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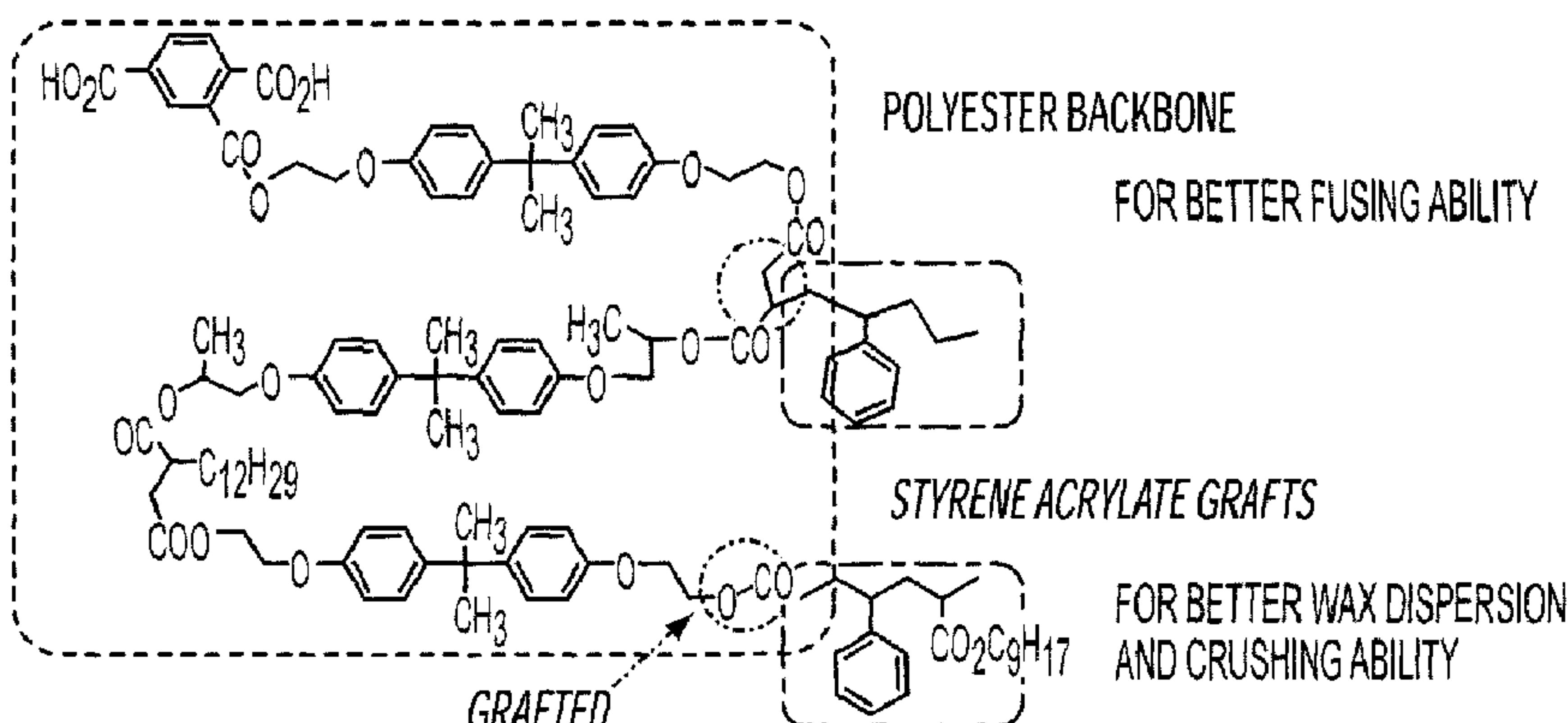
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(54) Title: EMULSION AGGREGATION TONER COMPRISING HYBRID LATEX



(57) Abrégé/Abstract:

A toner includes a core including a homogenized mixture of a first polyester latex, a styrene/acrylate latex, and a compatibilizing agent latex that includes a graft polyester-styrene/acrylate copolymer and a shell that includes a polyester latex. A process includes

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(57) Abrégé(suite)/Abstract(continued):

(1) homogenizing a mixture to form a plurality of core particles, the mixture including a first polyester latex, a styrene/acrylate latex, and a compatibilizing agent latex comprising a graft polyester-styrene/acrylate copolymer and (2) adding a shell polyester latex to the plurality of core particles to form a plurality of core-shell structures.

ABSTRACT

A toner includes a core including a homogenized mixture of a first polyester latex, a styrene/acrylate latex, and a compatibilizing agent latex that includes a graft polyester-styrene/acrylate copolymer and a shell that includes a polyester latex. A process includes (1) homogenizing a mixture to form a plurality of core particles, the mixture including a first polyester latex, a styrene/acrylate latex, and a compatibilizing agent latex comprising a graft polyester-styrene/acrylate copolymer and (2) adding a shell polyester latex to the plurality of core particles to form a plurality of core-shell structures.

EMULSION AGGREGATION TONER COMPRISING HYBRID LATEX

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BACKGROUND

[0001] The present disclosure relates to toners. In particular, the present disclosure relates to polyester based toners incorporating styrene/acrylate latexes to reduce production costs.

10 [0002] Attempts to reduce polyester latex fractions by replacement with less expensive poly(styrene/acrylate) latexes in toner particle production has been hampered by rejection of the latter latex either during aggregation/coalescence or during washing. Moreover, attempts to use these apparently disparate resins together have been frustrated by process complexity, causing significant changes in processing parameters

15 during aggregation/coalescence.

SUMMARY

[0003] In some aspects, embodiments herein relate to toners comprising a core comprising a homogenized mixture of a first polyester latex, a styrene/acrylate latex, and a compatibilizing agent latex comprising a graft polyester-styrene/acrylate copolymer; and a shell comprising a polyester latex.

20 [0004] In some aspects, embodiments herein relate to processes comprising homogenizing a mixture to form a plurality of core particles, the mixture comprising a first polyester latex, a styrene/acrylate latex, and a compatibilizing agent latex comprising a graft polyester-styrene/acrylate copolymer, and adding a shell polyester latex to the plurality of core particles to form a plurality of core-shell structures.

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BRIEF DESCRIPTION OF DRAWINGS

[0005] Various embodiments of the present disclosure will be described herein below with reference to the figures wherein:

[0006] FIG. 1 shows a compatabilizing agent in accordance with embodiments herein.

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DETAILED DESCRIPTION

[0007] Embodiments herein provide compositions and methods that incorporate poly(styrene/acrylate) latex as part of core particles during the aggregation/coalescence (A/C) process to reduce the overall cost of the toner due to the significantly lower cost of poly(styrene/acrylate) latex. Early attempts to incorporate poly(styrene/acrylate) latex into polyester latexes were hampered by expulsion of the poly(styrene/acrylate) into the mother liquor either in the A/C process or during washing.

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[0008] Embodiments herein overcome this expulsion problem by including a compatibilizing agent in latex form along with polyester and poly(styrene/acrylate) latexes during a standard A/C process. In embodiments, the compatibilizing agent comprises a graft co-polymer of a polyester and styrene/acrylate, as exemplified in Figure 1. Using this compatibilizing agent, the mother liquor filtrate was transparent in the A/C process which indicated that there was no latex rejection. The ability to substitute a fraction of the polyester latex with styrene/acrylate provides a substantial reduction in latex cost. Moreover, the resultant toner particles perform well in their intended toner particle role.

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[0009] Figure 1 shows the chemical structure of an exemplary compatibilizing agent.

The hybrid resin comprises a polyester backbone which may provide better fusing ability and styrene/acrylate grafts may improve wax dispersion. Moreover, the compatibilizing

agent may improve crushing ability, moisture sensitivity, and flexibility in polymer design. In embodiments, the ratio of polyester to styrene/acrylate graft can be readily controlled depending on the functional needs of the resin in toner system. Accordingly, the resin properties (such as Tg, Tm, and acid value) may change as the polyester to 5 styrene/acrylate graft ratio varies. Because the majority of compatibilizing agent is polyester and the styrene/acrylate grafts are on the end of polyester chains, it readily forms a latex with both polyester and poly(styrene/acrylate) on the particle surface. This dual surface display is believed to improve the compatibility between polyester and poly(styrene/acrylate) latexes particles allowing the three latexes to smoothly aggregate 10 and coalesce under standard A/C conditions.

[0010] In embodiments, there are provided toners comprising a core comprising a homogenized mixture of a first polyester latex, a styrene/acrylate latex, and a compatibilizing agent latex comprising a graft polyester-styrene/acrylate copolymer, the toners further comprising a shell comprising a polyester latex.

15 [0011] As used herein, "latex" refers to a liquid having polymeric resin particles dispersed therein. Latexes may be prepared directly from phase-inversion emulsification optionally with concomitant vacuum-assisted solvent removal.

[0012] In embodiments, the first polyester latex may be present in an amount from about 70 to about 90 weight percent of the core, or about 30 to about 90 weight percent of the 20 core, or about 40 to about 80 weight percent of the core, or about 50 to about 70 weight percent of the core.

[0013] In embodiments, the styrene/acrylate latex is present in an amount from about 5 to about 15 weight percent of the core, or about 1 to about 70 weight percent of the core, or about 10 to about 50 weight percent of the core.

[0014] In embodiments, the compatibilizing agent latex is present in an amount from 5 about 5 to about 15 weight percent of the core, or about 7 to about 12 weight percent of the core, or about 9 to about 11 weight percent of the core.

[0015] In embodiments, the ratio of polyester to styrene/acrylate in the graft polyester-styrene/acrylate copolymer is in a range from about 80:20 to about 90:10, or about 70:30 to about 99:1, or about 85:15 to about 95:5.

