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(57) Abrégé/Abstract:

Disclosed is a coated substrate, which includes a substrate comprising a cellulosic fiber material and a copolymer coated in a thin film on at least one surface of the substrate. The copolymer has at least two comonomer units of the formula: CX_2CYA, wherein each X is independently selected from the group consisting of H, C1 and F; Y is selected from the group consisting of H, Cl, F, $O(CZ_2)_nCZ_3$, $(CZ_2)_nCZ_3$, $(OCZ_2CZ_2)_nCZ_3$ and $(O(CZ_2)_n)_nCZ_3$, wherein each n is independently from about 1 to about 12 and each Z is independently selected from the group consisting of H, Cl and F; and A is selected from the group consisting of H, Cl and F; provided that for at least one comonomer unit, at least one of A, Y, and either X or any Z is Cl.

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(54) Title: CHLOROFLUOROPOLYMER COATED SUBSTRATES AND METHODS FOR PRODUCING THE SAME

(57) Abstract: Disclosed is a coated substrate, which includes a substrate comprising a cellulosic fiber material and a copolymer coated in a thin film on at least one surface of the substrate. The copolymer has at least two comonomer units of the formula: CX_2CYA, wherein each X is independently selected from the group consisting of H, C1 and F; Y is selected from the group consisting of H, C1, F, $O(CZ_2)_nCZ_3$, $(CZ_2)_nCZ_3$, $(OCZ_2CZ_2)_nCZ_3$ and $(O(CZ_2)_n)_nCZ_3$, wherein each n is independently from about 1 to about 12 and each Z is independently selected from the group consisting of H, Cl and F; and A is selected from the group consisting of H, Cl and F; provided that for at least one comonomer unit, at least one of A, Y, and either X or any Z is C1.

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CHLOROFLUOROPOLYMER COATED SUBSTRATES FOR PACKAGING MATERIALS

FIELD OF THE DISCLOSURE

[002] The present disclosure relates to aqueous chlorofluoropolymer dispersions used in substrate coating applications. In particular, the present disclosure relates to aqueous chlorofluoropolymer dispersions applied to cellulosic fiber substrates.

BACKGROUND

[003] The use of paper based products as packaging materials to pack, for example, food, alcoholic beverages, perfumes and cosmetics, medical and tobacco products, among others, is growing due to their bio-degradability and sustainability. Paper products, however, lack chemical, solvent, oil, and stain resistance, moisture and aroma-barrier, and heat sealability properties. Although laminating paper products with PVC imparts barrier and heat sealability properties to paper, they do not have chemical, solvent, oil and stain resistance.

[004] As such, it would be desirable to provide an improved coating for and methods for coating paper-based products that impart chemical, solvent, oil, and stain resistance to the paper based products, in addition to barrier and heat sealability properties while maintaining their bio-degradability. Furthermore, other desirable features and characteristics of the inventive subject matter will become apparent from the subsequent detailed description of the inventive subject

matter and the appended claims, taken in conjunction with this background of the inventive subject matter.

BRIEF SUMMARY

[005] In one exemplary embodiment, disclosed is a coated substrate, which includes a substrate including a cellulosic fiber material and a copolymer coated in a thin film on at least one surface of the substrate. The copolymer has at least two comonomer units of the formula: CX_2CYA, wherein C is carbon and wherein each X is independently selected from the group consisting of H, Cl and F; Y is selected from the group consisting of H, Cl, F, $O(CZ_2)_nCZ_3$, $(CZ_2)_nCZ_3$, $(OCZ_2CZ_2)_nCZ_3$ and $(O(CZ_2)_n)_nCZ_3$, wherein each n is independently from about 1 to about 12 and each Z is independently selected from the group consisting of H, Cl and F; and A is selected from the group consisting of H, Cl and F; provided that for at least one comonomer unit, at least one of A, Y, and either X or any Z is Cl.

[006] In another exemplary embodiment, disclosed is a method of coating a substrate, which includes the step of contacting at least one surface of a substrate including a cellulosic fiber material with an aqueous dispersion of a copolymer. The copolymer has at least two comonomer units of the formula: CX_2CYA, wherein each X is independently selected from the group consisting of H, Cl and F; Y is selected from the group consisting of H, Cl, F, $O(CZ_2)_nCZ_3$, $(CZ_2)_nCZ_3$, $(OCZ_2CZ_2)_nCZ_3$ and $(O(CZ_2)_n)_nCZ_3$, wherein each n is independently from about 1 to about 12 and each Z is independently selected from the group consisting of H, Cl and F; and A is selected from the group consisting of H, Cl and F; provided that for at least one comonomer unit, at least one of A, Y, and either X or any Z is Cl.

