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CA 2773741 C 2014/09/02

(11)(21) **2 773 741**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(22) Date de dépôt/Filing Date: 2012/04/05

(41) Mise à la disp. pub./Open to Public Insp.: 2012/10/11

(45) Date de délivrance/Issue Date: 2014/09/02

(30) Priorité/Priority: 2011/04/11 (US13/083,838)

(51) Cl.Int./Int.Cl. *G03G 9/08* (2006.01),
G03G 9/093 (2006.01), *C08L 67/02* (2006.01),
C08J 3/16 (2006.01)

(72) Inventeurs/Inventors:
ZHOU, KE, CA;
VANBESIEN, DARYL W., CA;
WOSNICK, JORDAN, CA;
MOFFAT, KAREN A., CA

(73) Propriétaire/Owner:
XEROX CORPORATION, US

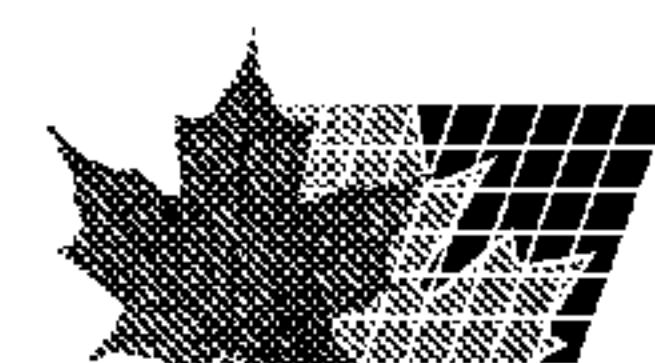
(74) Agent: SIM & MCBURNEY

(54) Titre : COMPOSITIONS D'ENCRE ET PROCEDES DE PRODUCTION CONNEXES

(54) Title: TONER COMPOSITIONS AND PROCESSES

(57) **Abrégé/Abstract:**

Toners are provided, which possess low melt properties capable of producing a low gloss finish. Methods for providing these resins and toners are also provided which include the process of controlling the gloss of the toner utilizing a slow acid addition during coalescence optionally combined with little or no chelating agent added during the aggregation process.



ABSTRACT

Toners are provided, which possess low melt properties capable of producing a low gloss finish. Methods for providing these resins and toners are also provided which include the process of controlling the gloss of the toner utilizing a slow acid addition during coalescence optionally combined with little or no chelating agent added during the aggregation process.

TONER COMPOSITIONS AND PROCESSES

TECHNICAL FIELD

[0001] The present disclosure is generally directed to toner processes, and more specifically, emulsion aggregation and coalescence processes, as well as toner compositions formed by such processes.

BACKGROUND

[0002] Numerous processes are within the purview of those skilled in the art for the preparation of toners. Emulsion aggregation (EA) is one such method. Emulsion aggregation toners may be used in forming print and/or electrophotographic images. Emulsion aggregation techniques may involve the formation of a polymer emulsion by heating a monomer and undertaking a batch or semi-continuous emulsion polymerization, as disclosed in, for example, U.S. Patent No. 5,853,943. Emulsion aggregation/coalescing processes for the preparation of toners are illustrated in a number of patents, such as U.S. Patents Nos. 5,290,654, 5,278,020, 5,308,734, 5,344,738, 6,593,049, 6,743,559, 6,756,176, 6,830,860, 7,029,817, and 7,329,476, and U.S. Patent Application Publication Nos. 2006/0216626, 2008/0107989, 2008/0107990, 2008/0236446, and 2009/0047593.

[0003] Polyester emulsion aggregation (EA) ultra low melt (ULM) toners have been prepared utilizing amorphous and crystalline polyester resins as illustrated, for example, in U.S. Patent Application Publication No. 2008/0153027.

[0004] EA processes often use an aggregating agent, such as aluminum sulfate, for toner particle aggregation and for promoting crosslinking within the particle to reach a desired

gloss level. However, the crosslinking agent may promote particle to particle sticking during coalescence, which could lead to a broad particle size distribution. Once the desired particle size is reached, a chelating agent, such as ethylene diamine tetraacetic acid (EDTA) is introduced to remove the extra aluminum after aggregation which helps prevent toner growth when the temperature is increased for coalescence. However, the addition of EDTA may prevent desired gloss modification from taking place. In addition, if the amount of EDTA utilized in the EA process is reduced, poor geometric size distribution (GSD) is obtained.

[0005] For many EA toners, there is a trade-off between obtaining desirable gloss and Minimum Fix (or Fusing) Temperature (MFT) characteristics. For example, many EA toners have high gloss and low melt properties. However, for applications where a lower gloss is desired, difficulties may arise in forming a toner having a lower gloss which still exhibits ultra low melt properties.

[0006] Improved toners and methods for their production thus remain desirable.

SUMMARY

[0007] The present disclosure provides processes for producing toners and toners produced by these processes. In embodiments, a process of the present disclosure includes contacting at least one amorphous resin with at least one crystalline resin and optionally one styrene/acrylate gel in a mixture; aggregating the mixture to form particles; adding a buffer having a pH of from about 3 to about 7 to the particles by metered addition to reach a desired pH over a period of from about 0.25 hours to about 10 hours; and coalescing the particles to form toner particles.

[0008] In other embodiments, a process of the present disclosure includes contacting at least one amorphous resin with at least one crystalline resin and optionally one styrene/acrylate gel in a mixture; aggregating the mixture to form core particles; contacting

the core particles with an emulsion including at least one amorphous resin to form a shell over the particles; slowly adding a buffer drop wise to the particles to reach a desired pH at a rate of from about 0.1 grams/minute per 100 grams of dry toner to about 5 grams/minute per 100 grams of dry toner; and coalescing the particles to form toner particles.

[0009] In yet other embodiments, a process of the present disclosure includes contacting at least one amorphous resin with at least one crystalline resin and optionally one styrene/acrylate gel in a mixture; aggregating the mixture to form core particles; contacting the core particles with an emulsion including at least one amorphous resin to form a shell over the particles; slowly adding a buffer system drop wise to the particles to reach a desired pH from about 4 to about 7, at a rate of from about 0.1 grams/minute per 100 grams of dry toner to about 5 grams/minute per 100 grams of dry toner; and coalescing the particles to form toner particles.

[0009a] In accordance with an aspect of the present invention there is provided a process for preparing low gloss, low melt toner particles comprising: contacting at least one amorphous resin with at least one crystalline resin and optionally one styrene/acrylate gel in a mixture; aggregating the mixture to form particles; adding a buffer having a pH of from about 3 to about 7 to the particles to lower the pH of the particles by metered addition to reach a desired reduced pH over a period of from about 0.25 hours to about 10 hours at a rate of about 0.005 pH units per minute to about 0.1 pH per minute; and coalescing the particles to form the low gloss, low melt toner particles.

[0009b] In accordance with a further aspect of the present invention there is provided a process for preparing low gloss, low melt toner particles comprising: contacting at least one amorphous resin with at least one crystalline resin and optionally one styrene/acrylate gel in a mixture; aggregating the mixture to form core particles; contacting the core particles with an emulsion comprising at least one amorphous resin to form a shell over the particles to form core/shell particles; slowly adding a buffer drop wise to the core/shell particles to reach a desired reduced pH at a rate of from about 0.1 grams/minute per 100 grams of dry toner to

about 5 grams/minute per 100 grams of dry toner; and coalescing the particles to form the low gloss, low melt toner particles.

[0009c] In accordance with a further aspect of the present invention there is provided a process for preparing low gloss, low melt toner particles comprising: contacting at least one amorphous resin with at least one crystalline resin and optionally one styrene/acrylate gel in a mixture; aggregating the mixture to form core particles; contacting the core particles with an emulsion comprising at least one amorphous resin to form a shell over the particles to form core/shell particles; slowly adding a buffer system drop wise to the core/shell particles to reach a desired reduced pH from about 4 to about 7, at a rate of from about 0.1 grams/minute per 100 grams of dry toner to about 5 grams/minute per 100 grams of dry toner; and coalescing the core/shell particles to form low gloss, low melt toner particles.

BRIEF DESCRIPTION OF THE FIGURES

[0010] Various embodiments of the present disclosure will be described herein below with reference to the figures wherein:

[0011] Figure 1 is a graph of the final particle size distribution for a comparative EA toner, as described in Comparative Example 1;

[0012] Figure 2 is a graph of the final particle size distribution for a comparative EA toner, as described in Comparative Example 2;

[0013] Figure 3 is a graph of the final particle size distribution for a comparative EA toner, as described in Comparative Example 3; and

[0014] Figure 4 is a graph of the final particle size distribution for an EA toner of the present disclosure.

DETAILED DESCRIPTION

[0015] In accordance with the present disclosure, processes for producing ultra low melt (ULM) EA toners are provided which include slowly reducing the pH during coalescence, by slow or metered feeding of a buffer system or acid to the reaction mixture, with little or no chelating agent utilized in the process. In embodiments, the buffer system is added through the use of a step-wise addition process, which includes feeding a small amount of acid or buffer slowly until the desired pH and the target particle size is reached. The processes of the present disclosure prevent particle to particle sticking from occurring, resulting in a narrow particle size distribution while achieving desired gloss and ultra low melt properties of a toner. Thus, toners of the present disclosure may be utilized to form ultra low melt toners having low gloss. In embodiments, the toners of the present disclosure possess a core-shell configuration, with the shell including at least one amorphous resin.

Resins

[0016] Any resin may be utilized in forming a toner of the present disclosure. In embodiments, the resins may be an amorphous resin, a crystalline resin, and/or a combination thereof. In embodiments, suitable resins may be polyester resins. The polyester resins may be linear, branched, combinations thereof, and the like. Polyester resins may include, in embodiments, those 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 as described in U.S. Patent No. 6,830,860.

[0017] In embodiments, a resin utilized in forming a toner may include an amorphous polyester resin. In embodiments, the resin may be a polyester resin formed by reacting a diol with a diacid or diester in the presence of an optional catalyst.

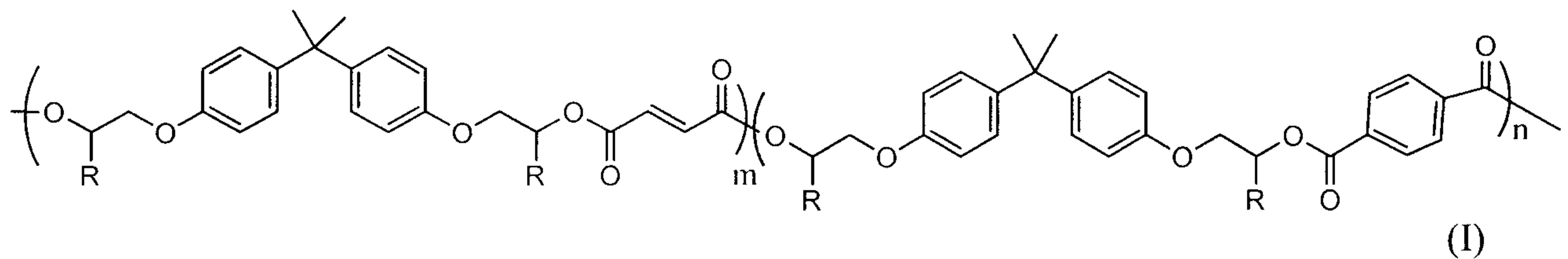
[0018] Examples of organic diols selected for the preparation of amorphous resins may include aliphatic diols with from about 2 to about 36 carbon atoms, such as 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,12-dodecanediol, and the like; alkali sulfo-aliphatic diols such as sodio 2-sulfo-1,2-ethanediol, lithio 2-sulfo-1,2-ethanediol, potassio 2-sulfo-1,2-ethanediol, sodio 2-sulfo-1,3-propanediol, lithio 2-sulfo-1,3-propanediol, potassio 2-sulfo-1,3-propanediol, mixture thereof, and the like. The aliphatic diol is, for example, selected in an amount of from about 45 to about 50 mole percent of the resin, and the alkali sulfo-aliphatic diol may be present in an amount of from about 1 to about 10 mole percent of the resin.