10 [0016] In embodiments the core further comprises a second polyester latex. In embodiments, the first polyester latex comprises an amorphous high molecular weight polyester of weight average molecular weight in a range from about 35 KDa to about 150 KDa. In embodiments the second polyester latex comprises an amorphous low molecular weight polyester of weight average molecular weight in a range from about 10 15 KDa to about 30 KDa.

[0017] In embodiments, the toners may further comprise a crystalline polyester latex.

[0018] In embodiments, the toners may further comprise a wax dispersion.

[0019] In embodiments, the toners may further comprise a colorant.

[0020] In embodiments, the toners may further comprise an aggregating agent.

20 Resins

[0021] In embodiments, the first polymer comprises a polyester. In embodiments, the second polymer comprises a polyester. In embodiments, the first polymer and the second polymer are the same. In embodiments, the polymer comprises a polyester. In

embodiments, the first or second polyester is amorphous. In embodiments, the first or second polyester is crystalline. Two types of amorphous acidic polyester resins (low Mw poly(co-propoxylated bisphenol A co-ethoxylated bisphenol A co-terephthalate co-fumarate co-dodecenyldsuccinate) and high Mw poly(co-propoxylated bisphenol A co-ethoxylated bisphenol A co-terephthalate co-dodecenyldsuccinate co-trimellitate), Kao Corporation, Japan) are commonly incorporated into Ultra-low-melt (ULM) toners, and these resins may account for about 75% to about 78% of the toner components. To make ULM toner, each resin is typically emulsified into an aqueous dispersion or emulsion (latex). Solvent-based PIE processes disclosed herein can be employed to 10 form the requisite polyester resin emulsions for making such toners.

[0022] In some embodiments, the first amorphous polyester and the second amorphous polyester may be present in a total amount in a range of from about 40% by weight to about 95% by weight of the latex. In some embodiments, first amorphous polyester and second amorphous polyester are present in a ratio from about 0.1: 0.9 to about 0.9:0.1, 15 including any ratio in between. In some embodiments, the polyester resin further comprises a crystalline polyester. In some embodiments, the crystalline polyester is present in an amount in a range of from about 1.0% by weight to about 35.0% by weight of the latex. In some embodiments, the polyester resin comprises a crystalline resin, but not an amorphous resin.

20 [0023] Any resin may be utilized in forming a latex emulsion of the present disclosure. In embodiments, the resins may be an amorphous resin, a crystalline resin, and/or a combination thereof. In embodiments, the resin may be a crystalline polyester resin with acidic groups having an acid number of about 1 mg KOH/g polymer to about 200

mg KOH/g polymer, in embodiments from about 5 mg KOH/g polymer to about 50 mg KOH/g polymer. In further embodiments, the resin may be a polyester resin, including the resins described in U.S. Patent Nos. 6,593,049 and 6,756,176. Suitable resins may also include a mixture of an amorphous polyester resin and a crystalline polyester resin

5 as described in U.S. Patent No. 6,830,860.

[0024] In embodiments, the resin may be a polyester resin formed by reacting a diol with a diacid in the presence of an optional catalyst. For forming a crystalline polyester, suitable organic diols include aliphatic diols with from about 2 to about 36 carbon atoms, such as 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 2,2-dimethylpropane-1,3-diol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonenediol, 1,10-decanediol, 1,12-dodecanediol and the like including their structural isomers. The aliphatic diol may be, for example, selected in an amount of from about 40 to about 60 mole percent, in embodiments from about 42 to about 55 mole percent, in embodiments from about 45 to about 53 mole percent, and a second diol can be

10 selected in an amount of from about 0 to about 10 mole percent, in embodiments from about 1 to about 4 mole percent of the resin.

[0025] Examples of organic diacids or diesters including vinyl diacids or vinyl diesters selected for the preparation of the crystalline resins include oxalic acid, succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, fumaric acid, dimethyl fumarate, dimethyl itaconate, cis, 1,4-diacetoxy-2-butene, diethyl fumarate, diethyl maleate, phthalic acid, isophthalic acid, terephthalic acid, naphthalene-2,6-dicarboxylic

acid, naphthalene-2,7-dicarboxylic acid, cyclohexane dicarboxylic acid, malonic acid and mesaconic acid, a diester or anhydride thereof. The organic diacid may be selected in an amount of, for example, in embodiments from about 40 to about 60 mole percent, in embodiments from about 42 to about 52 mole percent, in embodiments from 5 about 45 to about 50 mole percent, and a second diacid can be selected in an amount of from about 0 to about 10 mole percent of the resin.

[0026] Examples of crystalline resins include polyesters, polyamides, polyimides, polyolefins, polyethylene, polybutylene, polyisobutyrate, ethylene-propylene copolymers, ethylene-vinyl acetate copolymers, polypropylene, mixtures thereof, and 10 the like. Specific crystalline resins may be polyester based, such as poly(ethylene-adipate), poly(propylene-adipate), poly(butylene-adipate), poly(pentylene-adipate), poly(hexylene-adipate), poly(octylene-adipate), poly(ethylene-succinate), poly(propylene-succinate), poly(butylene-succinate), poly(pentylene-succinate), poly(hexylene-succinate), poly(octylene-succinate), poly(ethylene-sebacate), 15 poly(propylene-sebacate), poly(butylene-sebacate), poly(pentylene-sebacate), poly(hexylene-sebacate), poly(octylene-sebacate), poly(decylene-sebacate), poly(decylene-decanoate), poly(ethylene-decanoate), poly(ethylene dodecanoate), poly(nonylene-sebacate), poly(nonylene-decanoate), copoly(ethylene-fumarate)-copolymers, copoly(ethylene-sebacate), copoly(ethylene-fumarate)-copolymers, copoly(ethylene-decanoate), 20 copoly(ethylene-fumarate)-copolymers, copoly(ethylene-dodecanoate), copoly(2,2-dimethylpropane-1,3-diol-decanoate)-copolymers, poly(octylene-adipate). Examples of polyamides include poly(ethylene-adipamide), poly(propylene-adipamide), poly(butylene-adipamide), poly(pentylene-adipamide), poly(hexylene-adipamide),

poly(octylene-adipamide), poly(ethylene-succinimide), and poly(propylene-sebecamide).

Examples of polyimides include poly(ethylene-adipimide), poly(propylene-adipimide),

poly(butylene-adipimide), poly(pentylene-adipimide), poly(hexylene-adipimide),

poly(octylene-adipimide), poly(ethylene-succinimide), poly(propylene-succinimide), and

5 poly(butylene-succinimide).

[0027] The crystalline resin may be present, for example, in an amount of from about 1

to about 85 percent by weight of the toner components, in embodiments from about 5 to

about 50 percent by weight of the toner components. The crystalline resin can possess

various melting points of, for example, from about 30° C to about 120° C, in

10 embodiments from about 50° C to about 90° C. The crystalline resin may have a

number average molecular weight (Mn), as measured by gel permeation

chromatography (GPC) of, for example, from about 1,000 to about 50,000, in

embodiments from about 2,000 to about 25,000, and a weight average molecular weight

(Mw) of, for example, from about 2,000 to about 100,000, in embodiments from about

15 3,000 to about 80,000, as determined by GPC using polystyrene standards. The

molecular weight distribution (Mw/Mn) of the crystalline resin may be, for example, from

about 2 to about 6, in embodiments from about 3 to about 4.

[0028] Examples of diacids or diesters including vinyl diacids or vinyl diesters utilized for

the preparation of amorphous polyesters include dicarboxylic acids or diesters such as

20 terephthalic acid, phthalic acid, isophthalic acid, fumaric acid, trimellitic acid, dimethyl

fumarate, dimethyl itaconate, cis, 1,4-diacetoxy-2-butene, diethyl fumarate, diethyl

maleate, maleic acid, succinic acid, itaconic acid, succinic acid, succinic anhydride,

dodecylsuccinic acid, dodecylsuccinic anhydride, glutaric acid, glutaric anhydride, adipic

acid, pimelic acid, suberic acid, azelaic acid, dodecanediacid, dimethyl terephthalate, diethyl terephthalate, dimethylisophthalate, diethylisophthalate, dimethylphthalate, phthalic anhydride, diethylphthalate, dimethylsuccinate, dimethylfumarate, dimethylmaleate, dimethylglutarate, dimethyladipate, dimethyl dodecylsuccinate, and 5 combinations thereof. The organic diacids or diesters may be present, for example, in an amount from about 40 to about 60 mole percent of the resin, in embodiments from about 42 to about 52 mole percent of the resin, in embodiments from about 45 to about 50 mole percent of the resin.