[007] This brief summary is provided to introduce a selection of concepts in a simplified form that are further described below in the detailed description. This summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used as an aid in determining the scope of the claimed subject matter.

DETAILED DESCRIPTION

[008] Embodiments of the present disclosure are broadly directed to the application of chlorofluoro-olefin/fluoro-olefin copolymers to cellulosic fiber substrates. In an embodiment, cellulosic fiber substrates can include what will hereinafter be referred to as "paper" or "paper products." As used herein, the terms "paper" and "paper products" are intended to broadly and inclusively refer to the class of substrates that is derived from cellulosic fiber pulp and is provided in the form of dried sheets, paper or card boards of cellulosic fibers. An exemplary method for producing "paper" or "paper products" as used herein is briefly set forth below, by way of a non-limiting example. In addition to the pulp fibers derived from wood products, coatings in accordance with the present disclosure may be applied to the wood product itself (i.e., a hard wood product that has not been processed into pulp). As such, while some exemplary embodiments disclosed herein are directed to paper and paper based products, it will be understood that wood products serve as suitable substrates for the application coatings described herein as well.

[009] Cellulosic pulp is generally described in relation to cellulosic fibers derived from wood pulp. However, the embodiments described herein may be used in conjunction with any cellulosic fiber derived from any source. Exemplary cellulosic fibers include, but are not limited to, those derived from wood, such as wood pulp, as well as non-woody fibers from cotton, from straws and grasses, such as rice and esparto, from canes and reeds, such as bagasse, from bamboos, from stalks with bast fibers, such as jute, flax, kenaf, cannabis, linen and ramie, and from leaf fibers, such as abaca and sisal. It is also possible to use mixtures of one or more cellulosic fibers.

[0010] Wood fibers suitable for use in the described embodiments may be derived from either a softwood pulp source or hardwood pulp source or mixtures thereof. Exemplary softwood pulp sources include trees such as various pines (Slash pine, Loblolly pine, White pine, Caribbean pine), Western hemlock, various spruces, (e.g., Sitka Spruce), Douglas fir and/or mixtures of same. Exemplary hardwood pulp sources include trees such as sweet gum, black gum, maple, oak, eucalyptus, poplar, beech, and aspen or mixtures thereof.

[0011] As used herein, the term "pulp" simply refers to a mass or agglomeration of cellulose fibers. The pulp may be supplied in a dry form or as slurry. As used herein, the term "fiber" or "fibrous" is meant to refer to a particulate material wherein the length to diameter ratio of such particulate material is greater than about 10. In some embodiments, the cellulosic fibers are characterized by an average length, e.g., a WAFL length, between about 0.1 to 6 mm. In other embodiments, the average fiber length is between about 0.8 and 4 mm.

[0012] Cellulose pulp is produced using a primary pulping process as known in the art. Exemplary wood pulping operations generally entail a series of steps, such as digestion, deknotting and the like, that separate the pulp into individual fibers and remove impurities from the pulp. An exemplary wood pulping operation is the Kraft pulping process, as is known in the art. However, chemical pulping operations such as, but not limited to, sulfite pulping operations, and organic solvent pulping operations, may also be used.

[0013] As noted above, the use of paper based products as packaging materials to pack, for example, food, alcoholic beverages, perfumes and cosmetics, medical and tobacco products, among others, is growing due to their bio-degradability and sustainability. Paper products, however, lack chemical, solvent and oil resistance, moisture and aroma-barrier, and heat sealability properties. Although laminating paper products with PVC imparts barrier and heat sealability properties to paper, they do not have chemical and solvent resistance.

[0014] In order to overcome the aforementioned difficulties in using paper based products, it has been unexpectedly discovered by the inventors herein that chlorofluoro-olefin/fluoro-olefin copolymers impart desirable chemical, and solvent and oil resistance when applied to paper based products, in addition to the moisture-barrier and heat sealability properties that were previously known with regard to PVC coatings.

