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Canadian Intellectual Property Office

CA 2869876 C 2018/03/06

(11)(21) **2 869 876**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

(22) Date de dépôt/Filing Date: 2014/11/04
(41) Mise à la disp. pub./Open to Public Insp.: 2015/05/11
(45) Date de délivrance/Issue Date: 2018/03/06
(30) Priorité/Priority: 2013/11/11 (US14/077,024)

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

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(54) Titre : TONER A TRES FAIBLE POINT DE FUSION COMPORTANT DES PLASTIFIANTS A PETITES MOLECULES
(54) Title: SUPER LOW MELT TONER HAVING SMALL MOLECULE PLASTICIZERS

(57) Abrégé/Abstract:
An emulsion aggregation (EA) toner includes an amorphous polymeric resin, optionally a colorant, and a small molecule crystalline organic compound having molecular weight less than 1,000 g/mol and melting point less than the fusing temperature of the EA toner, wherein a mixture of the resin and the small molecule compound is characterized by a reduction in glass transition temperature from that of the resin and by the lack of a significant solid to liquid phase transition peak for the small molecule compound as determined by differential scanning calorimetry, the enthalpy of fusion for the small molecule compound in the mixture being measured to be less than 10% of the enthalpy of fusion of the compound in pure form. Furthermore, the EA toner may be configured to have a crease fix minimum fusing temperature (MFT) less than or equal to the crease fix MFT of a benchmark ultra-low-melt emulsion aggregation toner.

ABSTRACT

An emulsion aggregation (EA) toner includes an amorphous polymeric resin, optionally a colorant, and a small molecule crystalline organic compound having molecular weight less than 1,000 g/mol and melting point less than the fusing temperature of the EA toner, wherein a mixture of the resin and the small molecule compound is characterized by a reduction in glass transition temperature from that of the resin and by the lack of a significant solid to liquid phase transition peak for the small molecule compound as determined by differential scanning calorimetry, the enthalpy of fusion for the small molecule compound in the mixture being measured to be less than 10% of the enthalpy of fusion of the compound in pure form. Furthermore, the EA toner may be configured to have a crease fix minimum fusing temperature (MFT) less than or equal to the crease fix MFT of a benchmark ultra-low-melt emulsion aggregation toner.

SUPER LOW MELT TONER HAVING SMALL MOLECULE PLASTICIZERS

TECHNICAL FIELD

[0001] The presently disclosed embodiments are generally directed to toner compositions that include small molecule plasticizers. More specifically, the presently disclosed embodiments are directed to toner compositions that include small molecule crystalline organic compounds which are compatible with toner binder resins to provide low crease fix minimum fusing temperature.

BACKGROUND

[0002] Electrophotography, which is a method for visualizing image information by forming an electrostatic latent image, is currently employed in various fields. The term "electrostatographic" is generally used interchangeably with the term "electrophotographic." In general, electrophotography comprises the formation of an electrostatic latent image on a photoreceptor, followed by development of the image with a developer containing a toner, and subsequent transfer of the image onto a transfer material such as paper or a sheet, and fixing the image on the transfer material by utilizing heat, a solvent, pressure and/or the like to obtain a permanent image.

[0003] Crease fix Minimum Fusing Temperature (MFT) is a measurement used to determine the performance and energy efficiency of a particular toner in combination with a specific paper type and a specific fuser (which fixes the toner on the paper). Crease fix MFT is measured by folding the paper across a solid fill area of an image and then rolling a defined mass across the folded area. The paper can also be folded using a commercially available folder such as the Duplo D-590 paper folder. A plurality of sheets of paper with images that have been fused over a wide range of fusing temperatures are prepared. The sheets of paper are then unfolded and toner that has been loosened from the sheet of paper is wiped from the surface. Optical comparison of the crease area is then made to a reference chart which provides a definition of an acceptable level of toner adhesion; alternatively, the crease area may be quantified by computer image analysis. The smaller the area which has lost toner, the better the toner adhesion, and the temperature required to achieve an acceptable level of adhesion is defined as the crease fix MFT.

[0004] Currently, Ultra-Low-Melt (ULM) emulsion aggregation (EA) toners, such as described in U.S. Pat. No. 7,547,499 for example, have benchmark crease fix MFT of approximately -20 °C relative to styrene/acrylate EA toners. This improved crease fix MFT performance enables a reduction in fuser energy and enhanced fuser life when compared with EA toners. There is a desire to reduce the MFT even further, by an additional 10°C to 20°C, for example.

BRIEF SUMMARY

[0005] In embodiments, there is provided an emulsion aggregation (EA) toner comprising: an amorphous polymeric resin; optionally a colorant; and a small molecule crystalline organic compound having a molecular weight of less than 1,000 g/mol, and a melting point that is less than the fusing temperature of the emulsion aggregation toner; wherein a mixture of the amorphous polymeric resin and the small molecule crystalline organic compound is characterized by a reduction in glass transition temperature from that of the amorphous resin and by the lack of a significant solid to liquid phase transition peak for the small molecule crystalline organic compound as determined by differential scanning calorimetry, the enthalpy of fusion for the small molecule crystalline organic compound in the mixture being measured to be less than 10% of the enthalpy of fusion of the small molecule crystalline organic compound in pure form.

[0006] Another embodiment provides a method for making emulsion aggregation toner particles comprising: admixing polymeric amorphous resin emulsion, optionally at least one colorant emulsion, an optional wax emulsion, and a small molecule crystalline organic compound emulsion, the small molecule crystalline organic compound having a molecular weight of less than 1,000 g/mol and a melting point that is less than the fusing temperature of the emulsion aggregation toner particles, to form a composite emulsion; and adding an aggregating agent to the composite emulsion to form emulsion aggregation toner particles; wherein a mixture of the amorphous resin and the small molecule crystalline organic compound is characterized by a reduction in glass transition temperature from that of the polymeric amorphous resin and by the lack of a significant solid to liquid phase transition peak for the small molecule crystalline organic compound as determined by differential scanning calorimetry, the enthalpy of fusion for the small molecule crystalline organic compound in the mixture being measured to be less than 10% of the enthalpy of fusion of the small molecule crystalline organic compound in pure form.

[0006a] In accordance with an aspect, there is provided an emulsion aggregation (EA) toner comprising:

an amorphous polymeric resin;

optionally a colorant; and

a small molecule crystalline organic compound being selected from the group consisting of small molecule crystalline aromatic ethers having the formula

$$R_1{-}O{-}[(CH_2)_2O]_p{-}R_2,$$

wherein R_1 and R_2 are independently selected from the group consisting of an alkyl group, an arylalkyl group, an alkylaryl group, and an aromatic group, wherein at least one of R_1 and R_2 is an aromatic group, and wherein p is 0 or 1;

wherein a mixture of the amorphous polymeric resin and the small molecule crystalline organic compound is characterized by a reduction in glass transition temperature from that of the amorphous polymeric resin and by the lack of a significant solid to liquid phase transition peak for the small molecule crystalline organic compound as determined by differential scanning calorimetry, the enthalpy of fusion for the small molecule crystalline organic compound in the mixture being measured to be less than 10% of the enthalpy of fusion of the small molecule crystalline organic compound in pure form.

[0006b] In accordance with an aspect, there is provided a method for making emulsion aggregation toner particles comprising:

admixing polymeric amorphous resin emulsion, optionally at least one colorant emulsion, an optional wax emulsion, and a small molecule crystalline organic compound emulsion, the small molecule crystalline organic compound being selected from the group consisting of small molecule crystalline aromatic ethers having the formula

$$R_1{-}O{-}[(CH_2)_2O]_p{-}R_2,$$

wherein R_1 and R_2 are independently selected from the group consisting of an alkyl group, an arylalkyl group, an alkylaryl group, and an aromatic group, wherein at least one of R_1 and R_2 is an aromatic group, and wherein p is 0 or 1; and

adding an aggregating agent to the composite emulsion to form emulsion aggregation toner particles;

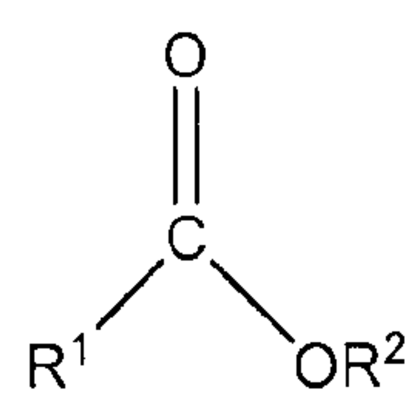
wherein a mixture of the amorphous resin and the small molecule crystalline organic compound is characterized by a reduction in glass transition temperature from that of the polymeric amorphous resin and by the lack of a significant solid to liquid phase transition peak for the small molecule crystalline organic compound as determined by differential scanning calorimetry, the enthalpy of fusion for the small molecule crystalline organic compound in the mixture being measured to be less than 10% of the enthalpy of fusion of the small molecule crystalline organic compound in pure form.

[0006c] In accordance with an aspect, there is provided an emulsion aggregation (EA) toner comprising:

an amorphous polymeric resin;

optionally a colorant; and

a small molecule crystalline organic compound being selected from the group consisting of small molecule crystalline monoesters having the formula:



wherein R^1 and R^2 are aromatic groups;

wherein a mixture of the amorphous polymeric resin and the small molecule crystalline organic compound is characterized by a reduction in glass transition temperature from that of the amorphous polymeric resin and by the lack of a significant solid to liquid phase transition peak for the small molecule crystalline organic compound as determined by differential scanning calorimetry, the enthalpy of fusion for the small molecule crystalline organic compound in the mixture being measured to be less than 10% of the enthalpy of fusion of the small molecule crystalline organic compound in pure form.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1 is a differential scanning calorimetry (DSC) curve of melt mixed di-tert-butyl isophthalate and an amorphous polyester resin;

[0008] Figure 2 is a DSC curve of melt mixed isophthalic acid, di-phenyl ester and an amorphous polyester resin;

[0009] Figure 3 is a DSC curve of melt mixed terephthalic acid, di-stearyl ester and an amorphous polyester resin;

[0010] Figure 4 is a differential scanning calorimetry (DSC) curve of benzyl 2-naphthyl ether;

[0011] Figure 5 is a DSC curve of melt mixed benzyl 2-naphthyl ether and an amorphous polyester resin;

[0012] Figures 6 & 7 are differential scanning calorimetry (DSC) curves 2-naphthyl benzoate, after first heating and cooling, and after second heating, respectively;

[0013] Figure 8 is a DSC curve of melt mixed 2-naphthyl benzoate and an amorphous polyester resin;

[0014] Figure 9 is a plot of gloss as a function of fuser roll temperature for a toner comprising N-benzyl phthalimide;

[0015] Figure 10 is a plot of crease area as a function of fuser roll temperature for determining the crease fix MFT of a toner comprising N-benzyl phthalimide;

[0016] Figure 11 is a plot of gloss as a function of fuser roll temperature for a toner comprising benzyl 2-naphthyl ether;

[0017] Figure 12 is a plot of crease area as a function of fuser roll temperature for determining the crease fix MFT of a toner comprising benzyl 2-naphthyl ether;

[0018] Figure 13 is a plot of crease area as a function of fuser roll temperature for determining the crease fix MFT of a toner comprising 2-naphthyl benzoate; and

[0019] Figure 14 is a plot of gloss as a function of fuser roll temperature for a toner comprising 2-naphthyl benzoate.

DETAILED DESCRIPTION

[0020] In accordance with the present disclosure, emulsion aggregation (EA) toners are provided which include small molecule crystalline organic compounds. In embodiments, the toner may comprise small molecule crystalline organic compounds and an amorphous polymeric resin, wherein a mixture of the amorphous polymeric resin and the small molecule crystalline organic compound is characterized by a reduction in glass transition temperature from that of the amorphous polymeric resin and by the lack of a significant solid to liquid phase transition peak for the small molecule crystalline organic compound as determined by differential scanning calorimetry. For example, the lack of a significant solid to liquid phase transition peak may be demonstrated by the enthalpy of fusion for the small molecule crystalline organic compound in the mixture being measured to be less than 20% of its original value, in embodiments less than 10% of its original value, and in some embodiments less than 5% of its original value, said original value representing the enthalpy of fusion for the small molecule when measured independently; this characterizes compatibility of the small molecule crystalline organic compounds with the amorphous polymeric resin. Furthermore, in some embodiments the small molecule crystalline organic compounds may have a melting point that is less than the fusing temperature of the EA toner. According to some embodiments, emulsion aggregation toners comprising small molecule crystalline organic compounds may achieve crease fix MFT at least comparable to nominal ULM EA toners, such as the Xerox® 700 Digital Color Press (DCP) toner available from Xerox Corp., for example, if not lower, by at least 5°C, or by 10°C to 20°C, for example.

[0021] **Resins**

[0022] Any toner resin may be utilized in the processes of the present disclosure. Such resins, in turn, may be made of any suitable monomer or monomers via any suitable polymerization method. In embodiments, the resin may be prepared by a method other than emulsion polymerization. In further embodiments, the resin may be prepared by condensation polymerization.

[0023] In embodiments, the resin may be a polyester, polyimide, polyolefin, polyamide, polycarbonate, epoxy resin, and/or copolymers thereof. In embodiments, the resin may be an amorphous resin, a crystalline resin, and/or a mixture of crystalline and amorphous resins. The crystalline resin may be present in the mixture of crystalline and amorphous resins, for example, in an amount of from 0 to about 50 percent by weight of the total toner resin, in embodiments from 5 to about 35 percent by weight of the toner resin. The amorphous resin may be present in the mixture, for example, in an amount of from about 50 to about 100 percent by weight of the total toner resin, in embodiments from 95 to about 65 percent by weight of the toner resin.

[0024] In embodiments, the amorphous resin may be selected from the group consisting of polyester, a polyamide, a polyimide, a polystyrene-acrylate, a polystyrene-methacrylate, a polystyrene-butadiene, or a polyester-imide, and mixtures thereof. In embodiments, the crystalline resin may be selected from the group consisting of polyester, a polyamide, a polyimide, a polyethylene, a polypropylene, a polybutylene, a polyisobutyrate, an ethylene-propylene copolymer, or an ethylene-vinyl acetate copolymer, and mixtures thereof. In further embodiments, the resin may be a polyester crystalline and/or a polyester amorphous resin. In embodiments, the polymer utilized to form 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 as described in U.S. Patent No. 6,830,860.