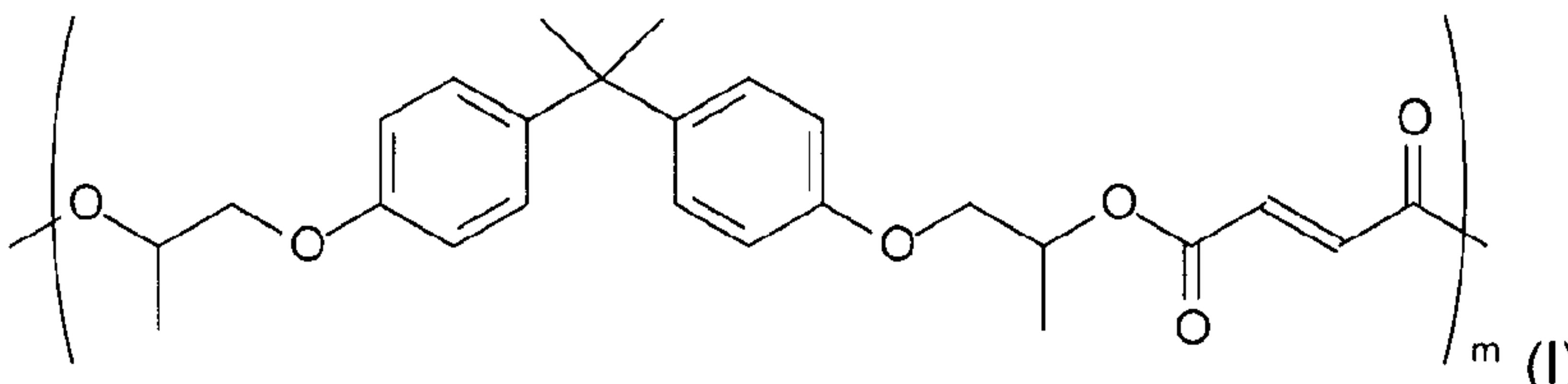
[0029] Examples of diols which may be utilized in generating the amorphous polyester 10 include 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, pentanediol, hexanediol, 2,2-dimethylpropanediol, 2,2,3-trimethylhexanediol, heptanediol, dodecanediol, bis(hydroxyethyl)-bisphenol A, bis(2-hydroxypropyl)-bisphenol A, 1,4-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, xylenedimethanol, cyclohexanediol, diethylene glycol, bis(2-hydroxyethyl) oxide, 15 dipropylene glycol, dibutylene, and combinations thereof. The amount of organic diols selected can vary, and may be present, for example, in an amount from about 40 to about 60 mole percent of the resin, in embodiments from about 42 to about 55 mole percent of the resin, in embodiments from about 45 to about 53 mole percent of the resin.

20 [0030] Polycondensation catalysts which may be utilized in forming either the crystalline or amorphous polyesters include tetraalkyl titanates, dialkyltin oxides such as dibutyltin oxide, tetraalkyltins such as dibutyltin dilaurate, and dialkyltin oxide hydroxides such as butyltin oxide hydroxide, aluminum alkoxides, alkyl zinc, dialkyl zinc, zinc oxide,

stannous oxide, or combinations thereof. Such catalysts may be utilized in amounts of, for example, from about 0.01 mole percent to about 5 mole percent based on the starting diacid or diester used to generate the polyester resin.

[0031] In embodiments, as noted above, an unsaturated amorphous polyester resin may 5 be utilized as a latex resin. Examples of such resins include those disclosed in U.S. Patent No. 6,063,827. Exemplary unsaturated amorphous polyester resins include, but are not limited to, poly(propoxylated bisphenol co-fumarate), poly(ethoxylated bisphenol co-fumarate), poly(butyloxylated bisphenol co-fumarate), poly(co-propoxylated bisphenol co-ethoxylated bisphenol co-fumarate), poly(1,2-propylene fumarate), 10 poly(propoxylated bisphenol co-maleate), poly(ethoxylated bisphenol co-maleate), poly(butyloxylated bisphenol co-maleate), poly(co-propoxylated bisphenol co-ethoxylated bisphenol co-maleate), poly(1,2-propylene maleate), poly(propoxylated bisphenol co-itaconate), poly(ethoxylated bisphenol co-itaconate), poly(butyloxylated bisphenol co-itaconate), poly(co-propoxylated bisphenol co-ethoxylated bisphenol co-itaconate), poly(1,2-propylene itaconate), and combinations thereof. 15

[0032] In embodiments, a suitable polyester resin may be an amorphous polyester such as a poly(propoxylated bisphenol A co-fumarate) resin having the following formula (I):

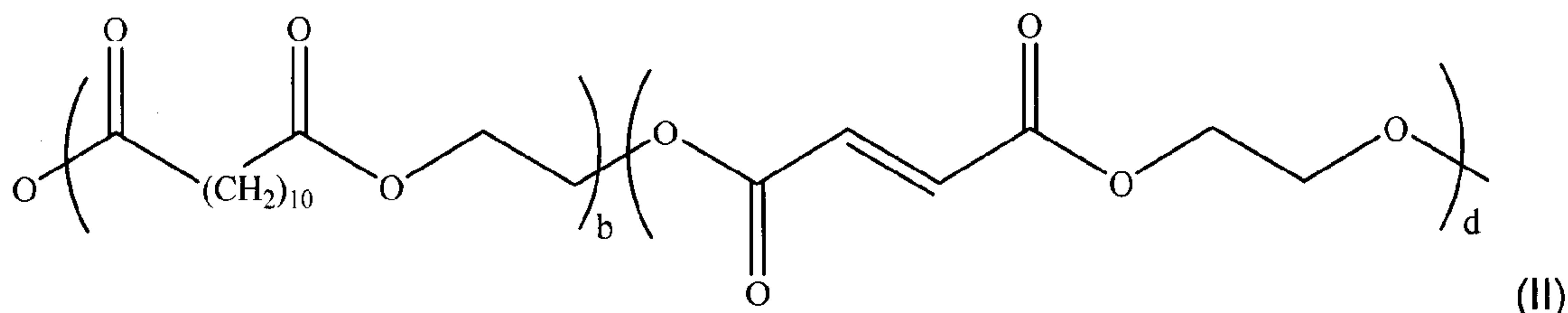


[0033] wherein m may be from about 5 to about 1000. Examples of such resins and 20 processes for their production include those disclosed in U.S. Patent No. 6,063,827.

[0034] In embodiments, a suitable polyester resin may be an amorphous polyester based on any combination of propoxylated bisphenol A, ethoxylated bisphenol A, terephthalic acid, fumaric acid, and dodecanyl succinic anhydride. Poly(co-propoxylated bisphenol A co-ethoxylated bisphenol A co-terephthalate co-fumarate co-
5 dodecenylsuccinate), available from Kao Corporation, Japan, is an example of such an amorphous ester.

[0035] An example of a linear propoxylated bisphenol A fumarate resin which may be utilized as a latex resin is available under the trade name SPARII from Resana S/A Industrias Quimicas, Sao Paulo Brazil. Other propoxylated bisphenol A fumarate resins
10 that may be utilized and are commercially available include GTUF and FPESL-2 from Kao Corporation, Japan, and EM181635 from Reichhold, Research Triangle Park, North Carolina, and the like.

[0036] Suitable crystalline resins which may be utilized, optionally in combination with an amorphous resin as described above, include those disclosed in U.S. Patent
15 Application Publication No. 2006/0222991. In embodiments, a suitable crystalline resin may include a resin formed of ethylene glycol and a mixture of dodecanedioic acid and fumaric acid co-monomers with the following formula:



[0037] wherein b is from about 5 to about 2000 and d is from about 5 to about 2000.

[0038] For example, in embodiments, a poly(propoxylated bisphenol A co-fumarate) resin of formula I as described above may be combined with a crystalline resin of formula II to form a latex emulsion.

[0039] An amorphous resin may be present, for example, in an amount of from about 5 to about 95 percent by weight of the toner components, in embodiments from about 30 to about 80 percent by weight of the toner components. In embodiments, the amorphous resin or combination of amorphous resins utilized in the latex may have a glass transition temperature (Tg) of from about 30°C to about 80°C, in embodiments from about 35°C to about 70°C. In further embodiments, the combined resins utilized in the latex may have a melt viscosity of from about 10 to about 1,000,000 Pa*S at about 130°C, in embodiments from about 50 to about 100,000 Pa*S.

[0040] One, two, or more resins may be used. In embodiments, where two or more resins are used, the resins may be in any suitable ratio (e.g., weight ratio) such as for instance of from about 1% (first resin)/99% (second resin) to about 99% (first resin)/ 1% (second resin), in embodiments from about 10% (first resin)/90% (second resin) to about 90% (first resin)/10% (second resin).

[0041] In embodiments the resin may possess acid groups which, in embodiments, may be present at the terminal of the resin. Acid groups which may be present include

carboxylic acid groups, and the like. The number of carboxylic acid groups may be controlled by adjusting the materials utilized to form the resin and reaction conditions.

[0042] In embodiments, the amorphous resin may be a polyester resin having an acid number from about 2 mg KOH/g of resin to about 200 mg KOH/g of resin, in

5 embodiments from about 5 mg KOH/g of resin to about 50 mg KOH/g of resin. The acid containing resin may be dissolved in tetrahydrofuran solution. The acid number may be detected by titration with KOH/ methanol solution containing phenolphthalein as the indicator. The acid number may then be calculated based on the equivalent amount of KOH/methanol required to neutralize all the acid groups on the resin identified as the
10 end point of the titration.

[0043] Solvent

[0044] In embodiments, the aprotic solvent is selected from the group consisting of a

ketone, an ester, an ether, or a nitrile. In some emobdiments, processes disclosed

herein may employ an aprotic solvent selected from the group consisting of methyl ethyl

15 ketone, acetone, methyl acetate, acetonitrile, or tetrahydrofuran. In embodiments, the aprotic solvent is MEK. In particular embodiments, the amount of aprotic solvent may be from about 0.1 % by weight to about 100 % by weight of the resin, in embodiments of from about 2 % by weight to about 50 % by weight of the resin, in other embodiments of from about 5 % by weight to about 35 % by weight of the resin.

20 [0045] In embodiments, the aprotic solvent to resin ratio may be about 0.1:10 to about 20:10, in other embodiments, from about 1.0:10 to about 5:10.

[0046] In embodiments, the aprotic solvent may be substantially miscible in water. In embodiments the aprotic solvent may be partially miscible in water. In embodiments,

the aprotic solvent may have sparing miscibility in water. In embodiments, the aprotic solvent may be immiscible in water and may have a boiling point of from about 30° C to about 80° C.