[0015] Chlorofluoro-olefin/fluoro-olefin copolymers, as used herein, are found to have many inherent advantages. Chlorofluoro-olefin/fluoro-olefin copolymers are abrasion resistant and when formed into a film have >90% solar light transmission. Chlorofluoro-olefin/fluoro-olefin copolymers have many fabricating advantages over PTFE, polytetrafluoroethylene-hexafluoropropylene copolymers (FEP) and polytetrafluoroethylene-hexafluoropropylene-vinylidenefluoride (THV, manufactured by Dyneon) terpolymers. Chlorofluoro-olefin/fluoro-olefin copolymers can be processed at mild, ambient temperatures and can be easily recoated by successive coatings of aqueous chlorofluoro-olefin/fluoro-olefin copolymer dispersions. Because chlorofluoro-olefin/fluoro-olefin copolymers have a relatively high surface tension, recoating with successive passes of these copolymers can be accomplished with very low levels of wetting agents, 0.1-2 weight % being typical depending on whether the wetting agent additive is fluorinated, perfluorinated, or non-fluorinated, or any mixture thereof. Chlorofluoro-olefin/fluoro-olefin copolymers are excellent film formers that facilitate the production of dispersion cast film for lamination onto fabric, or the direct coating/recoating of fabric to a desired thickness with low levels of wetting agents. Further, chlorofluoro-olefin/fluoro-olefin coatings resist solvents, acids, oils, stains, abrasion and UV and many other environmental impacts.

[0016] Certain chlorofluoro-olefin/fluoro-olefin copolymers are disclosed by McCarthy et al., *Proceedings of the Twenty-Fifth International Water-Borne, High Solids & Powder Coatings Symposium* 541 Feb. 18-20, (1998) and Bringer, *Encyclopedia of Polymer Science and Technology* (1st ed., vol. 7, Interscience Publishers, New York, 1967) p. 204, by International Patent Publication Nos. WO 97/11979 and WO 97/17381, and by U.S. Patent no. 6,759,131. Still further chlorofluoro-olefin/fluoro-olefin copolymers and methods for manufacturing the same are known in the art.

[0017] As noted above, chlorofluoro-olefin copolymers are capable of forming aqueous chlorofluoro-olefin copolymer dispersions, and as such are particularly suitable for use in the application thereof to paper and paper products as the paper and paper products can simply be immersed in the dispersion for a period time, and then dried. In particular, aqueous chlorofluoro-olefin copolymer dispersions can be prepared from ultrahigh molecular weight chlorofluoro-olefin copolymers that could not be otherwise formed by melt extrusion. When coalescing emulsion particles, entanglement of the chain ends between polymer particles is only needed, not a melt flow of the bulk. For aqueous dispersions of discrete submicron-sized particles, the minimum film formation temperature is the primary factor determining film formation. Coalescence is independent of polymer melt viscosity and polymer molecular weight.

[0018] Without being bound by any particular theory, it is believed that the high molecular weight of the chlorofluoro-olefin copolymers restricts the polymer chain mobility and limits UV-induced crystallization that would otherwise cause the formation of large, brittle spherulites, and any other morphological changes. It is also believed that the high molecular weight decreases the copolymer's tendency to move or deform permanently under the influence of stresses. Other benefits of the high polymer molecular weight include improved solvent resistance and increased toughness. In particular, the copolymers have a higher modulus and tensile strength and are more abrasion resistant.

[0019] All of the materials used to make the chlorofluoro-olefin copolymers of the present disclosure are commercially available. For example, CTFE is available from Honeywell International Inc. of Morristown, NJ, VDF is available from Solvay S.A. of Brussels, Belgium, and vinyl esters are from The Dow Chemical Company of Midland, MI. At least one comonomer from which the copolymer composition is prepared is a chlorofluoro-olefin. Suitable chlorofluoro-olefins include polychlorinated fluoroolefins such as CTFE, fluorotrichloroethylene, 1,1-dichlorodifluoroethylene, cis and trans isomers of 1,2-dichlorodifluoroethylene, 1-chloro-1-fluoroethylene, perchlorofluoroethers and perchlorofluorodioxoles.

[0020] Copolymer compositions may be prepared from up to three different chlorofluoro-olefin comonomers. Alternatively, one or two chlorofluoro-olefin comonomers may be copolymerized with one or two fluoro-olefins. Suitable fluoro-olefin comonomers from which the copolymer composition may be prepared have the formula CX_2CYA, wherein X, Y and A each do not include Cl but otherwise are as defined above. Preferred fluoro-olefin comonomers include partially and perfluorinated olefins such as VDF, TFE, HFP, vinylfluoride and 1,2-difluoroethylene, fluorinated alpha-olefins such as 3,3,4,4,4-penta-fluoro-1-butene, perfluoroethers such as perfluoro(propylvinylether) and perfluoro-dioxoles such as perfluoro(1,3-dioxole) and perfluoro(2,2-dimethyl-1,3-dioxole).