[0019] Examples of diacid or diesters selected for the preparation of the amorphous polyester may include dicarboxylic acids or diesters selected from the group consisting of terephthalic acid, phthalic acid, isophthalic acid, fumaric acid, maleic acid, itaconic acid, succinic acid, succinic anhydride, dodecylsuccinic acid, dodecylsuccinic anhydride, dodecenylsuccinic acid, dodecenylsuccinic 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, dimethyl dodecenylsuccinate, and mixtures thereof. The organic diacid or diester may be present, for example, from about 45 to about 52 mole percent of the resin.

[0020] Examples of suitable polycondensation catalyst for either the amorphous polyester resin include tetraalkyl titanates, dialkyltin oxide such as dibutyltin oxide, tetraalkyltin such as dibutyltin dilaurate, dialkyltin oxide hydroxide such as butyltin oxide hydroxide, aluminum alkoxides, alkyl zinc, dialkyl zinc, zinc oxide, stannous oxide, or mixtures thereof; and which catalysts are selected 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.

[0021] Exemplary 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), 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), a copoly(propoxylated bisphenol A co-fumarate)–copoly(propoxylated bisphenol A co-terephthalate), a terpoly(propoxylated bisphenol A co-fumarate)–terpoly(propoxylated bisphenol A co-terephthalate)–terpoly(propoxylated bisphenol A co-dodecylsuccinate), and combinations thereof. In embodiments, the amorphous resin utilized in the core may be linear.

[0022] In embodiments, a suitable amorphous resin may include alkoxylated bisphenol A fumarate/terephthalate based polyesters and copolyester resins. In embodiments, a suitable amorphous polyester resin may be a copoly(propoxylated bisphenol A co-fumarate)–copoly(propoxylated bisphenol A co-terephthalate) resin having the following formula (I):



wherein R may be hydrogen or a methyl group, and m and n represent random units of the copolymer and m may be from about 2 to 10, and n may be from about 2 to 10.

[0023] An example of a linear copoly(propoxylated bisphenol A co-fumarate) — copoly(propoxylated bisphenol A co-terephthalate) 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 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.

[0024] In embodiments, the amorphous polyester resin may be a saturated or unsaturated amorphous polyester resin. Illustrative examples of saturated and unsaturated amorphous polyester resins selected for the process and particles of the present disclosure include any of the various amorphous polyesters, such as polyethylene-terephthalate, polypropylene-terephthalate, polybutylene-terephthalate, polypentylene-terephthalate, polyhexalene-terephthalate, polyheptadene-terephthalate, polyoctalene-terephthalate, polyethylene-isophthalate, polypropylene-isophthalate, polybutylene-isophthalate, polypentylene-isophthalate, polyhexalene-isophthalate, polyheptadene-isophthalate, polyoctalene-isophthalate, polyethylene-sebacate, polypropylene sebacate, polybutylene-sebacate, polyethylene-adipate, polypropylene-adipate, polybutylene-adipate, polypentylene-adipate, polyhexalene-adipate, polyheptadene-adipate, polyoctalene-adipate, polyethylene-glutarate, polypropylene-glutarate, polybutylene-glutarate, polypentylene-glutarate, polyhexalene-glutarate, polyheptadene-glutarate, polyoctalene-glutarate polyethylene-pimelate, polypropylene-pimelate, polybutylene-pimelate, polypentylene-pimelate, polyhexalene-

pimelate, polyheptadene-pimelate, poly(ethoxylated bisphenol A-fumarate), poly(ethoxylated bisphenol A-succinate), poly(ethoxylated bisphenol A-adipate), poly(ethoxylated bisphenol A-glutarate), poly(ethoxylated bisphenol A-terephthalate), poly(ethoxylated bisphenol A-isophthalate), poly(ethoxylated bisphenol A-dodecenylsuccinate), poly(propoxylated bisphenol A-fumarate), poly(propoxylated bisphenol A-succinate), poly(propoxylated bisphenol A-adipate), poly(propoxylated bisphenol A-glutarate), poly(propoxylated bisphenol A-terephthalate), poly(propoxylated bisphenol A-isophthalate), poly(propoxylated bisphenol A-dodecenylsuccinate), SPAR (Dixie Chemicals), BECKOSOL (Reichhold Inc), ARAKOTE (Ciba-Geigy Corporation), HETRON (Ashland Chemical), PARAPLEX (Rohm & Haas), POLYLITE (Reichhold Inc), PLASTHALL (Rohm & Haas), CYGAL (American Cyanamide), ARMCO (Armco Composites), ARPOL (Ashland Chemical), CELANEX (Celanese Eng), RYNITE (DuPont), STYPOL (Freeman Chemical Corporation) and combinations thereof. The resins may also be functionalized, such as carboxylated, sulfonated, or the like, and particularly such as sodio sulfonated, if desired.

[0025] The amorphous polyester resin may be a branched resin. As used herein, the terms "branched" or "branching" includes branched resin and/or cross-linked resins. Branching agents for use in forming these branched resins include, for example, a multivalent polyacid such as 1,2,4-benzene-tricarboxylic acid, 1,2,4-cyclohexanetricarboxylic acid, 2,5,7-naphthalenetricarboxylic acid, 1,2,4-naphthalenetricarboxylic acid, 1,2,5-hexanetricarboxylic acid, 1,3-dicarboxyl-2-methyl-2-methylene-carboxylpropane, tetra(methylene-carboxyl)methane, and 1,2,7,8-octanetetracarboxylic acid, acid anhydrides thereof, and lower alkyl esters thereof, 1 to about 6 carbon atoms; a multivalent polyol such as sorbitol, 1,2,3,6-hexanetetrol, 1,4-sorbitane, pentaerythritol, dipentaerythritol, tripentaerythritol, sucrose, 1,2,4-butanetriol, 1,2,5-pentatriol, glycerol, 2-methylpropanetriol, 2-methyl-1,2,4-butanetriol, trimethylolethane, trimethylolpropane, 1,3,5-trihydroxymethylbenzene, mixtures thereof, and

the like. The branching agent amount selected is, for example, from about 0.1 to about 5 mole percent of the resin.

[0026] Linear or branched unsaturated polyesters selected for reactions include both saturated and unsaturated diacids (or anhydrides) and dihydric alcohols (glycols or diols). The resulting unsaturated polyesters are reactive (for example, crosslinkable) on two fronts: (i) unsaturation sites (double bonds) along the polyester chain, and (ii) functional groups such as carboxyl, hydroxy, and the like groups amenable to acid-base reactions. Typical unsaturated polyester resins may be prepared by melt polycondensation or other polymerization processes using diacids and/or anhydrides and diols.

[0027] In embodiments, a suitable amorphous resin utilized in a toner of the present disclosure may be a low molecular weight amorphous resin, sometimes referred to, in embodiments, as an oligomer, having a weight average molecular weight (M_w) of from about 500 daltons to about 10,000 daltons, in embodiments from about 1000 daltons to about 5000 daltons, in other embodiments from about 1500 daltons to about 4000 daltons.

[0028] The low molecular weight amorphous resin may possess a glass transition temperature of from about 58.5°C to about 66°C, in embodiments from about 60°C to about 62°C.

[0029] The low molecular weight amorphous resin may possess a softening point of from about 105°C to about 118°C, in embodiments from about 107°C to about 109°C.

[0030] The low molecular weight amorphous polyester resins may have an acid value of from about 8 to about 20 mg KOH/g, in embodiments from about 9 to about 16 mg KOH/g, and in embodiments from about 11 to about 15 mg KOH/g.

[0031] In other embodiments, an amorphous resin utilized in forming a toner of the present disclosure may be a high molecular weight amorphous resin. As used herein, the high molecular weight amorphous polyester resin may have, for example, a number average

molecular weight (M_n), as measured by gel permeation chromatography (GPC) of, for example, from about 1,000 to about 10,000, in embodiments from about 2,000 to about 9,000, in embodiments from about 3,000 to about 8,000, and in embodiments from about 6,000 to about 7,000. The weight average molecular weight (M_w) of the resin is greater than 45,000, for example, from about 45,000 to about 150,000, in embodiments from about 50,000 to about 100,000, in embodiments from about 63,000 to about 94,000, and in embodiments from about 68,000 to about 85,000, as determined by GPC using polystyrene standard. The polydispersity index (PD) is above about 4, such as, for example from about 4 to about 20, in embodiments from about 5 to about 10, and in embodiments from about 6 to about 8, as measured by GPC versus standard polystyrene reference resins. The PD index is the ratio of the weight-average molecular weight (M_w) and the number-average molecular weight (M_n). The high molecular weight amorphous polyester resins, which are available from a number of sources, may possess various melting points of, for example, from about 30°C to about 140°C, in embodiments from about 75°C to about 130°C, in embodiments from about 100°C to about 125°C, and in embodiments from about 115°C to about 124°C. High molecular weight amorphous resins may possess a glass transition temperature of from about 53°C to about 58°C, in embodiments from about 54.5°C to about 57°C.

[0032] The amorphous resin(s) is generally present in the toner composition in various suitable amounts, such as from about 50 to about 100 weight percent, in embodiments from about 60 to about 95 weight percent, of the toner or of the solids.

[0033] In further embodiments, the combined amorphous resins 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.

[0034] In embodiments, the toner composition, including the core, may include at least one crystalline resin. As used herein, "crystalline" refers to a polyester with a three dimensional

order. "Semicrystalline resins" as used herein refers to resins with a crystalline percentage of, for example, from about 10 to about 90 percent, in embodiments from about 12 to about 70 percent. Further, as used hereinafter "crystalline polyester resins" and "crystalline resins" encompass both crystalline resins and semicrystalline resins, unless otherwise specified.

[0035] In embodiments, the crystalline polyester resin is a saturated crystalline polyester resin or an unsaturated crystalline polyester resin.

[0036] For forming a crystalline polyester, suitable organic diols include aliphatic diols having from about 2 to about 36 carbon atoms, such as 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,12-dodecanediol, ethylene glycol, combinations thereof, and the like. 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 of the resin.

[0037] Examples of organic diacids or diesters selected for the preparation of the crystalline resins include oxalic acid, succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, fumaric acid, maleic acid, dodecanedioic acid, sebacic acid, 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, and combinations 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 55 mole percent, in embodiments from about 45 to about 53 mole percent.