Neutralizing agent

5 [0047] In embodiments, the neutralizing agent is selected from the group consisting of ammonium hydroxide, sodium carbonate, potassium hydroxide, sodium hydroxide, sodium bicarbonate, lithium hydroxide, potassium carbonate, triethyl amine, triethanolamine, pyridine, pyridine derivatives, diphenylamine, diphenylamine derivatives, poly(ethylene amine), poly(ethylene amine) derivatives, amine bases, and 10 pieprazine, and combinations thereof. In some embodiments, processes disclosed herein may employ a first portion of neutralizing agent and a second portion of neutralizing agent independently selected from the group consisting of ammonium hydroxide, potassium hydroxide, sodium hydroxide, sodium carbonate, sodium bicarbonate, lithium hydroxide, potassium carbonate, organoamines, and combinations 15 thereof.

[0048] In embodiments, the resin may be mixed with a weak base or neutralizing agent. In embodiments, the neutralizing agent may be used to neutralize acid groups in the resins, so a neutralizing agent herein may also be referred to as a “basic neutralization agent.” Any suitable basic neutralization reagent may be used in accordance with the 20 present disclosure. In embodiments, suitable basic neutralization agents may include both inorganic basic agents and organic basic agents. Suitable basic agents may include ammonium hydroxide, potassium hydroxide, sodium hydroxide, sodium carbonate, sodium bicarbonate, lithium hydroxide, potassium carbonate, combinations

thereof, and the like. Suitable basic neutralizing agents may also include monocyclic compounds and polycyclic compounds having at least one nitrogen atom, such as, for example, secondary amines, which include aziridines, azetidines, piperazines, piperidines, pyridines, bipyridines, terpyridines, dihydropyridines, morpholines, N-alkylmorpholines, 1,4-diazabicyclo[2.2.2]octanes, 1,8-diazabicycloundecanes, 1,8-diazabicycloundecenes, dimethylated pentylamines, trimethylated pentylamines, pyrimidines, pyrroles, pyrrolidines, pyrrolidinones, indoles, indolines, indanones, benzindazones, imidazoles, benzimidazoles, imidazolones, imidazolines, oxazoles, isoxazoles, oxazolines, oxadiazoles, thiadiazoles, carbazoles, quinolines, isoquinolines, naphthyridines, triazines, triazoles, tetrazoles, pyrazoles, pyrazolines, and combinations thereof. In embodiments, the monocyclic and polycyclic compounds may be unsubstituted or substituted at any carbon position on the ring.

[0049] The basic neutralizing agent may be utilized in an amount of from about 0.001 % by weight to 50% by weight of the resin, in embodiments from about 0.01% by weight to about 25 % by weight of the resin, in embodiments from about 0.1% by weight to 5 % by weight of the resin. In embodiments, the neutralizing agent may be added in the form of an aqueous solution. In other embodiments, the neutralizing agent may be added in the form of a solid.

[0050] Utilizing the above basic neutralizing agent in combination with a resin possessing acid groups, a neutralization ratio of from about 25% to about 500% may be achieved, in embodiments from about 50% to about 300%. In embodiments, the neutralization ratio may be calculated as the molar ratio of basic groups provided with the basic neutralizing agent to the acid groups present in the resin multiplied by 100%.

[0051] As noted above, the basic neutralization agent may be added to a resin possessing acid groups. The addition of the basic neutralization agent may thus raise the pH of an emulsion including a resin possessing acid groups from about 5 to about 12, in embodiments, from about 6 to about 11. The neutralization of the acid groups 5 may, in embodiments, enhance formation of the emulsion.

Surfactants

[0052] In embodiments, the process of the present disclosure may optionally include adding a surfactant, before or during the dissolution, to the polyester resin. In embodiments, the surfactant may be added prior to dissolution of the polyester resin at 10 an elevated temperature. Where utilized, a resin emulsion may include one, two, or more surfactants. The surfactants may be selected from ionic surfactants and nonionic surfactants. Anionic surfactants and cationic surfactants are encompassed by the term "ionic surfactants." In embodiments, the surfactant may be added as a solid or as a solution with a concentration of from about 5% to about 100% (pure surfactant) by 15 weight, in embodiments, from about 10% to about 95% by weight. In embodiments, the surfactant may be utilized so that it is present in an amount of from about 0.01% to about 20% by weight of the resin, in embodiments, from about 0.1% to about 16% by weight of the resin, in other embodiments, from about 1% to about 14% by weight of the resin.

20 [0053] Anionic surfactants which may be utilized include sulfates and sulfonates, sodium dodecylsulfate (SDS), sodium dodecylbenzene sulfonate, sodium dodecylnaphthalene sulfate, dialkyl benzenealkyl sulfates and sulfonates, acids such as abitic acid available from Aldrich, NEOGEN R™, NEOGEN SC™ obtained from Daiichi Kogyo Seiyaku,

combinations thereof, and the like. Other suitable anionic surfactants include, in embodiments, DOWFAX™™ 2A1, an alkyldiphenyloxide disulfonate from The Dow Chemical Company, and/or TAYCA POWER BN2060 from Tayca Corporation (Japan), which are branched sodium dodecylbenzene sulfonates. Combinations of these 5 surfactants and any of the foregoing anionic surfactants may be utilized in embodiments.

[0054] Examples of the cationic surfactants, which are usually positively charged, include, for example, alkylbenzyl dimethyl ammonium chloride, dialkyl benzenealkyl ammonium chloride, lauryl trimethyl ammonium chloride, alkylbenzyl methyl ammonium 10 chloride, alkyl benzyl dimethyl ammonium bromide, benzalkonium chloride, cetyl pyridinium bromide, C12, C15, C17 trimethyl ammonium bromides, halide salts of quaternized polyoxyethylalkylamines, dodecylbenzyl triethyl ammonium chloride, MIRAPOL™ and ALKAQUAT™, available from Alkaril Chemical Company, SANIZOL™ (benzalkonium chloride), available from Kao Chemicals, and the like, and mixtures 15 thereof.

[0055] Examples of nonionic surfactants that may be utilized for the processes illustrated herein include, for example, polyacrylic acid, methalose, methyl cellulose, ethyl cellulose, propyl cellulose, hydroxy ethyl cellulose, carboxy methyl cellulose, polyoxyethylene cetyl ether, polyoxyethylene lauryl ether, polyoxyethylene octyl ether, 20 polyoxyethylene octylphenyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitan monolaurate, polyoxyethylene stearyl ether, polyoxyethylene nonylphenyl ether, dialkylphenoxy poly(ethyleneoxy) ethanol, available from Rhone-Poulenc as IGEPAL CA-210™, IGEPAL CA-520™, IGEPAL CA-720™, IGEPAL CO-890™,

IGEPAL CO-720™, IGEPAL CO-290™, IGEPAL CA-210™, ANTAROX 890™ and ANTAROX 897™. Other examples of suitable nonionic surfactants may include a block copolymer of polyethylene oxide and polypropylene oxide, including those commercially available as SYNPERONIC PE/F, in embodiments SYNPERONIC PE/F 108.

5 Combinations of these surfactants and any of the foregoing surfactants may be utilized in embodiments.

Processing

[0056] In embodiments, there are provided processes comprising homogenizing a mixture to form a plurality of core particles, the mixture comprising a first polyester latex, 10 a styrene/acrylate latex, and a compatibilizing agent latex comprising a graft polyester-styrene/acrylate copolymer, the process further comprising adding a shell polyester latex to the plurality of core particles to form a plurality of core-shell structures.

[0057] In embodiments, the mixture further comprises a wax, a crystalline polyester, a colorant and an aggregating agent.

15 [0058] In embodiments, the processes may further comprise adjusting the pH.

[0059] In embodiments, processes may further comprise, before adding the shell polyester, heating the homogenized mixture to temperature from about 40 °C to about 60 °C.

[0060] In embodiments, after the homogenizing step, the plurality of core particles have 20 an effective diameter in a range from about 3 microns to about 7 microns. The resulting toner aggregates may also have a particle size of from about 3 microns to about 15 microns in volume average diameter, or from about 5 microns to about 9 microns in volume average diameter. Those skilled in the art will recognize that selections outside

this range may be achieved for alternate applications, including aggregates smaller than 3 microns, such as 2 microns, 1 micron, or 0.5 microns. Similarly, aggregates greater than about 15 microns may be accessed depending on the intended downstream application.

5 [0061] As noted above, the processes herein may employ more than one polyester latex. In some such embodiments, the polyester latexes may be all pre-blended together prior to processing. In some embodiments, one of a mixture resins may be a crystalline polyester latex and elevated temperatures may be employed in the process which may be a temperature above the crystallization temperature of the crystalline resin. In further embodiments, the resin may be a mixture of amorphous and crystalline resins and the temperature employed for dissolution may be above the Tg of the mixture.

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[0062] In some embodiments, emulsifying neutralized polyester resins may comprise adding water into the solution of neutralized resin until phase inversion occurs to form a 15 phase inverted latex emulsion. Emulsification may be followed by distilling the latex to remove organic solvent, water or a mixture of the two.

[0063] In embodiments, the neutralizing agent which may be utilized in the process of the present disclosure includes the agents mentioned hereinabove. In embodiments, an optional surfactant employed in the process may be any of the surfactants to ensure 20 that proper resin neutralization occurs and leads to a high quality latex with low coarse content.

[0064] In embodiments, the surfactant may be added to the one or more ingredients of the resin composition before, during, or after any mixing. In embodiments, the

surfactant may be added before, during, or after the addition of the neutralizing agent.

In embodiments, the surfactant may be added prior to the addition of the neutralizing agent. In embodiments, a surfactant may be added to a pre-blend mixture prior to dissolution.

5 [0065] In embodiments, a continuous phase inverted emulsion may be formed. Phase inversion can be accomplished by continuing to add an aqueous alkaline solution or basic agent, optional surfactant and/or water compositions to create a phase inverted emulsion which includes a disperse phase including droplets possessing the molten ingredients of the resin composition, and a continuous phase including a surfactant
10 and/or water composition.

