

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
5 August 2004 (05.08.2004)

PCT

(10) International Publication Number
WO 2004/065475 A1

- (51) International Patent Classification⁷: C08K 9/10, C09D 11/02, C09B 67/00, C09C 1/00, 3/00
- (21) International Application Number: PCT/US2004/001727
- (22) International Filing Date: 22 January 2004 (22.01.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 10/351,386 23 January 2003 (23.01.2003) US
- (71) Applicant (for all designated States except US): GENERAL ELECTRIC COMPANY [US/US]; 1 River Road, Schenectady, NY 12345 (US).

GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

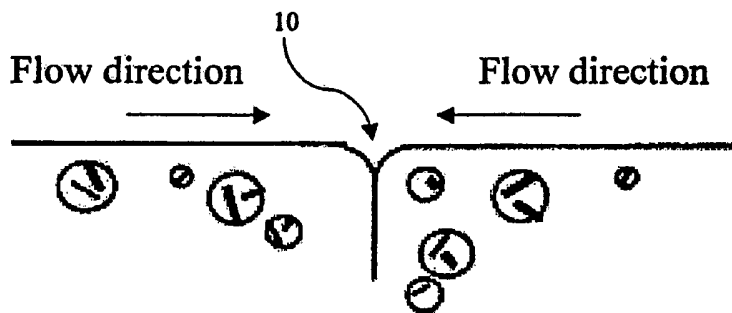
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations

Published:

- with international search report

[Continued on next page]

(54) Title: POLYMER ENCAPSULATION OF HIGH ASPECT RATIO MATERIALS AND METHODS OF MAKING SAME



(57) Abstract: Embodiments of this invention comprise a pigment comprising one or more substantially spherical-shaped beads, wherein each substantially spherical-shaped bead comprises one or more high aspect ratio particles encapsulated within an encapsulating material. Embodiments also comprise a resinous composition comprising said pigment. Yet further embodiments comprise a method of preparing said pigment via suspension polymerization. The substantially

spherical-shaped beads of this invention may be used to produce resinous compositions having a flowline-free colored, sparkling and/or metallescent appearance.

WO 2004/065475 A1



-
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

POLYMER ENCAPSULATION OF HIGH ASPECT RATIO MATERIALS AND METHODS OF MAKING SAME

Background of Invention

The present invention relates generally to pigments comprising high aspect ratio materials encapsulated in a polymer to form beads, and methods of making same. More specifically, the present invention relates to pigments comprising high aspect ratio flake particles encapsulated in a polymer to form substantially spherical beads that are useable for producing plastic products having a colored, sparkling, and/or metallescent or metal-like appearance, and methods of making same.

Current trends in consumer products have created an unprecedented demand for plastics having unique colors and looks. For example, cellular telephones having interchangeable plastic covers are now commonly available. These covers come in a variety of colors and/or special effects, giving consumers control over the aesthetic design of their phones. Many other injection molded plastic products, such as, for example, computers, stereos and other consumer and/or business equipment, automotive interiors, etc., would also benefit from having unique colors and looks.

Plastic products having a sparkling look, a metallescent or metal-like look, a true metal appearance, or any angular metameric appearance are desirable in many instances. Plastics having a sparkling or metallescent look can be created by incorporating free metal flakes into a plastic article at such loading that the individual flakes can be distinguished by the naked eye, resulting in an article with a sparkling or metallescent appearance. Plastics having a true metallic look can be created by using a much higher loading of free metal flakes. The drawback to products incorporating free metallic flakes is that the free flakes have a high aspect ratio, and therefore tend to change orientation at knitlines or other areas of non-uniform flow direction, aligning themselves with the flow field during processing, thereby causing visible flowlines, knitlines or weldlines in the finished product. Such flowlines, knitlines or weldlines produce unattractive streaks in the product. Therefore, there is an

increasing demand for sparkling, metallescent and/or metal-looking plastics that cannot be met effectively by incorporating free metallic flakes into plastic articles.

Many desirable pigments and additives for plastics, such as metallic particles, have a high aspect ratio, including, but not limited to, plate-like or flaky particle structures. As previously discussed, during processing such particles tend to orient parallel with the material flow. In some cases, this directionality can be an advantage, such as for improving the flexural modulus of extruded sheet moldings or thin-walled moldings. In other cases, however, this directionality can be disadvantageous, particularly in situations where the parts are complex and a uniform surface appearance is desired. Under such conditions, local variations in flow field direction can produce unacceptable variations in color or reflectivity. Metallic particles/flakes are particularly susceptible to this directionality problem because their reflectivity is high and very directional.

The geometry of the pigment particle is important in determining the optical effects that will be produced. The availability of multiple facets maximizes the reflectivity for a given particle orientation, while a more spherical shape is more hydrodynamically isotropic, thereby favoring the reduction or elimination of flowlines. High aspect ratio particles offer high sparkle efficiency, making them very effective as metallic pigments. However, these particles are also responsible for the appearance of visually objectionable flowlines.

There is presently no good way to ensure that pigments and additives having a high aspect ratio are optically anisotropic and rheologically isotropic when processed into plastic products. Cubes and octahedra seem to satisfy these two conditions, and in fact, existing techniques have attempted to resolve the directionality problem of flake materials by encapsulating the flake materials in a substantially cubic material. While cubic shaped materials are less sensitive to flow-induced orientation than flakes are, and thereby reduce the appearance of flowlines, this technique does not eliminate flowlines. Additionally, producing particles of complicated geometries (i.e., other than spheres and platelets) is nontrivial, and introduces unnecessary filler mass to the final product. As a result, considerable efforts have focused on the investigation of a

number of processing solutions to eliminate flowlines. Sequential gating, the use of complicated mold temperature profiles, and agitation of the mold have been found to reduce the appearance of flowlines considerably. However, these methods all require the use of highly specialized equipment, making them extremely uneconomical and impractical. Alternatively, using aluminum beads has been investigated as a possible solution. However, due to the absence of facets or sizeable reflective surfaces in aluminum beads, a reflective metallic look cannot be achieved in the end product.

Japanese Kokai Patent Application No. Hei 11[1999]-279434 describes a metallic pigment prepared by coating a transparent resin on at least one facet of glossy polyhedron particles. Japanese Kokai Patent Application No. Hei 11[1999]-21376 describes composite glittering agents that are cross-linked polymer particles containing glossy particles, resin compositions containing the glittering agents, and molded resin products made therefrom. However, neither of these references addresses the problem of glossy particles delaminating from the composite. Additionally, neither reference addresses the importance of cross-link density to overall physical properties or to the importance of restricting the size of the composite bead particles in obtaining defect free injection molded articles.

Thus, there is a need for systems and methods that ensure that the angular distribution of materials with high aspect ratios (for example, plate-like/flake pigments and additives) in complex flow fields remains optically anisotropic and rheologically isotropic when processed into plastic products. There is also a need for such systems and methods to be less expensive and less highly specialized than existing systems and methods. There is yet a further need for such systems and methods to substantially eliminate the appearance of flowlines. There is still a further need for such systems and methods to encapsulate high aspect ratio materials within a cross-linked or cross-linkable polymer. There is also a need for such systems and methods to provide higher flake-encapsulating bead yields than currently possible. There is yet still a further need for such systems and methods to utilize encapsulated high aspect ratio materials as pigments in injection molded or extruded plastics to create plastic articles substantially free of flowlines and having a sparkling and/or metallescent appearance. There is also a need to address the problem of high aspect ratio materials

delaminating from the encapsulant bead during compounding and/or molding operations. Finally, there is a need for such systems and methods to incorporate dyes therein to allow colored, sparkling and/or metallescent appearing products to be created.

Summary of Invention

Accordingly, the above-identified shortcomings of existing systems and methods are overcome by embodiments of the present invention, which relates to pigments comprising high aspect ratio materials encapsulated in a polymer to form substantially spherical beads, and methods of making same. These pigment beads are useable for producing plastic products having a colored, sparkling, and/or metallescent appearance. Embodiments of this invention comprise systems and methods that ensure that the angular distribution of high aspect ratio materials (for example, plate-like/flake pigments and additives) in complex flow fields remains optically anisotropic and rheologically isotropic when processed into plastic products. In some embodiments, the systems and methods of this invention may be less expensive and less highly specialized than existing systems and methods. In embodiments of this invention, the systems and methods may substantially eliminate the appearance of flowlines. Embodiments also encapsulate high aspect ratio materials within a cross-linked or cross-linkable polymer to form a bead, and can provide higher bead yields than currently possible. Furthermore, embodiments utilize encapsulated high aspect ratio materials as pigments in injection molded or extruded plastics to create plastic articles substantially free of flowlines and having a colored, sparkling, and/or metallescent appearance. Embodiments of this invention relate to specific processing conditions that can be employed to minimize the delamination of high aspect ratio materials from the encapsulant bead during compounding and/or molding operations. Finally, embodiments of this invention may incorporate dyes or colored pigments therein to allow colored sparkling and/or metallescent appearing products to be created.

Embodiments of this invention comprise a pigment comprising one or more substantially spherical-shaped beads, wherein each substantially spherical-shaped

bead comprises one or more high aspect ratio particles encapsulated within an encapsulating material. Embodiments of this invention also comprise methods to make said pigments.

Embodiments of this invention also comprise a resinous composition comprising a plastic matrix material and a pigment, the pigment comprising one or more substantially spherical-shaped beads, wherein each substantially spherical-shaped bead comprises one or more high aspect ratio particles encapsulated within an encapsulating material.

Embodiments of this invention also comprise molded articles made from said compositions.

Further features, aspects and advantages of the present invention will be more readily apparent to those skilled in the art during the course of the following description, wherein references are made to the accompanying figures which illustrate some preferred embodiments of the present invention, and wherein like characters of reference designate like parts throughout the drawings.