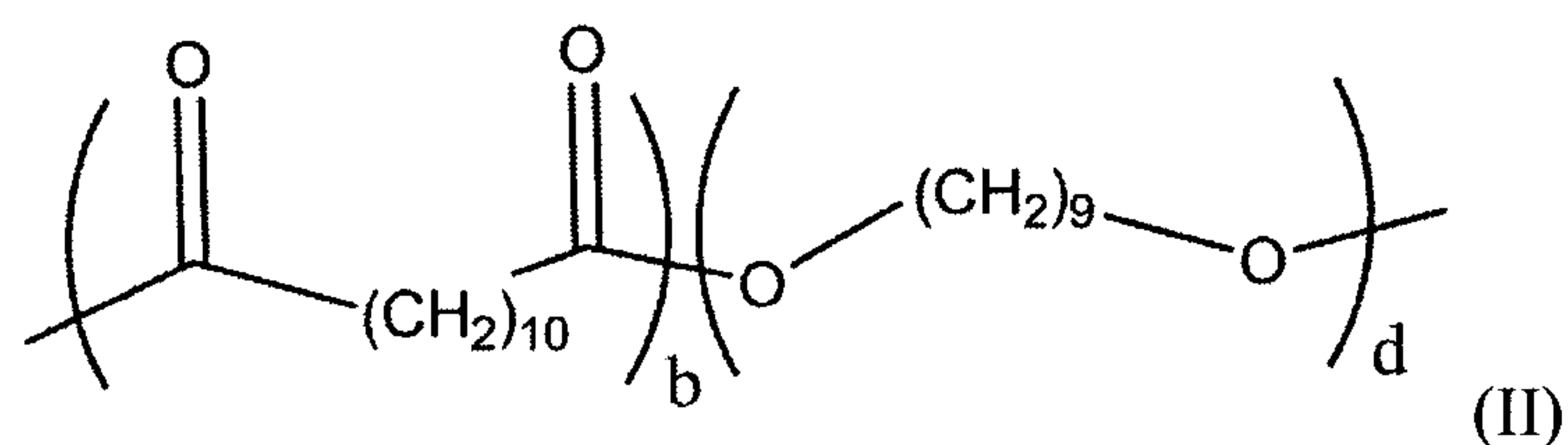
[0038] Specific crystalline resins may be polyester based, such as poly(ethylene-adipate), poly(propylene-adipate), poly(butylene-adipate), poly(pentylene-adipate), poly(hexylene-adipate), poly(octylene-adipate), poly(ethylene-succinate), poly(propylene-succinate), poly(butylene-succinate), poly(pentylene-succinate), poly(hexylene-succinate),

poly(octylene-succinate), poly(ethylene-sebacate), poly(propylene-sebacate), poly(butylene-sebacate), poly(pentylene-sebacate), poly(hexylene-sebacate), poly(octylene-sebacate), alkali copoly(5-sulfoisophthaloyl)-copoly(ethylene-adipate), poly(decylene-sebacate), poly(decylene-decanoate), poly-(ethylene-decanoate), poly-(ethylene-dodecanoate), poly(nonylene-sebacate), poly (nonylene-decanoate), copoly(ethylene-fumarate)-copoly(ethylene-sebacate), copoly(ethylene-fumarate)-copoly(ethylene-decanoate), copoly(ethylene-fumarate)-copoly(ethylene-dodecanoate), and combinations thereof. The crystalline resin may be present, for example, in an amount of from about 5 to about 25 percent by weight of the toner components, in embodiments from about 6 to about 15 percent by weight of the toner components.

[0039] The crystalline polyester resins, which are available from a number of sources, may possess various melting points of, for example, from about 30°C to about 120°C, in embodiments from about 50°C to about 90°C. The crystalline resins may have, for example, a number average molecular weight (M_n), as measured by GPC of, for example, from about 1,000 to about 50,000, in embodiments from about 2,000 to about 25,000, in embodiments from about 3,000 to about 15,000, and in embodiments from about 6,000 to about 12,000. The weight average molecular weight (M_w) of the resin is 50,000 or less, for example, from about 2,000 to about 50,000, in embodiments from about 3,000 to about 40,000, in embodiments from about 10,000 to about 30,000 and in embodiments from about 21,000 to about 24,000, as determined by GPC using polystyrene standards. The molecular weight distribution (M_w/M_n) of the crystalline resin is, for example, from about 2 to about 6, in embodiments from about 3 to about 4. The crystalline polyester resins may have an acid value of about 2 to about 20 mg KOH/g, in embodiments from about 5 to about 15 mg KOH/g, and in embodiments from about 8 to about 13 mg KOH/g. The acid value (or

neutralization number) is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of the crystalline polyester resin.

[0040] Suitable crystalline polyester resins include those disclosed in U.S. Patent No. 7,329,476 and U.S. Patent Application Publication Nos. 2006/0216626, 2008/0107990, 2008/0236446 and 2009/0047593. In embodiments, a suitable crystalline resin may include a resin composed of ethylene glycol or nonanediol and a mixture of dodecanedioic acid and fumaric acid co-monomers with the following formula (II):



wherein b is from about 5 to about 2000 and d is from about 5 to about 2000.

[0041] If semicrystalline polyester resins are employed herein, the semicrystalline resin may include poly(3-methyl-1-butene), poly(hexamethylene carbonate), poly(ethylene-p-carboxy phenoxy-butyrate), poly(ethylene-vinyl acetate), poly(docosyl acrylate), poly(dodecyl acrylate), poly(octadecyl acrylate), poly(octadecyl methacrylate), poly(behenylpolyethoxyethyl methacrylate), poly(ethylene adipate), poly(decamethylene adipate), poly(decamethylene azelaate), poly(hexamethylene oxalate), poly(decamethylene oxalate), poly(ethylene oxide), poly(propylene oxide), poly(butadiene oxide), poly(decamethylene oxide), poly(decamethylene sulfide), poly(decamethylene disulfide), poly(ethylene sebacate), poly(decamethylene sebacate), poly(ethylene suberate), poly(decamethylene succinate), poly(eicosamethylene malonate), poly(ethylene-p-carboxy phenoxy-undecanoate), poly(ethylene dithionesophthalate), poly(methyl ethylene terephthalate), poly(ethylene-p-carboxy phenoxy-valerate), poly(hexamethylene-4,4'-oxydibenzoate), poly(10-hydroxy capric acid), poly(isophthalaldehyde), poly(octamethylene

dodecanedioate), poly(dimethyl siloxane), poly(dipropyl siloxane), poly(tetramethylene phenylene diacetate), poly(tetramethylene trithiodicarboxylate), poly(trimethylene dodecane dioate), poly(m-xylene), poly(p-xylylene pimelamide), and combinations thereof.

[0042] As noted above, in embodiments a toner of the present disclosure may also include at least one high molecular weight branched or cross-linked amorphous polyester resin. This high molecular weight resin may include, in embodiments, for example, a branched amorphous resin or amorphous polyester, a cross-linked amorphous resin or amorphous polyester, or mixtures thereof, or a non-cross-linked amorphous polyester resin that has been subjected to cross-linking. In accordance with the present disclosure, from about 1% by weight to about 100% by weight of the high molecular weight amorphous polyester resin may be branched or cross-linked, in embodiments from about 2% by weight to about 50% by weight of the higher molecular weight amorphous polyester resin may be branched or cross-linked.

[0043] In embodiments, the resin may be formed by emulsion polymerization methods. Utilizing such methods, the resin may be present in a resin emulsion, which may then be combined with other components and additives to form a toner of the present disclosure.

Toner

[0044] The resins described above, in embodiments a combination of polyester resins, for example a low molecular weight amorphous resin, a high molecular weight amorphous resin, a crystalline resin, and optionally a styrene/acrylate gel, may be utilized to form toner compositions. Such toner compositions may include optional colorants, waxes, buffers, and other additives. Toners may be formed utilizing any method within the purview of those skilled in the art including, but not limited to, emulsion aggregation methods.

Surfactants

[0045] In embodiments, colorants, waxes, and other additives utilized to form toner compositions may be in dispersions including surfactants. Moreover, toner particles may be formed by emulsion aggregation methods where the resin and other components of the toner are placed in one or more surfactants, an emulsion is formed, toner particles are aggregated, coalesced, optionally washed and dried, and recovered.

[0046] One, two, or more surfactants may be utilized. 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 utilized so that it is present in an amount of from about 0.01% to about 5% by weight of the toner composition, for example from about 0.75% to about 4% by weight of the toner composition, in embodiments from about 1% to about 3% by weight of the toner composition.

[0047] Examples of nonionic surfactants that can be utilized 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, 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 include a block copolymer of polyethylene oxide and polypropylene oxide, including those commercially available as SYNPERONIC PE/F, in embodiments SYNPERONIC PE/F 108.

[0048] Anionic surfactants which may be utilized include sulfates and sulfonates, sodium dodecylsulfate (SDS), sodium dodecylbenzene sulfonate, sodium dodecyl naphthalene 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 dodecyl benzene sulfonates. Combinations of these surfactants and any of the foregoing anionic surfactants may be utilized in embodiments.

[0049] 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 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 thereof.

Colorants

[0050] 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. The colorant may be included in the toner in an amount of, for example, about 0.1 to about 35 percent by weight of the toner, or from about 1 to about 15 weight percent of the toner, or from about 3 to about 10 percent by weight of the toner.

[0051] As examples of suitable colorants, mention may be made of TiO₂; carbon black like REGAL 330[®] and NIPEX[®] 35; 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 the like. As colored pigments, there can be selected cyan, magenta, yellow, orange, 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.

[0052] Specific examples of pigments include SUNSPERSE 6000, FLEXIVERSE and AQUATONE 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[™], LEMON CHROME YELLOW DCC 1026[™], E.D. TOLUIDINE RED[™] and BON RED C[™] available from Dominion Color Corporation, Ltd., Toronto, Ontario, NOVAPERM YELLOW FGL[™], HOSTAPERM PINK E[™] from Hoechst, and CINQUASIA MAGENTA[™] available from E.I. DuPont de Nemours & Company, 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, 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, Pigment Blue 15:4 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 33 2,5-dimethoxy-4-sulfonanilide phenylazo-4'-chloro-2,5-dimethoxy acetoacetanilide, and Permanent Yellow FGL. Colored magnetites, such as mixtures of MAPICO BLACK™, and cyan components may also be selected as colorants. Other known colorants can be selected, such as Levanyl Black A-SF (Miles, Bayer) and Sunspere Carbon Black LHD 9303 (Sun Chemicals), and colored dyes such as Neopen Blue (BASF), Sudan Blue OS (BASF), PV Fast Blue B2G01 (American Hoechst), Sunspere Blue BHD 6000 (Sun Chemicals), Irgalite Blue BCA (Ciba-Geigy), Paliogen Blue 6470 (BASF), Sudan III (Matheson, Coleman, Bell), Sudan II (Matheson, Coleman, Bell), Sudan IV (Matheson, Coleman, Bell), Sudan Orange G (Aldrich), Sudan Orange 220 (BASF), Paliogen Orange 3040 (BASF), Ortho Orange OR 2673 (Paul Uhlich), Paliogen Yellow 152, 1560 (BASF), Lithol Fast Yellow 0991K (BASF), Paliotol Yellow 1840 (BASF), Neopen Yellow (BASF), Novoperm Yellow FG 1 (Hoechst), Permanent Yellow YE 0305 (Paul Uhlich), Lumogen Yellow D0790 (BASF), Sunspere Yellow YHD 6001 (Sun Chemicals), Suco-Gelb L1250 (BASF), Suco-Yellow D1355 (BASF), Hostaperm Pink E (American Hoechst), Fanal Pink D4830 (BASF), Cinquasia Magenta (DuPont), Lithol Scarlet D3700 (BASF), Toluidine Red (Aldrich), Scarlet for Thermoplast NSD PS PA (Ugine Kuhlmann of Canada), E.D. Toluidine Red (Aldrich), Lithol Rubine Toner (Paul Uhlich), Lithol Scarlet 4440 (BASF), Bon Red C (Dominion Color Company), Royal Brilliant Red RD-8192 (Paul Uhlich), Oracet Pink RF (Ciba-Geigy), Paliogen Red 3871K (BASF), Paliogen Red 3340 (BASF), Lithol Fast Scarlet L4300 (BASF), combinations of the foregoing, and the like. Other pigments that are available from various suppliers include various pigments in the following classes identified as Pigment Yellow 74, Pigment Yellow 14, Pigment Yellow 83, Pigment Orange 34, Pigment Red 238,

Pigment Red 122, Pigment Red 48:1, Pigment Red 269, Pigment Red 53:1, Pigment Red 57:1, Pigment Red 83:1, Pigment Violet 23, Pigment Green 7, combinations thereof, and the like.

Wax

The toners of the present disclosure may also optionally contain a wax, which can be either a single type of wax or a mixture of two or more different waxes. A single wax can be 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.