[0066] Stirring, although not necessary, may be utilized to enhance formation of the latex. Any suitable stirring device may be utilized. In embodiments, the stirring may be at a speed of from about 10 revolutions per minute (rpm) to about 5,000 rpm, in embodiments from about 20 rpm to about 2,000 rpm, in other embodiments from about
15 50 rpm to about 1,000 rpm. The stirring need not be at a constant speed, but may be varied. For example, as the mixture becomes more uniform, the stirring rate may be increased. In embodiments, a homogenizer (that is, a high shear device), may be utilized to form the phase inverted emulsion, but in other embodiments, the process of the present disclosure may take place without the use of a homogenizer. Where
20 utilized, a homogenizer may operate at a rate of from about 3,000 rpm to about 10,000 rpm.

[0067] Although the point of phase inversion may vary depending on the components of the emulsion, any temperature of heating, the stirring speed, and the like, phase

inversion may occur when the basic neutralization agent, optional surfactant, and/or water has been added so that the resulting resin is present in an amount from about 5 % by weight to about 70 % by weight of the emulsion, in embodiments from about 20 % by weight to about 65 % by weight of the emulsion, in other embodiments from about 30 % by weight to about 60 % by weight of the emulsion.

[0068] Following phase inversion, additional surfactant, water, and/or aqueous alkaline solution may optionally be added to dilute the phase inverted emulsion, although this is not required. Following phase inversion, the phase inverted emulsion may be cooled to room temperature if heat was employed, for example from about 20°C to about 25°C.

[0069] In embodiments, distillation may be performed to provide resin emulsion particles as a latex with an average diameter size of, for example, from about 50 nm to about 500 nm, in embodiments from about 120 nm to about 250 nm. In some embodiments, the distillate may be optionally recycled for use in a subsequent PIE process.

[0070] In embodiments, for example, the distillate from the process of the present disclosure may contain predominantly MEK, and optionally some isopropyl alcohol (IPA), with only small amounts of water, such as about less than about 10%, or less than about 25%, or less than about 35%. In alternate embodiments, the amount of water may be higher than about 35%, such as about 50 to about 60%. In embodiments, the MEK-water mixture may be re-used for the next phase inversion batch. In some embodiments, aprotic solvent may be removed by a vacuum distillation.

[0071] The emulsified polyester resin particles in the aqueous medium may have a submicron size, for example of about 1 μ m or less, in embodiments about 500 nm or less, such as from about 10 nm to about 500 nm, in embodiments from about 50 nm to

about 400 nm, in other embodiments from about 100 nm to about 300 nm, in some embodiments about 200 nm. Adjustments in particle size can be made by modifying the ratio of solvent to resin, the neutralization ratio, solvent concentration, and solvent composition.

5 [0072] Particle size distribution of any of the latexes disclosed herein may be from about 30 nm to about 500 nm, in embodiments, from about 125 nm to about 400 nm.

[0073] The coarse content of the latex of the present disclosure may be from about 0.01% by weight to about 5% by weight, in embodiments, from about 0.1% by weight to about 3% by weight. The solids content of the latex of the present disclosure may be 10 from about 10% by weight to about 50% by weight, in embodiments, from about 20% by weight to about 45% by weight.

[0074] The process of the present disclosure for the production of polyester emulsions using PIE may eliminate or minimize wasted product and produces particles with more efficient solvent stripping, solvent recovery, and permits recycling of the solvent.

15 [0075] The emulsions of the present disclosure may then be utilized to produce particles that are suitable for formation of toner particles.

Toner

[0076] In embodiments, processes disclosed herein further comprise forming toner particles from the latexes formed by PIE process. For example, once a polyester resin 20 has been converted into a latex, it may be utilized to form a toner by any process within the purview of those skilled in the art. The latex may be contacted with a colorant, optionally in a dispersion, and other additives to form an ultra low melt toner by a suitable process, in embodiments, an emulsion aggregation and coalescence process.

[0077] In embodiments, the optional additional ingredients of a toner composition including colorant, wax, and other additives, may be added before, during or after mixing the resin to form the emulsion. The additional ingredients may be added before, during or after formation of the latex emulsion. In further embodiments, the colorant 5 may be added before the addition of the surfactant.

Colorants

[0078] As the colorant to be added, various known suitable colorants, such as dyes, pigments, mixtures of dyes, mixtures of pigments, mixtures of dyes and pigments, and the like, may be included in the toner. In embodiments, the colorant may be included in 10 the toner in an amount of, for example, about 0.1 to about 35% by weight of the toner, or from about 1 to about 15% by weight of the toner, or from about 3 to about 10% by weight of the toner, although the amount of colorant can be outside of these ranges.

[0079] As examples of suitable colorants, mention may be made of carbon black like REGAL 330® (Cabot), Carbon Black 5250 and 5750 (Columbian Chemicals), 15 Sunperse Carbon Black LHD 9303 (Sun Chemicals); magnetites, such as Mobay magnetites MO8029™, MO8060™; Columbian magnetites; MAPICO BLACKS™ and surface treated magnetites; Pfizer magnetites CB4799™, CB5300™, CB5600™, MCX6369™; Bayer magnetites, BAYFERROX 8600™, 8610™; Northern Pigments magnetites, NP-604™, NP-608™; Magnox magnetites TMB-100™, or TMB-104™; and 20 the like. As colored pigments, there can be selected cyan, magenta, yellow, red, green, brown, blue or mixtures thereof. Generally, cyan, magenta, or yellow pigments or dyes, or mixtures thereof, are used. The pigment or pigments are generally used as water based pigment dispersions.

[0080] In general, suitable colorants may include Paliogen Violet 5100 and 5890 (BASF), Normandy Magenta RD-2400 (Paul Uhlrich), Permanent Violet VT2645 (Paul Uhlrich), Heliogen Green L8730 (BASF), Argyle Green XP-111-S (Paul Uhlrich), Brilliant Green Toner GR 0991 (Paul Uhlrich), Lithol Scarlet D3700 (BASF), Toluidine Red (Aldrich), Scarlet for Thermoplast NSD PS PA (Ugine Kuhlmann of Canada), Lithol Rubine Toner (Paul Uhlrich), Lithol Scarlet 4440 (BASF), NBD 3700 (BASF), Bon Red C (Dominion Color), Royal Brilliant Red RD-8192 (Paul Uhlrich), Oracet Pink RF (Ciba Geigy), Paliogen Red 3340 and 3871K (BASF), Lithol Fast Scarlet L4300 (BASF), Heliogen Blue D6840, D7080, K7090, K6910 and L7020 (BASF), Sudan Blue OS (BASF), Neopen Blue FF4012 (BASF), PV Fast Blue B2G01 (American Hoechst), Irgalite Blue BCA (Ciba Geigy), Paliogen Blue 6470 (BASF), Sudan II, III and IV (Matheson, Coleman, Bell), Sudan Orange (Aldrich), Sudan Orange 220 (BASF), Paliogen Orange 3040 (BASF), Ortho Orange OR 2673 (Paul Uhlrich), Paliogen Yellow 152 and 1560 (BASF), Lithol Fast Yellow 0991K (BASF), Paliotol Yellow 1840 (BASF), Novaperm Yellow FGL (Hoechst), Permanerit Yellow YE 0305 (Paul Uhlrich), Lumogen Yellow D0790 (BASF), Sunperse Yellow YHD 6001 (Sun Chemicals), Suco-Gelb 1250 (BASF), Suco-Yellow D1355 (BASF), Suco Fast Yellow D1165, D1355 and D1351 (BASF), Hostaperm Pink E™ (Hoechst), Fanal Pink D4830 (BASF), Cinquasia Magenta™ (DuPont), Paliogen Black L9984 (BASF), Pigment Black K801 (BASF), Levanyl Black A-SF (Miles, Bayer), combinations of the foregoing, and the like.

[0081] Other suitable water based colorant dispersions include those commercially available from Clariant, for example, Hostafine Yellow GR, Hostafine Black T and Black TS, Hostafine Blue B2G, Hostafine Rubine F6B and magenta dry pigment such as

Toner Magenta 6BVP2213 and Toner Magenta EO2 which may be dispersed in water and/or surfactant prior to use.

[0082] Specific examples of pigments include Sunperse BHD 6011X (Blue 15 Type), Sunperse BHD 9312X (Pigment Blue 15 74160), Sunperse BHD 6000X (Pigment 5 Blue 15:3 74160), Sunperse GHD 9600X and GHD 6004X (Pigment Green 7 74260), Sunperse QHD 6040X (Pigment Red 122 73915), Sunperse RHD 9668X (Pigment Red 185 12516), Sunperse RHD 9365X and 9504X (Pigment Red 57 15850:1, Sunperse YHD 6005X (Pigment Yellow 83 21108), Flexiverse YFD 4249 (Pigment Yellow 17 21105), Sunperse YHD 6020X and 6045X (Pigment Yellow 74 11741), 10 Sunperse YHD 600X and 9604X (Pigment Yellow 14 21095), Flexiverse LFD 4343 and LFD 9736 (Pigment Black 7 77226), Aquatone, combinations thereof, and the like, as water based pigment dispersions from Sun Chemicals, Heliogen Blue L6900™, D6840™, D7080™, D7020™, Pylam Oil Blue™, Pylam Oil Yellow™, Pigment Blue 1™ available from Paul Uhlich & Company, Inc., Pigment Violet 1™, Pigment Red 48™, 15 Lemon Chrome Yellow DCC 1026™, E.D. Toluidine Red™ and Bon Red C™ available from Dominion Color Corporation, Ltd., Toronto, Ontario, Novaperm Yellow FGL™, and the like. Generally, colorants that can be selected are black, cyan, magenta, or yellow, and mixtures thereof. Examples of magentas are 2,9-dimethyl-substituted quinacridone and anthraquinone dye identified in the Color Index as CI 60710, CI Dispersed Red 15, 20 diazo dye identified in the Color Index as CI 26050, CI Solvent Red 19, and the like. Illustrative examples of cyans include copper tetra(octadecyl sulfonamido) phthalocyanine, x-copper phthalocyanine pigment listed in the Color Index as CI 74160, CI Pigment Blue, Pigment Blue 15:3, and Anthrathrene Blue, identified in the Color

Index as CI 69810, Special Blue X-2137, and the like. Illustrative examples of yellows are diarylide yellow 3,3-dichlorobenzidine acetoacetanilides, a monoazo pigment identified in the Color Index as CI 12700, CI Solvent Yellow 16, a nitrophenyl amine sulfonamide identified in the Color Index as Foron Yellow SE/GLN, CI Dispersed Yellow 5 33 2,5-dimethoxy-4-sulfonanilide phenylazo-4'-chloro-2,5-dimethoxy acetoacetanilide, and Permanent Yellow FGL.