Brief Description of Drawings

The systems and methods of the present invention are described herein below with reference to the various figures, in which:

Figure 1 is a schematic diagram showing a cross-section of an injection molded part taken perpendicular to a knitline and showing the orientation of unencapsulated anisotropic particles;

Figure 2 is a schematic diagram showing a cross-section of an injection molded part taken perpendicular to a knitline and showing the random orientation of encapsulated anisotropic particles;

Figure 3 is a schematic diagram showing how the beads are separated by gravity sedimentation (the liquid medium in this embodiment may comprise a 5-20 weight %

potassium chloride solution that may contain 3-6 drops of a 0.1% Triton-X surfactant solution);

Figure 4 is a graph showing the aluminum flake distributions obtained by two methods of this invention;

Figure 5 shows the chemical structures of various additives that may be added to embodiments of this invention.

Detailed Description

For the purposes of promoting an understanding of the invention, reference will now be made to some preferred embodiments of the present invention as illustrated in FIGURES 1-5, and specific language used to describe the same. The terminology used herein is for the purpose of description, not limitation. Specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a basis for the claims as a representative basis for teaching one skilled in the art to variously employ the present invention. Any modifications or variations in the depicted systems and methods, and such further applications of the principles of the invention as illustrated herein, as would normally occur to one skilled in the art, are considered to be within the spirit of this invention.

Numerical values in the specification and claims of this application, particularly as they relate to polymer compositions, reflect average values for a composition that may contain individual polymers of different characteristics. Furthermore, the numerical values should be understood to include numerical values which are the same when reduced to the same number of significant figures and numerical values which differ from the stated value by less than the experimental error of the measurement technique used in the present application to determine the value.

Embodiments of the present invention comprise substantially spherical beads formed by encapsulation of high aspect ratio materials within a polymer. These beads may be used in various processes (for example, injection molding, extrusion, sheet molding,

solution-based processing techniques such as spin-coating or solution-casting, etc.) to form plastic products having a colored, sparkling, and/or metallescent appearance.

Referring now to Figure 1, there is shown a schematic diagram showing the directional orientation of unencapsulated (i.e., free) flakes in an injection molded polymer material. The high aspect ratio flakes or plate-like particles shown here tend to change orientation with the flow field at the knitline 10, aligning themselves with the knitline and increasing knitline visibility. This invention seeks to minimize or eliminate the visibility of these knitlines/flowlines.

Referring now to Figure 2, there is shown a schematic diagram of one embodiment of the present invention. In this embodiment, the random orientation of encapsulated flakes in a polymer material is shown. Once the flakes are encapsulated, they are substantially hydrodynamically isotropic, and are thereby substantially insensitive to flow direction. This reduces or eliminates the appearance of the knitlines 10. Additionally, the flakes encapsulated within the transparent, translucent and/or colored, substantially spherical polymer beads retain their very specular or mirror-like reflection characteristics. In this embodiment, the flake-encapsulating bead is optically anisotropic (i.e., the desired optical effect is preserved), but rheologically isotropic (i.e., there is no preferential flake orientation at knitlines and other areas of highly directional and/or nonuniform flow direction).

The present invention comprises materials having high aspect ratios (for example, flakes or plate-like particles) embedded or encapsulated in substantially spherical droplets or beads. As used herein, materials having high aspect ratios comprise those materials having an average aspect ratio of greater than about 1.5:1, greater than about 2:1, greater than about 4:1, greater than about 5:1, greater than about 8:1, greater than about 9:1, and greater than about 40:1, in various embodiments respectively. In other embodiments, materials having high aspect ratios comprise those materials having an average aspect ratio of about 2:1 to about 40:1, of about 5:1 to about 40:1, and of about 9:1 to about 40:1, in various embodiments respectively.

Materials having high aspect ratios that are suitable for use in this invention comprise materials having at least 2 facets, about 2 to about 100 facets, about 3 to about 50 facets, about 4 to about 10 facets, less than 4 facets, about 2 to about 4 facets, and about 2 to about 3 facets, in various embodiments respectively.

The high aspect ratio materials utilized in this invention may comprise any suitable material that provides the desired colored, metallic, sparkling and/or metallescent appearance in a resinous composition. Some non-limiting examples of such materials comprise aluminum, gold, silver, copper, nickel, titanium, stainless steel, nickel sulfide, cobalt sulfide, manganese sulfide, metal oxides, white mica, black mica, synthetic mica, mica coated with titanium dioxide, metal-coated glass flakes, colorants, including but not limited, to Perylene Red, or any other suitable high aspect ratio material that may be susceptible to forming flowlines when used by itself in an unencapsulated form in a resinous composition. Mixtures of high aspect ratio materials are also included in embodiments of the present invention. For example, a mixture of a high aspect ratio colorant and a high aspect ratio additive to provide metallic, sparkling and/or metallescent appearance may be employed. In many embodiments only one high aspect ratio additive is employed.

These substantially spherical beads may have an average aspect ratio of less than about 2:1, of less than about 1.5:1, of less than about 1.2:1, of less than about 1.1:1, or of about 1:1, in various embodiments respectively. Generally, it is desirable for the beads containing encapsulated high aspect ratio material to have an average aspect ratio of about 1:1 to ensure that there is little or no preferential orientation or alignment near knitlines, flowlines, etc. As used herein, the terms "knitline", "flowline", and "weldline" are all used interchangeably to mean areas of highly directional and/or non-uniform flow direction. Furthermore, as used herein, the terms "encapsulation", "flake-encapsulating" and any similar variations cover both flakes that are fully encapsulated within the bead, as well as flakes that are surface laminated to the bead. Both bead types may be present in varying degrees in materials prepared by methods described herein, and depending on which bead type comprises the majority of the bead population, the appropriate processing conditions, as described

below herein, may be applied to achieve plastic articles substantially free of visible flowlines.

The substantially spherical beads are also referred to in this application as an encapsulated pigment composition. The beads or particles in the encapsulated pigment composition are of a size that is suitable of imparting color and other visual effects to conventional objects, such as telephone covers, cell phones, computer bezels, keyboards, key caps and mice, television bezels, stereos, printers and other consumer and business equipment, as well as automotive interiors and exteriors and the like. As such, it will be appreciated that the particles in the pigment of the invention are small, as compared to the wall thickness of such articles so that dispersion is possible within the article.

The substantially spherical beads preferably have an average diameter that is at least equal to, or slightly exceeds, the average length of the high aspect ratio particle encapsulated therein. These beads may have an average diameter of between about 10 μ m to about 300 μ m, of between about 15 μ m to about 300 μ m, of between about 20 μ m to about 300 μ m, of between about 40 μ m to about 250 μ m, of between about 80 μ m to about 200 μ m, or of between about 90 μ m to about 140 μ m, in various embodiments respectively. Those skilled in the art will recognize that in these various embodiments, individual beads having a diameter less than or greater than the average diameters listed may exist, without causing the average bead diameter of the bead population to fall outside the specified ranges. The high aspect ratio particles that are encapsulated within the beads preferably have average values for their greatest dimension in the same range as the average diameters of the beads within which they are encapsulated, with the average value for the greatest dimension of the high aspect ratio particles preferably being equal to or slightly less than the average diameter of the beads within which they are encapsulated. For example, in one embodiment, the high aspect ratio particles encapsulated within the beads may comprise flakes having a maximum dimension of about 100 μ m or slightly less, with the beads having an average diameter of about 100 μ m.

The average amount (i.e., weight) of high aspect ratio material encapsulated within the polymer encapsulating bead material is typically an amount necessary to achieve a desired colored, metallic, sparkling and/or metallescent appearance for a particular concentration of beads in a resinous composition, wherein the average amount of high aspect ratio material may be determined by dividing the total weight of the high aspect ratio material used by the total weight of the beads. The average amount of high aspect ratio material encapsulated within the polymer encapsulating bead material may be less than about 25 wt. %, between about 0.1 and about 25 wt. %, between about 1 and about 20 wt. %, between about 2 and about 15 wt. %, between about 5 and about 10 wt. %, between about 10 to about 15 wt. %, between about 0.1 to about 5 wt. %, or between about 0.1 to about 4 wt. %, in various embodiments respectively, based on the weight of the pigment bead. Those skilled in the art will recognize that in the total bead populations of these various embodiments, there may be individual beads that have no high aspect ratio material encapsulated therein, and there may be individual beads that have greater than 25 wt. % high aspect ratio material encapsulated therein, without causing the average amount of high aspect ratio material encapsulated within the polymer beads of a given bead population to fall outside the specified ranges.

The polymer material (i.e., the encapsulating material) surrounding the high aspect ratio particles may comprise any material that has a sufficient amount of transparency and/or translucency to allow the desired optical effect in a plastic product to be achieved. Some non-limiting examples of such materials comprise a thermoset resin, a polymer prepared by suspension polymerization, or a polymer that is a thermoplastic.

Such thermoset resins may comprise, for example, epoxy, phenolic, acrylics, alkyds, polyester, polyimide, polyurethane, silicone, bis-maleimide, cyanate ester, vinyl, and/or benzocyclobutene resins. The thermoset resin composition may also comprise various catalysts, flame retardants, curing agents, fillers, reinforcing agents, and other components, if so desired. The various thermoset resin components may be used alone, in combination with one another, or in combination with another thermoplastic resin(s).