[0053] In accordance with the present disclosure, it has been found that a low melt toner producing a low gloss to matte finish may be obtained by including an amorphous polyester resin in the shell and a low percentage of wax. (Increasing the percentage of wax may result in poor charging of the toner particles.) Where utilized, the wax may be present in an amount of, for example, from about 1 weight percent to about 24 weight percent of the toner particles, in embodiments from about 3 weight percent to about 10 weight percent of the toner particles.

[0054] Waxes that may be selected include waxes having, for example, a weight average molecular weight 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, polypropylene, and polybutene waxes such as commercially available from Allied Chemical and Petrolite Corporation, for example POLYWAX™ polyethylene waxes 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 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, and 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 diethyleneglycol monostearate, dipropyleneglycol distearate, diglyceryl distearate, and triglyceryl tetrastearate; 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 6550™, SUPERSLIP 6530™ available from Micro Powder Inc., fluorinated waxes, for example POLYFLUO 190™, POLYFLUO 200™, POLYSILK 19™, POLYSILK 14™ available from Micro Powder Inc., mixed fluorinated, amide waxes, for example MICROSPERSION 19™ also available from Micro Powder Inc., imides, esters, quaternary amines, carboxylic acids or acrylic polymer emulsion, for example JONCRYL 74™, 89™, 130™, 537™, and 538™, 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, for example, fuser roll release agents.

Toner Preparation

[0055] The toner particles may be prepared by any method 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 method 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 toner-particle shape and morphology.

[0056] In embodiments, toner compositions may be prepared by emulsion aggregation processes, such as a process that includes aggregating a mixture of an optional wax and any other desired or required additives, and emulsions including the resins described above, optionally in surfactants as described above, and then coalescing the aggregate mixture. A mixture may be prepared by adding an optional wax or other materials, which may also be optionally in a dispersion(s) including a surfactant and/or colorant, to the emulsion, which may be a mixture of two or more emulsions containing the resin(s). 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 4.5. Additionally, in embodiments, the mixture may be homogenized. If the mixture is homogenized, homogenization may be accomplished by mixing at about 600 to about 4,000 revolutions per minute. Homogenization may be accomplished by any suitable means, including, for example, an IKA ULTRA TURRAX T50 probe homogenizer.

[0057] 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. Suitable

aggregating agents include, for example, aqueous solutions of a divalent cation or a multivalent cation material. The aggregating agent may be, for example, polyaluminum halides such as polyaluminum chloride (PAC), or the corresponding bromide, fluoride, or iodide, polyaluminum silicates such as polyaluminum sulfosilicate (PASS), and water soluble 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 aggregating agent may be added to the mixture at a temperature that is below the glass transition temperature (T_g) of the resin.

[0058] The aggregating agent may be added to the mixture utilized to form a toner in an amount of, for example, from about 0.1 parts per hundred (pph) to about 1 pph, in embodiments from about 0.25 pph to about 0.75 pph, in some embodiments about 0.5 pph. This provides a sufficient amount of agent for aggregation.

[0059] In order to control aggregation and coalescence of the particles, in embodiments the aggregating agent may be metered into the mixture over time. For example, the agent may be metered into the mixture over a period of from about 5 to about 240 minutes, in embodiments from about 30 to about 200 minutes. The addition of the agent may also be done while the mixture is maintained under stirred conditions, in embodiments from about 50 rpm to about 1,000 rpm, in other embodiments from about 100 rpm to about 500 rpm, and at a temperature that is below the glass transition temperature of the resin as discussed above, in embodiments from about 30 °C to about 90 °C, in embodiments from about 35°C to about 70 °C.

[0060] 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 from about 0.5 hours to about 6 hours, in embodiments from about hour 1 to about 5 hours, while maintaining stirring, to provide the aggregated particles. Once the predetermined desired particle size is reached, then the growth process is halted. In embodiments, the predetermined desired particle size is within the toner particle size ranges mentioned above.

[0061] The growth and shaping of the particles following addition of the aggregation agent may be accomplished under any suitable conditions. For example, the growth and shaping may be conducted under conditions in which aggregation occurs separate from coalescence. For separate aggregation and coalescence stages, the aggregation process may be conducted under thermal conditions at an elevated temperature, for example of from about 40°C to about 90°C, in embodiments from about 45°C to about 63°C, which may be below the glass transition temperature of the resin as discussed above.

[0062] In embodiments, the aggregate particles may have a volume average diameter (also referred to as "volume average particle diameter") of less than about 5 microns, in embodiments from about 4 microns to about 5 microns, in embodiments from about 4.5 microns to about 4.9 microns.

[0063] The gloss of a toner may be influenced by the amount of retained metal ion, such as Al^{3+} , in the particle. The amount of retained metal ion may be further adjusted by the addition of a chelating agent, such as for example EDTA. Where utilized, the amount of chelating agent may be from about 0.1 (parts per hundred) (pph) to about 10 pph, in

embodiments from about 0.2 pph to about 5 pph. In some embodiments, very little chelating agent may be required, from about 0 pph to about 0.8 pph based on the amount of dry toner, in embodiments from about 0.01 pph to about 0.75 pph, in embodiments from about 0.1 pph to about 0.6 pph.

[0064] In embodiments, the amount of retained crosslinker, for example Al^{3+} , in toner particles of the present disclosure may be from about 10 pph to about 1000 pph, in embodiments from about 100 pph to about 700 pph.

[0065] However, the addition of a chelating agent to remove the aggregating agent may prevent gloss modification. In order to tune current toner formulations to achieve low gloss levels, more aggregating agent may be left in the toner and thus, less EDTA may be utilized. However, poor GSD and particle to particle sticking may result when little or no EDTA is used in the aggregating step. Thus, as described in more detail below, use of little or no chelating agent to remove the crosslinking agent during aggregation, together with the addition of a buffer system to the toner slurry via a metered process during coalescence, may provide narrow particle size distribution and low gloss ULM toners. The buffer may be added in amounts of from about 2 to about 100 ml per 100 grams of dry toner, in embodiments from about 5 to about 50 ml per 100 grams of dry toner, over a period of time from about 0.25 hours to about 10 hours, in embodiments from about 0.5 hours to about 5 hours.

Shell resin

[0066] In embodiments, a shell may be applied to the formed aggregated toner particles. Any resin described above as suitable for the core resin may be utilized as the shell resin. The shell resin may be applied to the aggregated particles by any method within the purview of those skilled in the art. In embodiments, the shell resin may be in an emulsion including

any surfactant described above. The aggregated particles described above may be combined with said emulsion so that the resin forms a shell over the formed aggregates. In embodiments, at least one amorphous polyester resin may be utilized to form a shell over the aggregates to form toner particles having a core-shell configuration. In embodiments, an amorphous polyester and a crystalline resin may be utilized to form a shell over the aggregates to form toner particles having a core-shell configuration.

[0067] In embodiments, a suitable shell may include at least one amorphous polyester resin present in an amount from about 10 percent to about 90 percent by weight of the shell, in embodiments from about 20 percent to about 80 percent by weight of the shell, in embodiments from about 30 percent to about 70 percent by weight of the shell.

[0068] The shell resin may be present in an amount of from about 5 percent to about 40 percent by weight of the toner particles, in embodiments from about 24 percent to about 30 percent by weight of the toner particles.

[0069] 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 5 to about 10, and in embodiments from about 6 to about 8. 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. The base may be added in amounts from about 2 to about 25 percent by weight of the mixture, in embodiments from about 4 to about 10 percent by weight of the mixture.

Coalescence

[0070] Following aggregation to the desired particle size, with the formation of an optional shell as described above, the particles may then be coalesced to the desired final shape, the

coalescence being achieved by, for example, heating the mixture to a temperature of from about 55°C to about 105°C, in embodiments from about 65°C to about 100°C, in embodiments about 95°C, which may be below the melting point of the crystalline resin to prevent plasticization. Higher or lower temperatures may be used, it being understood that the temperature is a function of the resins used for the binder.

[0071] In embodiments, the pH of the mixture may then be reduced slowly with a buffer system of the present disclosure, as described below in greater detail. The adjustment of the pH may be conducted using a feeding pump to add the buffer system over a certain period of time, in embodiments from about 0.25 hour to about 10 hours, in embodiments from about 0.5 hours to about 5 hours. In embodiments, the pH of the mixture is reduced at a rate of from about 0.005 pH units per minute to about 0.1 pH units per minute, in embodiments of from about 0.01 pH units per minute to about 0.09 pH units per minute.

[0072] In embodiments, as mentioned above, the slow metered addition of a buffer system to the reaction slurry for reducing the pH of the mixture during coalescence, optionally in combination with the use of the little or no chelating agent during coalescence, may provide narrow final toner GSD volume and prevent particle to particle sticking.

[0073] In embodiments, the buffer system may be added to the toner particles at a rate of from about 0.1 grams/minute per 100 grams of dry toner to about 5 grams/minute per 100 grams of dry toner, in embodiments from about 0.5 grams/minute per 100 grams of dry toner to about 4 grams/minute per 100 grams of dry toner.

[0074] Coalescence may proceed and be accomplished over a period of from about 0.05 hours to about 10 hours, in embodiments from about 0.5 hours to about 5 hours.

[0075] After coalescence, the mixture may be cooled to a lower temperature, such as from about 20°C to about 40°C. The cooling may be rapid or slow, as desired. A suitable cooling method 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 method for drying including, for example, freeze-drying.

Buffers

[0076] In embodiments, the buffer system may include at least two of acids, salts, bases, organic compounds, and combinations thereof in a solution with deionized water as the solvent. The buffer may be present in a solution at a concentration from about 1 percent by weight to about 60 percent by weight, in embodiments from about 5 percent by weight to about 50 percent by weight.

[0077] Suitable acids which may be utilized to form the buffer system include, but are not limited to, aliphatic acids and/or aromatic acids such as acetic acid, citric acid, formic acid, oxalic acid, phthalic acid, salicylic acid, combinations thereof, and the like. Suitable salts which may be utilized to form the buffer system include, but are not limited to, metallic salts of aliphatic acids or aromatic acids, such as sodium acetate, sodium acetate trihydrate, potassium acetate, zinc acetate, sodium hydrogen phosphate, potassium formate, sodium oxalate, sodium phthalate, potassium salicylate, combinations thereof, and the like.

[0078] In embodiments, a suitable buffer system may include a combination of acids and salts. For example, in embodiments, a buffer system may include sodium acetate and acetic acid.

[0079] In embodiments, a buffer system of the present disclosure may be in a solution with deionized water as the solvent.

[0080] The amount of acid and salts utilized in forming the buffer system, as well as deionized water utilized in forming a buffer solution, may vary depending upon the acid used, the salt used, and the composition of the toner particles. As noted above, in embodiments a buffer system may include both an acid and a salt. In such a case, the amount of acid in the

buffer system may be from about 1 % by weight to about 40 % by weight of the buffer system, in embodiments from about 2 % by weight to about 30 % by weight of the buffer system. The amount of salt in the buffer system may be from about 10 % by weight to about 60 % by weight of the buffer system, in embodiments from about 20 % by weight of the buffer system to about 50 % by weight of the buffer system.

[0081] The amount of acid and/or salt in the buffer system may be in amounts so that the pH of the buffer system is from about 3 to about 7, in embodiments from about 4 to about 6. The buffer system may be added to the toner slurry as described above so that the pH of the toner slurry is from about 4 to about 7, in embodiments from about 5.8 to about 6.5.