[0025] 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, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,12-dodecanediol, 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.

[0026] 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.

[0027] Examples of crystalline resins include polyesters, polyamides, polyimides, polyolefins, polyethylene, polybutylene, polyisobutyrate, ethylene-propylene copolymers, ethylene-vinyl acetate copolymers, polypropylene, mixtures thereof, and 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), 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-decanedioate), poly-(ethylene-decanedioate), poly-(ethylene-dodecanedioate), poly(nonylene-sebacate), poly (nonylene-decanedioate), poly(nonylene-dodecanedioate), poly(decylene-dodeanedioate), copoly(ethylene-fumarate)-copoly(ethylene-sebacate), copoly(ethylene-fumarate)-copoly(ethylene-decanedioate), and copoly(ethylene-fumarate)-copoly(ethylene-dodecanedioate). The crystalline resin, when utilized, may be present, for example, in an amount of from about 5 to about 50 percent by weight of the toner components, in embodiments from about 10 to about 35 percent by weight of the toner components.

[0028] The crystalline resin can 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 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 3,000 to about 80,000, as determined by Gel Permeation Chromatography 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 2 to about 4.

[0029] Examples of diacid or diesters selected for the preparation of amorphous polyesters include dicarboxylic acids or diesters such as terephthalic acid, phthalic acid, isophthalic acid, fumaric acid, maleic acid, succinic acid, itaconic acid, succinic acid, succinic anhydride, dodecenylsuccinic acid, dodecenylsuccinic anhydride, glutaric acid, glutaric anhydride, adipic acid, pimelic acid, suberic acid, azelaic acid, dodecanedioic acid, dimethyl terephthalate, diethyl terephthalate, dimethyl isophthalate, diethyl isophthalate, dimethyl phthalate, phthalic anhydride, diethyl phthalate, dimethyl succinate, dimethyl fumarate, dimethyl maleate, dimethyl glutarate, dimethyl adipate, dimethyl dodecenylsuccinate, and 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 55 mole percent of the resin, in embodiments from about 45 to about 53 mole percent of the resin.

[0030] Examples of diols utilized in generating the amorphous polyester 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, dipropylene glycol, dibutylene glycol, and combinations thereof. The amount of organic diol 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.

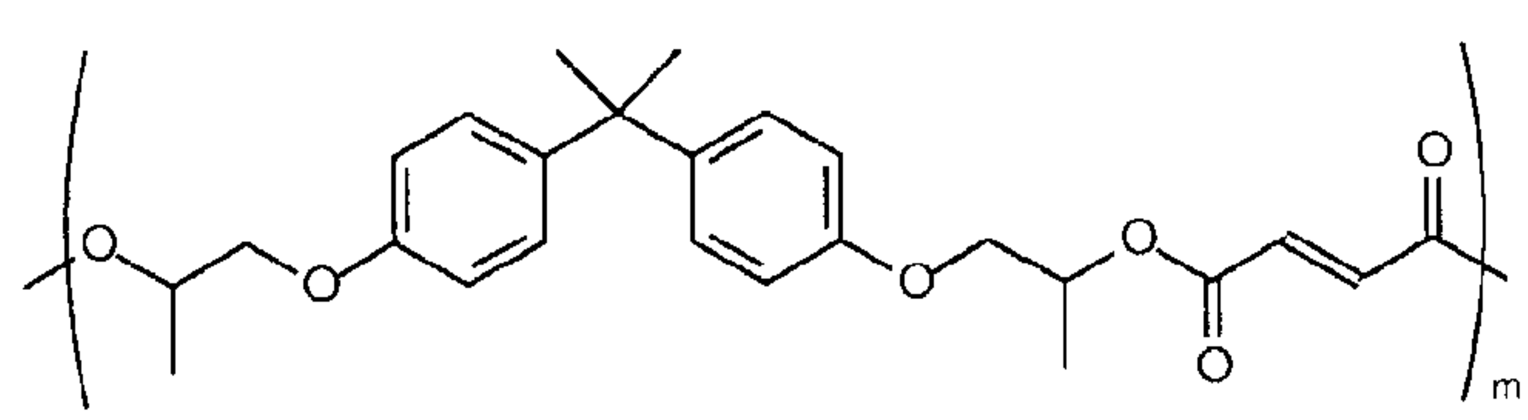
[0031] In embodiments, polycondensation catalysts may be used in forming the polyesters. Polycondensation catalysts which may be utilized for either the crystalline or amorphous polyesters include tetraalkyl titanates, dialkyltin oxides such as dibutyltin oxide, tetraalkyltins such as dibutyltin dilaurate, and dialkyltin oxide hydroxides such as butyltin oxide hydroxide, tin octoate, 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.

[0032] In embodiments, suitable amorphous resins include polyesters, polyamides, polyimides, polyolefins, polyethylene, polybutylene, polyisobutyrate, ethylene-propylene copolymers, ethylene-vinyl acetate copolymers, polypropylene, combinations thereof, and the like. Examples of amorphous resins which may be utilized include alkali sulfonated-polyester resins, branched alkali sulfonated-polyester resins, alkali sulfonated-polyimide resins, and branched alkali sulfonated-polyimide resins. Alkali sulfonated polyester resins may be useful in embodiments, such as the metal or alkali salts of copoly(ethylene-terephthalate)-copoly(ethylene-5-sulfo-isophthalate), copoly(propylene-terephthalate)-copoly(propylene-5-sulfo-isophthalate), copoly(diethylene-terephthalate)-copoly(diethylene-5-sulfoisophthalate), copoly(propylene-diethylene-terephthalate)-copoly(propylene-diethylene-5-sulfoisophthalate), copoly(propylene-butylene-terephthalate)-copoly(propylene-butylene-5-sulfoisophthalate), and copoly(propoxylated bisphenol-A-fumarate)-copoly(propoxylated bisphenol A-5-sulfo-isophthalate).

[0033] In embodiments, an unsaturated, amorphous polyester resin may 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), 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.

[0034] The amorphous resin can possess various glass transition temperatures (Tg) of, for example, from about 40° C to about 100° C, in embodiments from about 45° C to about 70° C, in some embodiments from 50 °C to about 65 °C. The crystalline resin may have a number average molecular weight (M_n), for example, from about 1,000 to about 50,000, in embodiments from about 2,000 to about 25,000, in some embodiments from about 2,000 to about 10,000 and a weight average molecular weight (M_w) of, for example, from about 2,000 to about 100,000, in embodiments from about 3,000 to about 80,000, in some embodiments from about 4,000 to about 20,000, as determined by Gel Permeation Chromatography (GPC) using polystyrene standards. The molecular weight distribution (M_w/M_n) of the crystalline resin may be, for example, from about 2 to about 6, in embodiments from about 2 to about 5, and in some embodiments about 2 to about 4.

[0035] For example, in embodiments, an amorphous polyester resin may be a poly(propoxylated bisphenol A co-fumarate) resin having the following formula (I):



(I)

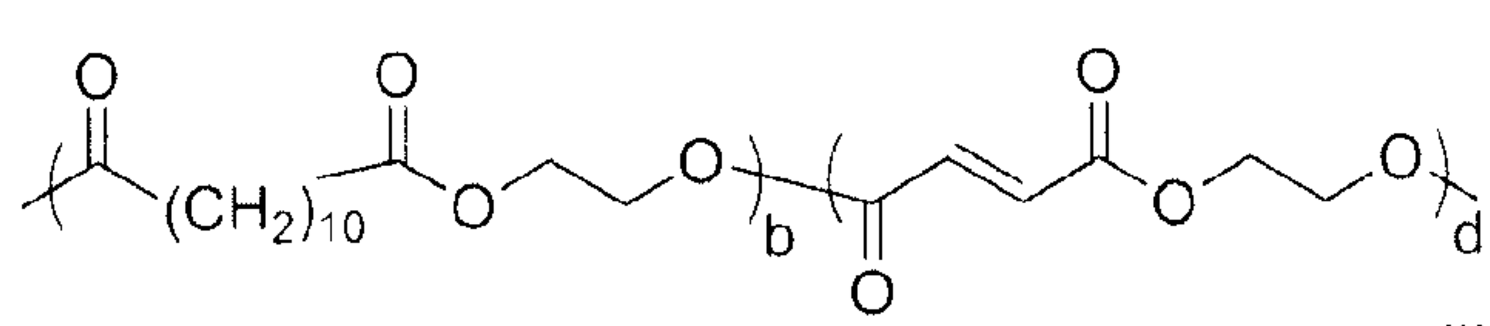
wherein m may be from about 5 to about 1000, in embodiments from about 10 to about 500, in other embodiments from about 15 to about 200. Examples of such resins and processes for their production include those disclosed in U.S. Patent No. 6,063,827.

[0036] An example of a linear propoxylated bisphenol A fumarate resin which may be utilized as a toner 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.

[0037] In embodiments, the amorphous polyester resin may be a co-polymer of alkoxylated Bisphenol A with at least one diacid. The alkoxylated Bisphenol A may include ethoxylated Bisphenol A, propoxylated Bisphenol A, and/or ethoxylated-propoxylated Bisphenol A. Suitable diacids include fumaric acid, terephthalic acid, dodecenylsuccinic acid, and/or trimellitic acid.

[0038] In embodiments, a combination of low Mw and high Mw amorphous resins may be used to form a toner. Low-Mw resins may have a weight-average molecular weight of approximately 10 kg/mol to approximately 20 kg/mol, and a number-average molecular weight of approximately 2 kg/mol to approximately 5 kg/mol. High-Mw resins may have a weight-average molecular weight of approximately 90 kg/mol to approximately 160 kg/mol, and a number-average molecular weight of approximately 4 kg/mol to approximately 8 kg/mol. The ratio, by weight, of low Mw to high Mw amorphous resins may be from about 0:100 to about 100:0, in embodiments from about 70:30 to about 30:70, and in some embodiments from about 60:40 to about 40:60.

[0039] Further examples of crystalline resins which may be utilized, optionally in combination with an amorphous resin as descried above, include those disclosed in U.S. Patent 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 (II):



(II)

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

[0040] 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 resin suitable for forming a toner.

[0041] Examples of other toner resins or polymers which may be utilized include those based upon styrenes, acrylates, methacrylates, butadienes, isoprenes, acrylic acids, methacrylic acids, acrylonitriles, and combinations thereof. Exemplary additional resins or polymers include, but are not limited to, poly(styrene-butadiene), poly(methylstyrene-butadiene), poly(methyl methacrylate-butadiene), poly(ethyl methacrylate-butadiene), poly(propyl methacrylate-butadiene), poly(butyl methacrylate-butadiene), poly(methyl acrylate-butadiene), poly(ethyl acrylate-butadiene), poly(propyl acrylate-butadiene), poly(butyl acrylate-butadiene), poly(styrene-isoprene), poly(methylstyrene-isoprene), poly(methyl methacrylate-isoprene), poly(ethyl methacrylate-isoprene), poly(propyl methacrylate-isoprene), poly(butyl methacrylate-isoprene), poly(methyl acrylate-isoprene), poly(ethyl acrylate-isoprene), poly(propyl acrylate-isoprene), poly(butyl acrylate-isoprene); poly(styrene-propyl acrylate), poly(styrene-butyl acrylate), poly(styrene-butadiene-acrylic acid), poly(styrene-butadiene-methacrylic acid), poly(styrene-butadiene-acrylonitrile-acrylic acid), poly(styrene-butyl acrylate-acrylic acid), poly(styrene-butyl acrylate-methacrylic acid), poly(styrene-butyl acrylate-acrylonitrile), and poly(styrene-butyl acrylate-acrylonitrile-acrylic acid), and combinations thereof. The polymer may be block, random, or alternating copolymers.

[0042] In further embodiments, the resins utilized in the toner may have a melt viscosity of from about 10 to about 1,000,000 Pascal-seconds (Pa*s) at about 130°C, in embodiments from about 20 to about 100,000 Pa*s.

[0043] One, two, or more toner resins may be used. In embodiments where two or more toner resins are used, the toner resins may be in any suitable ratio (e.g., weight ratio) such as for instance about 10% (first resin)/90% (second resin) to about 90% (first resin)/10% (second resin).

[0044] In embodiments, the polymer latex may be formed by emulsification 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.

[0045] The polymer resin may be present in an amount of from about 65 to about 95 percent by weight, in embodiments from about 70 to about 90 percent by weight, and in some embodiments from about 75 to about 85 percent by weight of the toner particles (that is, toner particles exclusive of external additives) on a solids basis. Where the resin is a combination of a crystalline resin and one or more amorphous resins, the ratio of crystalline resin to amorphous resin(s) can be in embodiments from about 1:99 to about 30:70, in embodiments from about 5:95 to about 25:75, in some embodiments from about 5:95 to about 15:85.

[0046] **Surfactants**

[0047] In embodiments, resins, 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.

[0048] 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.

[0049] 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.

[0050] 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 dodecyl benzene sulfonates. Combinations of these surfactants and any of the foregoing anionic surfactants may be utilized in embodiments.

[0051] 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, C_{12}, C_{15}, C_{17} 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.

[0052] **Colorants**

[0053] As the optional 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.

[0054] As examples of suitable colorants, mention may be made of carbon black like REGAL 330®; 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, 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.

[0055] 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, 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-dichlorobenzidene 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 Sunsperse Carbon Black LHD 9303 (Sun Chemicals), and colored dyes such as Neopen Blue (BASF), Sudan Blue OS (BASF), PV Fast Blue B2G01 (American Hoechst), Sunsperse 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), Sunsperse 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.

[0056] **Wax**

[0057] Optionally, a wax may also be combined with the resin and optional colorant in forming toner particles. When included, the wax may be present in an amount of, for example, from about 1 weight percent to about 25 weight percent of the toner particles, in embodiments from about 5 weight percent to about 20 weight percent of the toner particles.

[0058] Waxes that may be selected include waxes having, for example, a weight average molecular weight (Mw) 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.

[0059] **Shell Resins**

[0060] 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 resin and a crystalline resin may be utilized to form a shell over the aggregates to form toner particles having a core-shell configuration. 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.