[0083] In embodiments, the colorant may include a pigment, a dye, combinations thereof, carbon black, magnetite, black, cyan, magenta, yellow, red, green, blue, brown, combinations thereof, in an amount sufficient to impart the desired color to the toner. It 10 is to be understood that other useful colorants will become readily apparent based on the present disclosures.

[0084] In embodiments, a pigment or colorant may be employed in an amount of from about 1% by weight to about 35% by weight of the toner particles on a solids basis, in other embodiments, from about 5% by weight to about 25% by weight. However, 15 amounts outside these ranges can also be used, in embodiments.

Wax

[0085] Optionally, a wax may also be combined with the resin and a colorant in forming toner particles. The wax may be provided in a wax dispersion, which may include a single type of wax or a mixture of two or more different waxes. A single wax may be 20 added to toner formulations, for example, to improve particular toner properties, such as toner particle shape, presence and amount of wax on the toner particle surface, charging and/or fusing characteristics, gloss, stripping, offset properties, and the like.

Alternatively, a combination of waxes can be added to provide multiple properties to the toner composition.

[0086] When included, the wax may be present in an amount of, for example, from about 1% by weight to about 25% by weight of the toner particles, in embodiments from 5 about 5% by weight to about 20% by weight of the toner particles, although the amount of wax can be outside of these ranges.

[0087] When a wax dispersion is used, the wax dispersion may include any of the various waxes conventionally used in emulsion aggregation toner compositions. Waxes that may be selected include waxes having, for example, an average molecular weight 10 of from about 500 to about 20,000, in embodiments from about 1,000 to about 10,000. Waxes that may be used include, for example, polyolefins such as polyethylene including linear polyethylene waxes and branched polyethylene waxes, polypropylene including linear polypropylene waxes and branched polypropylene waxes, polyethylene/amide, polyethylenetetrafluoroethylene, 15 polyethylenetetrafluoroethylene/amide, and polybutene waxes such as commercially available from Allied Chemical and Petrolite Corporation, for example POLYWAX™ polyethylene waxes such as commercially available from Baker Petrolite, wax emulsions available from Michaelman, Inc. and the Daniels Products Company, EPOLENE N-15™ commercially available from Eastman Chemical Products, Inc., and 20 VISCOL 550-P™, a low weight average molecular weight polypropylene available from Sanyo Kasei K. K.; plant-based waxes, such as carnauba wax, rice wax, candelilla wax, sumacs wax, and jojoba oil; animal-based waxes, such as beeswax; mineral-based waxes and petroleum-based waxes, such as montan wax, ozokerite, ceresin, paraffin

wax, microcrystalline wax such as waxes derived from distillation of crude oil, silicone waxes, mercapto waxes, polyester waxes, urethane waxes; modified polyolefin waxes (such as a carboxylic acid-terminated polyethylene wax or a carboxylic acid-terminated polypropylene wax); Fischer-Tropsch wax; ester waxes obtained from higher fatty acid and higher alcohol, such as stearyl stearate and behenyl behenate; ester waxes obtained from higher fatty acid and monovalent or multivalent lower alcohol, such as butyl stearate, propyl oleate, glyceride monostearate, glyceride distearate, and pentaerythritol tetra behenate; ester waxes obtained from higher fatty acid and multivalent alcohol multimers, such as diethylene glycol monostearate, dipropylene glycol distearate, diglyceryl distearate, and triglyceryl tetra stearate; sorbitan higher fatty acid ester waxes, such as sorbitan monostearate, and cholesterol higher fatty acid ester waxes, such as cholesteryl stearate. Examples of functionalized waxes that may be used include, for example, amines, amides, for example AQUA SUPERSLIP 6550TM, SUPERSLIP 6530TM available from Micro Powder Inc., fluorinated waxes, for example 10 POLYFLUO 190TM, POLYFLUO 200TM, POLYSILK 19TM, POLYSILK 14TM available from Micro Powder Inc., mixed fluorinated, amide waxes, such as aliphatic polar amide functionalized waxes; aliphatic waxes consisting of esters of hydroxylated unsaturated fatty acids, for example MICROSPERSION 19TM also available from Micro Powder Inc., imides, esters, quaternary amines, carboxylic acids or acrylic polymer emulsion, for 15 example JONCRYL 74TM, 89TM, 130TM, 537TM, and 538TM, all available from SC Johnson Wax, and chlorinated polypropylenes and polyethylenes available from Allied Chemical and Petrolite Corporation and SC Johnson wax. Mixtures and combinations of the foregoing waxes may also be used in embodiments. Waxes may be included as, 20

for example, fuser roll release agents. In embodiments, the waxes may be crystalline or non-crystalline.

[0088] In embodiments, the wax may be incorporated into the toner in the form of one or

more aqueous emulsions or dispersions of solid wax in water, where the

5 [0089] solid wax particle size may be in the range of from about 100 to about 300 nm.

Toner Preparation

[0090] The toner particles may be prepared by any process within the purview of one

skilled in the art. Although embodiments relating to toner particle production are

described below with respect to emulsion aggregation processes, any suitable process

10 of preparing toner particles may be used, including chemical processes, such as

suspension and encapsulation processes disclosed in U.S. Patent Nos. 5,290,654 and

5,302,486. In embodiments, toner compositions and toner particles may be prepared

by aggregation and coalescence processes in which small-size resin particles are

aggregated to the appropriate toner particle size and then coalesced to achieve the final

15 toner particle shape and morphology.

[0091] In embodiments, toner compositions may be prepared by emulsion aggregation

processes, such as a process that includes aggregating a mixture of an optional

colorant, an optional wax and any other desired or required additives, and emulsions

including the polyester resins described above, optionally in surfactants, and then

20 coalescing the aggregate mixture. A mixture may be prepared by adding a colorant and

optionally a wax or other materials, which may also be optionally in a dispersion(s)

including a surfactant, to the emulsion, which may be a mixture of two or more

emulsions containing the resin. The pH of the resulting mixture may be adjusted by an acid such as, for example, acetic acid, nitric acid or the like. In embodiments, the pH of the mixture may be adjusted to from about 2 to about 5. Additionally, in embodiments, the mixture may be homogenized. If the mixture is homogenized, homogenization may

5 be accomplished by mixing at about 600 to about 6,000 revolutions per minute.

Homogenization may be accomplished by any suitable means, including, for example, an IKA ULTRA TURRAX T50 probe homogenizer.

[0092] Following the preparation of the above mixture, an aggregating agent may be added to the mixture. Any suitable aggregating agent may be utilized to form a toner.

10 Suitable aggregating agents include, for example, aqueous solutions of a divalent cation or a multivalent cation material. The aggregating agent may be, for example, an inorganic cationic aggregating agent such as polyaluminum halides such as polyaluminum chloride (PAC), or the corresponding bromide, fluoride, or iodide, polyaluminum silicates such as polyaluminum sulfosilicate (PASS), and water soluble

15 metal salts including aluminum chloride, aluminum nitrite, aluminum sulfate, potassium aluminum sulfate, calcium acetate, calcium chloride, calcium nitrite, calcium oxylate, calcium sulfate, magnesium acetate, magnesium nitrate, magnesium sulfate, zinc acetate, zinc nitrate, zinc sulfate, zinc chloride, zinc bromide, magnesium bromide, copper chloride, copper sulfate, and combinations thereof. In embodiments, the

20 aggregating agent may be added to the mixture at a temperature that is below the Tg of the resin.

[0093] Suitable examples of organic cationic aggregating agents include, for example, dialkyl benzenealkyl ammonium chloride, lauryl trimethyl ammonium chloride,

alkylbenzyl methyl ammonium chloride, alkyl benzyl dimethyl ammonium bromide, benzalkonium chloride, cetyl pyridinium bromide, C12, C15, C17 trimethyl ammonium bromides, halide salts of quaternized polyoxyethylalkylamines, dodecylbenzyl triethyl ammonium chloride, combinations thereof, and the like.

5 [0094] Other suitable aggregating agents also include, but are not limited to, tetraalkyl titinates, dialkyltin oxide, tetraalkyltin oxide hydroxide, dialkyltin oxide hydroxide, aluminum alkoxides, alkyl zinc, dialkyl zinc, zinc oxides, stannous oxide, dibutyltin oxide, dibutyltin oxide hydroxide, tetraalkyl tin, combinations thereof, and the like.

10 Where the aggregating agent is a polyion aggregating agent, the agent may have any desired number of polyion atoms present. For example, in embodiments, suitable polyaluminum compounds have from about 2 to about 13, in other embodiments, from about 3 to about 8, aluminum ions present in the compound.