Such thermoplastics may comprise, for example, polyesters, such as polyethylene terephthalate (PET); polybutylene terephthalate (PBT); polyethylene naphthalate (PEN); polybutylene naphthalate (PBN); polycyclohexane dimethanol terephthalate (PCT); polyethylene-co-cyclohexane dimethanol terephthalate (PETG); liquid crystal polyester (LCP) and the like; polyolefins, such as polyethylene (PE), polypropylene (PP), polybutylene, polymethylpentene and the like; resins comprising structural units derived from styrene monomer such as polystyrene, styrene-acrylonitrile copolymer (SAN), acrylonitrile-styrene-butadiene (ABS) and acrylonitrile-styrene-acrylate (ASA); polyoxymethylene (POM); polyamide (PA); polycarbonate (PC); bisphenol A polycarbonate; polyvinyl chloride (PVC); polyphenylene sulfide (PPS); polyphenylene ether (PPE); polyimide (PI); polyamide imide (PAI); polyetherimide (PEI); polysulfone (PSU); polyether sulfone (PES); polyketone (PK); polyether ketone (PEK); polyether ether ketone (PEEK); polyarylate (PAR); phenol resins (novolac type or the like); phenoxy resins; fluorocarbon resins; or, furthermore, thermoplastic elastomers, examples of which include, but are not limited to, a polystyrene type, a polyolefin type, a polyurethane type, a polyester type, a polyamide type, a polybutadiene type, polyisoprene type, a fluorine type, a siloxane type, a natural rubber, a synthetic rubber, or the like; or copolymers or modifications of any of the these substances, or combinations of two or more of these substances or the like. Examples of copolymers include, but are not limited to, polydimethyl siloxane-polycarbonate copolymer, polyestercarbonate copolymer, ethylene-propylene copolymer, and ethylene-propylene diene modified copolymer (EPDM). Thermoplastics and elastomers may optionally be appropriately modified using means known in the art to introduce crosslinkable sites therein. In a particular embodiment thermoplastics or elastomers may be comprise allyl or olefinic groups, and may be prepared from monomers comprising allyl or olefinic groups. Preferably, in the case of suspension polymerization, the encapsulating material comprises polystyrene (PS), polymethyl methacrylate (PMMA), styrene acrylonitrile copolymer (SAN), methyl methacrylate styrene acrylonitrile copolymer, acrylonitrile-styrene-acrylate (ASA) resins, or combinations thereof.

At least one cross-linking agent may be included in the polymer material (i.e., the encapsulating material) surrounding the high aspect ratio particles, and the inclusion of a cross-linking agent is of particular importance when a suspension polymerization process is employed. In some embodiments the inclusion of a cross-linking agent may impart mechanical strength and/or melt stability to the pigment beads when they are processed in a composition to make a final extruded or molded product. An illustrative cross-linking agent is divinylbenzene. The amount of cross-linking agent employed may affect the physical properties of the final product. The amount of cross-linking agent that may be incorporated in the encapsulating material is determined by such factors as the physical properties desired in the final product, the properties of the thermoplastic carrier resin, and the compounding conditions used (for example, all-throat feeding vs. down-stream feeding during extrusion), and may be determined by those skilled in the art without undue experimentation. For example, in some embodiments at the same cross-linker loading, compositions extruded using down-stream feeding may be less ductile than those produced using all-throat feeding.

In some embodiments molded parts may become less ductile with increased cross-linker loading. Increasing the loading of pigment beads themselves may also result in decreased ductility in certain embodiments. The ductility of the final molded product will depend, in part, on the properties of the carrier resin used.

Other additives may be included in the encapsulating bead material. Such additives may be included for various reasons. Such additives may help maintain a desired visual effect and/or may help the beads retain their substantially spherical shape when processed into the final product. Other additives may be added to improve the bead yield over those currently possible. For example, chain transfer agents may be added, and/or retarders and/or inhibitors may be added to improve the bead manufacturing process. Additionally, dyes may be added so that colored sparkling and/or metallescent appearing products can be created. Some non-limiting examples of suitable additives comprise any suitable colorant, Solvent Blue 35, Solvent Blue 36, Disperse Violet 26, Solvent Green 3, Anaplast Orange LFP, Perylene Red, Morplas Red 36, thermal stabilizers, oxidation inhibitors, butylated hydroxytoluene (BHT),

radical scavengers, any vinyl-based monomer, filler (for example, titanium dioxide, carbon black and/or graphite), impact modifiers, UV absorbers, and/or fire retardants, etc.

These pigment beads comprising high aspect ratio material encapsulated in a polymer may be used to create plastic products having a colored, sparkling, metallescent, metal-like, true metal, and/or an angular metameric appearance. Such products may be created by dispersing such pigment beads in a plastic matrix. Suitable plastic matrix materials comprise those materials that are prone to visible flowline formation when they contain only unencapsulated high aspect ratio materials. In particular embodiments suitable plastic matrix materials include, but are not limited to, all those plastic and elastomeric materials listed hereinabove for encapsulating high aspect ratio materials. In addition to the pigment beads, these plastic matrices may also comprise additives, such as, for example, dyes or any other suitable colorants, thermal stabilizers, oxidation inhibitors, radical scavengers, fillers (for example, titanium dioxide, carbon black and/or graphite), impact modifiers, UV absorbers, and/or fire retardants, provided that the desired colored, sparkling, metallescent, true metal or angular metameric appearance is preserved when such additives are present. In some embodiments the plastic matrices may comprise unencapsulated high aspect ratio material in addition to that added in encapsulated form. The presence of all or at least a portion of the unencapsulated material in compositions comprising encapsulated material may result from delamination of encapsulated material during processing, from contamination of encapsulated material with unencapsulated material, or from the deliberate addition of unencapsulated material to the composition. The amount of unencapsulated high aspect ratio material in compositions comprising encapsulated material is such that the presence of flowlines, knitlines, or weldlines in molded parts derived from said compositions is substantially eliminated or at least reduced compared to compositions not containing encapsulated high aspect ratio material.

When the article in which encapsulated pigment composition of the invention is incorporated is larger in size, for example laptop computer covers TV bezels and other larger items, additional fine tuning and control of the process may be required to achieve the best remediation of visual defects specific to large and/or thin walled

applications. In particular, it has been observed that for thin-walled (< 1.5 mm) and/or large parts, where laminar flow of > 4 6 inches is required to fill the part on injection molding, larger beads were found to congregate at the melt front(s) rather than disperse evenly throughout the part. This resulted in objectionable visual defects in which these areas are darker in color to than the rest of the molded parts. This problem is more extreme the larger the bead particles become and is extenuated at increasingly thin wall sections. In addition to defects from bead size segregation at the melt front, at lower cross-link densities i.e. when divinylbenzene concentration is less than approximately 0.2 parts per hundred in the bead forming reaction, larger beads also become more objectionable as specks of non-uniformly high aluminum content. This problem becomes more extreme the darker the accompanying pigment/resin package becomes. The reason these are more objectionable at lower cross-link densities is that these beads are softer and therefore become stretched on injection molding in the direction of resin flow. For long laminar flow parts, for which resin velocity can be significantly higher than in smaller applications, this bead stretching phenomenon is even more extreme. Lower cross-link densities are desirable for achieving acceptable physical properties, in particular, ductile impact. The smaller the bead size achieved the better the overall aesthetics of an injection molded part will be.

In order to solve both of these problems while maintaining physical properties as well as acceptable yields from the process, beads with size no greater than 150 microns, with cross-link densities optimized for both surfactant and monomer ratios used in making the beads as well as the thermoplastic resin used. For example, using a 92:8 styrene/acrylonitrile monomer ratio and a PVA surfactant system, a cross-link density of 0.2 parts per hundred DVB provides the ideal compromise between bead stability and overall physical properties for a given resin. The cross-link densities are relative to the initial amount of cross-linking agent, in this case DVB, and are not absolute numbers. Using a different monomer ratio may require a change in cross-link density. For example, using an 85:15 styrene/acrylonitrile ratio with a PVA surfactant system requires a cross-link density of around 0.25 parts per hundred for equivalent flow line and physical performance. Additionally, using a 92:8 styrene/acrylonitrile monomer

ratio but a PVA/KI surfactant system requires around 0.3 parts per hundred DVB for similar results to a 0.2 parts per hundred material made in a PVA surfactant system. As well, as the effects of factors associated with bead and surfactant composition, incorporation of beads into a resin requiring higher processing temperatures in turn requires a bead with increased cross-link density. For example, a bead with cross-link density optimized for a resin compounded at 275 °C is not sufficiently stable for use in a resin compounded at 310 °C resulting in the appearance of flowlines in molded parts. Thus, to cover all potential thermoplastic resins a wide range of cross-link densities is required. These two key facets to achieving this target are process optimization within the suspension polymerization reaction used to make the beads (i.e, the selection of the appropriate amount of cross-linking agent and the amount of encapsulating material relative to the amount of pigment) and post reaction sieving/screening of the isolated beads to remove these large particles. As used in the specification and claims of this application, the term "maximum diameter" refers to the nominal screen size. Thus particles with a maximum diameter of 150 microns are particles which have been passed through a 150 micron screen or sieve. It will be appreciated that particles which are not perfectly symmetrical but which will pass through the screen/sieve in one direction even though they are larger than 150 microns in diameter in another direction are included in this definition.

The loading of such pigments comprising high aspect ratio materials dispersed within such plastic matrices is typically an amount necessary to achieve the desired colored, sparkling, metallescent, metal-like, true metal and/or angular metameric appearance in the final plastic article created therewith. For example, the loading of such pigments may comprise values in the range of about 0.05 to about 10 wt. %, of about 0.05 to about 5 wt. %, of about 0.05 to about 4 wt. %, of about 0.05 to about 3 wt. %, or of about 0.1 to about 3 wt. %, in various embodiments respectively.

In some embodiments the polymer encapsulating material of the beads may substantially match the refractive index of the plastic matrix in which the beads are contained. For example, the refractive index difference between the polymer encapsulating material of the beads and the plastic matrix in which the beads are contained may be less than about 0.01 to yield a substantially transparent final product

(if the plastic matrix itself is substantially transparent and no other pigmentation is added). Alternatively, the refractive index difference between the polymer encapsulating material of the beads and the plastic matrix in which the beads are contained may be in the range of between about 0.01 and about 0.05, or could even be greater than about 0.05, to yield final products having various degrees of translucency.