[0061] 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.

[0062] 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. Furthermore, the addition of an EDTA solution may be used to freeze the shell growth. In embodiments, a combination of EDTA solution and base solution may be used to freeze the toner particle growth.

[0063] <u>Small Molecule Crystalline Organic Compounds</u>

[0064] In embodiments, small molecule crystalline organic compounds, which are crystalline solids at room temperature, are added to the toner for reduction in minimum fusing temperature (MFT) of the toner. In particular embodiments, the small molecule crystalline organic compounds are added to emulsion aggregation (EA) toners, completely or partially replacing a crystalline polymer component, if included, where the small molecule crystalline organic compounds are compatible with the toner amorphous binder resin(s). Compatibility may be shown by characterizing a melt mixture of the amorphous resin and the small molecule crystalline organic compound(s) – the amorphous resin and small molecule crystalline organic compound(s) are considered to be compatible when the melt mixture is characterized by a reduction in glass transition temperature from that of the amorphous resin and by the lack of a significant solid to liquid phase transition peak for the small molecule crystalline organic compound(s) as determined by differential scanning calorimetry, the enthalpy of fusion for the small molecule crystalline organic compound in the mixture being measured to be less than 20% of its original value, in embodiments less than 10% of its original value, and in some embodiments less than 5% of its original value, said original value representing the enthalpy of fusion for the small molecule when measured independently. Furthermore, in embodiments the small molecule crystalline organic compounds have a melting point that is less than the fusing temperature of the EA toner. According to some embodiments, emulsion aggregation toners comprising small molecule crystalline organic compounds may achieve crease fix MFT at least comparable to nominal ULM toners, such as the Xerox® 700 DCP toner available from Xerox Corp, for example, if not lower, by at least 5°C, or by 10°C to 20°C, for example.

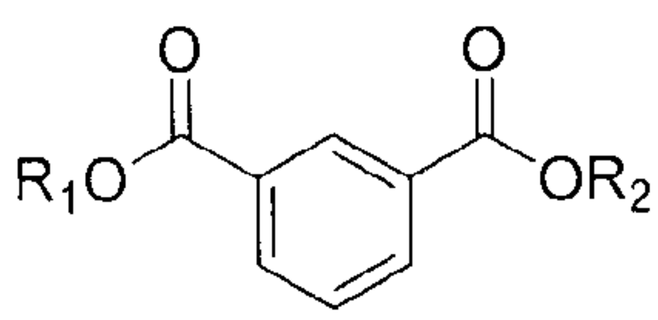
[0065] In some embodiments the small molecule crystalline organic compounds have a molecular weight of less than 1,000 g/mol; in further embodiments, the small molecule crystalline organic compounds have a molecular weight of less than 750 g/mol; and yet further embodiments the small molecule crystalline organic compounds have a molecular weight of less than 500 g/mol.

[0066] In brief, the compatibility test for the amorphous resin and the small molecule crystalline compounds proceeds as follows. A small molecule crystalline compound is mixed with an amorphous resin in a ratio similar to that in the toner itself. The mixture is heated to at least above the melting point of the crystalline component for a time sufficient for complete melting with mixing, then cooled to room temperature. The resulting material is analyzed by DSC. In this test, small molecules that are not compatible with the resin are thought to re-crystallize from the molten mixture as it cools, and the resulting DSC trace shows both (1) a clear melting peak corresponding to the small molecule and (2) the original glass transition of the amorphous resin (which may or may not be shifted to a slightly lower temperature). When incorporated into an EA toner, small molecules with this characteristic generally do not provide low-melt toner properties. In contrast, small molecules that are compatible with the resin generally do not re-crystallize from the molten mixture. In these cases, the resulting DSC traces show both (1) a weak or completely absent melting transition and (2) a weakened and / or shifted glass transition, indicating plasticization of the amorphous resin by the small molecule. When incorporated into EA toner, these small molecules generally do provide low-melt properties, when the melting point of the small molecules is below the typical fusing temperature of the toner (between about 110°C and 120°C for a typical ULM EA toner, such as Xerox® 700 DCP toner, for example). Furthermore, to measure the extent of compatibility, the enthalpy of crystallization may be measured - for full compatibility a value of less than 5% of the original value is obtained, whereas for full incompatibility, a value of greater than 20% of the original value is obtained, said original value representing the enthalpy of fusion for the small molecule when measured independently.

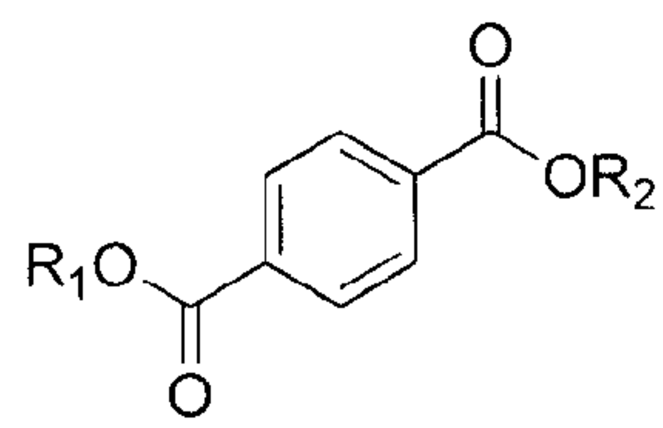
[0067] Provided herein are some examples of groups of small molecule crystalline organic compounds which may be suitable for adding to the toner for reduction in minimum fusing temperature (MFT) of the toner. These examples are not intended to be limiting - other groups of organic compounds may also be suitable for adding to the toner for reduction in minimum fusing temperature (MFT) of the toner, such as aliphatic esters and diesters, aliphatic ethers, amides, ketones, aldehydes, and the like.

[0068] Small Molecule Crystalline Aromatic Diester Compounds

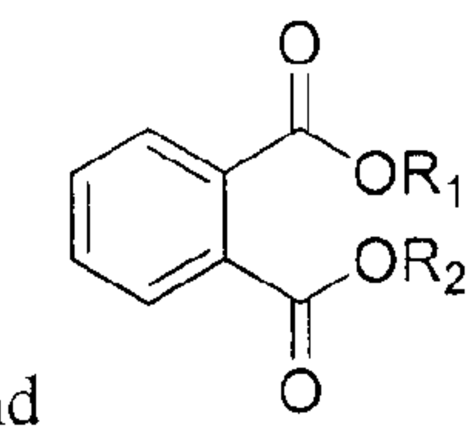
[0069] In embodiments, small molecule crystalline aromatic diester compounds are added to the toner for reduction in minimum fusing temperature (MFT) of the toner. Examples of suitable aromatic diesters include those of the formulas (III, IV, V)



(III),



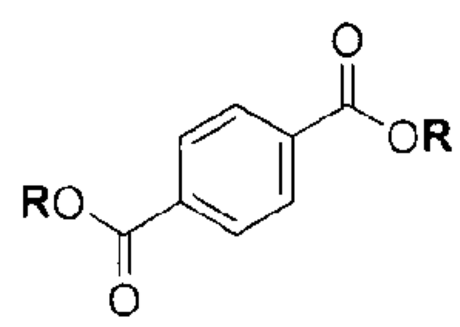
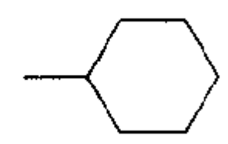
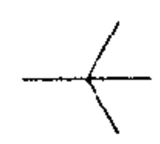
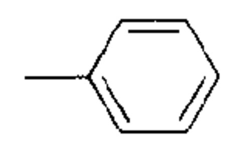
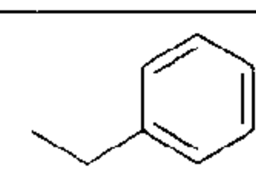
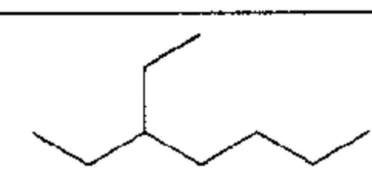
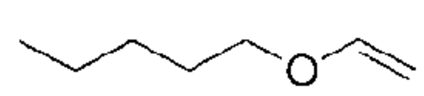
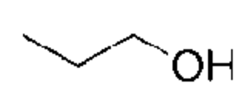
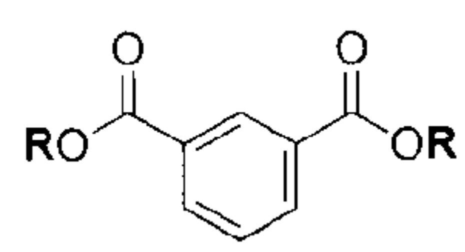
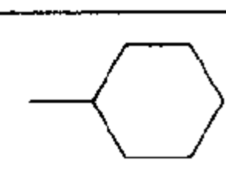
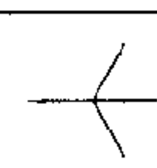
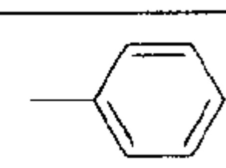
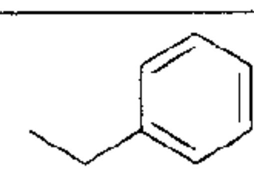
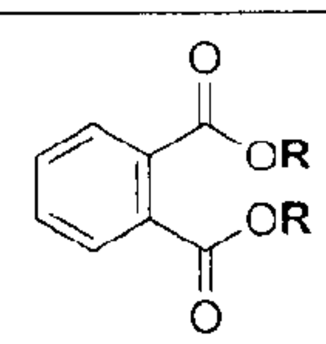
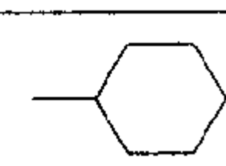
(IV), and



(V),

wherein R_1 and R_2 can be the same or different. In embodiments, R_1 and R_2 may be selected from the group consisting of aryl, alkyl, aryl-aklyl, and alkyl-aryl groups. In particular embodiments, the aromatic diester has a carbon-to-oxygen ratio between 3.5 to 6, similar in range to the carbon-to-oxygen ratio of the resins used in the toner. Thermal properties of these aromatic diesters for specific examples of R_1 and R_2 are provided in Table 1.

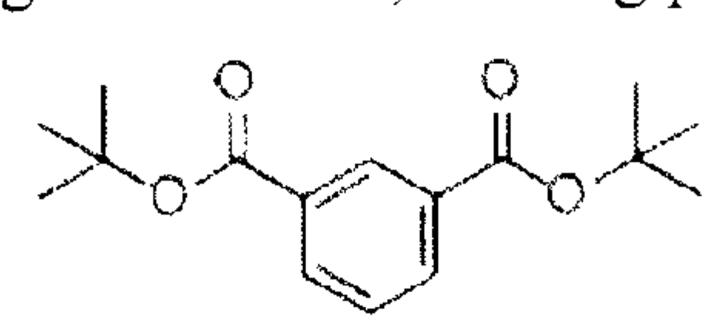
[0070] **Table 1.** Thermal properties of aromatic diesters.

#	Core structure	-R	T_{melt} (°C)*	T_{crys} (°C)*	T_{melt} − T_{crys} (°C)
T1		$-CH_3$	143	132	11
T2			88	42	46
T3			117	75	42
T4			191	**	
T5			95	39	56
T6			32	**	
T7			45	**	
T8			107	62	45
I1		$-CH_3$	68	29	39
I2			**	**	
I3			83		
I4			138	88	50
I5			149	38	111
P1		$-CH_3$	2	**	
P2			65	**	

* T_{melt} = melting temperature, and T_{crys} = crystallization temperature, as determined by DSC at a rate of 10 °C/min.

** Data not available or not measured.

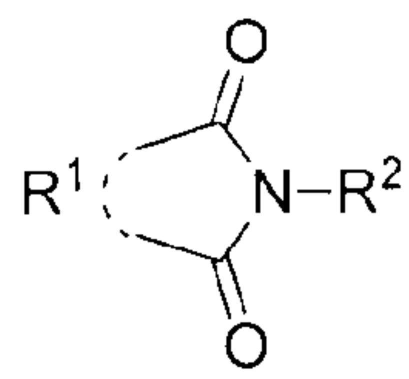
[0071] In a particular embodiment, the aromatic diester is di-tert-butyl isophthalate (carbon-to-oxygen ratio of 4, melting point 83°C), with the formula (VI):



(VI).

[0072] Small Molecule Crystalline Imides

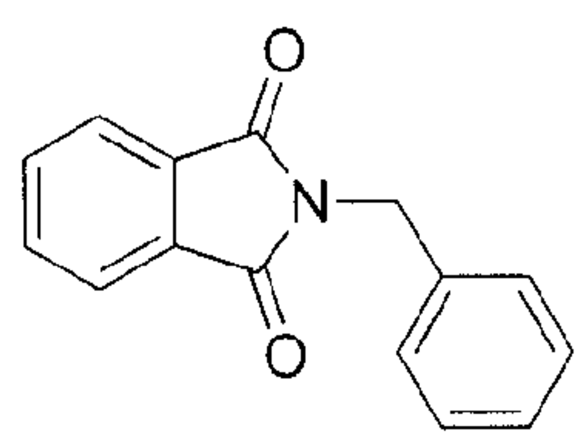
[0073] In embodiments, small molecule crystalline imides are added to the toner for reduction in minimum fusing temperature (MFT) of the toner. Examples of suitable imides include those of the general structure (VII):



(VII)

wherein R^1 is an optional connection (either a direct connection as in the case of succinimides, a methylene unit as in the case of glutarimides, a 1,2-phenylene unit as in the case of phthalimides, or a related connector unit) and R^2 is an alkyl or aryl unit such as benzyl, phenyl, methyl, ethyl, or a related structure. The imides specified herein include both cyclic aliphatic imides (e.g. succinimides) and aromatic imides (e.g. phthalimides) as well as acyclic imides, with or without alkyl or aryl substituents on the central nitrogen atom.

[0074] In a particular embodiment, the small molecule crystalline imide is N-benzyl phthalimide (m.p. 119°C), with the formula (VIII):



(VIII).