15 [0095] The aggregating agent may be added to the mixture utilized to form a toner in an amount of, for example, from about 0% to about 10% by weight, in embodiments from about 0.2% to about 8% by weight, in other embodiments from about 0.5% to about 5% by weight, of the resin in the mixture. This should provide a sufficient amount of agent for aggregation.

20 [0096] The particles may be permitted to aggregate until a predetermined desired particle size is obtained. A predetermined desired size refers to the desired particle size to be obtained as determined prior to formation, and the particle size being monitored during the growth process until such particle size is reached. Samples may be taken during the growth process and analyzed, for example with a Coulter Counter, for average particle size. The aggregation thus may proceed by maintaining the elevated

temperature, or slowly raising the temperature to, for example, from about 40 °C to about 100 °C, and holding the mixture at this temperature for a time of from about 0.5 hours to about 6 hours, in embodiments from about 1 hour to about 5 hours, while maintaining stirring, to provide the aggregated particles. Once the predetermined 5 desired particle size is reached, then the shell resin latex is added.

[0097] Shell Resin

[0098] In embodiments, after aggregation, but prior to coalescence, a resin coating may be applied to the aggregated particles to form a shell thereover. In embodiments, the core may thus include a crystalline resin, as described above. Any resin described 10 above may be utilized as the shell. In embodiments, a polyester amorphous resin latex as described above may be included in the shell. In embodiments, the polyester amorphous resin latex described above may be combined with a different resin, and then added to the particles as a resin coating to form a shell.

[0099] In embodiments, resins which may be utilized to form a shell include, but are not 15 limited to, a crystalline resin latex described above, and/or the amorphous resins described above. In embodiments, an amorphous resin which may be utilized to form a shell in accordance with the present disclosure includes an amorphous polyester, optionally in combination with a crystalline polyester resin latex described above. Multiple resins may be utilized in any suitable amounts. In embodiments, a first 20 amorphous polyester resin, for example an amorphous resin of formula I above, may be present in an amount of from about 20 percent by weight to about 100 percent by weight of the total shell resin, in embodiments from about 30 percent by weight to about 90 percent by weight of the total shell resin. Thus, in embodiments, a second resin may

be present in the shell resin in an amount of from about 0 percent by weight to about 80 percent by weight of the total shell resin, in embodiments from about 10 percent by weight to about 70 percent by weight of the shell resin.

[00100] The shell resin may be applied to the aggregated particles by any process 5 within the purview of those skilled in the art. In embodiments, the resins utilized to form the shell may be in an emulsion including any surfactant described above. The emulsion possessing the resins, optionally the crystalline polyester resin latex described above, may be combined with the aggregated particles described above so that the shell forms over the aggregated particles.

10 [00101] The formation of the shell over the aggregated particles may occur while heating to a temperature of from about 30°C to about 80°C, in embodiments from about 35°C to about 70°C. The formation of the shell may take place for a period of time of from about 5 minutes to about 10 hours, in embodiments from about 10 minutes to about 5 hours.

15 [00102] The shell may be present in an amount of from about 1 percent by weight to about 80 percent by weight of the latex particles, in embodiments of from about 10 percent by weight to about 40 percent by weight of the latex particles, in still further embodiments from about 20 percent by weight to about 35 percent by weight of the latex particles.

20 [00103] Once the desired final size of the toner particles is achieved, the pH of the mixture may be adjusted with a base to a value of from about 3 to about 10, and in embodiments from about 5 to about 9. The adjustment of the pH may be utilized to freeze, that is to stop, toner growth. The base utilized to stop toner growth may include

any suitable base such as, for example, alkali metal hydroxides such as, for example, sodium hydroxide, potassium hydroxide, ammonium hydroxide, combinations thereof, and the like. In embodiments, ethylene diamine tetraacetic acid (EDTA) may be added to help adjust the pH to the desired values noted above.

5 [00104] In embodiments, the final size of the toner particles may be of from about 2 μm to about 12 μm , in embodiments of from about 3 μm to about 10 μm .

[00105] Coalescence

[00106] Following aggregation to the desired particle size and application of any optional shell, the particles may then be coalesced to the desired final shape, the 10 coalescence being achieved by, for example, heating the mixture to a temperature of from about 45 °C to about 150 °C, in embodiments from about 55 °C to about 99 °C, which may be at or above the T_g temperature of the resins utilized to form the toner particles, and/or reducing the stirring, for example to from about 20 rpm to about 1000 rpm, in embodiments from about 30 rpm to about 800 rpm. Coalescence may be 15 accomplished over a period of from about 0.01 to about 9 hours, in embodiments from about 0.1 to about 4 hours.

[00107] After aggregation and/or coalescence, the mixture may be cooled to room 20 temperature, such as from about 20 °C to about 25 °C. The cooling may be rapid or slow, as desired. A suitable cooling process may include introducing cold water to a jacket around the reactor. After cooling, the toner particles may be optionally washed with water, and then dried. Drying may be accomplished by any suitable process for drying including, for example, freeze-drying.

[00108] Additives

[00109] In embodiments, the toner particles may also contain other optional additives, as desired or required. For example, the toner may include positive or negative charge control agents, for example in an amount of from about 0.1 to about 10% by weight of the toner, in embodiments from about 1 to about 3% by weight of the toner. Examples 5 of suitable charge control agents include quaternary ammonium compounds inclusive of alkyl pyridinium halides; bisulfates; alkyl pyridinium compounds, including those disclosed in U.S. Patent No. 4,298,672; organic sulfate and sulfonate compositions, including those disclosed in U.S. Patent No. 4,338,390; cetyl pyridinium tetrafluoroborates; distearyl dimethyl ammonium methyl sulfate; aluminum salts such as 10 BONTRON E84™ or E88™ (Orient Chemical Industries, Ltd.); combinations thereof, and the like.

[00110] There can also be blended with the toner particles external additive particles after formation including flow aid additives, which additives may be present on the surface of the toner particles. Examples of these additives include metal oxides such as 15 titanium oxide, silicon oxide, aluminum oxides, cerium oxides, tin oxide, mixtures thereof, and the like; colloidal and amorphous silicas, such as AEROSIL®, metal salts and metal salts of fatty acids inclusive of zinc stearate, calcium stearate, or long chain alcohols such as UNILIN 700, and mixtures thereof.

[00111] In general, silica may be applied to the toner surface for toner flow, tribo 20 enhancement, admix control, improved development and transfer stability, and higher toner blocking temperature. TiO₂ may be applied for improved relative humidity (RH) stability, tribo control and improved development and transfer stability. Zinc stearate, calcium stearate and/or magnesium stearate may optionally also be used as an external

additive for providing lubricating properties, developer conductivity, tribo enhancement, enabling higher toner charge and charge stability by increasing the number of contacts between toner and carrier particles. In embodiments, a commercially available zinc stearate known as Zinc Stearate L, obtained from Ferro Corporation, may be used. The 5 external surface additives may be used with or without a coating.

[00112] Each of these external additives may be present in an amount of from about 0.1% by weight to about 5% by weight of the toner, in embodiments of from about 0.25% by weight to about 3% by weight of the toner, although the amount of additives can be outside of these ranges. In embodiments, the toners may include, for example, 10 from about 0.1% by weight to about 5% by weight titania, from about 0.1% by weight to about 8% by weight silica, and from about 0.1% by weight to about 4% by weight zinc stearate.

[00113] Suitable additives include those disclosed in U.S. Patent Nos. 3,590,000, 3,800,588, and 6,214,507.

15 [00114] The following Examples are being submitted to illustrate embodiments of the present disclosure. These Examples are intended to be illustrative only and are not intended to limit the scope of the present disclosure. Also, parts and percentages are by weight unless otherwise indicated. As used herein, "room temperature" refers to a temperature of from about 20 ° C to about 25° C.

20

EXAMPLES

Example 1

[00115] This example describes the formation of a latex using a hybrid resin.

[00116] 6.0 parts of methyl ethyl ketone (MEK) and 1.8 parts of isopropyl alcohol (IPA) 5 were used to dissolve 10 parts hybrid resin HBA-1 (polyester with styrene-acrylate graft) shown in Figure 1 (KAO Specialties Americas LLC). A small portion (6.25 parts) water with 0.208 parts ammonia were added to promote the polyester dissolution. After the neutralization with 0.418 parts ammonia, 13.74 parts of water was slowly added to form the latex at 40°C. Table 1 lists the components of the HBA-1 latex.

10

Table 1

Chemicals	Parts	Percentage (%)
HBA-1 Resin (Figure 1)	10	26.0
MEK	6	15.6
IPA	1.8	4.7
aqueous ammonia (I)	0.208	0.5
deionized water (I)	6.25	16.3
aqueous ammonia (II)	0.418	1.1
D I water (II)	13.74	35.8
Total	38.42	100

The acid value of HBA-1 was 24.3 mg KOH/g. The neutralization ratio in this PIE was 85%.

[00117] This HBA-1 latex was distilled to reduce volatile organic compounds (VOCs) 15 below 300 ppm to meet specification. The final latex D_{50} , (which represents diameter of 50% of the particle distribution) particle size was 146.9 nm with 130 nm width measured by Nanotrac. This latex represents a reduced particle size (latex for typical toner applications is often about 200 ± 25 nm, 146.9 nm is smaller than the typical particle) in order to enlarge the contacting surface area with polyester and poly(styrene/acrylate)

5 latexes particles in downstream toner preparation. Note, with both polyester and poly(styrene/acrylate) on particle surface, this HBA-1 latex was expected to behave as a compatibilizing agent to improve the compatibility between polyester (EP33&34) and poly(styrene/acrylate) (EP7) latexes, in forming mixed resin latex particles. 2.5 parts per hundred (pph) surfactant (Dowfax 2A1, The Dow Chemical Company) was added into distilled HBA-1 latex to stabilize the particles after distillation.