[0021] Exemplary copolymers contain predominantly chlorotrifluoroethylene, and at least one fluoro-olefin selected from the group: VDF, hexafluoropropylene, tetrafluoroethylene, vinylfluoride, trifluoroethylene, and fluorinated or perfluorinated alkylvinylethers such as perfluoropropyl vinylether. In another exemplary embodiment, the comonomers used to make the copolymer composition are selected from CTFE, VDF and a fluorinated vinyl ester. For example, the comonomers may have the formula CX_2CYA, wherein X, Y and A are as defined above, excluding olefins in which each X and A are hydrogen, provided that at least one comonomer unit contains a chlorine atom. In an exemplary preferred embodiment, the comonomers used to make the copolymer composition are CTFE and VDF.

[0022] The copolymer compositions may optionally include a chloro-olefin comonomer. Essentially any chloro-olefin may be employed, and among the suitable chloro-olefins are vinylidene chloride, vinyl chloride and trichloroethylene.

[0023] The copolymer compositions may also optionally include a non-halogenated vinyl ester or an acid as a comonomer in addition to the halogenated olefins, provided that at least two halogenated olefin comonomers are employed. The vinyl ester is preferably an alkyl vinylester, in which the alkyl group contains from about 1 to about 12 carbon atoms. The acid comonomers include acrylic acid, methacrylic acid, methyl methacrylate and other alkyl acrylates. Both vinyl ester and acid comonomers are all commercially available from, for instance, The Dow Chemical Company of Midland, MI.

[0024] Preferred vinyl esters include vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl hexanoate, vinyl stearate, neononanoate ethenyl ester, vinyl esters of n-valeric, caproic, lauric, versatic, isovaleric, 2-ethyl hexanoic, 2,2-dimethyl octanoic, 2-methyl-2-propyl pentanoic and 4-methyl-4-butyl hexanoic acids, as well as neoacid vinylesters. Preferred acids include acrylic and methacrylic acids.

[0025] The copolymerization of vinyl esters with fluoro-olefins is known in the art. U.S. Pat. Nos. 3,451,978; 3,531,441; 3,318,850 and 3,449,305 describe the copolymerization of either vinylfluoride (VF) or VDF with some quantity of a vinylester. In each of these embodiments, the major component is VF or VDF, another component is TFE, and a third component including a vinylester.

[0026] Regarding the vinylester that may be incorporated into the polymer, vinyl propionate and vinyl butyrate serve as suitable non-limiting examples. Vinyl propionate is a partially water-soluble olefin which accelerates the emulsion polymerization of chlorofluoro-olefins and fluoro-olefins. Because of the slightly branched nature of vinyl propionate, it also slows crystallization and the formation of large spherulites, while not preventing their formation. Non-halogenated olefins such as ethylene or propylene can also be incorporated into the polymer.

[0027] The amount of each monomeric unit used to prepare the copolymer will mostly depend on the application in which the material will be used (e.g., a room temperature application generally requires a composition with a glass transition temperature close to room temperature). In the case of chlorofluoro-olefins, generally, increasing levels of comonomer leads to decreasing glass transition temperatures. One skilled in the art can readily and without undue experimentation optimize these ranges to obtain an essentially amorphous chlorofluoropolymer composition having the desired properties.

[0028] Exemplary polymers contain less than about 90 weight % of a chlorofluoro-olefin, up to about 30 weight % of a fluoro-olefin, and from about 0 to about 10 weight % of a vinylester and/or a non-fluorinated olefin. When the comonomers used to make the copolymer composition are CTFE and VDF, the CTFE is present in an amount of from about 70 to about 95 weight %, for example from about 75 to about 94 weight %, and such as from about 80 to about 90 weight %. When the comonomers used to prepare the copolymer composition are CTFE, VDF and a vinylester, the vinylester is present in an amount of from about 0.1 to about 5 weight %, for example from about 0.5 to about 3 weight %, the VDF component is present in an amount of from about 5 to about 25 weight %, for example from about 10 to about 25 weight %, and the CTFE component is present in an amount less than about 88 weight %, for example less than about 85 weight %.