The encapsulation of the high aspect ratio material, and an optional further cross-linking of the polymer encapsulation material, may be accomplished in a number of different manners, such as, for example, spray drying techniques, the Wurster process, or in-situ suspension polymerization. In some embodiments when suspension polymerization is utilized, the method may comprise the steps of: dispersing high aspect ratio particles in at least one of a monomer or a polymer and a cross-linking agent to form a suspension mixture; adding the suspension mixture to an aqueous mixture comprising a suspension agent; heating and mixing the aqueous reaction mixture to encourage the formation of beads, wherein most beads encapsulate one or more high aspect ratio particles; quenching the aqueous reaction mixture after the beads are formed; and collecting the beads. This method may further comprise suspending the one or more high aspect ratio particles in the suspension mixture by sonicating the suspension mixture prior to adding the suspension mixture to the aqueous mixture. It may also comprise utilizing gravity sedimentation or centrifugation to separate the beads into various batches, and drying the beads thereafter.

In the case of suspension polymerization, the use of a cross-linking agent such as divinylbenzene provides superior particle stability in the product, as this prevents melting and dispersion of the particle and encapsulated pigment during compounding in the resin of choice. In addition, for most efficient pigment encapsulation, it is desirable that the pigment partitions between the suspension mixture (suspended phase) and the aqueous phase in such a manner that the pigment resides substantially in the suspended phase over the course of polymerization. As used in the specification and claims of this application, the phrase "resides substantially" indicates that at least 95% of the pigment resides in the suspended phase. More

preferably, greater than 99 % of the pigment resides in the suspended phase. Greater amounts residing in the aqueous phase lead to lower yields of encapsulated pigment, and can result in unencapsulated pigment in the final product leading to flowlines when used in injection molded applications. Surface modification of the pigment particles, for example to increase hydrophobicity, can be used to enhance the partition ratio for a given pigment.

The gravity sedimentation utilized in embodiments of this invention may comprise: a) removing from the beads the microemulsion caused by the suspension polymerization process; b) filtering the beads; c) reslurrying the beads in a salt solution (for example, 5-20 weight % potassium chloride) to form a separation system having an original volume; d) mixing the separation system, for example by shaking the system up; e) allowing the separation system to stand still to come to equilibrium; f) removing a fraction of useable beads from the separation system; g) filtering the fraction of useable beads that is obtained from the separation system; h) washing the filtered fraction of useable beads to remove any excess slurry solution; i) adding a quantity of deionized water to the remaining beads and slurry solution in the separation system to bring the volume of the separation system back to the original volume; and j) repeating steps d)-i) as necessary until all the beads have been removed from the separation system. If necessary, the first fraction of beads that are obtained may be discarded since that fraction may also contain free (i.e., unencapsulated) high aspect ratio particles that could cause flowlines in the final product.

In one embodiment, aluminum flakes having diameters of less than about 100 micrometers are encapsulated in a polymer. This encapsulation may be achieved via suspension polymerization of monomers in the presence of the aluminum flakes. A cross-linking agent may be included to impart mechanical strength and melt stability to the encapsulated beads when they are processed into the final extruded or molded product. The flakes may also incorporate surface functionalization thereon, so that growth of the encapsulant polymer is a surface-promoted process. In the case of suspension polymerization, surface functionalization may also be necessary for flakes that have a hydrophilic surface.

In order to make high aspect ratio materials such as flakes having a hydrophilic surface compatible with organic monomers, such materials may need to be treated with a compatibilizer, such as, for example, oleic acid. Unencapsulated high aspect ratio materials can be divided into two categories with respect to their behavior in organic media: organic compatible and organic non-compatible. The material's behavior may be tested by preparing a biphasic mixture such as toluene/water, and then adding the material into that mixture. If the material stays in the organic portion of the mixture, the material is organic compatible (i.e., hydrophobic). If the material prefers the aqueous layer of the mixture, the material is organic non-compatible (i.e., hydrophilic). The test is indicative of the material's preference for one of these two phases: hydrophobic or hydrophilic. For higher encapsulation efficiency, it is desirable to have organic compatible (i.e., hydrophobic) materials. Therefore, in cases where materials are found non-compatible, surface treatment/modifications may be carried out to render such materials organic compatible.

Rendering such materials organic compatible may entail the use of organic molecules that can bind to the surface of the material. Once binding is achieved, the organic layer should be hydrophobic enough to render the material organic compatible. In general, such molecules, often called surface modifiers, comprise a long alkyl chain and a polar end group such as, for example, thiols, sulfonic acids, phosphonic acids, carboxylic acids, carboxylates, amines, and/or quaternary ammonium salts. Surface modifiers may be polymeric, and may comprise, for example, sulfonated polystyrene, polystyrene bearing amino groups and sulfonated EPDM. The nature of the polar end group will depend on the nature of the surface. Depending on the substrate, a convenient end group may be chosen to achieve an interaction that can be ionic, covalent or non-covalent in nature. The surface modifier can also contain, besides the end group and hydrophobic portion, other reactive groups. Such reactive groups can be used to carry out further reactions. This procedure to render such materials organic compatible can also be used when the material or the surface modifier is wet or contains organic components that can be removed by known procedures such as, for example, simple or azeotropic distillation. [0047] Numerous flake particles are commercially available, such as, for example, aluminum flakes. Many times, these

flake particles are contained in a carrier agent, such as mineral oil. In various embodiments the flakes may be used as received, or the carrier agent may be removed by washing the flakes in a suitable solvent. In either case, the flakes may be added directly to the suspension of reactants in water, or the flakes may first be suspended in the monomer(s) by sonication at room temperature, and then be added to an aqueous solution comprising polyvinyl alcohol (PVA) as a suspension agent.

Example One: Coated glass pigments may be compatibilized (i.e., made to be compatible with organic monomers) using oleic acid. In one embodiment, about 11.4g of coated glass flake (30 micrometers), about 50 ml of toluene, and about 2.85g of oleic acid as a surface modifier (20 weight % with respect to the flake, 90% purity from Aldrich) were put into a round bottom flask fitted with a Dean-Stark trap and a stirrer. The mixture was stirred under azeotropic conditions for about two hours. The compatibility of the flakes was then tested, as mentioned above, by adding water and toluene. It was found that the surface of these treated flakes was now hydrophobic, as evidenced by the fact that most of the surface treated flakes stayed in toluene, whereas only some of the non-surface treated flakes stayed in toluene.

EXAMPLE TWO: About 11.4g of coated glass flake (30-90 micrometers), about 50 ml of styrene, and about 2.85g of oleic acid (20 weight % with respect to the flake, 90% purity from Aldrich) were put into a round bottom flask fitted with a condenser and a stirrer. The heterogeneous solution was stirred at about 80°C for about two hours. The resulting mixture was then used for suspension polymerization. The resulting beads contained a higher amount of encapsulated glass flake than did beads made using glass flake that had not been surface treated.

In both EXAMPLE ONE and EXAMPLE TWO, surface modifiers containing a carboxylic acid end group were used for purposes of flake/monomer compatibility. Aluminum flakes were also modified with vinyl benzoic acid and 4,4"-azobis(4-cyano valeric acid). Vinyl benzoic acid and 4,4"-azobis(4-cyano valeric acid) can be classified as reactive surface modifiers since they can be employed as monomers and initiators in radical polymerization, respectively.

Once formed, the beads may be separated into various batches of beads of differing densities via gravity sedimentation (also called gravity separation, gradient sedimentation, and/or gradient separation, or the like). The beads may also be separated via centrifugation, or in any other suitable manner. A general description of the gravity sedimentation process followed in embodiments of this invention will now be described. After removing the microemulsion (i.e., white water) from the beads, the beads were filtered. Filtering was done using a Buchner funnel and filter paper. Thereafter, the wet beads were reslurried in an original volume of about 5-20 weight % potassium chloride or sodium chloride. In one particular embodiment, the wet beads were reslurried in a 15 wt. % potassium chloride or sodium chloride solution, and were then transferred into a 4 liter separation funnel. Occasionally, 2 to 3 droplets of a 0.1 weight % Triton X-100 solution in water was added to improve the wetting of the beads, when and if necessary. The slurry was then shaken up and left to stand for about 15-30 minutes until the system was in equilibrium. The empty beads tended to float to the top of the slurry, the flake-encapsulating beads tended to float but remain below the empty beads in the slurry, and the free flakes tended to sink to the bottom of the slurry, as shown in Figure 3. The first fraction of the useable beads (about a 250ml volume) was removed/drained, filtered and washed with deionized water to remove any excess potassium or sodium chloride. This first fraction of beads was usually discarded, if necessary, since this fraction often contained some free aluminum flakes, which can cause flowlines in the final product. This was particularly the case if only styrene was used as the monomer. Next, deionized water was added to the separation funnel to return the volume in the funnel to approximately the original volume, and to dilute the slurry and decrease its density. By changing the density of the slurry, beads having a different amount of aluminum flake content could be collected in each pass, as confirmed by photography, the result of which are shown graphically in shown in Figure 4. This allowed beads having specific aluminum contents to be used in a given product, thereby allowing different visual/optical effects to be created just by varying the beads that were combined to make the finished product. After shaking, the standing, removing/draining, filtering, washing and diluting procedure was repeated until there were almost no beads remaining in the funnel, which typically took about 12-15 dilutions. The beads were

then dried in a vacuum oven at about 50-60°C for at least about 48 hours. After sieving through a 300µm stainless steel sieve, the beads were ready for use in such processes as compounding, extruding and/or injection molding.