Additives

[0082] In embodiments, the toner particles may also contain other optional additives, as desired or required. For example, the toner may include any known charge additives in amounts of from about 0.1 to about 10 weight percent, and in embodiments of from about 0.5 to about 7 weight percent of the toner. Examples of such charge additives include alkyl pyridinium halides, bisulfates, the charge control additives of U.S. Patent Nos. 3,944,493, 4,007,293, 4,079,014, 4,394,430 and 4,560,635, negative charge enhancing additives like aluminum complexes, and the like.

[0083] Surface additives can be added to the toner compositions of the present disclosure after washing or drying. Examples of such surface additives include, for example, metal salts, metal salts of fatty acids, colloidal silicas, metal oxides, strontium titanates, mixtures thereof, and the like. Surface additives may be present in an amount of from about 0.1 to about 10 weight percent, and in embodiments of from about 0.5 to about 7 weight percent of the toner. Examples of such additives include those disclosed in U.S. Patent Nos. 3,590,000, 3,720,617,

3,655,374 and 3,983,045. Other additives include zinc stearate and AEROSIL R972® available from Degussa. The coated silicas of U.S. Patent Nos. 6,190,815 and 6,004,714, can also be present in an amount of from about 0.05 to about 5 percent, and in embodiments of from about 0.1 to about 2 percent of the toner, which additives can be added during the aggregation or blended into the formed toner product.

[0084] The characteristics of the toner particles may be determined by any suitable technique and apparatus. Volume average particle diameter (D_{50v}), volume average geometric size distribution (GSD_v), and number average geometric size distribution (GSD_n) may be measured by means of a measuring instrument such as a Beckman Coulter Multisizer 3, operated in accordance with the manufacturer's instructions. Representative sampling may occur as follows: a small amount of toner sample, about 1 gram, may be obtained and filtered through a 25 micrometer screen, then put in isotonic solution to obtain a concentration of about 10%, with the sample then run in a Beckman Coulter Multisizer 3.

[0085] Toners produced in accordance with the present disclosure may possess excellent charging characteristics when exposed to extreme relative humidity (RH) conditions. The low-humidity zone (C zone) may be about 10°C/15% RH, while the high humidity zone (A zone) may be about 28°C/85% RH. Toners of the present disclosure may also possess a parent toner charge per mass ratio (Q/M) of from about -3 $\mu\text{C/g}$ to about -35 $\mu\text{C/g}$, and a final toner charging after surface additive blending of from -10 $\mu\text{C/g}$ to about -45 $\mu\text{C/g}$.

[0086] Utilizing the methods of the present disclosure, the toner formulation design may be adjusted so that the levels of glossiness become tunable and the GSD narrow. As noted above, this may be accomplished by reducing the amount of chelating agent in the toner during the aggregation process, combined with slow addition of a buffer system when

reducing pH during the coalescence process. Thus, for example, the gloss level of a toner of the present disclosure may have a gloss as measured in Gardner Gloss Units (ggu) by a Gardner 75° Gloss Meter, of from about 25 ggu to about 85 ggu, in embodiments from about 35 ggu to about 75 ggu.

[0087] In other embodiments, toners of the present disclosure may possess a low gloss of less than about 30 ggu, in embodiments from about 0.1 ggu to about 30 ggu, in embodiments from about 5 ggu to about 25 ggu, in embodiments from about 10 ggu to about 20 ggu.

[0088] In embodiments, toners of the present disclosure may be utilized as ultra low melt (ULM) toners. In embodiments, the dry toner particles, exclusive of external surface additives, may have the following characteristics:

[0089] (1) Volume average diameter of from about 2.5 to about 20 microns, in embodiments from about 2.75 to about 18 microns, in other embodiments from about 3 to about 15 microns.

[0090] (2) Number Average Geometric Standard Deviation (GSDn) and/or Volume Average Geometric Standard Deviation (GSDv) of from about 1.17 to about 1.3, in embodiments from about 1.18 to about 1.28.

[0091] (3) Circularity of from about 0.9 to about 1 (measured with, for example, a Sysmex FPIA 2100 analyzer), in embodiments from about 0.94 to about 0.985, in other embodiments from about 0.95 to about 0.98.

[0092] (4) A minimum fixing temperature of from about 100°C to about 180°C, in embodiments from about 120°C to about 150°C.

Developers

[0093] The toner particles thus formed may be formulated into a developer composition. The toner particles may be mixed with carrier particles to achieve a two-component

developer composition. The toner concentration in the developer may be from about 1% to about 25% by weight of the total weight of the developer, in embodiments from about 2% to about 15% by weight of the total weight of the developer.

Carriers

[0094] Examples of carrier particles that can be utilized for mixing with the toner include those particles that are capable of triboelectrically obtaining a charge of opposite polarity to that of the toner particles. Illustrative examples of suitable carrier particles include granular zircon, granular silicon, glass, steel, nickel, ferrites, iron ferrites, silicon dioxide, and the like. Other carriers include those disclosed in U.S. Patent Nos. 3,847,604, 4,937,166, and 4,935,326.

[0095] The selected carrier particles can be used with or without a coating. In embodiments, the carrier particles may include a core with a coating thereover which may be formed from a mixture of polymers that are not in close proximity thereto in the triboelectric series. The coating may include fluoropolymers, such as polyvinylidene fluoride resins, terpolymers of styrene, methyl methacrylate, and/or silanes, such as triethoxy silane, tetrafluoroethylenes, other known coatings and the like. For example, coatings containing polyvinylidenefluoride, available, for example, as KYNAR 301F™, and/or polymethylmethacrylate, for example having a weight average molecular weight of about 300,000 to about 350,000, such as commercially available from Soken, may be used. In embodiments, polyvinylidenefluoride and polymethylmethacrylate (PMMA) may be mixed in proportions of from about 30 to about 70 weight % to about 70 to about 30 weight %, in embodiments from about 40 to about 60 weight % to about 60 to about 40 weight %. The coating may have a coating weight of, for example, from about 0.1 to about 5% by weight of the carrier, in embodiments from about 0.5 to about 2% by weight of the carrier.

[0096] In embodiments, PMMA may optionally be copolymerized with any desired comonomer, so long as the resulting copolymer retains a suitable particle size. Suitable comonomers can include monoalkyl, or dialkyl amines, such as a dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, diisopropylaminoethyl methacrylate, or t-butylaminoethyl methacrylate, and the like. The carrier particles may be prepared by mixing the carrier core with polymer in an amount from about 0.05 to about 10 percent by weight, in embodiments from about 0.01 percent to about 3 percent by weight, based on the weight of the coated carrier particles, until adherence thereof to the carrier core by mechanical impaction and/or electrostatic attraction.

[0097] Various effective suitable means can be used to apply the polymer to the surface of the carrier core particles, for example, cascade roll mixing, tumbling, milling, shaking, electrostatic powder cloud spraying, fluidized bed, electrostatic disc processing, electrostatic curtain, combinations thereof, and the like. The mixture of carrier core particles and polymer may then be heated to enable the polymer to melt and fuse to the carrier core particles. The coated carrier particles may then be cooled and thereafter classified to a desired particle size.

[0098] In embodiments, suitable carriers may include a steel core, for example of from about 25 to about 100 μm in size, in embodiments from about 50 to about 75 μm in size, coated with about 0.5% to about 10% by weight, in embodiments from about 0.7% to about 5% by weight of a conductive polymer mixture including, for example, methylacrylate and carbon black using the process described in U.S. Patent Nos. 5,236,629 and 5,330,874.

[0099] The carrier particles can be mixed with the toner particles in various suitable combinations. The concentrations are may be from about 1% to about 20% by weight of the toner composition. However, different toner and carrier percentages may be used to achieve a developer composition with desired characteristics.

[00100]

Imaging

[00101] The toners can be utilized for electrophotographic processes, including those disclosed in U.S. Patent No. 4,295,990. In embodiments, any known type of image development system may be used in an image developing device, including, for example, magnetic brush development, jumping single-component development, hybrid scavengless development (HSD), and the like. These and similar development systems are within the purview of those skilled in the art.

[00102] Imaging processes include, for example, preparing an image with an electrophotographic device including a charging component, an imaging component, a photoconductive component, a developing component, a transfer component, and a fusing component. In embodiments, the development component may include a developer prepared by mixing a carrier with a toner composition described herein. The electrophotographic device may include a high speed printer, a black and white high speed printer, a color printer, and the like.

[00103] Once the image is formed with toners/developers via a suitable image development method such as any one of the aforementioned methods, the image may then be transferred to an image receiving medium such as paper and the like. In embodiments, the toners may be used in developing an image in an image-developing device utilizing a fuser member. The fusing member can be of any desired or suitable configuration, such as a drum or roller, a belt or web, a flat surface or platen, or the like. The fusing member can be applied to the image by any desired or suitable method, such as by passing the final recording substrate through a nip formed by the fusing member and a back member, which can be of any desired or effective configuration, such as a drum or roller, a belt or web, a flat surface or platen, or the like. In embodiments, a fuser roll can be used. Fuser roll members are contact fusing devices

that are within the purview of those skilled in the art, in which pressure from the roll, optionally with the application of heat, may be used to fuse the toner to the image-receiving medium. Optionally, a layer of a liquid such as a fuser oil can be applied to the fuser member prior to fusing.

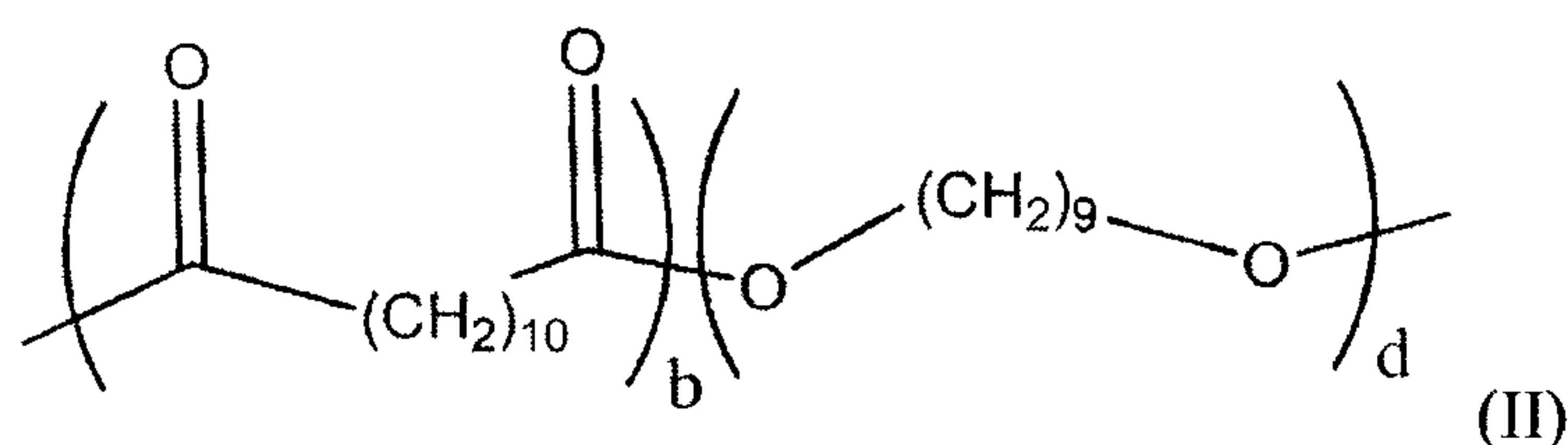
[00104] Toners of the present disclosure may have excellent blocking, i.e., the ability of the toner to resist sticking together during shipping and/or storage.

[00105] 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 30° C.

EXAMPLESCOMPARATIVE EXAMPLE 1

[00106] Preparation of toner without ethylene diamine tetraacetic acid (EDTA).