[0029] The copolymers of the invention have a crystallinity index from 0 to about 10%. Polymers having a crystallinity index of no greater than 5% are most preferred. For copolymer compositions consisting of an aqueous dispersion of 0.05 to 0.5 micron spherical emulsion particles, weight-average molecular weights between about 2,000,000 and about 20,000,000 Daltons are suitable. Weight-average molecular weights less than 10,000,000 Daltons are typical, with a weight-average molecular weight of about 8,000,000 Daltons being particularly suitable.

[0030] The copolymers suitable for use in accordance with the present disclosure are polymerized by conventional free-radical polymerization methods. Any commercially available radical initiator may be used in accordance with the embodiments described herein. Suitable candidates include thermal initiators and oxidation-reduction or "redox" initiator systems. Thermal initiators include: metal persulfates like potassium persulfate and ammonium persulfate; organic peroxides or hydroperoxides such as diacyl peroxides, ketone peroxides, peroxyesters, dialkyl peroxides and peroxy ketals; azo initiators such as 2,2'-azobisisobutyronitrile and water-soluble analogues thereof; and mixtures of any of the foregoing.

[0031] Any redox initiator system known to be useful in the preparation of fluoropolymers such as PCTFE may be used in the present invention. Exemplary redox initiator systems include: 1) an organic or inorganic oxidizing agent or mixtures thereof; and 2) an organic or inorganic reducing agent or mixtures thereof. Suitable oxidizing agents include metal persulfates such as potassium persulfate and ammonium persulfate; peroxides such as hydrogen peroxide, potassium peroxide, ammonium peroxide, tertiary butyl hydroperoxide ("TBHP") ($(CH_3)_3COOH$), cumene hydroperoxide, and t-amyl hydroperoxide; manganese triacetate; potassium permanganate; ascorbic acid and mixtures thereof. Suitable reducing agents include sodium sulfites such as sodium bisulfite, sodium sulfite, sodium pyrosulfite, sodium-m-bisulfite ("MBS") ($Na_2S_2O_5$) and sodium thiosulfate; other sulfites such as ammonium bisulfite; hydroxylamine; hydrazine; ferrous irons; organic acids such as oxalic acid, malonic acid, citric acid and mixtures thereof.

[0032] A suitable free radical initiating system is one that serves to simultaneously emulsify the polymer while initiating the polymerization, thus eliminating the need for large quantities of surfactants. Redox initiator systems are suitable for this purpose. Exemplary redox initiator systems use an MBS reducing agent and a TBHP oxidizing agent. For example, the redox initiator system is used in conjunction with a transition metal accelerator. Accelerators can greatly reduce the polymerization time. Any commercially available transition metal may be used as an accelerator in the invention. Exemplary transition metals include copper, silver, titanium, ferrous iron and mixtures thereof.

[0033] The amount of radical initiator used in the process depends on the relative ease with which the various monomers copolymerize, the molecular weight of the polymer and the rate of reaction desired. Generally, from about 10 to about 100,000 ppm of initiator may be used, for example from about 100 to about 10,000 ppm.

[0034] Optionally, in order to further accelerate the polymerization, the redox initiator system may include additional peroxide-based compounds. The amount of additional peroxide-based compound used ranges from about 10 to about 10,000 ppm, for example from about 100 to about 5,000 ppm.

[0035] The radical initiator may be added before, simultaneous with and/or shortly after the addition and/or consumption of the monomers used to make the copolymer. When an additional peroxide-based compound is used it may be added at the same interval specified for the primary radical initiator.

[0036] The chlorofluoropolymer compositions of the present disclosure may be made by a two-step polymerization reaction. In one example, monomers, water, and an initial charge of radical initiator are introduced into suitable polymerization vessel. Additional monomer is added throughout the reaction at a rate equal to the rate of consumption to maintain a constant pressure. Incremental additional charges of initiator are introduced into the vessel over the duration of the reaction to sustain the polymerization. The reaction mixture is maintained at a controlled temperature while all reactants are being charged to the vessel and throughout the polymerization reaction.

[0037] The only requirement for the reaction vessel used to prepare the composition described herein is that it be capable of being pressurized and agitated. Conventional commercial autoclaves which can be sealed and pressurized to the required reaction pressures (preferably in excess of 3.36 MPa (500 psig)) are preferred. Horizontally inclined autoclaves are preferred to vertically inclined autoclaves, although both geometries can be used.