EXAMPLE THREE: In this embodiment, novel special effects in injection molded or extruded plastics were created using common polymer processing techniques. This embodiment comprised aluminum flakes encapsulated in polystyrene. This reaction system included the use of about a 1-2 weight % aqueous solution of polyvinyl alcohol (PVA) (molecular weight 124000-186000, 87-89% hydrolyzed) as the suspending medium. The monomer, styrene in this embodiment, was mixed with about 1-2 weight % (based on the monomer) of divinylbenzene (a cross-linker), and the mixture was then sonicated. After sonication, about 0.3 weight % (based on the monomer) benzoyl peroxide (an initiator) OLE_LINK3 was added to the styrene mixture, and the new mixture was briefly shaken. The OLE_LINK3 monomer system comprising styrene monomer and initiator was added to the aqueous suspending agent (PVA dissolved in water) without stirring, and comprised about 10-20 weight % of the suspending medium/agent. The aluminum flakes were added directly to the suspension of reactants in water, or the flakes were first suspended in the pure monomer by sonication at room temperature, and then added to the aqueous PVA solution. The reaction mixture was then stirred at about 300 rpm and heated at about 80°C for about one hour, followed by heating at about 85°C for about two more hours. The reaction mixture was then quenched (for example, by cooling or diluting the mixture), the microemulsion was removed, and the resultant beads were then collected by filtration (for example, by gravity sedimentation as described in detail above, or by centrifugation) and washed with water.

The product beads, comprising metallic flakes encapsulated within the cross-linked polymer spheres, may then be compounded into a target resin system (i.e., a plastic matrix) using traditional polymer processing techniques (for example, extrusion, injection molding, sheet molding, solution-based processing techniques such as spin-coating or solution-casting, etc.). This embodiment yields pigment particles comprising faceted aluminum flakes/particles encapsulated in a substantially spherical polymer bead. This substantially spherical shape makes the particles relatively

insensitive to flow fields when these beads are processed into plastic products. The substantially spherical shape, combined with the faceted nature of the embedded flakes/particles, should theoretically produce parts having virtually no visible flowlines and a sparkling, metallescent or true metal look, depending on the concentration of the encapsulated aluminum pigment that is used.

When styrene and divinylbenzene were used as the only monomers using the preparation method of EXAMPLE THREE, the encapsulation method was not 100% effective. The majority of aluminum flakes were merely surface laminated to the polymer beads instead of being fully encapsulated within the beads, and many empty beads were apparent via optical microscopy. Additionally, there were some visible flowlines in the final molded product that incorporated these beads in a plastic matrix of polystyrene when the composition was processed (before molding) by extrusion compounding with all composition components being throat-fed. Investigation showed that some of these surface laminated flakes became delaminated from the encapsulant bead under the high shear conditions during extrusion and/or injection molding, causing some visible flowlines.

When surface laminated flakes, rather than fully encapsulated flakes, are present in plastic matrices, extrusion compounding with all-throat-feeding of the composition components can result in the appearance of flowlines in subsequently molded parts. Although this invention is in no way dependent upon theory, the appearance of flowlines is believed to be generally a result of laminated flakes detaching from the surface of beads to form free flakes under the high shear conditions associated with extrusion. The amount of free (i.e., unencapsulated) high aspect ratio material that can tolerably be present in compositions comprising encapsulated high aspect ratio material in a plastic matrix may be less than about 1 wt. %, less than about 0.5 wt. %, less than about 0.2 wt. %, less than about 0.1 wt. %, less than about 0.05 wt. %, less than about 0.01 wt. %, or less than about 0.005 wt. %, in various embodiments respectively, based on the weight of the entire composition. These range limits for unencapsulated material in compositions comprising encapsulated material apply when the presence of all or at least a portion of the unencapsulated material results from delamination of encapsulated material, or from contamination of encapsulated

material by unencapsulated material, or when all or at least a portion of unencapsulated material is deliberately added to the composition. In general, at comparable weight percent loading in the composition, it has been observed that smaller diameter free flakes may result in more prominently visible flowlines than larger diameter free flakes.

One way to stop laminated flakes from detaching from the surface of beads is to add the pigment bead material to the plastic matrix resin prior to molding and then compounding during molding. This typically results in such flakes remaining laminated to the bead surface, and may result in an aesthetically pleasing molded part when the pigment beads can be well dispersed throughout the plastic matrix. In some embodiments, when pigment beads cannot easily be well dispersed in the plastic matrix, then dispersion may be improved by employing all, or at least a portion, of the plastic matrix resin in the form of a powder, which has a higher surface area and will therefore promote mixing and dispersion of pigment during molding. Another solution to this problem is to decrease the amount of time that resin beads of Type II are exposed to high-shear conditions that may promote delamination. In one embodiment, all, or at least a portion, of pigment beads are provided to an extrusion compounder at a feed inlet at some barrel segment following the feed-throat, wherein all, or at least a portion, of the remaining blend components comprising plastic matrix resin have been throat-fed (so-called "down-stream feeding"). This results in the pigment beads experiencing a high shear environment for shorter periods of time, which leads to a decrease in delamination, and therefore elimination of objectionable flowlines, or a diminution of objectionable flowlines in comparison to a similar composition prepared by throat feeding all the components:

EXAMPLE FOUR: Encapsulated aluminum flakes were prepared in beads comprising polystyrene cross-linked with divinylbenzene. The beads in each of these compositions contained about 3.9 wt. % aluminum flake on average, as measured by thermogravimetric analysis (TGA). Three different compositions were prepared comprising pigment beads and polystyrene matrix resin, the compositions respectively comprising 0.3 wt. % (7.6 wt. % bead), 0.7 wt. % (17.9 wt. % bead), and 1.2 wt. % (30.8 wt. % bead) of aluminum flake. A portion of the polystyrene matrix resin was

in the form of powder. Individually, each of these compositions was added directly to a molding machine for preparing molded parts. The resulting molded parts made from these encapsulated beads did not show flowlines. For comparison, three similar compositions were prepared using unencapsulated aluminum flakes, and each of these compositions was then also added directly to a molding machine for preparing molded parts. The resulting molded parts made from compositions comprising these unencapsulated aluminum flakes showed visible flowlines.

EXAMPLE FIVE: Three different compositions of encapsulated aluminum flakes were prepared as beads comprising polystyrene (PS) cross-linked with divinylbenzene. These bead compositions were then extruded along with a polystyrene matrix resin, wherein at least a portion of the blend components were throat-fed, and at least a portion of the blend components were fed down-stream via a side feeder at barrel 5 of an 8-barrel extruder. Table 1 shows the blend compositions and processing conditions used in this example. For comparison, one similar composition (5-D) was prepared by throat-feeding all the blend components, and another similar composition (5-E) was prepared by down-stream feeding all the unencapsulated aluminum flakes in the composition. All components in this example are in wt. %, based on the weight of the entire composition. Parts molded from compositions 5-A, 5-B and 5-C all had significantly fewer flowlines visible than did parts molded from compositions 5-D and 5-E.

Composition	Throat-fed Components		Down-stream Fed Components		
	Polystyrene ^a (PS)	PS-encapsulated Al flakes	Free Al flakes ^b	PS-encapsulated Al flakes	PS
5-A	88.50	--	--	7.70	3.3
5-B	81.55	--	--	17.95	--
5-C	68.80	--	--	30.70	--
5-D	79.55	19.95	--	--	--
5-E	98.62	--	0.875	--	--

^a Throat-fed PS contained 0.5 parts of organic lubricant.

^b Unencapsulated Al flakes.

In order to enhance the design flexibility and improve the possibility of varying the refractive index of the encapsulation materials to match a broader range of matrix resins, it would be highly desirable to have a process that allows for the use of more than one monomer. Therefore, in some embodiments, the polymer beads comprise a combination of monomers, in variable ratios, with optional cross-linking. Any monomer that can be used in free radical suspension polymerization may be used here, such as, for example, styrene in combination with at least one of the following: acrylonitrile, methyl methacrylate (MMA), butadiene, or any other vinylic or olefinic monomer.

EXAMPLE SIX: In this embodiment, a higher solids content (i.e., higher monomers/water ratios), ranging from about 20-49 weight % gave a higher amount of beads per batch. The PVA concentration in water in this embodiment ranged from about 0.25 weight % to about 4 weight %. A different temperature profile during the initial stages of the suspension polymerization was also used here. Furthermore, it was found that by changing the way the monomer/flake mixture was added to the aqueous PVA solution, the final aluminum flake distribution in the beads could be influenced. In this embodiment, it was found that by adding the previously-sonicated monomer/flake mixture to a stirred aqueous PVA solution (as opposed to the non-

turbulent, non-stirred aqueous PVA solution used in the previous examples), a much more uniform overall aluminum flake distribution in the beads was produced.

This embodiment was created using a 6 liter jacketed kettle reactor equipped with a six-blade Rushton stirrer. In this reactor, an aqueous solution of 59 grams of PVA (i.e., about 87-89% hydrolyzed, MW = 124000-186000) and 2250 grams of deionized water was kept at 40°C, stirred at about 100rpm, and purged with nitrogen for about 60 minutes. About 1128 grams of styrene, about 373 grams of acrylonitrile, about 23 grams of divinylbenzene and about 28 grams of aluminum flakes were combined in a volumetric flask, placed in an ultrasonic bath, and sonicated for about 10 minutes while shaking occasionally. After sonication, about 4.5 grams of benzoyl peroxide (the radical initiator) was added to the mix.

The monomer/flake/initiator mixture was then added to the aqueous PVA solution in one of two ways: (1) to the non-turbulent, non-stirred PVA solution in such a way that a two-phase system was obtained. After the addition of the monomer/flake/initiator mixture was complete, the stirring was switched on at about 250rpm; or(2) to the stirred PVA solution while it was being stirred at about 250rpm.

Either way, once the monomer/flake/initiator mixture was added, the system was allowed to equilibrate for about 15 minutes at about 40°C, then the temperature was raised to about 70°C within about 30 minutes. After holding at about 70°C for about 90 minutes, the temperature was raised to about 75°C, and held for about 120 minutes. Then the temperature was raised to about 80°C, and held for about 150 minutes while being stirred at about 300rpm. Finally, the temperature was raised to about 85°C, and held for about 120 minutes while being stirred at about 350rpm. Recovery, isolation and separation of the beads were accomplished in the same way as described in the previous examples.