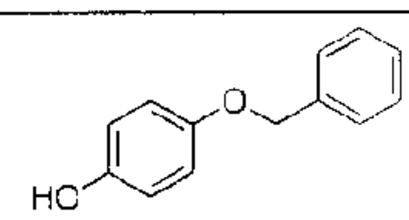
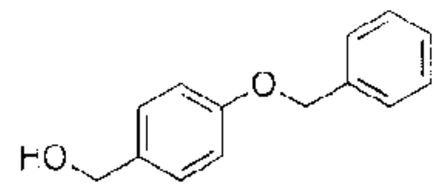
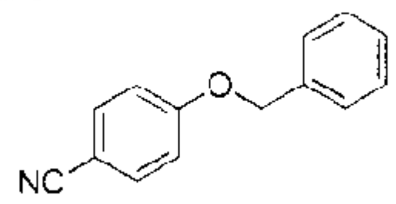
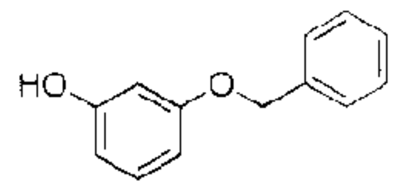
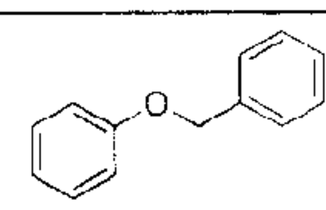
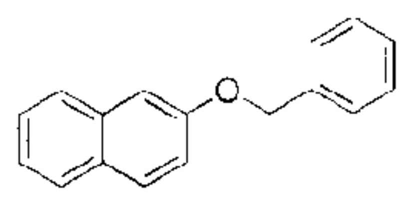
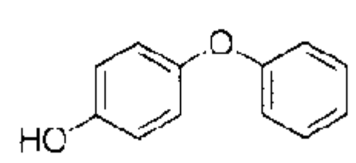
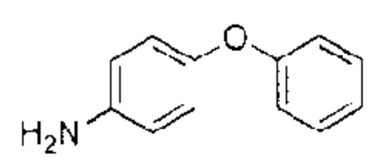
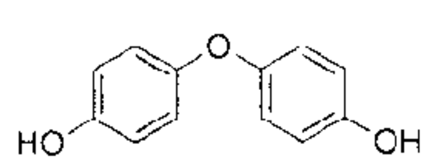
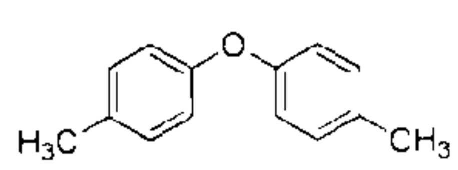
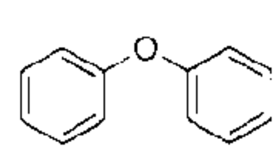
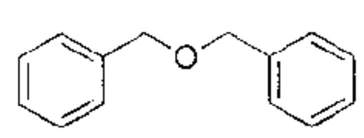
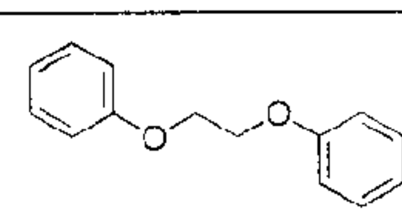
[0075] Small Molecule Crystalline Aromatic Ether Compounds

[0076] In embodiments, small molecule crystalline aromatic ether compounds are added to the toner for reduction in minimum fusing temperature (MFT) of the toner. Examples of suitable aromatic ethers include those of the formulas (IX):

$$R_1{-}O{-}[(CH_2)_2O]_p{-}R_2 \quad \text{(IX)}$$

wherein R_1 and R_2 are independently selected from the group consisting of (i) an alkyl group; (ii) an arylalkyl group; (iii) an alkylaryl group and (iii) an aromatic group; and mixtures thereof, provided that at least one of R_1 and R_2 is an aromatic group; and p is 0 or 1. Thermal properties of these aromatic ethers for specific examples of R_1 and R_2 are provided in Table 2.

[0077] **Table 2.** Thermal properties of aromatic ethers.

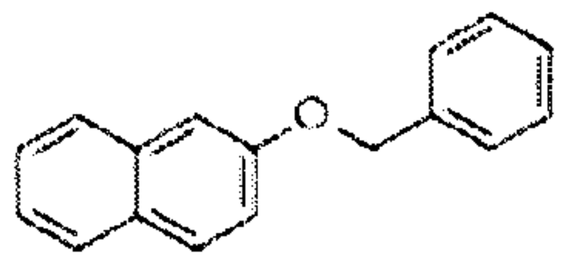
Compound #	Structure	T_{melt} (°C)*	T_{crys} (°C)*	$T_{melt} - T_{crys}$ (°C)
1		121	100	21
2		90	77	13
3		97 (1stH) & 81 (2ndH)***	36	61
4		50	**	**
5		39	**	**
6		102	65	37
7		88	4 (2ndH)***	84
8		85	29	56
9		168	**	**
10		48	**	**
11		26 - 30	**	**
12		4	**	**
13		98	77	21

*Determined by DSC at a rate of 10 °C/min or melting point data from commercial source.

**Data not available or not measured.

***Second Heating

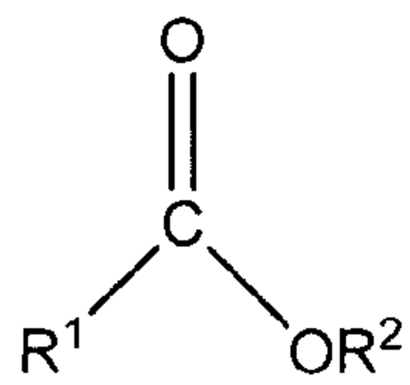
[0078] In a particular embodiment, the aromatic ether is benzyl 2-naphthyl ether (melting point 102°C), of the formula (X):



(X).

[0079] Small Molecule Crystalline Aromatic Monoester Compounds

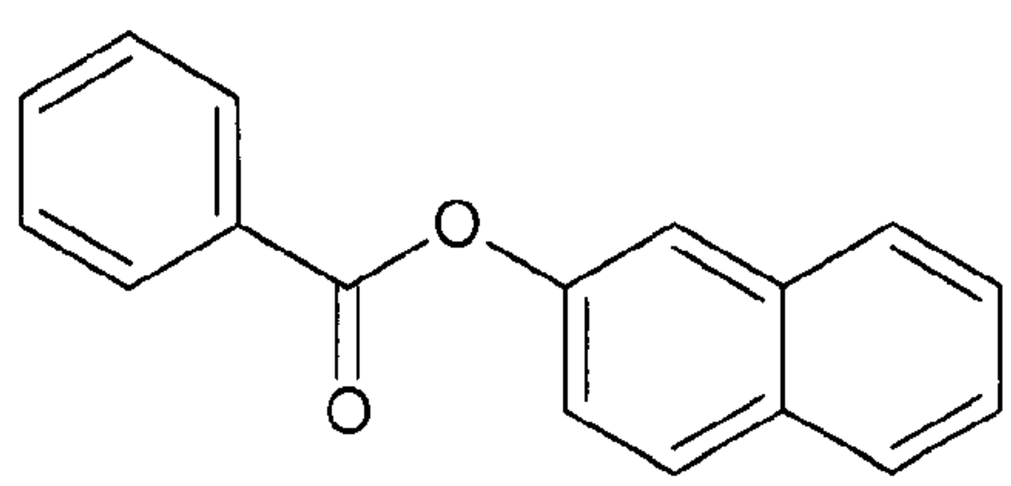
[0080] In embodiments, small molecule crystalline aromatic monoester compounds are added to the toner for reduction in minimum fusing temperature (MFT) of the toner. Examples of suitable aromatic monoesters include those of the formula (XI):



(XI)

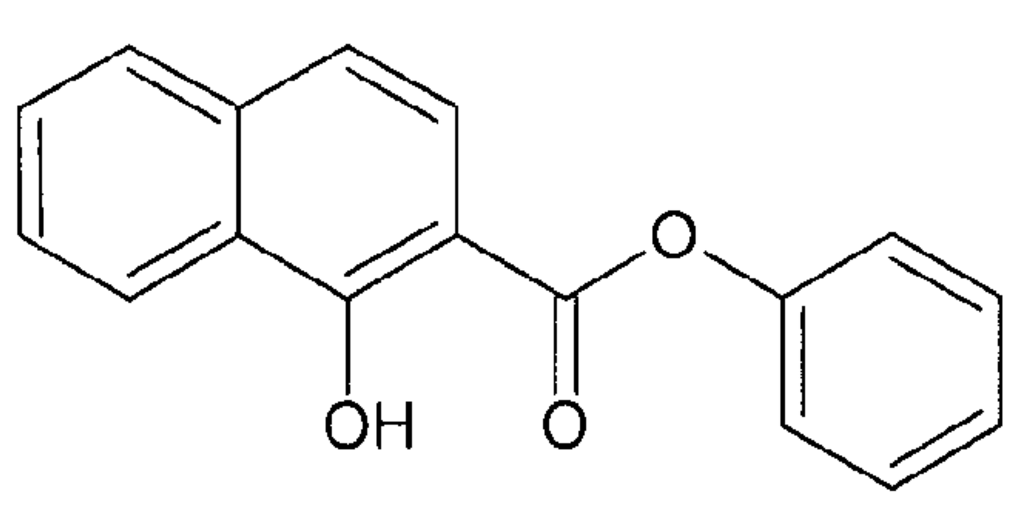
wherein R^1 and R^2 can be the same or different, and at least one of R^1 and R^2 is an aromatic group. In embodiments, R^1 and R^2 may be selected from the group consisting of aryl, alkyl, aryl-aklyl, and alkyl-aryl groups. In particular embodiments, the aromatic monoester has a carbon-to-oxygen ratio between 3.5 and 6, similar in range to the carbon-to-oxygen ratio of the resins used in the toner..

[0081] In a particular embodiment, the aromatic monoester is 2-Naphthyl benzoate (melting point 107°C), of the formula (XII):



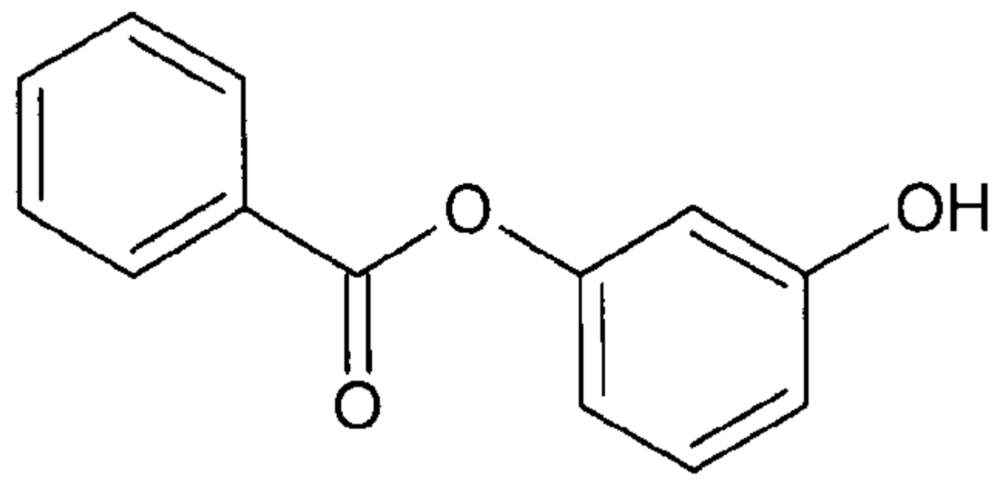
(XII).

Other suitable aromatic monoesters may include, for example, phenyl-1-hydroxy-2-naphthoate (melting point 95°C), of the formula (XIII):



(XIII);

and benzoic acid 3-hydroxyphenyl ester (melting point 136°C), of the formula (XIV):



(XIV).

[0082] Toner Preparation

[0083] 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, for example. 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.

[0084] 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 resins and at least one or more of the small molecule crystalline organic compounds described above, optionally in surfactants as described above, and then coalescing the aggregate mixture. Examples of potentially suitable colorants, waxes and/or other additives are described above. In some embodiments the small molecule crystalline organic compound(s) is about 5% to about 25% by dry weight of the toner, not including any external additives, in embodiments from about 10% to about 20%, and in some embodiments the small molecule crystalline organic compound(s) is about 15% by dry weight of the toner. In embodiments, emulsions of each of the components are prepared and then combined together. Furthermore, in some embodiments the toner comprises both a small molecule crystalline organic compound and a crystalline resin. For example, the crystalline resin may be the crystalline polyester resin described above and/or any of the other crystalline resins described herein. In some embodiments the crystalline resin is about 3% to about 20% by dry weight of the toner, not including any external additives, in embodiments from about 5% to about 15%, and in some embodiments the small molecule crystalline organic compound(s) is about 5% to about 10% by dry weight of the toner.

[0085] A mixture may be prepared by adding optional colorant(s), wax(es) and/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 as needed.

[0086] Following the preparation of the above mixture, an aggregating agent or flocculent 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 (Tg) of the resin.

[0087] 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 as needed, and holding the mixture at this temperature for the time required to form the desired particle size, while maintaining stirring, to provide the aggregated particles. Once the predetermined desired particle size is reached, emulsions of resins are added to grow a shell, providing core-shell structured particles. The shell is grown until the desired core-shell toner particle size is reached, then the growth process is halted by increasing the pH of the reaction slurry by the addition of a base, such as NaOH, followed by the addition of an EDTA solution.

[0088] After halting the particle growth the reaction mixture is heated, to for example 85°C, to coalesce the particles. The toner slurry is then cooled to room temperature, and the toner particles are separated by sieving and filtration, followed by washing and freeze drying.

[0089] The characteristics of the toner particles may be determined by any suitable technique and apparatus, as described in more detail below.

EXAMPLES

[0090] The examples set forth herein below are illustrative of different compositions and conditions that can be used in practicing the present embodiments. All proportions are by weight unless otherwise indicated. It will be apparent, however, that the present embodiments can be practiced with many types of compositions and can have many different uses in accordance with the disclosure above and as pointed out hereinafter.