[0038] The aqueous medium in which the polymerization is conducted is deionized, nitrogen-purged water. Generally, an amount equivalent to approximately half the capacity of the vessel, such as an autoclave, is used. The ratio of polymer to water is chosen in such a way to obtain a dispersion of about 20 to about 60% polymer solids in water. The water is pre-charged to the autoclave. The process is a surfactant-free emulsion polymerization process that does not require a separate post-concentration step to obtain high levels of emulsified polymer in water.

[0039] The monomers may be charged to the reactor vessel either in a semicontinuous or a continuous manner during the course of the polymerization. "Semicontinuous," as used herein, means that a number of batches of the monomers are charged to the reactor during the course of the polymerization reaction. The batch size is determined by the desired operating pressure. The molar ratio of total monomer consumed to radical initiator will depend upon the overall particle size and molecular weight desired. In an embodiment, the overall mole ratio of monomer to initiator would be from about 10 to about 10,000, for example from about 50 to about 1,000, and such as from about 100 to about 500 moles of total monomer to one mole of initiator.

[0040] The radical initiator is generally added incrementally over the course of the reaction. For purposes of this disclosure, "initial charge" or "initial charging" of initiator refers to a rapid, large, single or incremental addition of initiator to effect the onset of polymerization. In the initial charge, generally between about 10 ppm/min to about 1,000 ppm/min is added over a period of from about 3 to about 30 minutes, either before, after, or during the charging of the monomers. As further used herein, "continuous charge" or "continuous charging" means the slow, small, incremental addition of initiator over a period of from about 1 hour to about 6 hours, or until polymerization has concluded. In the continuous charge, generally between about 0.1 ppm/min to about 30 ppm/min of initiator is added.

[0041] During the initiation of the polymerization reaction, the sealed reactor and its contents are maintained at the desired reaction temperature, or alternately to a varying temperature profile which varies the temperature during the course of the reaction. Control of the reaction temperature is a factor for establishing the final molecular weight of the chlorofluoropolymers produced. As a general rule, polymerization temperature is inversely proportional to product molecular weight. Typically, the reaction temperature should range between about 0°C to about 120°C, although temperatures above and below these values are also contemplated. The reaction pressure is between from about 172 KPa to about 5.5 MPa, and for example from about 345 KPa to about 4.2 MPa. Elevated pressures and temperatures will yield greater reaction rates.

[0042] The polymerization is conducted under agitation to ensure proper mixing. An adjustment of the agitation rate during the polymerization may be desirable to prevent premature coagulation of the particles. Although the agitation rate and reaction time will typically depend upon the amount of chlorofluoropolymer product desired, one of ordinary skill in the art can readily optimize the conditions of the reaction without undue experimentation to get the claimed results. The agitation rate will generally be in the range of from about 5 to about 800 rpm and, for example from about 25 to about 700 rpm, depending on the geometry of the agitator and the size of the vessel. The reaction time will generally range from about 1 to about 24 hours, for example from about 1 to about 8 hours.

[0043] The chlorofluoropolymers produced using the above surfactant-free process are self-emulsifiable chlorofluorinated macromolecules having inorganic, "surfactant-like" functional end groups that impart excellent latex stability to the polymer when present in very low concentration. The chlorofluoropolymers produced are thereby dispersed in the aqueous medium by the attachment of these inorganic fragments onto the end of the polymer repeating units, thus creating a surface active agent having both a hydrophobic component and a hydrophilic component. This attachment leads to micelle formation, or, if the concentration of functionalized end groups is high enough, to their complete dissolution in water.

[0044] The type of "surfactant-like" end groups produced depends upon the type of initiator system selected and the optional addition of compounds that might be incorporated into the polymer through chain transfer reactions. Examples of such emulsifying functional end groups include, but are not limited to, sulfonates, carboxylates, phosphonates, phosphates and salts and acids thereof, ammonium salts and any mixture thereof.

[0045] The presence of sulfonic acid end groups has been discovered to most significantly affect the emulsification of the chlorofluoropolymers in water. The amount of these functional end groups in the dispersion can be determined by first purifying the dispersion by methods known to the art, such as by ion exchange or dialysis, titrating the dispersion with any known base such as aqueous sodium hydroxide or ammonium hydroxide, and then expressing the amount in terms of molar equivalents of titrated base. The amount of these functional end groups expressed in moles of equivalent NaOH may range between from about 0.0001 to about 0.5 moles of functional end groups per liter of chlorofluoropolymer dispersion obtained. The molar ratio of these functional end groups per fluoropolymer produced may range from about 1:10 to 10,000, for example from about 1:10 to 1,000, such as from about 1:50 to 500. An exemplary chlorofluoropolymer dispersion within the scope of this disclosure contains about 0.01 molar equivalents/kg of dry polymer.