If addition method (1) was used, typically approximately 700 grams of beads having a diameter smaller than about 300µm were obtained per batch. This is approximately a 47% yield based on the monomers used. The average diameter of these beads was

about $100 \pm 50\mu\text{m}$. The aluminum content of these beads ranged from about 15 to about 1 weight % as determined by thermogravimetric analysis (TGA).

If addition method (2) was used, typically approximately 900 grams of beads having a diameter smaller than about $300\mu\text{m}$ were obtained per batch. This is approximately a 60% yield based on the monomers used. The average diameter of these beads was about $100 \pm 50\mu\text{m}$. The aluminum content of these beads ranged from about 8.5 to about 1.2 weight % as determined by TGA. The aluminum flake distributions that were obtained by the two methods of this example are shown in Figure 6.

The beads produced by this method were compounded with clear ABS and molded into flowline-sensitive parts. The results obtained were favorable. The parts obtained did not exhibit any flowlines, even if high shear processing conditions (i.e., throat feeding all of the blend components) were used. This indicates that this process (EXAMPLE SIX) yields beads having few surface laminated flakes or free flakes. Furthermore, EXAMPLES FOUR, FIVE, and SIX demonstrate the importance of the relationship between bead morphology and the compounding/processing conditions that is necessary for achieving a final product having a flowline-free appearance.

EXAMPLE SEVEN: In this embodiment, various dyes, together with aluminum flakes, were incorporated into cross-linked polymeric beads to create a colored visual effect in a matrix resin. Some of the dyes used in this embodiment are shown in Figure 7. This embodiment yielded flakes that were encapsulated within small, colored beads. This example disregarded the effect of the molecular structure of the dye on the reaction yield.

In this embodiment, dye was added to the mixture of aluminum flakes and monomer of EXAMPLE SIX prior to sonication. Ideally, the dye should be soluble in the monomer solution, and preferably, the dye should be significantly more soluble in the organic/monomer phase than in the aqueous phase used in the suspension polymerization reaction. Upon dissolution of the dye, and subsequent sonication, the mixture was then added to the aqueous phase in the normal manner, and the appropriate stirring and temperature profiles for the monomer were used (i.e., the

profiles that were described above in EXAMPLE SIX). Isolation of the final beads was then carried out using the standard gravity sedimentation technique previously discussed above.

By varying the loading of the dye, the color and strength of the end effect was varied. More loading of the dye produced beads having a more vibrant color, while less loading of the dye produced beads having less color. Additionally, high loading of the colored beads in a matrix resin resulted in a colored, sparkling matrix that was not significantly different in sparkling appearance from a resin containing colorless beads. However, at low loading of the beads, the colored beads remained resolved (i.e., optically separated) from the color of the surrounding resin matrix, giving a flowline-free sparkling effect where the aluminum flakes appeared to be colored.

Once these beads were created, 40 grams of these colored beads were compounded and injection molded in 500 grams of clear acrylonitrile butadiene styrene plastic (ABS). These beads yielded a colored sparkling product that was substantially free of visible flowlines.

EXAMPLE EIGHT: In this embodiment, specific dyes, together with aluminum flakes, were incorporated into the cross-linked polymeric beads. These specific dyes provided better bead yields than embodiments produced without any dye. Typical bead yields when co-polymerizing styrene and acrylonitrile without any dye are in the 50-60% range. Such a yield is below the typical acceptable yield for large-scale industrial processes for reasons such as raw material costs, separation of product from impurities, and cost of by-product disposal. It has been found that, in the presence of certain anthraquinone-derived dyes, styrene acrylonitrile (SAN) bead yields of greater than about 90% are obtainable. In addition to the dramatically increased yield of the suspension polymerization, this method also decreased the amount of microemulsion, an unwanted side-product.

In this embodiment, Solvent Blue 35, or more preferably Solvent Blue 36, was added to the mixture of aluminum flakes and monomer prior to sonication. The chemical structures of Solvent Blue 35 and Solvent Blue 36 are shown in Figure 5. Upon

dissolution of the dye, and subsequent sonication, the mixture was then added to the aqueous phase in the normal manner, and the appropriate stirring and temperature profiles for the monomer were used.

For example, a mixture of about 1125 grams of styrene, about 375 grams of acrylonitrile, about 22.5 grams of divinylbenzene, about 28.5 grams of aluminum flakes, and about 900 mg of Solvent Blue 36 was prepared and sonicated for about 15 minutes. About 4.5 grams of benzoyl peroxide was then added to this mixture, and the resulting mixture was then added to a nitrogen-purged solution of about 59 grams of polyvinyl alcohol in about 2250 ml of water. Standard stirring (at about 250-280 rpm) and temperature profiles, as detailed in EXAMPLE SIX, were then followed. Recovery, isolation and separation of the beads were accomplished in the same way as described in the previous examples.

The color of the mixture began changing a few minutes after the monomer solution was added to PVA/water solution. After about 3 hours, the reaction was sufficiently thick that about 200ml of water was added, and stirring was then increased to about 350 rpm. The reaction was stopped and the product isolated in the same manner as outlined above in the previous examples. The final beads in this example were noticeably violet in color, and about a 90% yield (based on the monomers) was obtained.

Alternatively, a smaller amount of dye was used (about 238 mg of Solvent Blue 36). This provided about a 78% yield, and the beads had only a slightly violet tint.

Using about 238-900 mg of Solvent Blue 36 provided a yield of about 78-90%. Subsequent acetone washing/slurrying yielded beads having little or no violet coloration.

Beads with different amounts of incorporated dye were compounded with ABS, or ABS comprising methyl methacrylate as the co-monomer, and molded into flowline sensitive parts. Visible flowlines were eliminated. Increasing the amount of the active dye induced an increasingly positive effect on yield, and resulted in beads having more color. A loading of dye sufficiently low to result in insignificant

discoloration of the SAN beads (for example, about 240 mg) resulted in yields around 80%. Upon bead isolation, washing with a solvent that causes a certain swelling of the beads (i.e., acetone) removed a significant amount of the dye from the bead matrix. This provided a way to produce essentially colorless beads at a much higher yield than previously possible. It was also observed that when these beads were received from the polymerization process, they contained tiny bubbles, but after they were acetone-washed, the beads were free of bubbles. Such bubbles were not observed in beads produced in any of the preceding examples.

By varying the loading of the dye, and by varying the amount of washing done to the beads, the color and strength of the end effect could be varied. More loading of the dye and less washing of the beads produced beads having a more vibrant color, while less loading of the dye and more washing of the beads produced beads having less color.

EXAMPLE NINE : In this embodiment, a modified reaction from those above is used upon scale-up of the reaction from 1 and 6 liter glass reactors to a 40 liter steel reactor. The reactor was charged with an aqueous PVA solution comprising 1.2 kg of PVA dissolved in 24.5 liters of water and stirred at 400 rpm at 75 °C. Into a charge tank connected to the reactor, 9.2 kg of styrene is added and agitation is set to 950rpm. To this was added 28.54 g of divinylbenzene followed by 1186 g of aluminum flake. This was stirred for 20 minutes after which time 797 g of acrylonitrile and 30 g of benzoyl peroxide was added. This mixture was stirred for 10 minutes then added to the reactor by way of releasing a valve between to two tanks. The reaction is then stirred at 400 rpm for 4 hours. At this time a solution of 1050 g of PVA in 2 liters of water is added over 10 minutes. Stirring at 400 rpm and 75 °C is continued for another 4 hours then raised to 82 °C and stirred for a further 3 hours. The resulting beads are separated from microemulsion product then washed and dried using standard techniques.

The additional PVA batch added during the reaction substantially improves the process compared to scaling up the exact process described earlier at 1 and 6 liter

scale. The additional PVA reduces the amount of cleaning required in the reactor after completion, leads to less agglomeration of beads and increases the yield of beads.

EXAMPLE TEN : In this embodiment, an alternative surfactant system is used for a reaction in a 40 liter steel reactor. The reactor was charged with an aqueous solution comprising 1.53 kg of PVA and 1.4 g of potassium iodide dissolved in 24.2 liters of water and stirred at 400 rpm at 75 °C. Into a charge tank connected to the reactor, 9.2 kg of styrene is added and agitation is set to 950rpm. To this was added 28.54 g of divinylbenzene followed by 1186 g of aluminum flake. This was stirred for 20 minutes after which time 797 g of acrylonitrile and 78.9 g of benzoyl peroxide was added. This mixture was stirred for 10 minutes then added to the reactor by way of releasing a valve between to two tanks. The reaction is then stirred at 450 rpm for 2 hours, then for a further 6 hours at 400 rpm and 75 °C. Finally, the temperature is raised to 82 °C and stirred for a further 3 hours. The resulting beads are separated from microemulsion product then washed and dried using standard techniques.

The use of a modified surfactant system avoids the need for an additional PVA step during the reaction. It also provides for greater control over the size of bead produced with a much smaller size distribution from within one reaction batch. This approach also leads to higher yield and a reduced amount of small, microemulsion particles which must subsequently be removed.

The beads isolated from this process require an extra step before compounding as they do not feed efficiently down the feed throat of an extruder in their current form. This can be solved by adding a 0.2% by weight amount of micronised barium sulphate to the beads.

EXAMPLE ELEVEN: A series of experiments was carried out in which two different surfactant systems, PVA and PVA/KI, were used, and divinylbenzene cross-linker content was varied between 0.1 and 0.3 parts per hundred and the resulting beads were screened at sieve sizes of 106, 150, 180, 212 and 250 microns. These beads were then compounded into a LEXAN EXL based resin at 9% bead loading and laptop covers in which the visual defects described above are prevalent were molded.