[0091] Compatibility studies of examples of the aforementioned groups of small molecule crystalline organic compounds and an amorphous polyester toner binding resin were investigated by separately melt mixing the small molecule crystalline organic compounds with a low Mw linear amorphous resin A (an alkoxylated bisphenol-A co-polyester with fumaric, terephthalic and dodecenylsuccinic acids). The melt mixing is carried out on a hot plate at 150 °C, over a 20 min period, followed by cooling and characterization by DSC. Table 3 summarizes the experimental data obtained. Furthermore, toners prepared with these small molecule crystalline organic compounds (small molecules are about 15 dry weight percent of the toner particles, excluding external additives), as described herein, are tested to determine their low melt properties.

[0092] Table 3: Description of small molecule melting properties, compatibility with amorphous polyester resin, and low-melt properties of the resulting toner.

Molecule name	Melting point[a] °C	Compatibility test: crystalline melting peak observed?[b]	Compatibility test: amorphous resin Tg shifted?[c]	Toner low-melt?[d]
N-benzyl phthalimide	119	no	slightly	yes
Diphenyl isophthalate	138	no	slightly	no
Di-tert-butyl isophthalate	85	no	slightly	yes
Naphthyl benzoate	107	no	> 5 °C	yes
Benzyl naphthyl ether	102	no	> 10 °C	yes
HBPA diacetate	138	no	slightly	no
Distearyl terephthalate	89	yes	slightly	no

[a] Melting point of the small molecule in its pure state.

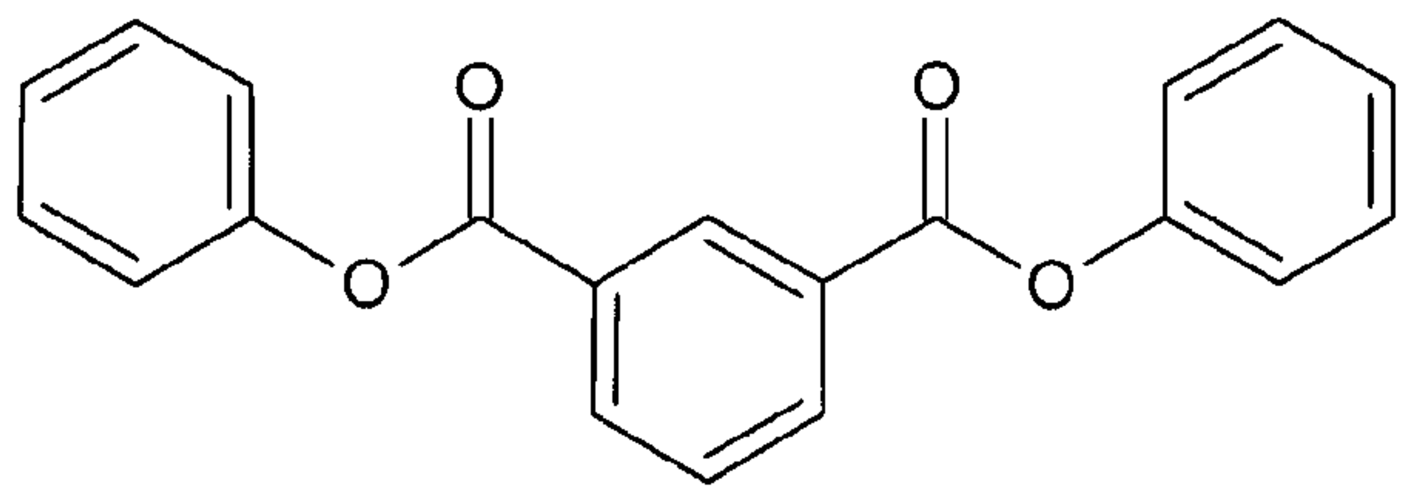
[b] Observation of the melting transition of the small molecule after heating and melt-mixing with low Mw linear amorphous resin A

[c] Shift in the glass transition of low Mw linear amorphous resin A after heating and melt-mixing

[d] Toner has MFT equal to or lower than the MFT of Xerox® 700 DCP toner when measured in a Xerox® 700 DCP fusing apparatus

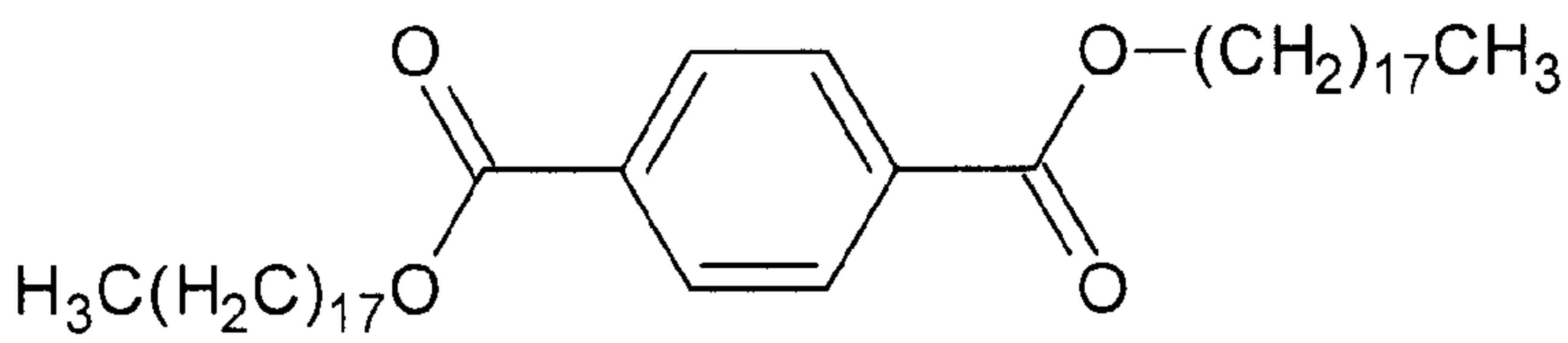
[0093] Some specific examples of DSC plots are provided in Figures 1 through 7. These plots are discussed in more detail below.

[0094] The aromatic diester used in an example herein is di-tert-butyl isophthalate (carbon-to-oxygen ratio of 4, melting point 83°C), of the formula (VI). Two other aromatic diesters are used in comparative examples: Isophthalic acid, di-phenyl ester (carbon-to-oxygen ratio of 5, melting point 138°C), of the formula (XV):



(XV);

and Terephthalic acid, di-stearyl ester (carbon-to-oxygen ratio of 11, melting point 89°C), of the formula (XVI):



(XVI).

[0095] The compatibility of these aromatic diesters with the linear amorphous polyester resin A were investigated using DSC. The small molecule crystalline aromatic diester compounds display melting peaks at around 83°C, 138°C, and 89°C, respectively; the linear amorphous resin A displays a glass transition temperature, Tg, at about 60°C. Figure 1 is a DSC curve of melt mixed di-tert-butyl isophthalate and linear amorphous polyester resin A. The Tg of resin A was depressed from about 60°C to about 48.9°C, and no solid to liquid phase transition peak for the crystalline compound was observed, which indicates that di-tert-butyl isophthalate is fully compatible with the linear amorphous polyester resin A. Figure 2 is a DSC curve of melt mixed Isophthalic acid, di-phenyl ester and linear amorphous polyester resin A. The Tg of resin A was depressed from about 60°C to about 46.4°C, and no solid to liquid phase transition peak for the crystalline compound was observed, which indicates that Isophthalic acid, di-phenyl ester is fully compatible with the linear amorphous polyester resin A. Figure 3 is a DSC curve of melt mixed terephthalic acid, di-stearyl ester and linear amorphous polyester resin A. The enthalpy of crystallization is greater than 20% of the original value for terephthalic acid di-stearyl ester, indicating full incompatibility.

[0096] The small molecule crystalline imide used in the example herein is N-benzyl phthalimide, of the formula (VIII). Compatibility studies of this imide and an amorphous polyester toner binding resin A were investigated by DSC. The small molecule crystalline imide shows a sharp melting transition at 119°C and recrystallization at 72°C; the linear amorphous resin A displays a glass transition temperature, Tg, at about 60°C. For the mixture of small molecule crystalline imide N-benzyl phthalimide and linear amorphous polyester resin A, a glass transition at about 29°C and no melting transition is observed by DSC, indicating complete compatibility.

[0097] The aromatic ether used in an example herein is benzyl 2-naphthyl ether (melting point 102°C), of the formula (X). Differential scanning calorimetry (DSC) was used to measure the thermal properties of the benzyl 2-naphthyl ether – Figure 4 shows very sharp melting and recrystallization peaks at about 102°C and 63°C, respectively. Figure 5 is a DSC curve of melt mixed benzyl 2-naphthyl ether and linear amorphous polyester resin A. The Tg of resin A was depressed from about 60°C to about 37.1°C, and no solid to liquid phase transition peak for the crystalline compound was observed, which indicates that benzyl 2-naphthyl ether is fully compatible with the linear amorphous polyester resin A.

[0098] A DSC plot for the aromatic monoester 2-Naphthyl benzoate (melting point 107°C), of the formula (XII) is shown in Figures 6 & 7. Differential scanning calorimetry (DSC) was used to measure the thermal properties of the 2-Naphthyl benzoate – Figure 6 shows very sharp melting and recrystallization peaks at about 107°C and 63°C, respectively, for first heating and cooling; Figure 7 shows a sharp melting peak at about 107°C for second heating. Note that a second heating is used for complicated materials, where the first scan erases thermal history and the second scan is better for comparisons.

[0099] As shown in Figures 6 & 7, the small molecule crystalline aromatic monoester compound 2-Naphthyl benzoate displays a melting peak at around 107°C; the linear amorphous resin A displays a glass transition temperature, Tg, at about 60°C. Figure 8 is a DSC curve of melt mixed 2-Naphthyl benzoate and linear amorphous polyester resin A. The Tg of resin A was depressed from about 60°C to about 42°C, and no solid to liquid phase transition peak for the crystalline compound was observed, which indicates that 2-Naphthyl benzoate is fully compatible with the linear amorphous polyester resin A.

[00100] <u>**Comparative Example 1**</u>

[00101] <u>Preparation of toner comprised of 15% Isophthalic acid, di-phenyl ester</u>

[00102] Into a 2 liter glass reactor equipped with an overhead mixer was added 227.72 g of Isophthalic acid, di-phenyl ester dispersion (7.18 wt%, made by ball milling isophthalic acid diphenyl ester obtained from Sigma-Aldrich Chemical Company with 9% anionic surfactant), 61.54 g high Mw linear amorphous polyester resin B in an emulsion (35.22 wt %), 62.34 g low Mw linear amorphous polyester resin A in an emulsion (34.84 wt %), 30.56 g wax dispersion (wax available from International Group Inc., 30.19 wt %) and 34.83 g cyan pigment PB15:3 (17.21 wt %). The linear amorphous resin B is a co-polyester of alkoxylated Bisphenol A with terephthalic and dodecenylsuccinic acids. Separately, 3.58 g $Al_2(SO4)_3$ (27.85 wt %) was added as a flocculent under homogenization at 3500 rpm. The mixture was heated to 40 °C to aggregate the particles while stirring at 200 rpm. The particle size was monitored with a Coulter Counter until the core particles reached a volume average particle size of 4.35 microns with a GSD volume of 1.36, and then a mixture of 40.55 g and 41.07 g, respectively, of the afore mentioned A and B resin emulsions were added as shell material, resulting in core-shell structured particles with an average particle size of 6.21 microns, GSD volume 1.27. Thereafter, the pH of the reaction slurry was increased to 8.5 using 4 wt% NaOH solution followed by 7.69g EDTA (39 wt%) to freeze the toner growth. After freezing, the reaction mixture was heated to 85°C and the toner particles were coalesced at 85°C, pH 8.4. The toner was quenched after coalescence, resulting in a final particle size of 7.66 microns, GSD volume of 1.37, GSD number 1.35 and Circularity of 0.967. The toner slurry was then cooled to room temperature, separated by sieving (25 μm), filtered, and then washed and freeze dried.

[00103] <u>**Comparative Example 2**</u>

[00104] <u>Preparation of toner comprised of 15% terephthalic acid, di-stearyl ester</u>

[00105] Into a 2 liter glass reactor equipped with an overhead mixer was added 488.12 g of emulsion containing terephthalic acid, di-stearyl ester, high Mw linear amorphous resin A, and low Mw linear amorphous resin B in the ratio of 15:21.3:21.3 (12 wt%, made by co-emulsification), 30.15 g wax dispersion (wax available from International Group Inc., 30.19 wt %) and 34.39 g cyan pigment PB15:3 (17.21 wt %). Separately, 1.18 g $Al_2(SO4)_3$ (27.85 wt %) was added as a flocculent under homogenization at 3500 rpm. The mixture was heated to 38.2 °C to aggregate the particles while stirring at 300 rpm. The particle size was monitored with a Coulter Counter until the core particles reached a volume average particle size of 5.25 micron with a GSD volume of 1.38, and then a mixture of 40.55 g and 40.03 g, respectively, of the afore mentioned A and B resin emulsions were added as shell material, resulting in core-shell structured particles with an average particle size of 5.83 microns, GSD volume 1.23. Thereafter, the pH of the reaction slurry was increased to 8 using 4 wt% NaOH solution followed by 7.6g EDTA (39 wt%) to freeze the toner growth. After freezing, the reaction mixture was heated to 85°C and the toner particles were coalesced at 85°C, pH 7. The toner was quenched after coalescence, resulting in a final particle size of 6.41 microns, GSD volume of 1.25, GSD number 1.31 and Circularity of 0.958. The toner slurry was then cooled to room temperature, separated by sieving (25 μm), filtered, and then washed and freeze dried.

[00106] **Comparative Example 3**

[00107] Preparation of hydrogenated bisphenol A diacetate

[00108] 60 g of 4,4′-isopropylidenedicyclohexanol (also known as hydrogenated Bisphenol A), obtained from Sigma-Aldrich, was combined with 63.7 g of acetic anhydride in a 1-L flask with stirring. Eight drops of concentrated sulfuric acid were then added, after which heat was observed to be generated and the solid reaction mixture became homogeneous. The mixture was stirred for 2.5 hours, then poured onto approximately 500 g of crushed ice. After stirring overnight, the mixture was filtered and air-dried. The resulting solid was recrystallized twice from boiling methanol, filtered, and dried under vacuum at 60 °C, providing 25.3 g of hydrogenated bisphenol A diacetate. The structure was confirmed by 1H and 13C NMR (nuclear magnetic resonance) spectroscopy.