[00107] About 239.48 grams of a low molecular weight amorphous resin emulsion including an alkoxyated bisphenol A with terephthalic acid, fumaric acid, and dodecenylsuccinic acid co-monomers (about 36.80 % by weight), about 229.50 grams of a high molecular weight amorphous resin emulsion alkoxyated bisphenol A with terephthalic acid, trimellitic acid, and dodecenylsuccinic acid co-monomers (about 38.40% by weight), about 76.85 grams of a crystalline polyester resin emulsion of the following formula:



wherein b was from about 5 to about 2000 and d was from about 5 to about 2000 (about 36.10 % by weight), about 128.27 grams of a styrene acrylate gel latex (about 24.51% by weight), about 144.46 grams cyan Pigment Blue 15:3 (about 16.60% by weight), and about 120.59 grams of IGI wax in a dispersion (about 30.60 % by weight), was added to a 2 liter glass reactor equipped with an overhead mixer. To this mixture, about 199.48 grams of aluminum sulfate (about 1.0 weight %) was added as a flocculent under homogenization by mixing at a speed of from about 3000 to about 4000 rpm for about 10 minutes.

[00108] The toner slurry was then heated to begin aggregation. The toner slurry was heated to about 45.1°C with mixing at a speed of about 370 rpm. During aggregation, the toner particle size was closely monitored with a Coulter Counter until the core particles reached a volume average particle size of about 4.68 micrometers with a GSDv of about 1.22.

A shell including about 155.22 grams of the low molecular weight amorphous resin emulsion (about 50 % by weight) and about 148.75 of the high molecular amorphous weight resin emulsion (about 50 % by weight) utilized in the core was added, resulting in core-shell structured particles with an average particle size of about 5.65 microns and a GSDv of about 1.21.

[00109] Thereafter, the pH of the slurry was adjusted to about 8.5 using sodium hydroxide (NaOH) (about 4 % by weight) to freeze, i.e. stop, the aggregation step.

[00110] After freezing, the reaction mixture was heated to about 95°C while the pH of the toner slurry was reduced quickly to about 6.08 by the addition of a NaAc/HAc (sodium acetate/acetic acid) buffer having a pH of about 5.7, over a period of about 5 minutes, for coalescence. The toner was quenched after coalescence. As shown in FIG. 1, the final toner particle size was about 6.48 microns, the GSDv was about 1.30, and the circularity was about 0.948.

[00111] The toner slurry was then cooled to room temperature, screened through a 25 micron sieve, and the product was filtrated, washed and freeze dried.

COMPARATIVE EXAMPLE 2

[00112] Preparation of toner with 0.5 pph EDTA.

[00113] The same materials, in the same amounts, were utilized to form a toner slurry as described above in Comparative Example 1.

[00114] Again, the toner slurry was heated to about 45.1°C at a stirring speed of about 370 rpm. During aggregation, the toner particle size was closely monitored with a Coulter Counter until the core particles reached a volume average particle size of about 4.94 micrometers with a GSDv of 1.24. A shell as described above in Comparative Example 1

was added, resulting in core-shell structured particles with an average particle size of about 5.65 microns and a GSDv of about 1.21.

[00115] Thereafter, the pH of the slurry was adjusted to about 8.5 using sodium hydroxide (NaOH) (about 4 % by weight) and about 5.13 grams of EDTA (about 39 % by weight) to freeze, i.e. stop, the aggregation step.

[00116] After freezing, the reaction mixture was heated to about 95°C while the pH of the toner slurry was reduced quickly to about 6 by the addition of a NaAc/HAc (sodium acetate/acetic acid) buffer having a pH of about 5.7, over a period of about 5 minutes, for coalescence. The toner was quenched after coalescence. As shown in FIG. 2, the final toner particle size was about 6.02 microns, the GSDv was about 1.34, and the circularity was about 0.948.

[00117] The toner slurry was then cooled to room temperature, screened through a 25 micron sieve, and the product was filtrated, washed and freeze dried.

COMPARATIVE EXAMPLE 3

[00118] Preparation of toner with 0.7 pph EDTA and 1 pph extra DOWFAX® 2A1, an alkyldiphenyloxide disulfonate, before pH reduction.

[00119] The same materials, in the same amounts, were utilized to form the toner slurry as described above in Comparative Example 1.

[00120] Again the toner slurry was heated to about 45.1°C at a stirring speed of about 370 rpm. During aggregation, the toner particle size was closely monitored with a Coulter Counter until the core particles reached a volume average particle size of about 5.04 micrometers with a GSDv of 1.28. A shell as described above in Comparative Example 1 was added, resulting in core-shell structured particles with an average particle size of about 5.65 microns and a GSDv of about 1.21.

[00121] Thereafter, the pH of the slurry was adjusted to about 8.5 using sodium hydroxide (NaOH) (about 4 % by weight) and about 7.69 grams of EDTA (about 39 % by weight) to freeze, i.e. stop, the aggregation step.

[00122] After freezing, the reaction mixture was heated to about 95°C while the pH of the toner slurry was reduced quickly to about 6 by the addition of a NaAc/HAc (sodium acetate/acetic acid) buffer having a pH of about 5.7, over a period of about 5 minutes, for coalescence. Thereafter, about 8.56 grams of DOWFAX®2A1, an alkyldiphenyloxide disulfonate (commercially available from the Dow Chemical Company) was introduced to the reaction mixture. The toner was quenched after coalescence. As shown in FIG. 3, the final toner particle size was about 6.02 microns, the GSDv was about 1.30, and the circularity was about 0.972.

[00123] The toner slurry was then cooled to room temperature, screened through a 25 micron sieve, and the product was filtrated, washed and freeze dried.

EXAMPLE 1

[00124] Preparation of toner without EDTA.

[00125] About 245.82 grams of the low molecular weight amorphous resin emulsion described above in Comparative Example 1 (about 36.12 % by weight), about 231.22 grams of the high molecular weight amorphous resin emulsion described above in Comparative Example 1 (about 38.40% by weight), about 78.61 grams of the crystalline polyester resin emulsion described above in Comparative Example 1 (about 35.56 % by weight), about 129.24 grams of a styrene acrylate gel latex (about 24.51% by weight), about 145.54 grams cyan Pigment Blue 15:3 (about 16.60% by weight), and about 121.49 grams of IGI wax in a dispersion (about 30.60 % by weight) was added to a 2 liter glass reactor equipped with an overhead mixer. To this mixture, about 200.98 grams of aluminum sulfate (about 1.0 weight

%) was added as a flocculent under homogenization by mixing at a speed of from about 3000 to about 4000 rpm for about 10 minutes.

[00126] The toner slurry was then heated to begin aggregation. The toner slurry was heated to about 44.2°C at a stirring speed of about 370 rpm. During aggregation, the toner particle size was closely monitored with a Coulter Counter until the core particles reached a volume average particle size of about 4.78 micrometers with a GSDv of 1.25. A shell including about 159.33 grams of the low molecular weight amorphous resin emulsion (about 50 % by weight) and about 149.87 of the high molecular amorphous weight resin emulsion (about 50 % by weight) utilized in the core was added, resulting in core-shell structured particles with an average particle size of about 5.65 microns and a GSDv of about 1.21.

[00127] Thereafter, the pH of the slurry was adjusted to about 8.5 using sodium hydroxide (NaOH) (about 4 % by weight) to freeze, i.e. stop, the aggregation step.

[00128] After freezing, the reaction mixture was heated to about 95°C while the pH of the toner slurry was slowly reduced to about 6.05 by the addition of a pH 5.7 NaAc/HAc (sodium acetate/acetic acid) buffer, over about 1 hour, at about 95°C using a feeding pump, for coalescence. The toner was quenched after coalescence. As shown in FIG. 4, the final toner particle size was about 6.48 microns, the GSDv was about 1.23, and the circularity was about 0.966.

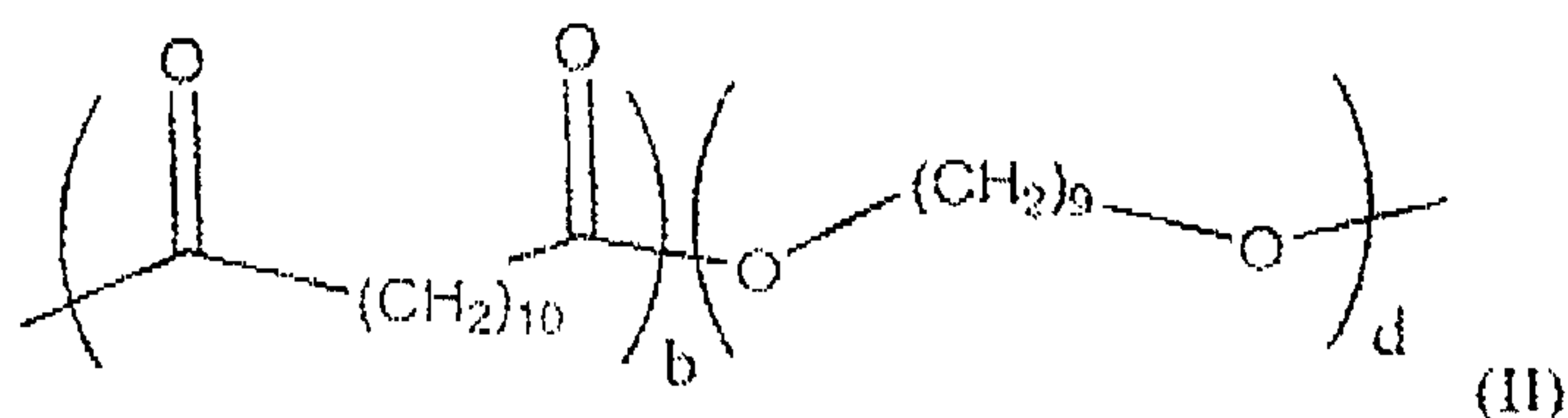
[00129] The toner slurry was then cooled to room temperature, screened through a 25 micron sieve, and the product was filtrated, washed and freeze dried.

[00130] It will be appreciated that various of the above-disclosed and other features and functions, or alternatives thereof, may be desirably combined into many other different systems or applications. Also that various alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art which are also intended to be encompassed by the invention. Unless

specifically recited in a claim, steps or components of claims should not be implied or imported from the specification or any other claims as to any particular order, number, position, size, shape, angle, color, or material.

WHAT IS CLAIMED IS:

1. A process for preparing low gloss, low melt toner particles comprising:
 - contacting at least one amorphous resin with at least one crystalline resin and optionally one styrene/acrylate gel in a mixture;
 - aggregating the mixture to form particles;
 - adding a buffer having a pH of from about 3 to about 7 to the particles to lower the pH of the particles by metered addition to reach a desired reduced pH over a period of from about 0.25 hours to about 10 hours at a rate of from about 0.005 pH units per minute to about 0.1 pH unit per minute; and
 - coalescing the particles to form the low gloss, low melt toner particles.
2. The process according to claim 1, further comprising adding a chelating agent in an amount from about 0.01 pph to about 0.75 pph.
3. The process according to claim 1, wherein the at least one amorphous resin comprises at least one amorphous polyester resin including an alkoxyated bisphenol A fumarate/terephthalate based polyester or copolyester resin, and the at least one crystalline polyester resin is of the formula



wherein b is from about 5 to about 2000 and d is from about 5 to about 2000.

4. A process according to claim 1, wherein adding the buffer solution to the particles includes adding the buffer at a rate of from about 0.1 grams/minute per 100 grams of dry toner to about 5 grams/minute per 100 grams of dry toner.
5. A process according to claim 1, wherein the buffer comprises acids selected from the group consisting of acetic acid, citric acid, formic acid, oxalic acid, phthalic acid,

salicylic acid, and combinations thereof, salts selected from the group consisting of sodium acetate, sodium acetate trihydrate, potassium acetate, zinc acetate, sodium hydrogen phosphate, potassium formate, sodium oxalate, sodium phthalate, potassium salicylate, and combinations thereof, and wherein the desired pH is from about 4 to about 7.