The resulting parts were visually assessed to compare and pass/fail the visual defects for each formulation. For the PVA system, little difference was seen in beads ranging from 0.2 - 0.3 pph DVB. Thus 0.2 pph DVB is favored as this is known to provide the best resin physical properties within this range. For the PVA/KI system, beads with the nominal cross-link density of 0.2 pph DVB were not sufficiently stable when compounded in the same LEXAN EXL grade. Beads with 0.3 pph DVB made under PVA/KI conditions were found to give similar overall performance to 0.2 pph DVB beads made under PVA conditions.

Screening beads to 106 microns afforded the best results in terms of both large particle observation and melt-front congregation. Particle sizes of 212 and 250 microns gave unacceptable defects with respect to the melt front as well as large specks being observed. Both 180 and 150 microns gave acceptable melt front performance, but the large specks were visually objectionable for beads screened at \leq 180 microns.

As described above, the systems and methods of the present invention allow a user to encapsulate high aspect ratio materials within a polymer to form substantially spherical beads. These beads may then be used to create plastic products having a sparkling and/or metallescent appearance. Figure 8 shows a comparison of two molded parts, each comprising a polystyrene matrix, wherein one part was prepared using free metallic flakes and the other part was prepared using aluminum flakes encapsulated in polystyrene cross-linked with divinylbenzene. Each composition was prepared by mixing the blend components in a molding machine. Advantageously, these systems and methods created plastic products that were visually flowline free, something that was not easily or economically obtained before this invention.

Various embodiments of the invention have been described in fulfillment of the various needs that the invention meets. It should be recognized that these embodiments are merely illustrative of the principles of various embodiments of the present invention. Reaction conditions may vary from equipment to equipment, and therefore adjustments to these above-described processes may be necessary to produce good beads. Numerous other modifications and adaptations thereof will be

apparent to those skilled in the art without departing from the spirit and scope of the present invention. Thus, it is intended that the present invention cover all suitable modifications and variations as come within the scope of the appended claims and their equivalents.

Claims

1. An encapsulated pigment composition comprising one or more substantially spherical-shaped beads, wherein each substantially spherical-shaped bead comprises one or more high aspect ratio particles encapsulated within an encapsulating material and wherein the substantially spherical-shaped beads have an average diameter of 10 μ m to 300 μ m.
2. The encapsulated pigment composition of claim 1, wherein the high aspect ratio particles comprise at least one of: aluminum, gold, silver, copper, nickel, titanium, stainless steel, nickel sulfide, cobalt sulfide, manganese sulfide, metal oxides, white mica, black mica, synthetic mica, mica coated with titanium dioxide, metal-coated glass flakes, or colorants.
3. The encapsulated pigment composition of claim 1 or 2, wherein the encapsulating material comprises a polymer with structural units derived from at least one monomer selected from the group consisting of styrene, alpha-methyl styrene, para-methyl styrene, acrylonitrile, alkyl acrylate, alkyl methacrylate, methyl methacrylate, divinyl benzene, and mixtures thereof.
4. The encapsulated pigment composition of claim 1 or 2, wherein the encapsulating material comprises at least one of: polystyrene, polymethyl methacrylate, styrene acrylonitrile copolymer, methyl methacrylate styrene acrylonitrile copolymer, or an acrylonitrile-styrene-acrylate resin.
5. The encapsulated pigment composition of any of claims 1 to 4, wherein the encapsulated pigment composition further comprises at least one additive.
6. The encapsulated pigment composition of claim 5, wherein the at least one additive comprises at least one of: a colorant, a thermal stabilizer, an oxidation inhibitor, butylated hydroxytoluene, a radical scavenger, a vinyl-based monomer, a filler, an impact modifier, a UV absorber, or a fire retardant.

7. The encapsulated pigment composition of claim 6, wherein the colorant comprises at least one of: Solvent Blue 35, Solvent Blue 36, Disperse Violet 26, Solvent Green 3, Anaplast Orange LFP, Morplas Red 36, or Perylene Red.
8. The encapsulated pigment composition of any of claims 1 to 7, wherein the encapsulating material is transparent.
9. The encapsulated pigment composition of any of claims 1 to 7, wherein the encapsulating material is translucent.
10. The encapsulated pigment composition of any of claims 1 to 9, wherein the substantially spherical-shaped beads have an average aspect ratio of 1:1 to 2:1.
11. The encapsulated pigment composition of any of claims 1 to 10 claim 1, wherein the high aspect ratio particles have an average aspect ratio of greater than 1.5:1.
12. The encapsulated pigment composition of any of claims 1 to 10, wherein the high aspect ratio particles have an average aspect ratio of 1.5:1 to 40:1.
13. The encapsulated pigment composition of any of claims 1 to 12, , wherein the substantially spherical-shaped beads have an average diameter of 75 to 125 microns.
14. The encapsulated pigment composition of claim 13, wherein the substantially spherical-shaped beads have a maximum diameter of 150 microns.
15. The encapsulated pigment composition of any of claims 1 to 14, wherein an average weight percent of high aspect ratio particles encapsulated within an encapsulating material comprises 0.1 to 25 weight percent, based on the weight of the pigment bead.
16. The encapsulated pigment composition of any of claims 1 to 15, wherein the high aspect ratio particles comprise 2 to 100 facets.
17. The encapsulated pigment composition of any of claims 1 to 16, wherein the encapsulating material is cross-linked.

18. The encapsulated pigment composition of claim 17, wherein the cross-link density is from 0.15 to 0.8 parts per hundred parts of cross-linking agent.
19. The encapsulated pigment composition of claim 18, wherein the cross-link density is 0.2 parts per hundred parts of cross-linking agent.
20. An encapsulated pigment composition comprising one or more substantially spherical-shaped beads, wherein each substantially spherical-shaped bead comprises one or more high aspect ratio aluminum flakes encapsulated within an encapsulating material comprising a polymer with structural units derived from at least one monomer which is styrene, wherein the flakes have an average aspect ratio of 1.5:1 to 40:1 and wherein the encapsulated pigment composition comprises 0.1 to 25 weight percent of the flakes.
21. A resinous composition comprising a plastic matrix material and an encapsulated pigment composition according to any of claims 1-20.
22. The resinous composition of claim 21, wherein the plastic matrix material comprises at least one member selected from the group consisting of thermoplastics, polyesters, polyolefins, polyethylene, polypropylene, polybutylene, polymethylpentene; resins comprising structural units derived from styrene monomer, polystyrene, styrene-acrylonitrile copolymer, acrylonitrile-styrene-butadiene, acrylonitrile-styrene-acrylate; polyamide; polycarbonate; bisphenol A polycarbonate; polyphenylene ether; polyimide; polyamide imide; polyetherimide; polysulfone; polyether sulfone; polyketone; polyether ketone; polyether ether ketone; polyarylate; phenoxy resins; fluorocarbon resins; thermoplastic elastomers; thermoplastic elastomers derived from polystyrene, from polyolefin, from polyurethane, from polyester, from polyamide, from polybutadiene, from polyisoprene, from fluorine-containing monomer; a natural rubber, a synthetic rubber, copolymers or modifications of any of the these substances, and combinations of two or more of these substances.
23. The resinous composition of claim 21, wherein the plastic matrix material comprises acrylonitrile-styrene-butadiene copolymer.

24. The resinous composition of claim 23, wherein the plastic matrix material further comprises polycarbonate.

25. A molded article made from the composition of any of claims 21 to 24.

26. The molded article of claim 25 which is substantially free of visible flowlines.

27. The molded article of claim 25 or 26 formed by a process which comprises compounding the composition during molding.

28. A method of preparing an encapsulated pigment composition via suspension polymerization, the encapsulated pigment composition comprising one or more substantially spherical-shaped beads, wherein the substantially spherical-shaped beads comprise one or more high aspect ratio particles encapsulated within an encapsulating material, the method comprising the steps of:

dispersing high aspect ratio particles in at least one of a monomer or a polymer and a cross-linking agent to form a suspension mixture;

adding the suspension mixture to an aqueous mixture comprising a suspension agent;

heating and mixing the aqueous reaction mixture to encourage the formation of substantially spherical-shaped beads, wherein most of the substantially spherical-shaped beads encapsulate one or more high aspect ratio particles to an extent that the high aspect ratio particles will not become delaminated during processing;

quenching the aqueous reaction mixture after the substantially spherical-shaped beads are formed; and

collecting the substantially spherical-shaped beads.

29. The method of claim 28, further comprising:

suspending the one or more high aspect ratio particles in the suspension mixture by sonicating the suspension mixture prior to adding the suspension mixture to the aqueous reaction mixture.

30. The method of claim 29, the method further comprising utilizing at least one of gravity sedimentation and centrifugation to separate the substantially spherical-shaped beads into various batches.

31. The method of claim 30, wherein the gravity sedimentation comprises:

a) reslurrying the substantially spherical-shaped beads in a slurry solution to form a separation system having an original volume;

b) mixing the separation system;

c) allowing the separation system to stand still to come to equilibrium;

d) removing a fraction of useable substantially spherical-shaped beads from the separation system;

e) filtering the fraction of useable substantially spherical-shaped beads that is obtained from the separation system;

f) washing the filtered fraction of useable substantially spherical-shaped beads to remove any excess slurry solution; and

g) adding a quantity of deionized water to the remaining substantially spherical-shaped beads and slurry solution in the separation system to bring the volume of the separation system back to the original volume; and

h) repeating steps b)-g) as necessary until all the substantially spherical-shaped beads have been removed from the separation system.

32. The method of claim 31, further comprising drying the substantially spherical-shaped beads.

33. The method of claim 32, further comprising utilizing the substantially spherical-shaped beads in a resinous composition.

34. The method of any of claims 28 to 33, wherein the pigment further comprises at least one member selected from the group consisting of: a colorant, Solvent Blue

35, Solvent Blue 36, Disperse violet 26, Solvent Green 3, Anaplast Orange LFP, Morplas Red 36, and Perylene Red.

35. The method of claim 34, wherein the pigment is selected from the group consisting of: Solvent Blue 35 and Solvent Blue 36.