[0046] In the absence of added surfactant, the resulting particle size distribution of the dispersion produced according to the process of the invention will be monodisperse and narrow. "Monodisperse distribution" as used herein means a single distribution of particle sizes. Generally, the particle distribution ranges between about 0.1 microns and about 0.4 microns, and for example from about 0.1 to about 0.3 microns.

[0047] The dispersions as described herein are prepared using a surfactant-free emulsion process to obtain stable dispersions having up to 45 weight % solids in water, which are obtained without a concentration step. Low levels of surfactants are added if further particle size control is desired, or to obtain higher levels of emulsified polymer in water (i.e., 40-60 weight %). Any commercially available surfactant may optionally be pre-charged or added batch-wise during or subsequent to the onset of polymerization to further manipulate particle size, particle number and particle distribution. It is well known in the art that the addition of more surfactant during the course of polymerization to emulsions already containing surfactants sometimes creates new particles and thus produces a bimodal distribution of particles or a broad distribution of particles.

[0048] Suitable surfactants will readily occur to those skilled in the art and include anionic, cationic and nonionic surfactants. An exemplary dispersion is an anionic surfactant stabilized latex emulsion having from 0 to 0.25 weight % of an anionic emulsifier. Examples of suitable perfluorinated anionic surfactants include perfluorinated ammonium octanoate, perfluorinated alkyl/aryl ammonium (metal) carboxylates and perfluorinated alkyl/aryl lithium (metal) sulfonates wherein the alkyl group has from about 1 to about 20 carbon atoms. Suitable surfactants also include fluorinated ionic or nonionic surfactants, hydrocarbon-based surfactants such as the alkylbenzenesulfonates or mixtures of any of the foregoing.

[0049] The chlorofluoropolymers produced by the process of the invention may be isolated by conventional methods such as evaporating the water medium, freeze-drying the aqueous suspension, or adding a minor amount of an agglomerating or coagulating agent such as ammonium carbonate, followed by filtration or centrifuging. Alternatively and preferably the chlorofluoropolymer dispersion produced is used as is.

[0050] As noted briefly above, unlike other fluoropolymers which must be processed at temperatures greater than 260°C (i.e., PTFE, FEP, PFA, ETFE etc.), dispersions of chlorofluoro-olefin/fluoro-olefin copolymers as described in the present disclosure and the vinylester terpolymers thereof can be coated at temperatures lower than 120°C onto paper and paper products. Non-limiting examples of industrial uses for such paper and paper products include packaging food, alcoholic beverages, perfumes and cosmetics, medical and tobacco products, In particular, the coated paper imparted with moisture barrier property will be useful as a lid foil for blister packs in pharmaceutical packaging. In addition, coating value documents with aqueous dispersions of chlorofluoroolefin/fluoro-olefin copolymers as described in the present disclosure provides stain resistance to such documents.

[0051] In one embodiment, the chlorofluoro-olefin/fluoro-olefin copolymers are coated on a paper or paper product substrate in multi-pass processes, although a single-pass process may also be used. For example, the paper product may be immersed in the above-described aqueous dispersions of chlorofluoro-olefin/fluoro-olefin copolymers for a period of time ranging between about 60 seconds to 1 hour. As noted above, due to the unique nature of this particular dispersion, the application process is able to occur at ambient temperatures, for example from about 20 – 30°C. Thereafter, the paper product may be removed from the aqueous dispersion, and allowed to dry. Drying may be performed at an elevated temperature to increase the speed at which the paper product dries, for example from about 70 – 120 C in an oven. The drying process may also be expedited with air or nitrogen Thereafter, the application process can be repeated any number of times to produce the desired thickness of coating on the paper product, for example one, two, three, four, five, or more times.

[0052] The resulting coated paper or paper product desirably is hydrophobic, and does not allow solvent such as isopropyl alcohol ("IPA"), toluene, or ethanol, for example, to penetrate through the paper. The coated paper also does not allow oil or grease to penetrate through the paper and resistant to stain. Furthermore, the coated paper seals itself upon heating and the sealed paper maintains its properties. The coated paper further provides a barrier to moisture and aroma, and the moisture and aroma-barrier property can be tailored by adjusting the thickness and kind (for example, one-sided or two-sided) of coating.