Example 2

[00118] This Example shows the preparation of a laboratory scale control toner batch lacking the HBA-1 latex of Example 1 as a compatibilizing agent.

10 [00119] Core particles were formed from the materials indicated in Table 2 below by homogenizing for a total of 30 minutes and adjusting the slurry to pH 4.2. After homogenization the slurry was transferred into a 2L baffle-less reactor at 49°C for 70 min. After the target particle size was reached the shell materials in Table 3 were added to the core to form the shell. The shell latex may be applied until the desired final size of the toner particles is achieved, in embodiments from about 3 microns to about 15 microns, in other embodiments from about 4 microns to about 9 microns. In other 15 embodiments, the toner particles may be prepared by in-situ seeded semi-continuous emulsion copolymerization of the latex with the addition of the shell latex once aggregated particles have formed. The shell materials were added over 10 minutes at pH of approximately 3.3. After 40 minutes the pH was increased to 7.8 and the 20 temperature raised to 85°C until the target size was obtained.

Table 2

Raw Material	Supplier	Reagent	Weight	Percentage
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			type	(g)	(%)
Water			deionized (continuous phase)	781.6	52.1
poly(co-propoxylated bisphenol A co- ethoxylated bisphenol A co-terephthalate co- dodecenylsuccinate co-trimellitate) resin latex (EP34 latex)	Kao Corporation Japan		amorphous high- molecular weight polyester	221.6	14.8
poly(co-propoxylated bisphenol A co- ethoxylated bisphenol A co-terephthalate co- fumarate co- dodecenylsuccinate) resin latex (EP33 latex)	Kao Corporation Japan		amorphous low- molecular weight polyester	221.6	14.8
poly(dodecanedioic acid-co-nanediol)	DIC Corporation		crystalline polyester latex	70.5	4.7
Cyan Pigment Dispersion	Sun Chemical		colorant	105.8	7.1
Wax Dispersion	International Group Inc.		Fischer Tropsch	92.3	6.2
ALS	Alesco		aluminum sulfate	5.4	0.4
Total				1499	100

Table 3

Raw Material	Weight (g)	Percentage (%)
DI Water	91.0	27.0
poly(co- propoxylated bisphenol A co- ethoxylated bisphenol A co- terephthalate co- dodecenylsuccinate co-trimellitate) resin latex (EP34 latex)	122.5	36.5
poly(co- propoxylated bisphenol A co-	122.5	36.5

ethoxylated bisphenol A co- terephthalate co- fumarate co- dodecenylsuccinate) resin latex (EP33 latex)		
Total	336	100

EXAMPLE 3

[00120] This Example shows the preparation of a laboratory scale control toner batch including the HBA-1 latex of Example 1 as a compatibilizing agent.

5 [00121] Core particles were formed from the materials in Table 4 below were homogenized using a lab homogenizer for a total of 30 minutes adjusting to a slurry pH of 4.2. After homogenization we transferred the slurry into a 2L baffle-less reactor where we ran at 49°C for 80 min. After the particle size target was reached we added the shell materials in **Table 5** over a span of 10 minutes below at a pH of approximately 10 3.3. After 40 minutes we then increased the pH to 7.8 and raised the temperature to 85°C until we reached our size target.

Table 4

Raw Material	Weight (g)	Percentage (%)
DI Water	648.6	47.9
poly(co-propoxylated bisphenol A co- ethoxylated bisphenol A co-terephthalate co- dodecenylsuccinate co- trimellitate) resin latex (EP34 latex)	177.3	13.1
poly(co-propoxylated bisphenol A co- ethoxylated bisphenol A co-terephthalate co- fumarate co- dodecenylsuccinate)	177.3	13.1

resin latex (EP33 latex)		
Hybrid HBA-1 Latex (Example 1)	39.8	2.9
EP07 Latex (styrene/acrylate latex)	37.8	2.8
poly(dodecanedioic acid- co-nonanediol) latex	70.5	5.2
Cyan Pigment Dispersion	105.8	7.8
Wax Dispersion	92.3	6.8
ALS	5.4	0.4
Total	1355	100

Table 5

Raw Material	Weight (g)	Percentage (%)
DI Water	91.0	27.0
poly(co- propoxylated bisphenol A co- ethoxylated bisphenol A co- terephthalate co- dodecenylsuccinate co-trimellitate) resin latex (EP34 latex)	122.5	36.5
poly(co- propoxylated bisphenol A co- ethoxylated bisphenol A co- terephthalate co- fumarate co- dodecenylsuccinate) resin latex (EP33 latex)	122.5	36.5
Total	336	100

[00122] Example 2 and Example 3 Comparison

5 [00123] Without the compatibilizing agent, Example 1 latex, a great deal of latex rejection was observed when attempts were made to place EP07 (polystyrene/acrylate latex) into the Example 2 formulation for a direct control toner comparison. With the

compatibilizing agent included, as in Example 3, very little latex rejection was observed. This was confirmed by measuring the amount of latex remaining in the mother liquor. Having a comparable amount of material in the mother liquor control Example 2 and Example 3 with compatibilizing agent demonstrated that the polystyrene latex was fully 5 incorporated as shown in Table 6 below which indicates the mother liquor (ML) composition. Overall the incorporation of the polystyrene is nearly complete and we see less overall latex in the mother liquor solution. Lower free latex shows better overall incorporation.

Table 6

Batch	Polyester Latex in ML (mg/mL)	Polystyrene Latex in ML (mg/mL)	Overall Latex in ML (mg/mL)
Example 2 ML	1.1	0	1.1
Example 3 ML	0.78	0.062	0.842

10 [00124] With this data on the mother liquor composition, along with the observed XPS (surface ions) data (Table 7) and changes in the rheology (Table 8), incorporation of polystyrene into the latex formulation via compatibilizing agent HBA-1 was confirmed. Thus, using the compatibilizing agent, the amount of polystyrene can be increased in 15 the core particle to help reduce cost, while at the same time altering the overall rheological properties with the proportional use of the latexes and still creating a usable particle for toner production. Table 7 shows the XPS results of the final particle (dry) batches. While using the same amount of wax, a significant increase in carbon was observed. This observation was expected because polystyrene has no oxygen atoms 20 while polyesters contain a significant number of oxygen atoms in the polymer backbone.

Table 7

Batch	XPS % C	XPS % O	XPS % Na

Example 2	80.3	19.3	0.38
Example 3	82.8	16.8	0.33

[00125] Table 8 shows rheology data at 10 radians per second at 100 °C. Due to the more crystalline nature of the polystyrene versus the amorphous nature of the polyester, we expect the G' and viscosity to increase and the Tan δ to decrease assuming the 5 same quantities of CPE/Pigment/Wax.

Table 8

Batch	G' (Pa)	G'' (Pa)	η (Pa s)	Tan δ
Example 2	12,937	24,462	2,767	1.89
Example 3	13,835	25,491	2,900	1.84

WHAT IS CLAIMED IS:

1. A toner comprising:
 - a core comprising a homogenized mixture of:
 - 5 a first polyester latex;
 - a styrene/acrylate latex; and
 - a compatibilizing agent latex comprising a graft polyester-styrene/acrylate copolymer; and
 - a shell comprising a polyester latex.
- 10 2. The toner of claim 1, wherein the first polyester latex is present in an amount from about 30 to about 90 weight percent of the core.
3. The toner of claim 1 or 2, wherein the styrene/acrylate latex is present in an amount from about 1 to about 70 weight percent of the core.
4. The toner of any one of claims 1 to 3, wherein the compatibilizing agent latex is 15 present in an amount from about 5 to about 15 weight percent of the core.
5. The toner of any one of claims 1 to 4, wherein the weight ratio of polyester to styrene/acrylate in the graft polyester-styrene/acrylate copolymer is in a range from about 70:30 to about 99:1.
6. The toner of any one of claims 1 to 5, wherein the core further comprises a 20 second polyester latex.
7. The toner of claim 6, wherein the first polyester latex comprises an amorphous high molecular weight polyester of weight average molecular weight in a range from about 35 KDa to about 150 KDa.
8. The toner of claim 6 or 7, wherein the second polyester latex comprises an 25 amorphous low molecular weight polyester of weight average molecular weight in a range from about 10 KDa to about 30 KDa.
9. The toner of any one of claims 1 to 8, further comprising a crystalline polyester latex.
10. The toner of any one of claims 1 to 9, further comprising a wax dispersion.
- 30 11. The toner of any one of claims 1 to 10, further comprising a colorant.
12. The toner of any one of claims 1 to 11, further comprising an aggregating agent.

13. A process comprising:

homogenizing a mixture to form a plurality of core particles, the mixture comprising:

a first polyester latex;

5 a styrene/acrylate latex; and

a compatibilizing agent latex comprising a graft polyester-styrene/acrylate copolymer; and

adding a shell polyester latex to the plurality of core particles to form a plurality of core-shell structures.

10 14. The process of claim 13, wherein the mixture further comprises a wax.

15. The process of claim 13 or 14, wherein the mixture further comprises crystalline polyester.

16. The process of any one of claims 13 to 15, wherein the mixture further comprises a colorant.

15 17. The process of any one of claims 13 to 16, wherein the mixture further comprises an aggregating agent.

18. The process of any one of claims 13 to 17, wherein after the homogenizing step, the plurality of core particles have an effective diameter in a range from about 3 microns to about 7 microns.

20 19. The process of any one of claims 13 to 18, further comprising adjusting the pH.

20. The process of any one of claims 13 to 19, further comprising, before adding the shell polyester, heating the homogenized mixture to temperature from about 40 °C to about 60 °C.