36. The method of any of claims 28-35, wherein the high aspect ratio particles comprise at least one of: aluminum, gold, silver, copper, nickel, titanium, stainless steel, nickel sulfide, cobalt sulfide, manganese sulfide, metal oxides, white mica, black mica, synthetic mica, mica coated with titanium dioxide, metal-coated glass flakes, or colorants.

37. The method of any of claims 28-36, wherein the suspension mixture comprises at least one of: styrene, methyl methacrylate, styrene acrylonitrile, divinylbenzene, or modified bisphenol A.

38. The method of claim any of claims 28-37, wherein the cross-link density is from 0.175 to 0.25 parts per hundred parts of cross-linking agent.

39. The method of any of claims 28-37, wherein the cross-link density is from 0.20 parts per hundred parts of cross-linking agent.

40. The method of any of claims 28-39, further comprising the step of screening the collected substantially spherical-shaped beads produced to obtain a composition wherein the the substantially spherical-shaped beads have an average diameter of 75 to 125 microns.

41. The method of any of claims 28-40, wherein the substantially spherical-shaped beads are screened to have a maximum diameter of 150 microns.

42. A resinous composition comprising an encapsulated pigment composition prepared by the method of any of claims 28-41.

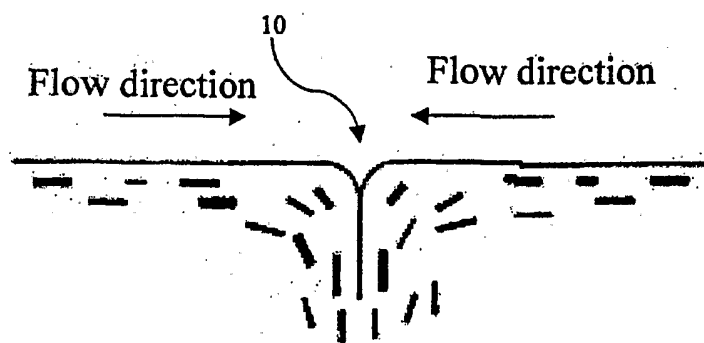


FIGURE 1

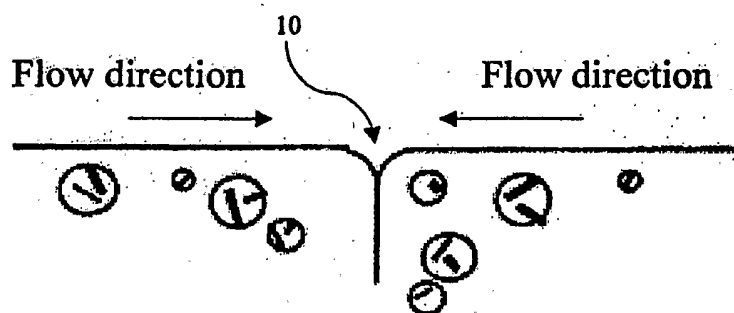


FIGURE 2

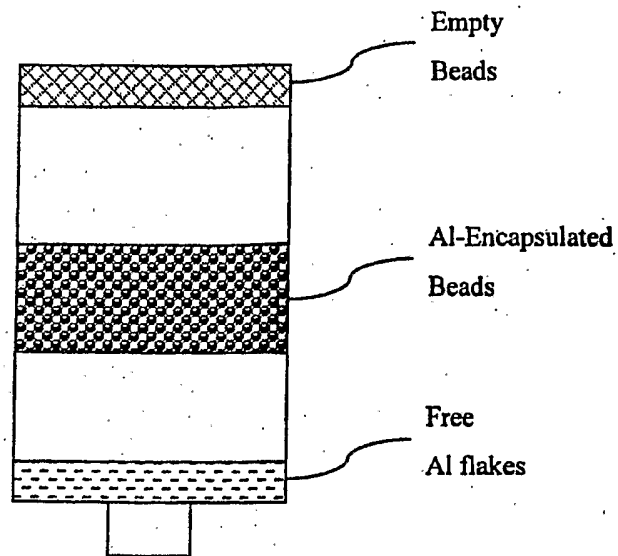


Figure 3

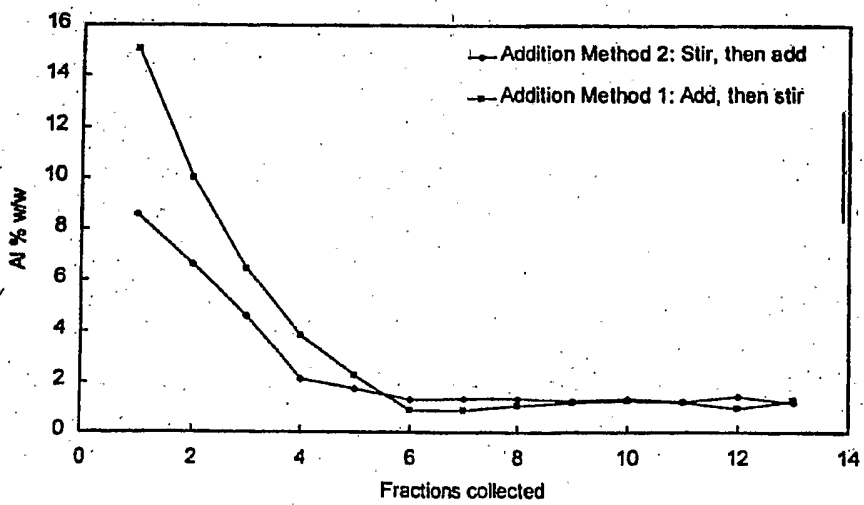
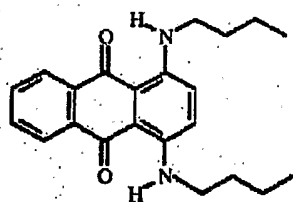
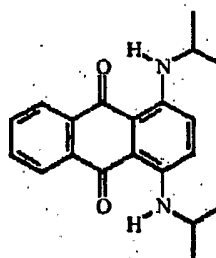


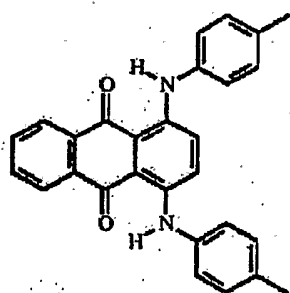
Figure 4



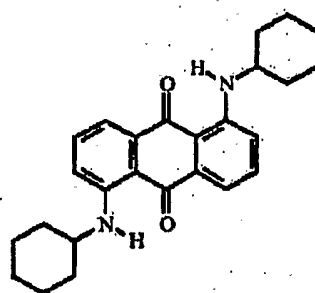
Solvent Blue 35



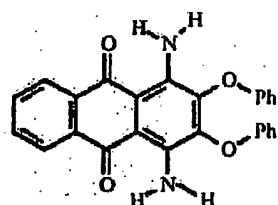
Solvent Blue 36



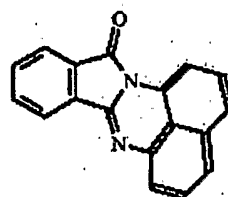
Solvent Green 3



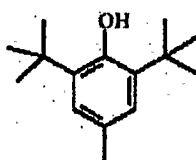
Morplas Red 36



Disperse violet 26



Anaplasti Orange LFP



BHT

Figure 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/001727

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08K9/10 C09D11/02 C09B67/00 C09C1/00 C09C3/00		
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 C08K C09D C09B C09C		
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, PAJ, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 108 863 A (HSIEH BING R ET AL) 28 April 1992 (1992-04-28) column 14, line 62 claims 1-4; examples I,III-IX column 1, lines 57,58	1-42
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 10, 31 August 1999 (1999-08-31) & JP 11 140343 A (NIPPON PAINT CO LTD), 25 May 1999 (1999-05-25) abstract	1-42
----- -/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
° Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
Date of the actual completion of the international search	Date of mailing of the international search report	
5 July 2004	13/07/2004	
Name and mailing address of the ISA	Authorized officer	
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Von Kuzenko, M	

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/001727

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 154 739 A (MARTIN ROBERT W) 18 September 1985 (1985-09-18) page 8, lines 1-32 page 19, line 5 - page 20, line 12 page 47, lines 21-24 claim 1	1-42
X	----- US 4 771 086 A (MARTIN ROBERT W) 13 September 1988 (1988-09-13) column 24, lines 5-32 claim 1	1
X	----- US 4 598 020 A (PANUSH SOL) 1 July 1986 (1986-07-01) column 7, lines 12-17; claim 1 -----	1

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/US2004/001727

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5108863	A	28-04-1992	NONE	
JP 11140343	A	25-05-1999	NONE	
EP 0154739	A	18-09-1985	AU 576513 B2	01-09-1988
			AU 3207284 A	05-09-1985
			CA 1255032 A1	30-05-1989
			EP 0154739 A2	18-09-1985
			JP 60203673 A	15-10-1985
			US RE34145 E	15-12-1992
			US 4608401 A	26-08-1986
US 4771086	A	13-09-1988	AU 1861783 A	08-03-1984
			AU 576513 B2	01-09-1988
			BR 8304723 A	10-04-1984
			CA 1255031 A1	30-05-1989
			EP 0104498 A2	04-04-1984
			US RE34145 E	15-12-1992
			US 4608401 A	26-08-1986
US 4598020	A	01-07-1986	AU 577257 B2	15-09-1988
			AU 6114586 A	19-02-1987
			BR 8603852 A	24-03-1987
			CA 1279425 C	22-01-1991
			EP 0214922 A2	18-03-1987
			ES 2001754 A6	16-06-1988
			JP 2108475 C	06-11-1996
			JP 8003059 B	17-01-1996
			JP 62109869 A	21-05-1987
			MX 168183 B	10-05-1993
			NZ 217227 A	28-06-1989
			PH 21631 A	13-01-1988
			ZA 8606179 A	25-03-1987