[0053] While at least one exemplary embodiment has been presented in the foregoing detailed description of the inventive subject matter, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the inventive subject matter in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the inventive subject matter. It being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the inventive subject matter as set forth in the appended claims.

[0054] **Example 1**

Preparation of CTFE/VDF/Vinyl Propionate Terpolymer Dispersion

CTFE/VDF/Vinyl propionate terpolymer dispersion was prepared having 80.1 weight % chlorotrifluoroethylene, 16.5 weight % vinylidenefluoride and 3.4 weight % vinyl propionate. To prepare the polymer, a 3 Gallon glass-lined autoclave was first filled with 1.57 gallons of deionized water and then nitrogen sparged to remove oxygen. The autoclave was then filled with 585 g of CTFE and 116 grams of VDF and heated to 19 ° C (66.2 ° F). 5.7 G of 70% solution of tertiary butyl hydroperoxide (TBHP) in water was further diluted to 35.7 mL with deionized water. 4.4 grams of sodium metabisulfite (MBS) and 0.9 grams of ferrous sulfate heptahydrate were also diluted to 35.7 mL with deionized water. The two solutions were then separately added to the autoclave over a ten minute period to initiate the polymerization. The temperature in the autoclave was maintained throughout the entire polymerization between 19 – 20° C. The polymerization was continued by the slow addition of two separate solutions consisting of TBHP (20.6 g in 142 mL deionized water) and MBS (16.8 g in 142.8 mL in deionized water). After 25 minutes into the polymerization, 108.4 mL of vinyl propionate was pumped into the autoclave throughout the polymerization at a rate equal to the consumption rate of CTFE and VDF. After the consumption of the initial charges of CTFE and VDF, additional CTFE and VDF were added to the autoclave over a period of 4 hours to maintain a reactor pressure from 50-160 psig. Total amounts of CTFE and VDF added to maintain the pressure equals to 4222 grams and 837 grams of VDF, respectively. After the consumption of all the monomers (pressure drops to <90 psig) the autoclave was vented, yielding 2 gallons of aqueous terpolymer dispersion containing 31.2% polymer solids by weight.

[0055] **Example 2**

Coating of a paper using the dispersion from Example 1

To the dispersion obtained in Example 1 was added 2.0 weight % (based on the weight of dispersion) of Capstone™ FS-32 fluorosurfactant (from Du Pont) and mixed thoroughly. The mixture was then coated onto a laminated paper (from Coldenhove, Netherlands) at room temperature using multiple passes to achieve a thickness of 1.5 mils coating on each side of the paper. Total thickness of the coated paper corresponds to 4.9 mils. The coated paper was dried in an air oven at 80 °C between coats. The coated paper was then subjected to MOCON testing at 40 °C and 70% relative humidity to give a water vapor transmission rate of 0.0929 grams/100in^2

–day. Upon heating the coated paper to 175 °C (~ 350 °F), it heat seals itself and the attempts to break the seal results the paper getting ripped indicating the seal is intact

What is claimed is:

1. A coated packaging substrate with water vapor transmission barrier and self-heat-sealing properties consisting of:

a paper or paper product substrate consisting of a cellulosic fiber material derived from wood pulp; and

a copolymer coating consisting of a copolymer applied on both surfaces of the substrate, wherein the copolymer consists of a terpolymer of chlorotrifluoroethylene, vinylidene fluoride, and vinylpropionate with the chlorotrifluoroethylene being present in the copolymer at a weight-% of less than 88%, the vinylidene fluoride being present in the copolymer at a weight-% of from 5% to 25%, and the vinylpropionate being present in the copolymer at a weight-% of from 0.1% to 5%,

wherein the copolymer has a weight-average molecular weight between 2,000,000 and 20,000,000 Daltons and is applied to the substrate as an aqueous dispersion of 0.05 to 0.5 micron spherical emulsion particles, and

wherein the cellulosic fiber material is provided in the form of dried sheets, paper, or cardboards of cellulosic fibers, and wherein the paper or paper product substrate is in the form of packaging materials to pack food, alcoholic beverages, perfumes and cosmetics, and medical or tobacco products, and

wherein the copolymer coating has a coating thickness on the surfaces of the substrate that inhibits the passage of water vapor from one surface of the substrate through to the other surface of the substrate and provides for sealability of the substrate to itself upon heating.

2. The coated packaging substrate of claim 1, wherein the copolymer has a crystallinity index from 0% to 10%.