (i) glass microbubbles;
      (ii) a coating on the glass microbubbles, wherein the coating comprises a phosphate ester and optionally comprises surface tension reducer;
   (b) resin selected from the group consisting of epoxy, urethane, and unsaturated polyester; and
   (c) optional resin curing agent, catalyst, or initiator;

wherein the volume loading of coated glass microbubbles is at least about 40 percent based on the total volume of the uncured resin composition; and wherein the coated microbubbles provide a density decrease of at least about 2 percent at constant viscosity according to Test Procedure II.
23. The composition of claim 22 wherein the coated glass microbubbles provide at least about a 10 percent reduction in viscosity at constant volume loading according to Test Procedure II.

24. The composition of claim 22 wherein the coated glass microbubbles provide at least about a 20 percent reduction in viscosity at constant volume loading according to Test Procedure II.

25. The composition of claim 22 wherein the coated glass microbubbles provide at least about a 30 percent reduction in viscosity at constant volume loading according to Test Procedure II.

26. An uncured resin composition comprising:
   (a) glass microbubbles;
   (b) resin selected from the group consisting of epoxy, urethane, and unsaturated polyester;
   (c) phosphate ester;
   (d) optional surface tension reducer; and
   (e) optional resin curing agent, catalyst, or initiator;

   wherein the volume loading of glass microbubbles is at least about 40 percent based on the total volume of the uncured resin composition; wherein the phosphate ester and optional surface tension reducer in combination with the glass microbubbles provide a density decrease of at least about 2 percent at constant viscosity according to Test Procedure III; and wherein the uncured resin composition is formed by combining the glass microbubbles, resin, phosphate ester, optional surface tension reducer, and optional resin curing agent, initiator, or catalyst in situ.

27. The composition of claim 26 wherein the phosphate ester and optional surface tension reducer in combination with the glass microbubbles provide at least about a 10 percent reduction in viscosity at constant volume loading according to Test Procedure III.
28. The composition of claim 26 wherein the phosphate ester and optional surface tension reducer in combination with the glass microbubbles provide at least about a 20 percent reduction in viscosity at constant volume loading according to Test Procedure III.

29. The composition of claim 26 wherein the phosphate ester and optional surface tension reducer in combination with the glass microbubbles provide at least about a 30 percent reduction in viscosity at constant volume loading according to Test Procedure III.

30. The composition of claim 22 or 26 wherein said curable resin is selected from the group consisting of epoxy, urethane, and unsaturated polyester.

31. The composition of claim 22 or 26 wherein the phosphate ester comprises a phosphorylated copolymer comprising a polyoxyethylene residue.

32. The uncured resin of claim 31 wherein the phosphate ester comprises a phosphorylated reaction product of a methoxy endcapped polyoxyethylene and caprolactone, the phosphate ester having a number average molecular weight of less than about 1200.

33. The composition of claim 22 or 26 having a loading of microbubbles of at least about 50 percent by volume based on the total volume of the uncured resin composition.

34. The uncured resin composition of claim 33 having a loading of microbubbles of at least about 60 percent by volume based on the total volume of the uncured resin composition.

35. A cured syntactic foam composition comprising:
   (a) glass microbubbles; and
   (b) the reaction product of a composition comprising an uncured resin, a phosphate ester comprising a phosphorylated copolymer comprising a polyoxyethylene residue, an optional surface tension reducer, and a component selected from the
group consisting of resin curing agents, catalysts, and initiators, and combinations thereof; and

wherein the loading of the glass microbubbles is at least about 50 percent by volume based on the total volume of the glass microbubbles, the uncured resin, and the component.

36. The cured syntactic foam composition of claim 35 having a density of less than about 0.65 g/cc.

37. The composition of claim 35, wherein the loading of the glass microbubbles is at least about 55 percent by volume based on the total volume of the glass microbubbles, uncured resin, and optional resin curing agent, catalyst, or initiator.

38. The composition of claim 35 wherein the loading of the glass microbubbles is at least about 60 percent by volume based on the total volume of the glass microbubbles, uncured resin, and optional resin curing agent, initiator, or catalyst.

39. The composition of claim 35, wherein the loading of the glass microbubbles is at least about 70 percent by volume based on the total volume of the glass microbubbles, uncured resin, and optional resin curing agent, initiator, or catalyst.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 CO3C11/00 CO3C17/28

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 7 CO3C

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)

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>X</td>
<td>EP 0 630 956 A (ALDERLEY MATERIALS LTD) 28 December 1994 (1994-12-28) cited in the application page 5, line 14 page 6, line 1 - line 55</td>
<td>1-39</td>
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Date of the actual completion of the international search: 10 January 2001

Date of mailing of the international search report: 18/01/2001

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