6. A process according to claim 1, wherein the buffer is present in a solution at a concentration from about 1 percent by weight to about 60 percent by weight.

7. A process according to claim 1, wherein the toner has a gloss from about 0.1 ggu to about 30 ggu.

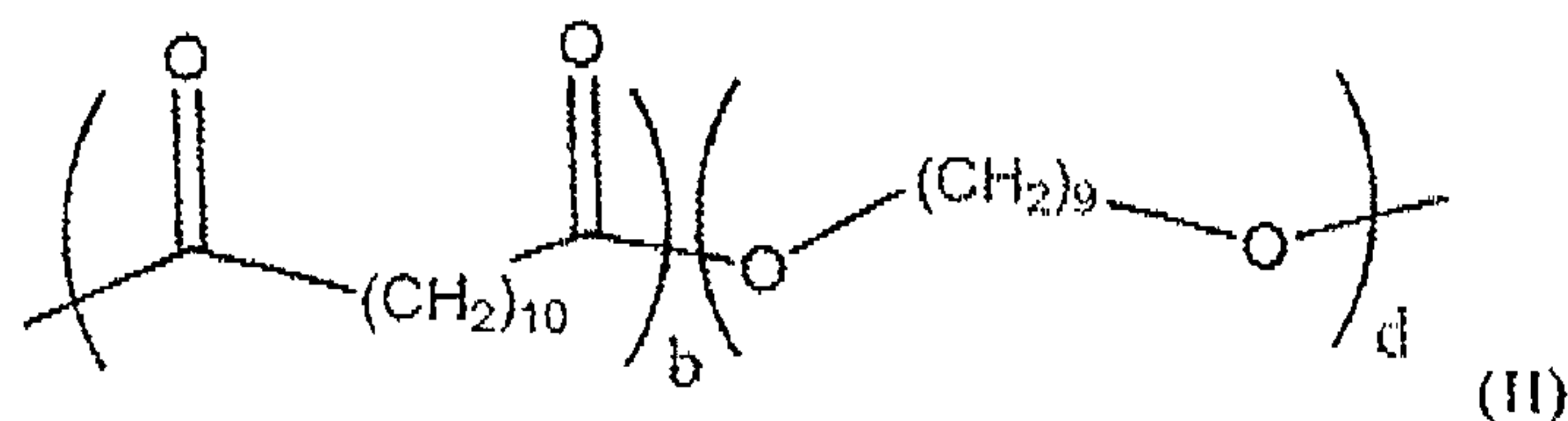
8. A process for preparing low gloss, low melt toner particles comprising:
 contacting at least one amorphous resin with at least one crystalline resin
 and optionally one styrene/acrylate gel in a mixture;
 aggregating the mixture to form core particles;
 contacting the core particles with an emulsion comprising at least one
 amorphous resin to form a shell over the particles to form core/shell particles;
 slowly adding a buffer drop wise to the core/shell particles to reach a desired
 reduced pH at a rate of from about 0.1 grams/minute per 100 grams of dry toner to about 5
 grams/minute per 100 grams of dry toner; and
 coalescing the particles to form the low gloss, low melt toner particles.

9. A process according to claim 8, wherein the desired pH is from about 4 to about 7.

10. A process according to claim 8, wherein the at least one amorphous resin includes a low molecular weight amorphous resin and high molecular weight amorphous resin.

11. A process according to claim 8, wherein the at least one amorphous resin comprises at least one amorphous polyester resin including an alkoxyated bisphenol A

fumarate/terephthalate based polyester or copolyester resin, and the at least one crystalline polyester resin is of the formula



wherein b is from about 5 to about 2000 and d is from about 5 to about 2000.

12. A process according to claim 8, wherein the buffer comprises acids selected from the group consisting of acetic acid, citric acid, formic acid, oxalic acid, phthalic acid, salicylic acid, and combinations thereof, salts selected from the group consisting of sodium acetate, sodium acetate trihydrate, potassium acetate, zinc acetate, sodium hydrogen phosphate, potassium formate, sodium oxalate, sodium phthalate, potassium salicylate, and combinations thereof.

13. A process according to claim 8, wherein the buffer is present in a solution at a concentration from about 1 percent by weight to about 60 percent by weight.

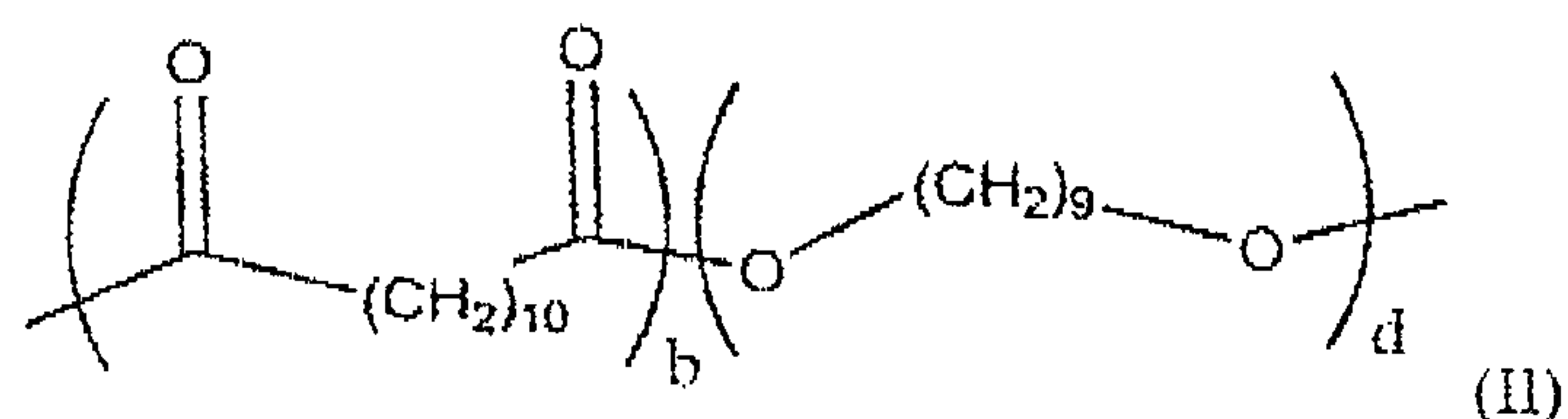
14. A process according to claim 8, wherein the shell includes at least one amorphous polyester resin present in an amount from about 10 percent to about 90 percent by weight of the shell.

15. A process for preparing low gloss, low melt toner particles comprising:

- contacting at least one amorphous resin with at least one crystalline resin and optionally one styrene/acrylate gel in a mixture;
- aggregating the mixture to form core particles;
- contacting the core particles with an emulsion comprising at least one amorphous resin to form a shell over the particles to form core/shell particles;
- slowly adding a buffer system drop wise to the core/shell particles to reach a desired reduced pH from about 4 to about 7, at a rate of from about 0.1 grams/minute per 100 grams of dry toner to about 5 grams/minute per 100 grams of dry toner; and

coalescing the core/shell particles to form low gloss, low melt toner particles.

16. A process according to claim 15, wherein the at least one amorphous resin comprises at least one amorphous polyester resin including an alkoxyated bisphenol A fumarate/terephthalate based polyester or copolyester resin, and the at least one crystalline polyester resin is of the formula



wherein b is from about 5 to about 2000 and d is from about 5 to about 2000.

17. A process according to claim 15, wherein the buffer system comprises acids selected from the group consisting of acetic acid, citric acid, formic acid, oxalic acid, phthalic acid, salicylic acid, and combinations thereof, salts selected from the group consisting of sodium acetate, sodium acetate trihydrate, potassium acetate, zinc acetate, sodium hydrogen phosphate, potassium formate, sodium oxalate, sodium phthalate, potassium salicylate, and combinations thereof.

18. A process according to claim 15, wherein the buffer is present in a solution at a concentration from about 1 percent by weight to about 60 percent by weight.

19. A process according to claim 15, wherein the shell includes at least one amorphous polyester resin present in an amount from about 10 percent to about 90 percent by weight of the shell.

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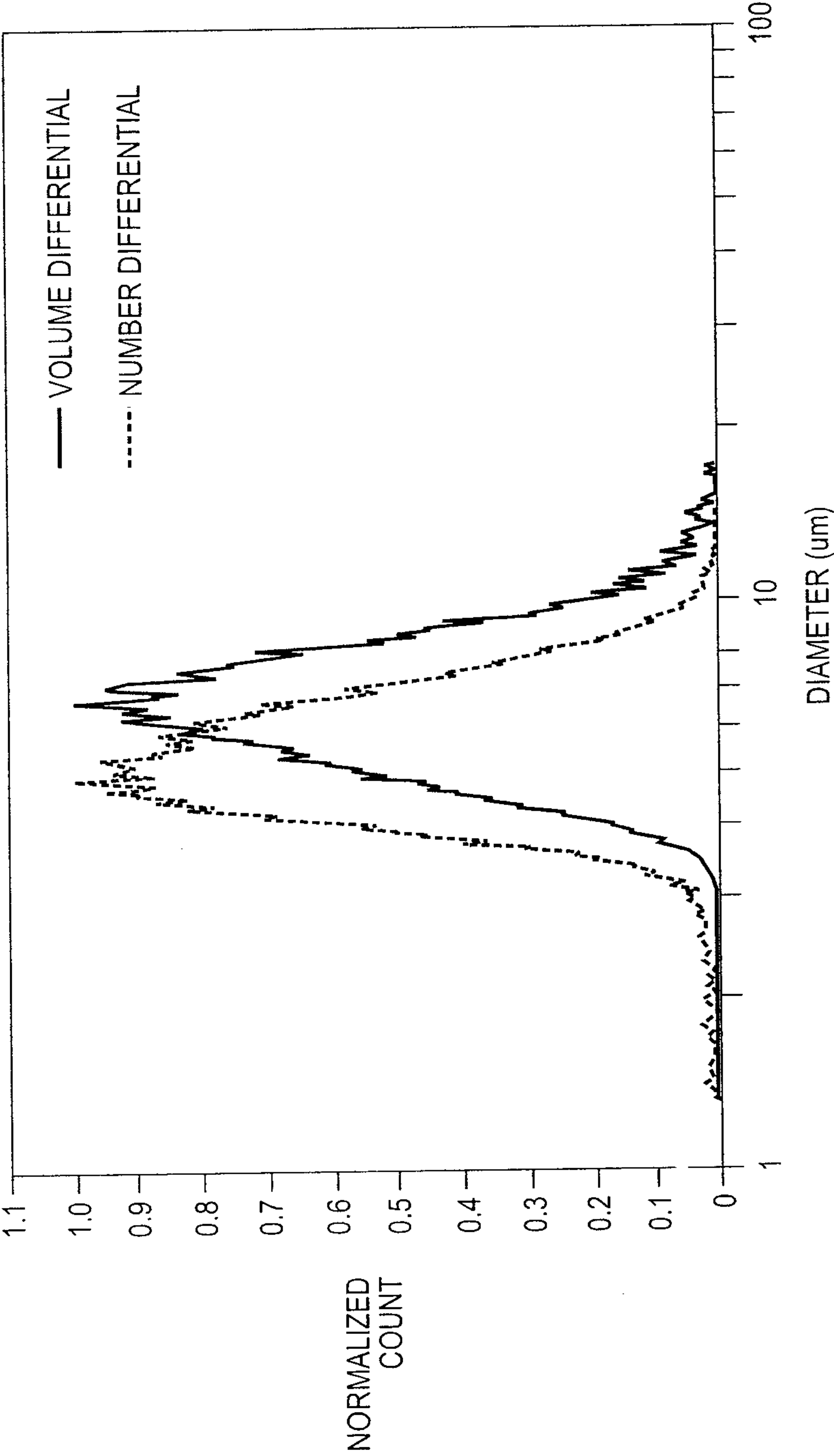