[00109] **Comparative Example 4**

[00110] Preparation of toner comprised of 15% hydrogenated bisphenol A diacetate

[00111] Into a 2 liter glass reactor equipped with an overhead mixer was added 310.8 g of hydrogenated bisphenol A diacetate dispersion (5.3 wt%, made by ball milling the material of Comparative Example 3 with 9% anionic surfactant), 61.54 g high Mw linear amorphous polyester resin B in an emulsion (35.22 wt %), 62.34 g low Mw linear amorphous polyester resin A in an emulsion (34.84 wt %), 30.56 g wax dispersion (wax available from International Group Inc., 30.19 wt %) and 34.83 g cyan pigment PB15:3 (17.21 wt %). Separately, 3.58 g $Al_2(SO_4)_3$ (27.85 wt %) was added as a flocculent under homogenization at 3500 rpm. The mixture was heated to 40 °C to aggregate the particles while stirring at 200 rpm. The particle size was monitored with a Coulter Counter until the core particles reached a volume average particle size of 4.2 microns with a GSD volume of 1.26, and then a mixture of 40.55 g and 41.07 g, respectively, of the afore mentioned A and B resin emulsions were added as shell material, resulting in core-shell structured particles with an average particle size of 5.90 microns, GSD volume 1.26. Thereafter, the pH of the reaction slurry was increased to 8.0 using 4 wt% NaOH solution followed by 7.69g EDTA (39 wt%) to freeze the toner growth. After freezing, the reaction mixture was heated to 85°C and the toner particles were coalesced at 85°C, pH 7.8. The toner was quenched after coalescence, resulting in a final particle size of 7.34 microns, GSD volume of 1.30, GSD number 1.33 and Circularity of 0.948. The toner slurry was then cooled to room temperature, separated by sieving (25 μm), filtered, and then washed and freeze dried.

[00112] **Example 1**

[00113] Preparation of N-benzyl phthalimide dispersion

[00114] Into a 250 ml plastic bottle equipped with about 700g of stainless steel beads, was added 10.33 grams N-benzyl phthalimide obtained from TCI America, 1.98 g of the nonionic surfactant DOWFAX available from The Dow Chemical Co. (47wt%), and 70g deionized water (DIW). The bottle was then milled for 7days. A dispersion of particle sizes with an average particle diameter of 414 nm was obtained.

[00115] **Example 2**

[00116] Preparation of benzyl 2-naphthyl ether dispersion

[00117] Into a 250 ml plastic bottle equipped with about 700g of stainless steel beads, was added 20 grams of benzyl 2-naphthyl ether obtained from TCI America, 3.34 g of the nonionic surfactant DOWFAX available from the Dow Chemical Co. (47wt%), and 70g of deionized water (DIW). The bottle was then milled for 7days. A dispersion of particle sizes with an average particle diameter of 367 nm was obtained.

[00118] **Example 3**

[00119] Preparation of 2-Naphthyl benzoate dispersion

[00120] Into a 250 ml plastic bottle equipped with about 700g of stainless steel beads, was added 17.45 grams of 2-Naphthyl benzoate obtained from TCI America, 3.34 g of the nonionic surfactant DOWFAX available from the Dow Chemical Co. (47wt%), and 70g of deionized water (DIW). The bottle was then milled for 7days. A dispersion of particle sizes with an average particle diameter of 484 nm was obtained.

[00121] **Example 4**

[00122] Preparation of toner comprised of 15% di-tert-butyl isophthalate

[00123] Into a 2 liter glass reactor equipped with an overhead mixer was added 417.33 g di-tert-butyl isophthalate dispersion (2.86 wt%, made by ball milling with 9% anionic surfactant), 44.93 g high Mw amorphous resin B in an emulsion (35.22 wt %), 45.51 g low Mw linear amorphous resin A in an emulsion (A, 34.84 wt %), 22.31 g wax dispersion (wax available from International Group Inc., 30.19 wt %) and 25.43 g cyan pigment PB15:3 (17.21 wt %). Separately, 2.62 g $Al_2(SO4)_3$ (27.85 wt %) was added as a flocculent under homogenization at 3500 rpm. The mixture was heated to 41.1 °C to aggregate the particles while stirring at 200 rpm. The particle size was monitored with a Coulter Counter until the core particles reached a volume average particle size of 3.96 microns with a GSD volume of 1.26, and then a mixture of 29.60 g and 29.98 g, respectively, of the afore mentioned A and B resin emulsions were added as shell material, resulting in core-shell structured particles with an average particle size of 6.48 microns, GSD volume 1.27. Thereafter, the pH of the reaction slurry was increased to 7.8 using 4 wt% NaOH solution followed by 5.62g EDTA (39 wt%) to freeze the toner growth. After freezing, the reaction mixture was heated to 85°C and the toner particles were coalesced at 85°C pH 8.4. The toner was quenched after coalescence, resulting in a final particle size of 7.50 microns, GSD volume of 1.31, GSD number 1.33 and Circularity of 0.960. The toner slurry was then cooled to room temperature, separated by sieving (25 μm), filtered, and then washed and freeze dried.

[00124] **Example 5**

[00125] Preparation of toner comprised of 15% N-benzyl phthalimide

[00126] Into a 2 liter glass reactor equipped with an overhead mixer was added 493.32 g of the N-benzyl phthalimide dispersion of Example 1 (2.32 wt%), 43.08 g high Mw linear amorphous resin B in an emulsion (35.22 wt %), 43.63 g low Mw linear amorphous resin A in an emulsion (34.84 wt %), 21.39 g wax dispersion (wax available from International Group Inc., 30.19 wt %) and 24.38 g cyan pigment PB15:3 (17.21 wt %). Separately, 2.51 g $Al_2(SO4)_3$ (27.85 wt %) was added as a flocculent under homogenization at 3500 rpm. The mixture was heated to 43 °C to aggregate the particles while stirring at 200 rpm. The particle size was monitored with a Coulter Counter until the core particles reached a volume average particle size of 4.05 microns with a GSD volume of 1.30, and then a mixture of 28.38 g and 28.75 g, respectively, of the afore mentioned A and B resin emulsions were added as shell material, resulting in core-shell structured particles with an average particle size of 6.21 microns, GSD volume 1.25. Thereafter, the pH of the reaction slurry was increased to 8 using 4 wt% NaOH solution followed by 5.39g EDTA (39 wt%) to freeze the toner growth. After freezing, the reaction mixture was heated to 85°C and the toner particles were coalesced at 85°C pH 7.7. The toner was quenched after coalescence, resulting in a final particle size of 8.15 microns, GSD volume of 1.36, GSD number 1.35. The toner slurry was then cooled to room temperature, separated by sieving (25 μm), filtered, and then washed and freeze dried.

[00127] **Example 6**

[00128] Preparation of toner comprised of 15% benzyl 2-naphthyl ether

[00129] Into a 2 liter glass reactor equipped with an overhead mixer was added 165.99 g of the benzyl 2-naphthyl ether dispersion of Example 2 (9.85 wt%), 61.54 g high Mw linear amorphous resin B in an emulsion (35.22 wt %), 62.34 g low Mw linear amorphous resin A in an emulsion (34.84 wt %), 30.56 g wax dispersion (wax available from International Group Inc., 30.19 wt %) and 34.83 g cyan pigment PB15:3 (17.21 wt %). Separately, 3.58 g $Al_2(SO4)_3$ (27.85 wt %) was added as a flocculent under homogenization at 3500 rpm. The mixture was heated to 39.4 °C to aggregate the particles while stirring at 200 rpm. The particle size was monitored with a Coulter Counter until the core particles reached a volume average particle size of 4.40 microns with a GSD volume of 1.26, and then a mixture of 40.55 g and 41.07 g, respectively, of the afore mentioned A and B resin emulsions were added as shell material, resulting in core-shell structured particles with an average particle size of 5.96 microns, GSD volume 1.33. Thereafter, the pH of the reaction slurry was increased to 8 using 4 wt% NaOH solution followed by 7.69g EDTA (39 wt%) to freeze the toner growth. After freezing, the reaction mixture was heated to 85°C and the toner particles were coalesced at 85°C pH 8. The toner was quenched after coalescence, resulting in a final particle size of 6.34 microns, GSD volume of 1.32, GSD number 1.30. The toner slurry was then cooled to room temperature, separated by sieving (25 µm), filtered, and then washed and freeze dried.

[00130] **Example 7**

[00131] Preparation of toner comprised of 15% 2-Naphthyl benzoate

[00132] Into a 2 liter glass reactor equipped with an overhead mixer was added 225.21 g of the 2-Naphthyl benzoate dispersion of Example 3 (7.26 wt%), 61.54 g high Mw linear amorphous resin B in an emulsion (35.22 wt %), 62.34 g low Mw linear amorphous resin A in an emulsion (34.84 wt %), 30.56 g wax dispersion (wax available from International Group Inc., 30.19 wt %) and 34.83 g cyan pigment PB15:3 (17.21 wt %). Separately, 3.58 g $Al_2(SO4)_3$ (27.85 wt %) was added as a flocculent under homogenization at 3500 rpm. The mixture was heated to 45.3 °C to aggregate the particles while stirring at 200 rpm. The particle size was monitored with a Coulter Counter until the core particles reached a volume average particle size of 4.05 microns with a GSD volume of 1.22, and then a mixture of 40.55 g and 41.07 g, respectively, of the afore mentioned A and B resin emulsions were added as shell material, resulting in core-shell structured particles with an average particle size of 5.96 microns, GSD volume 1.27. Thereafter, the pH of the reaction slurry was increased to 7.8 using 4 wt% NaOH solution followed by 7.69g EDTA (39 wt%) to freeze the toner growth. After freezing, the reaction mixture was heated to 85°C and the toner particles were coalesced at 85°C pH 7.8. The toner was quenched after coalescence, resulting in a final particle size of 6.97 microns, GSD volume of 1.35, GSD number 1.32 and Circularity of 0.951. The toner slurry was then cooled to room temperature, separated by sieving (25 µm), filtered, and then washed and freeze dried.

[00133] **Fusing Results**

[00134] The toners of Examples 4 and 7, Comparative Examples 1 and 2 and controls were evaluated using the fusing apparatus of a Xerox® 700 Digital Color Press printer. The toners were fused at 220 mm/s onto Xerox® Color Xpressions® paper for gloss, MFT, cold offset performance and hot offset performance. The fusing performance of the toners is provided in Tables 4 through 7.

The control toners are a Xerox® 700 DCP toner, including a crystalline resin with a melting temperature between 65 °C and 85 °C, and a Xerox® EA high-gloss (HG) toner as used in the Xerox® DC250 printer. The fuser is the fusing apparatus of a Xerox® 700 Digital Color Press printer.

[00135]

Table 4. Fusing results of toners containing Isophthalic acid, di-phenyl ester, or Isophthalic acid, di-stearyl ester

	ULM Control (Xerox® 700 DCP toner)	Comparative Example 1	Comparative Example 2
Crystalline Material	Crystalline Resin	15% Isophthalic acid, di-phenyl ester	15% Terephthalic acid, di-stearyl ester
Cold offset (CO) on CX+	113	110	120
Gloss at MFT on CX+	17.6	20.0	13.8
Peak Gloss on CX+	65.6	52.8	51.9
T(Gloss 50) on CX+	144	175	166
$MFT_{CA=80}$ (extrapolated MFT)	112	135	126
ΔMFT (Relative to Xerox® EA high-gloss toner fused the same day)	-26	-3	-12
Mottle/Hot Offset (HO) CX+220mm/s	185 / 190	210 / >210	210 / >210
Fusing Latitude HO-MFT on DCX+	72 / 77	>75 / >75	>84 / >84

CX+ and DCX+ are the paper types utilized, available from Xerox Corp.

T(Gloss 50) is the temperature at which the gloss achieved is 50 Gardner gloss units (ggu)

$MFT_{CA=80}$ is the MFT with a crease area of 80 units

Xerox® EA high-gloss toner as used in the Xerox® DC250 printer

[00136] As shown in Table 4, crease fix MFT's of toners containing isophthalic acid, di-phenyl ester, or terephthalic acid, di-stearyl ester are greater than the ULM EA control toner. The control toner MFT was 112°C while the small molecule samples started at 117°C and went up to 135°C. The two Comparative Example toners with small molecules did not produce low-melt properties.

[00137] In the case of isophthalic acid, di-phenyl ester, even though it is compatible with the amorphous polyester resins, as described above, and has a carbon to oxygen ratio of 5 (for comparison the carbon-to-oxygen ratios for the amorphous polyester resins A and B are 4.85 and 4.95, respectively), it has a melting point of 138°C, which is too high to allow melting of the crystalline aromatic diester when the toner is fused. In the case of terephthatlic acid, di-stearyl ester, it has a melting point of 83°C, but it is too hydrophobic, with a carbon to oxygen ratio of 11, making it incompatible with the amorphous polyester resins, as described above.

[00138] Table 5. Fusing results of toners with di-tert-butyl isophthalate

	Example 4	ULM Control (Xerox® 700 DCP toner)
Crystalline material	15% di-tert-butyl isophthalate	Crystalline Resin
Cold offset on CX+	102	129
Gloss at MFT on CX+	8.2	30.0
Peak Gloss on CX+	53.5	67.8
T(Gloss 50) on CX+	158	140
$MFT_{CA=80}$ (extrapolated MFT)	111	122*
ΔMFT (Relative to Xerox® EA high-gloss toner fused the same day)	-32	-23*
Mottle/Hot Offset CX+220mm/s	210/>210	200/210
Fusing Latitude HO-MFT/CO on CX+	97/>97	71/81

[00139] As shown in Table 5, incorporation of the di-tert-butyl isophthalate in the toner provides a cold offset temperature (100°C versus 129°C) and a crease fix MFT (111°C versus 122°C) shifted to much lower temperatures relative to the Xerox® 700 DCP toner. (The crease fix MFT values are accurate to roughly ± 3 or 4 degrees centigrade.) The mottle/hot offset temperature was higher (210°C versus 200°C), which resulted in much larger fusing latitude (97°C vs. 71°C).