FIG. 1

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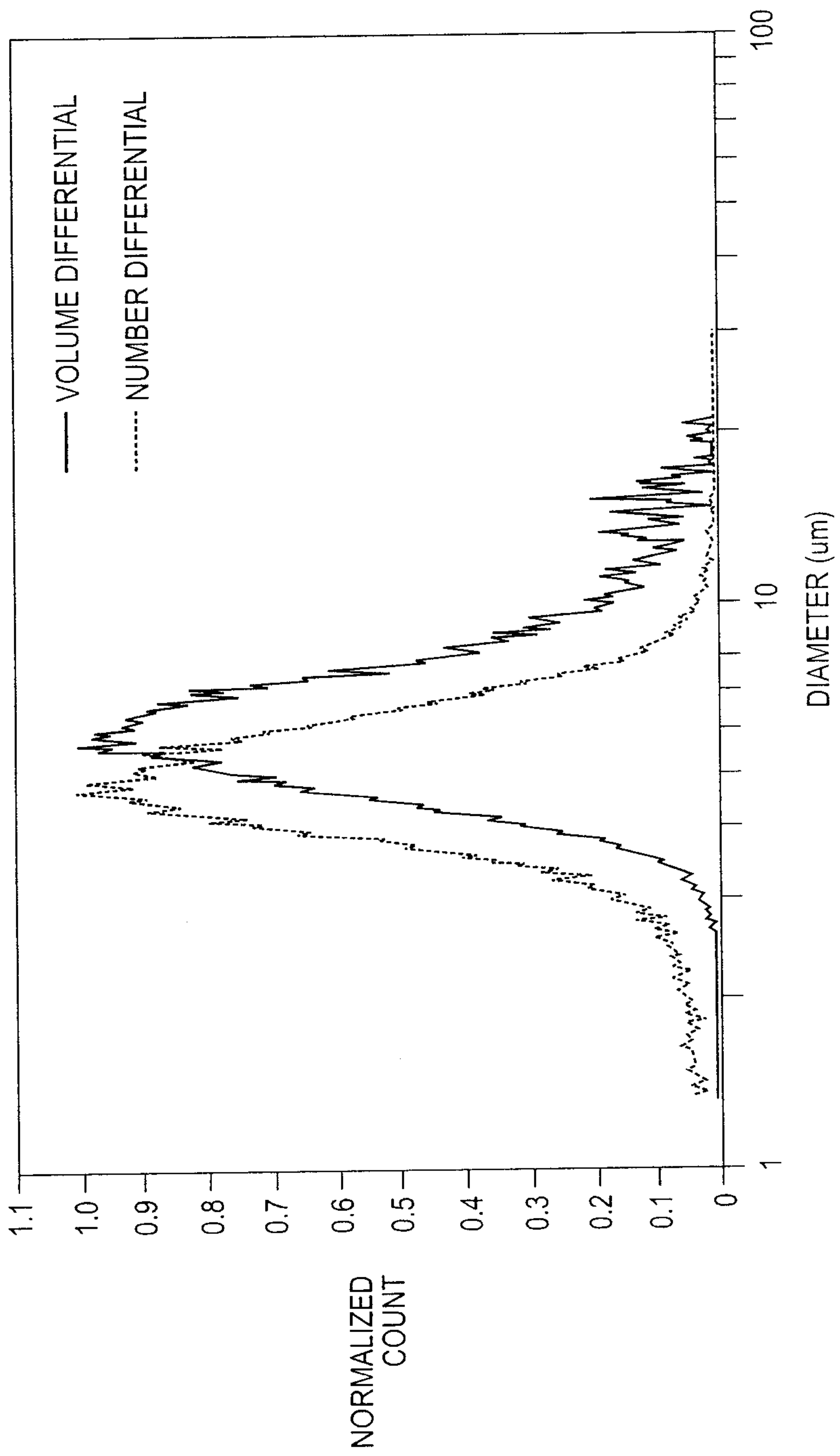


FIG. 2

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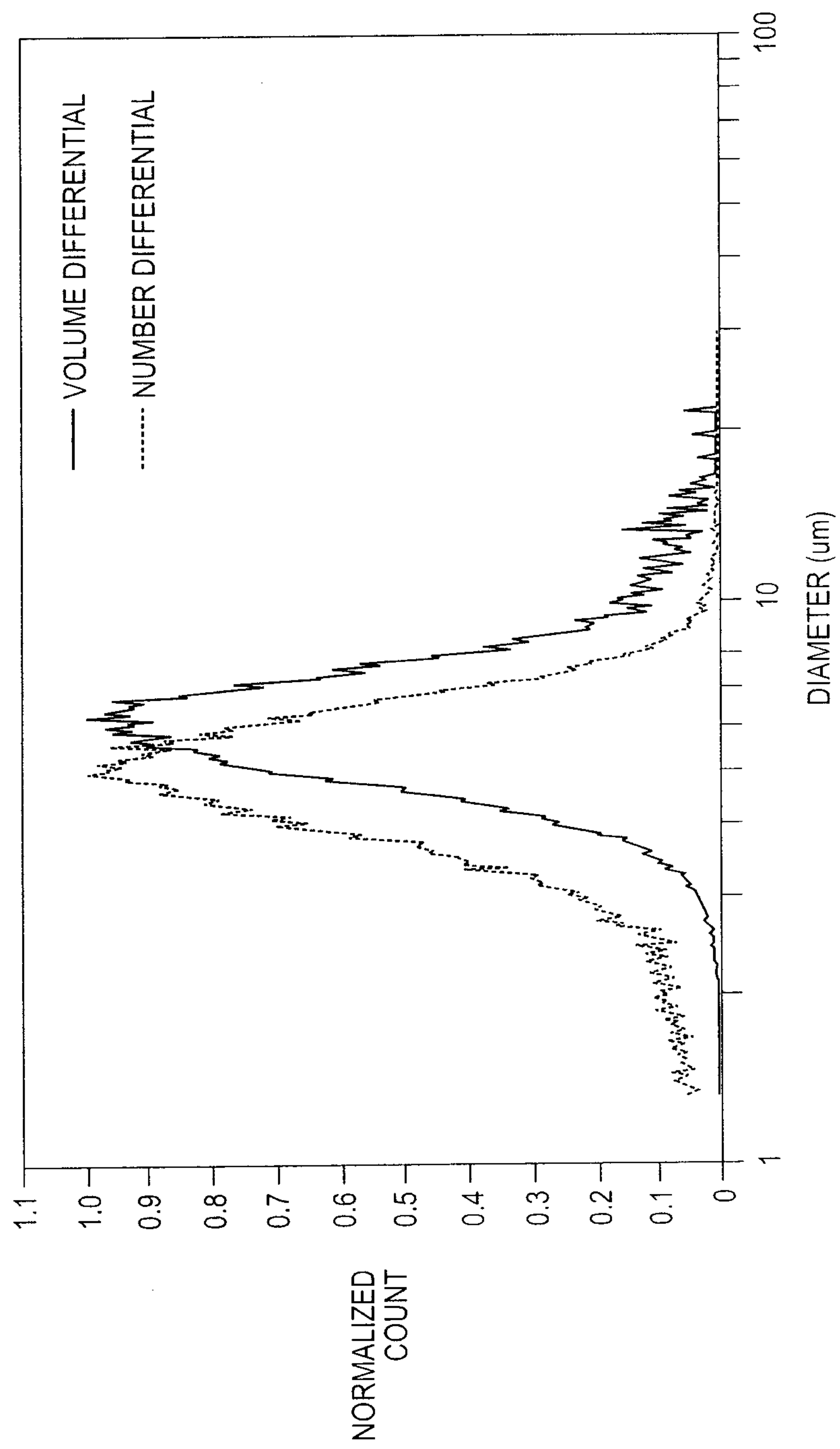


FIG. 3

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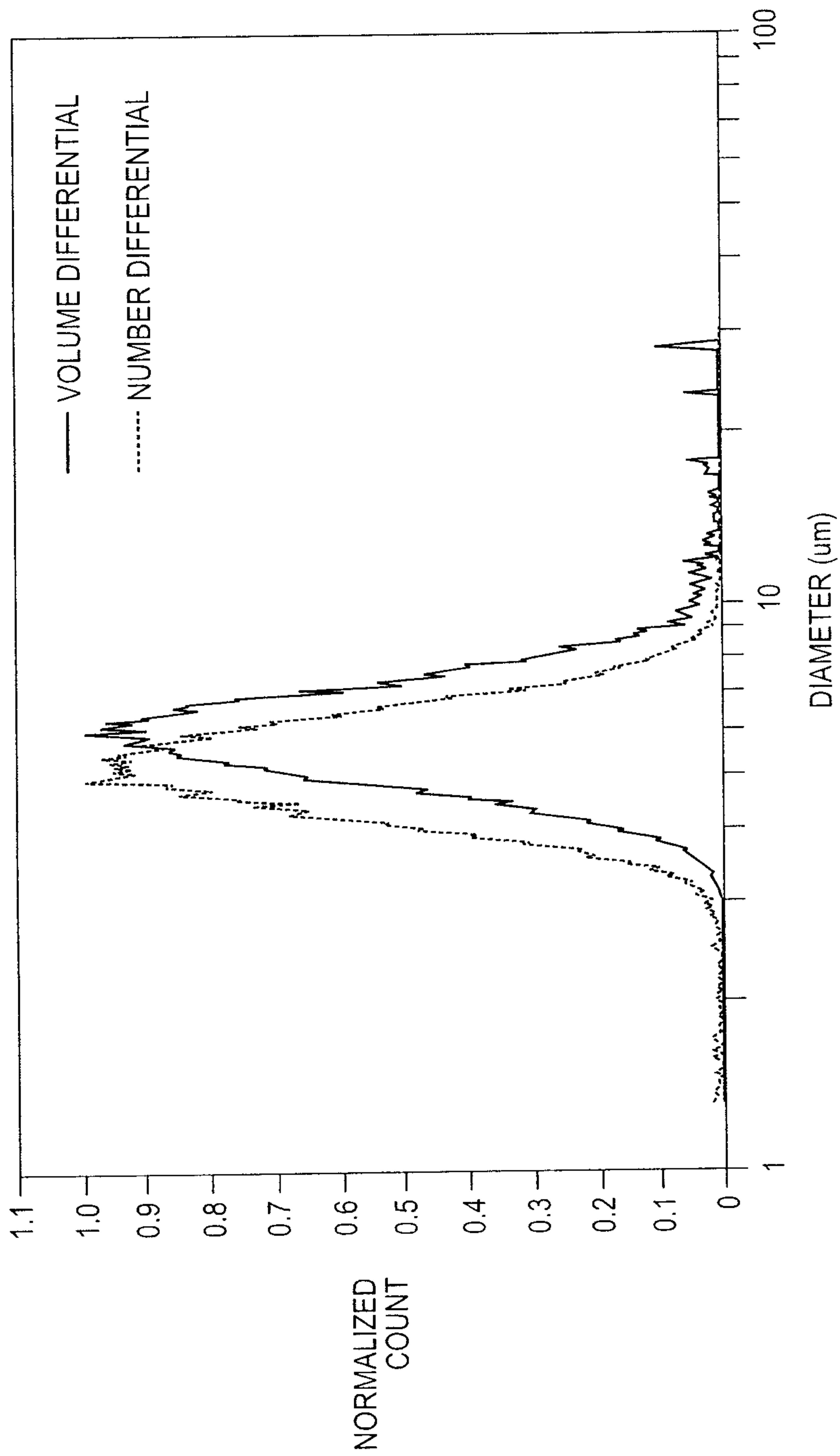


FIG. 4