[00140] The toner of Example 5 and controls were evaluated using the fusing apparatus from a Xerox® 700 Digital Color Press printer. The toners were fused at 220 mm/s onto Color Xpressions® paper (90 gsm) with a toner mass per unit area (TMA) of 1.00 mg/cm^2 for gloss, MFT, cold offset performance and hot offset performance. The temperature of the fuser roll was varied from cold offset to hot offset (up to 210°C) for gloss and crease measurements. The fusing performance of the toners is shown in Figures 9 & 10.

[00141] Figures 9 & 10 show plots of print gloss and print crease area, respectively, against fusing temperature for the toner of Example 5 containing 15% N-benzyl phthalimide and

Xerox® high-gloss toner and the ULM EA Xerox® 700 DCP toner. Relative to the controls, the toner containing N-benzyl phthalimide exhibits somewhat lower gloss and lower crease fix MFT. Notably, the experimental toner exhibits a very low cold-offset temperature and a high hot-offset temperature, providing an unexpectedly wide fusing latitude.

[00142] The toner of Example 6 and controls were evaluated using the fusing apparatus from a Xerox® 700 Digital Color Press printer. The toners were fused at 220 mm/s onto Color Xpressions® paper (90 gsm) with a toner mass per unit area (TMA) of 1.00 mg/cm^2 for gloss, MFT, cold offset performance and hot offset performance. The temperature of the fuser roll was varied from cold offset to hot offset (up to 210°C) for gloss and crease measurements. The fusing performance of the toners is shown in Figures 11 & 12 and in Table 6.

[00143] Table 6 shows the fusing results of the toner of Example 6, including the small molecule crystalline benzyl 2-naphthyl ether, compared with those of Xerox® 700 DCP toner as a control toner containing a crystalline resin. The fuser is the fusing apparatus of a Xerox® 700 Digital Color Press printer.

[00144] Table 6. Fusing results of toners containing benzyl 2-naphthyl ether

	ULM Control (Xerox® 700 DCP toner)	Example 6
Crystalline material	Crystalline Resin	15% benzyl 2-naphthyl ether
Cold offset on CX+	113	100
Gloss at MFT on CX+	13.1	14.0
Peak Gloss on CX+	66.0	64.7
T(Gloss 50) on CX+	143	144
MFT_{CA-80} (extrapolated MFT)	117	104
ΔMFT (Relative to Xerox® EA high-gloss toner fused the same day)	-28	-41
Mottle/Hot Offset CX+220mm/s	190 / >210	200 / >210
Fusing Latitude HO-MFT on DCX+	73/>93	96 / >106

[00145] As shown in Table 6, incorporation of the benzyl 2-naphthyl ether in the toner provides a cold offset temperature (100°C versus 113°C) and a crease fix MFT (104°C versus 117°C) shifted to much lower temperatures relative to the Xerox® 700 DCP toner. (The crease fix MFT values are accurate to roughly ± 3 or 4 degrees centigrade.) The mottle/hot offset temperature was higher (200°C versus 190°C), which resulted in much larger fusing latitude (96°C versus 73°C).

[00146] Figures 11 & 12 show plots of print gloss and print crease area, respectively, against fusing temperature for the toner of Example 6 containing 15% benzyl 2-naphthyl ether, Xerox® high-gloss toner and the ULM EA Xerox® 700 DCP toner. Relative to the ULM EA control, the toner containing benzyl 2-naphthyl ether exhibits somewhat lower gloss, and relative to both controls a lower crease fix MFT.

[00147] The toner of Example 7 and controls were evaluated using the fusing apparatus from a Xerox® 700 Digital Color Press printer. The toners were fused at 220 mm/s onto Color Xpressions® paper (90 gsm) with a toner mass per unit area (TMA) of 1.00 mg/cm^2 for gloss, MFT, cold offset performance and hot offset performance. The temperature of the fuser roll was varied from cold offset to hot offset (up to 210°C) for gloss and crease measurements. The fusing performance of the toners is shown in Figures 13 & 14 and in Table 7.

[00148] Table 7 shows the fusing results of the toner of Example 7, including the small molecule crystalline 2-Naphthyl benzoate, compared with those of Xerox® 700 DCP toner as a control toner containing a crystalline resin. The fuser is the fusing apparatus of a Xerox® 700 Digital Color Press printer.

[00149] Table 7. Fusing results of toners containing 2-Naphthyl benzoate

	ULM Control (Xerox® 700 DCP toner)	Example 7
Crystalline material	Crystalline Resin	15% 2-Naphthyl benzoate
Cold offset on CX+	129	100
Gloss at MFT on CX+	30.0	8.2
Peak Gloss on CX+	67.8	53.5
T(Gloss 50) on CX+	140	158
$MFT_{CA=80}$ (extrapolated MFT)	122	111
ΔMFT (Relative to Xerox® EA high-gloss toner fused the same day)	-23	-34
Mottle/Hot Offset CX+220mm/s	200/210	210 / >210
Fusing Latitude HO-MFT on CX+	71/81	99 / >99

[00150] As shown in Table 7 and Fig. 13, incorporation of the 2-Naphthyl benzoate in the toner provides a cold offset temperature (100°C versus 129°C) and a crease fix MFT (111°C versus 122°C) shifted to much lower temperatures relative to the Xerox® 700 DCP toner. (The crease fix MFT values are accurate to roughly ± 3 or 4 degrees centigrade.) The mottle/hot offset temperature was higher (>210°C versus 210°C), which resulted in much larger fusing latitude (99°C versus 71°C).

[00151] Figures 13 & 14 show plots of print crease area and print gloss, respectively, against fusing temperature for the toner of Example 2 containing 15% 2-Naphthyl benzoate, Xerox® high-gloss toner and the ULM EA Xerox® 700 DCP toner. Relative to the ULM EA control, the toner containing 2-Naphthyl benzoate exhibits somewhat lower gloss, and relative to both controls a lower crease fix MFT.

[00152] **<u>Developer Charging Results</u>**

[00153] Toner samples as described above were blended with Xerox® 700 DCP additives and carrier to provide developer samples. The developer samples were conditioned overnight in A and J zones and then charged using a Turbula mixer for about 60 minutes. The A zone is a high humidity zone at about 28°C and 85% relative humidity (RH) and the J zone is a low humidity zone at about 21°C and 10% RH. Toner charge (Q/d) was measured using a charge spectrograph with a 100 V/cm field, and was measured visually as the midpoint of the toner charge distribution. The toner charge per mass ratio (Q/m) was determined by the total blow-off charge method, measuring the charge on a faraday cage containing the developer after removing the toner by blow-off in a stream of air. The total charge collected in the cage is divided by the mass of toner removed by the blow-off, by weighing the cage before and after blow-off to give the Q/m ratio.

[00154] The toners of Examples 4-7 were tested and the charging results were found to be acceptable – similar to results for a nominal ULM toner used as a control. Moreover, the toner charging properties may be optimized, improving both Q/m and Q/d for instance, by: adjusting the toner shell thickness; varying the weight percentage of crystalline material; incorporating both small molecule crystalline organic compounds and a crystalline polymer and optimizing the ratio; adjusting the toner agglomeration/coalescence process, for instance adjusting the coalescence temperature.

[00155] It will be appreciated that variants of the above-disclosed and other features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently unforeseen or unanticipated 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 following claims.

WHAT IS CLAIMED IS:

1. An emulsion aggregation (EA) toner comprising:

an amorphous polymeric resin;

optionally a colorant; and

a small molecule crystalline organic compound being selected from the group consisting of small molecule crystalline aromatic ethers having the formula

$$R_1{-}O{-}[(CH_2)_2O]_p{-}R_2,$$

wherein R_1 and R_2 are independently selected from the group consisting of an alkyl group, an arylalkyl group, an alkylaryl group, and an aromatic group, wherein at least one of R_1 and R_2 is an aromatic group, and wherein p is 0 or 1;

wherein a mixture of the amorphous polymeric resin and the small molecule crystalline organic compound is characterized by a reduction in glass transition temperature from that of the amorphous polymeric resin and by the lack of a significant solid to liquid phase transition peak for the small molecule crystalline organic compound as determined by differential scanning calorimetry, the enthalpy of fusion for the small molecule crystalline organic compound in the mixture being measured to be less than 10% of the enthalpy of fusion of the small molecule crystalline organic compound in pure form.

2. The EA toner of claim 1, wherein the amorphous polymeric resin is a polyester resin.

3. The EA toner of claim 2, wherein the polyester resin comprises a poly(propoxylated bisphenol A co-fumarate) resin.

4. The EA toner of any one of claims 1 to 3, wherein the enthalpy of fusion for the small molecule crystalline organic compound in the mixture is measured to be less than 5% of the enthalpy of fusion of the small molecule crystalline organic compound in pure form.

5. The EA toner of any one of claims 1 to 4, further comprising a wax.

6. The EA toner of any one of claims 1 to 5, wherein the small molecule crystalline organic compound has a carbon-to-oxygen ratio between 3.5 and 6.

7. The EA toner of any one of claims 1 to 6, wherein the small molecule crystalline organic compound is about 5% to about 25% by dry weight of the emulsion aggregation toner.

8. The EA toner of any one of claims 1 to 7, further comprising a crystalline polymeric resin.

9. The EA toner of claim 8, wherein the crystalline polymeric resin is a crystalline polyester resin.

10. The EA toner of any one of claims 1 to 9, wherein the emulsion aggregation toner is configured to have a crease fix minimum fusing temperature of less than or equal to about -20°C.

11. The EA toner of claim 10, wherein the crease fix minimum fusing temperature of the toner is at least 5°C less than -20°C.

12. A method for making emulsion aggregation toner particles comprising:

admixing polymeric amorphous resin emulsion, optionally at least one colorant emulsion, an optional wax emulsion, and a small molecule crystalline organic compound emulsion, the small molecule crystalline organic compound being selected from the group consisting of small molecule crystalline aromatic ethers having the formula

$$R_1{-}O{-}[(CH_2)_2O]_p{-}R_2\,,$$

wherein R_1 and R_2 are independently selected from the group consisting of an alkyl group, an arylalkyl group, an alkylaryl group, and an aromatic group, wherein at least one of R_1 and R_2 is an aromatic group, and wherein p is 0 or 1; and

adding an aggregating agent to the composite emulsion to form emulsion aggregation toner particles;

wherein a mixture of the amorphous resin and the small molecule crystalline organic compound is characterized by a reduction in glass transition temperature from that of the polymeric amorphous resin and by the lack of a significant solid to liquid phase transition peak for the small molecule crystalline organic compound as determined by differential scanning calorimetry, the enthalpy of fusion for the small molecule crystalline organic compound in the mixture being measured to be less than 10% of the enthalpy of fusion of the small molecule crystalline organic compound in pure form.

13. The method of claim 12, wherein the small molecule crystalline organic compound is about 5% to about 25% by dry weight of the emulsion aggregation toner particles.

14. The method of claim 12 or 13, wherein the admixing further includes a crystalline polymeric resin emulsion.

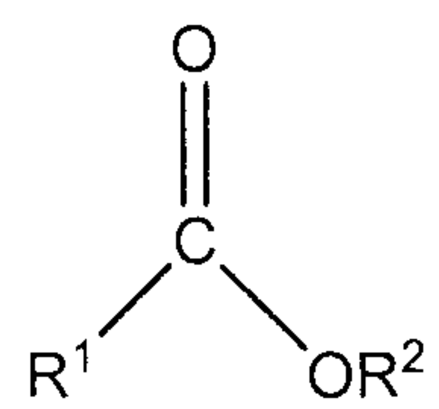
15. The method of any one of claims 12 to 14, wherein the polymeric amorphous resin emulsion is a polyester resin emulsion.

16. An emulsion aggregation (EA) toner comprising:

an amorphous polymeric resin;

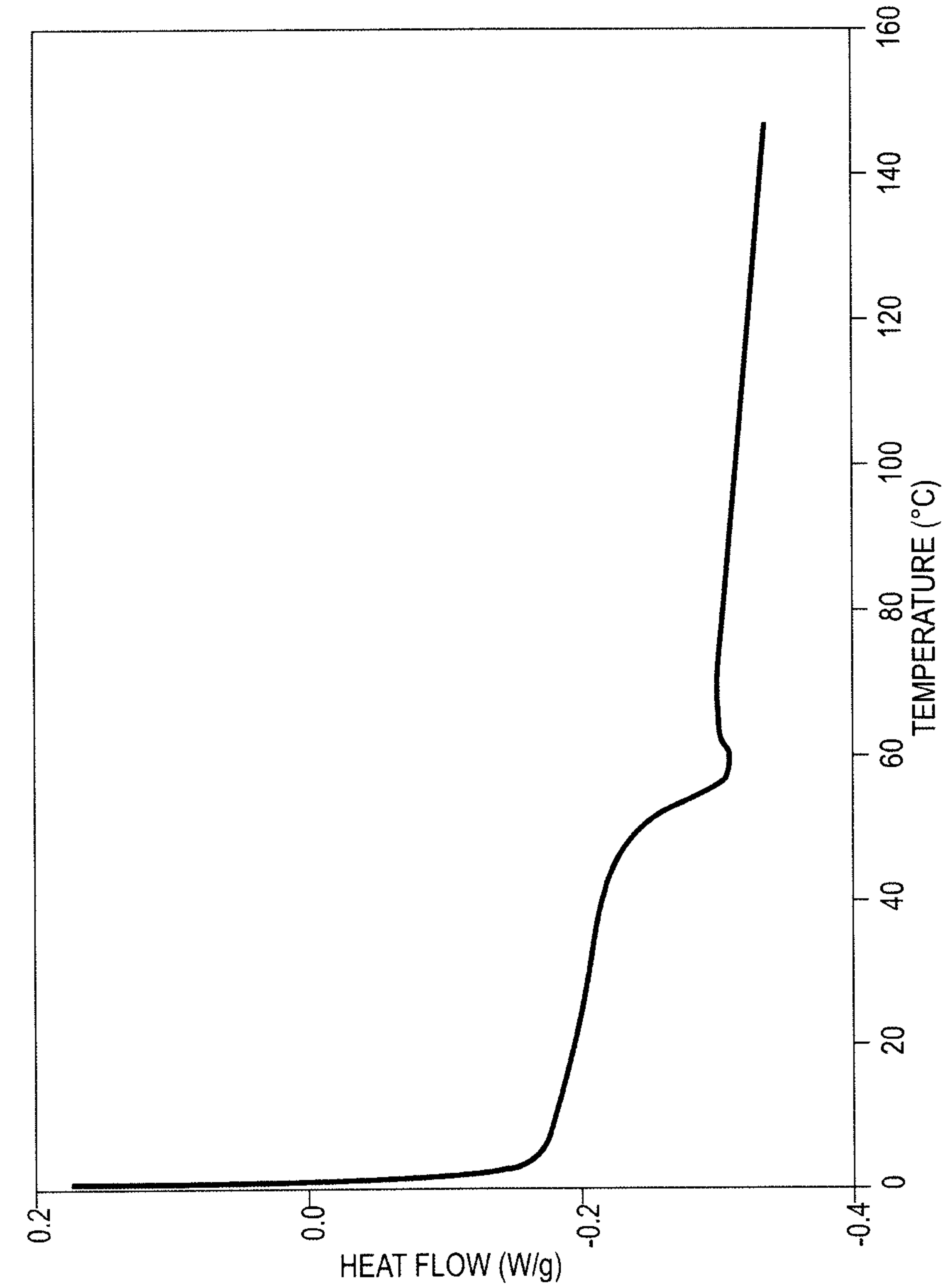
optionally a colorant; and

a small molecule crystalline organic compound being selected from the group consisting of small molecule crystalline monoesters having the formula:



wherein R^1 and R^2 are aromatic groups;

wherein a mixture of the amorphous polymeric resin and the small molecule crystalline organic compound is characterized by a reduction in glass transition temperature from that of the amorphous polymeric resin and by the lack of a significant solid to liquid phase transition peak for the small molecule crystalline organic compound as determined by differential scanning calorimetry, the enthalpy of fusion for the small molecule crystalline organic compound in the mixture being measured to be less than 10% of the enthalpy of fusion of the small molecule crystalline organic compound in pure form.


0
20
40
60
80
100
120
140
160
TEMPERATURE (°C)
0.2
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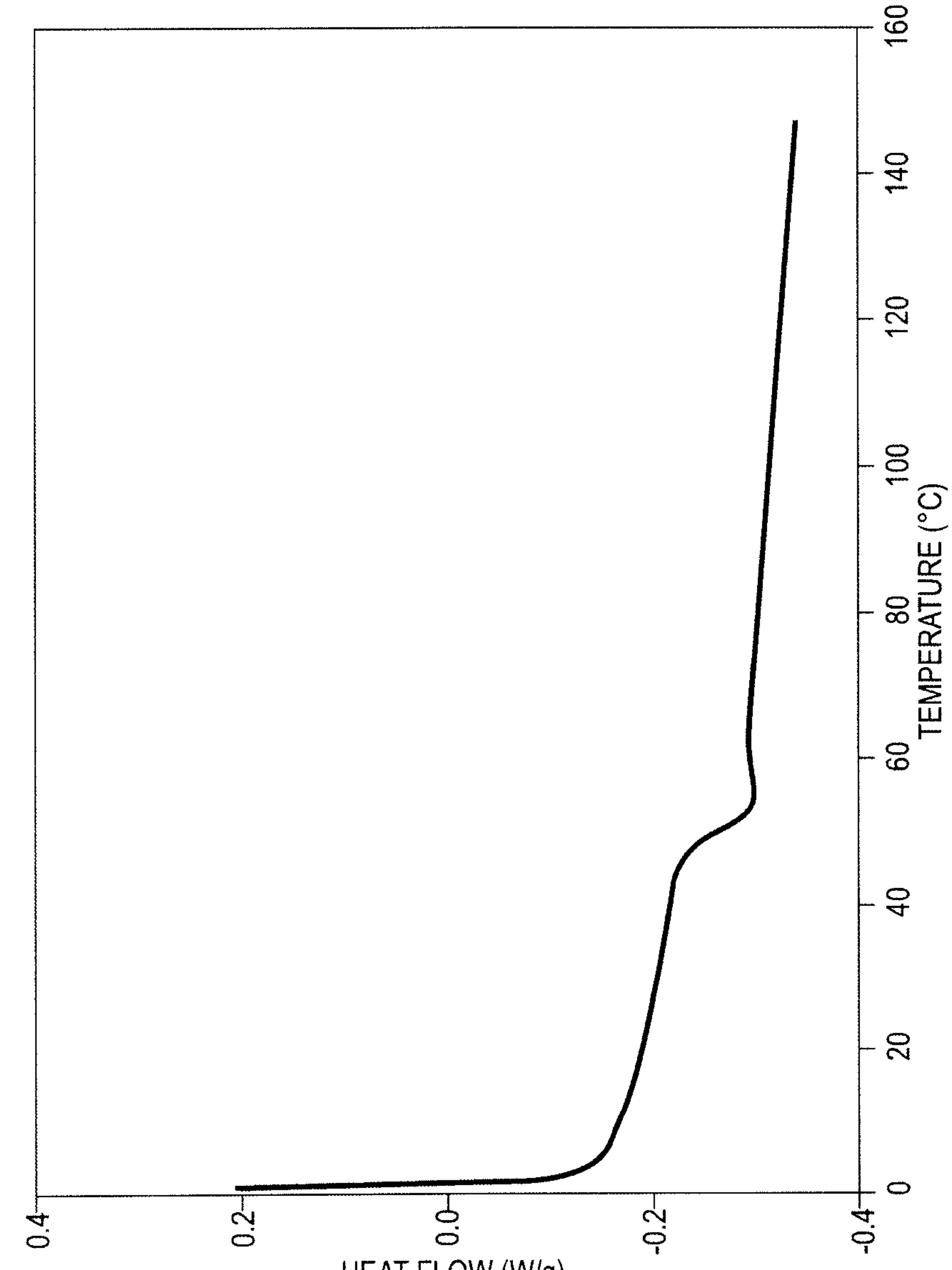
-0.2
-0.4
HEAT FLOW (W/g)

FIG. 1


HEAT FLOW (W/g)
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0.2
0.0
-0.2
-0.4
TEMPERATURE (°C)
0
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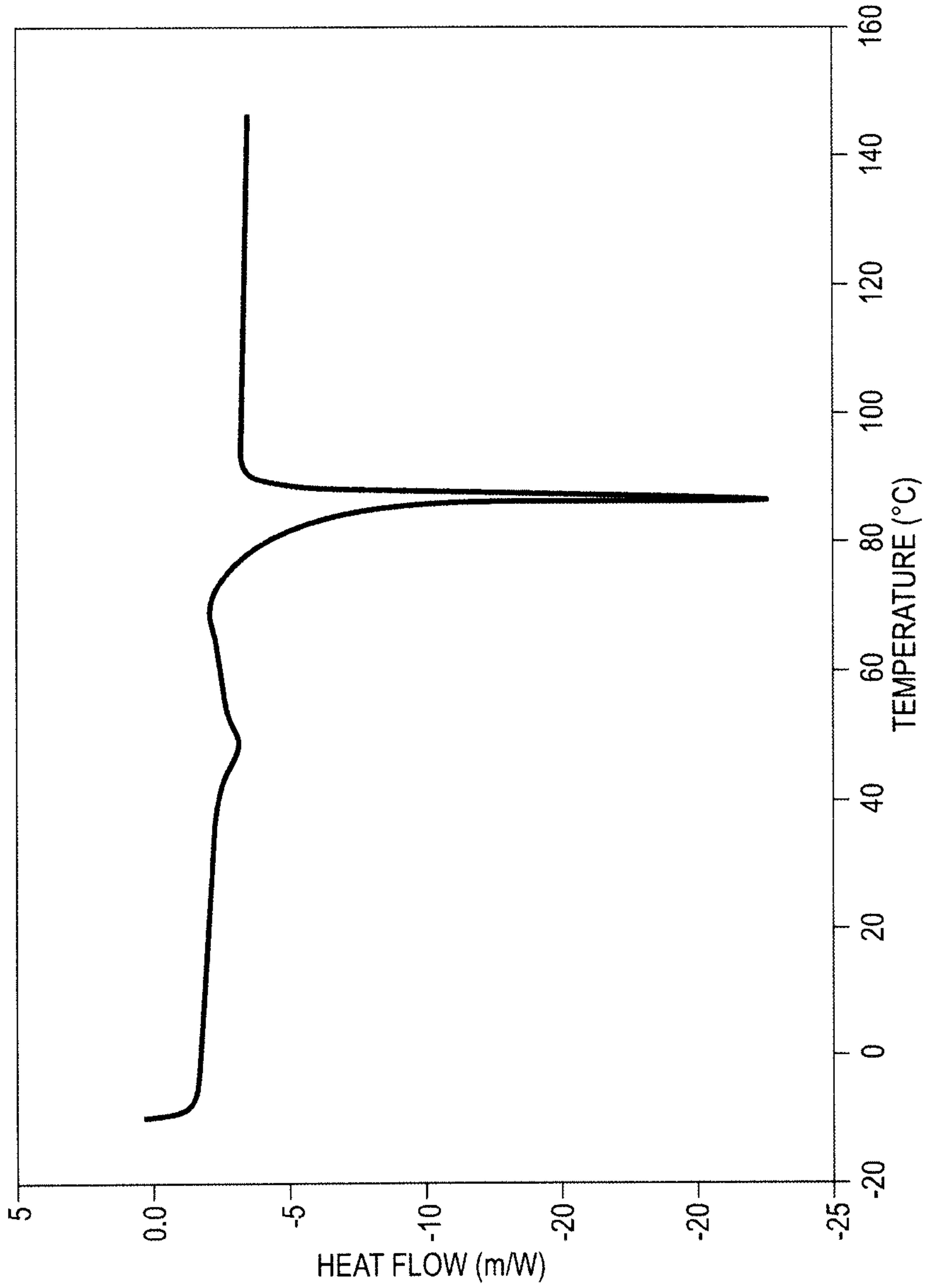
40
60
80
100
120
140
160

FIG. 2


HEAT FLOW (m/W)
5
0.0
-5
-10
-20
-20
-25
TEMPERATURE (°C)
-20
0
20
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60
80
100
120
140
160

FIG. 3

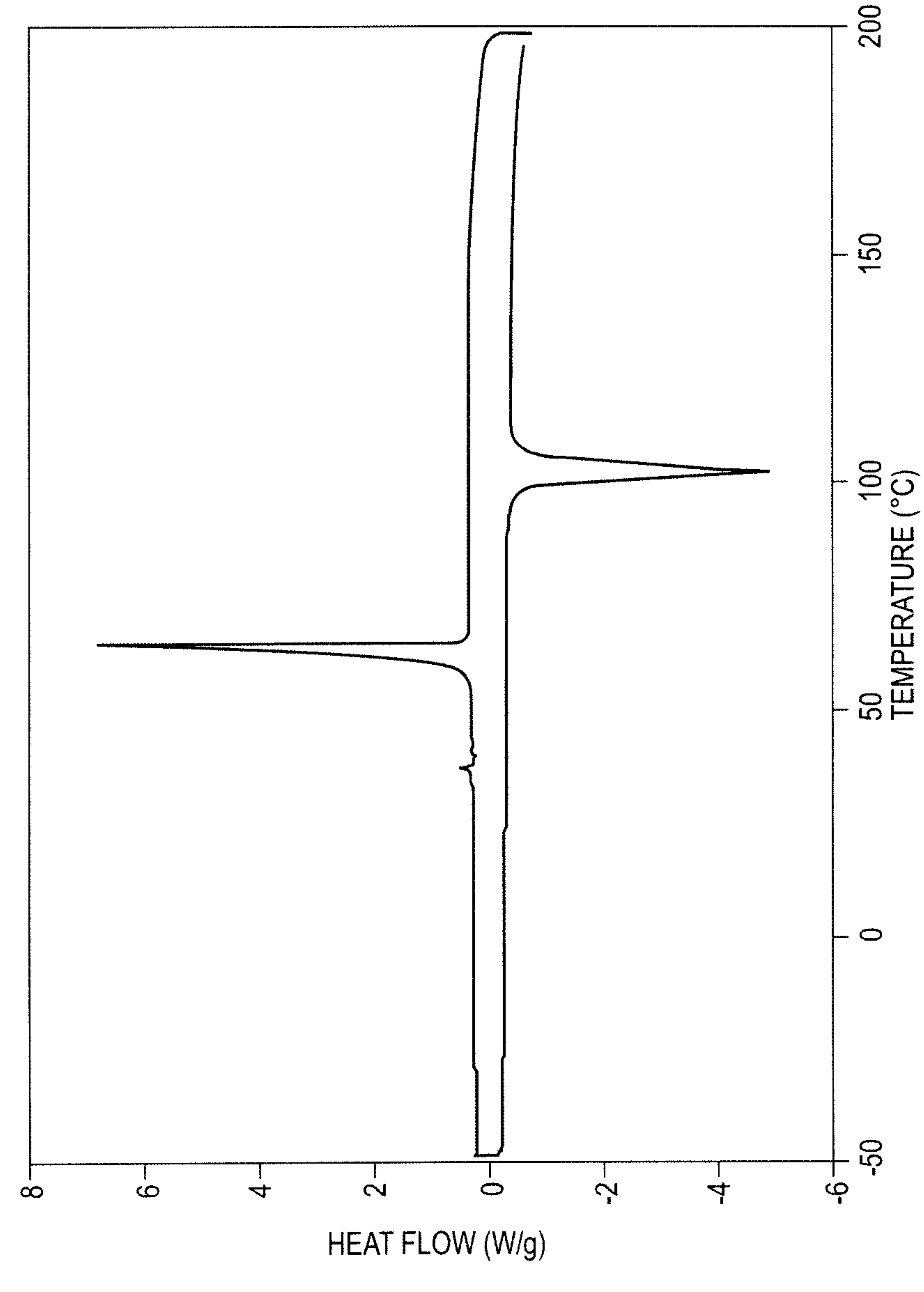
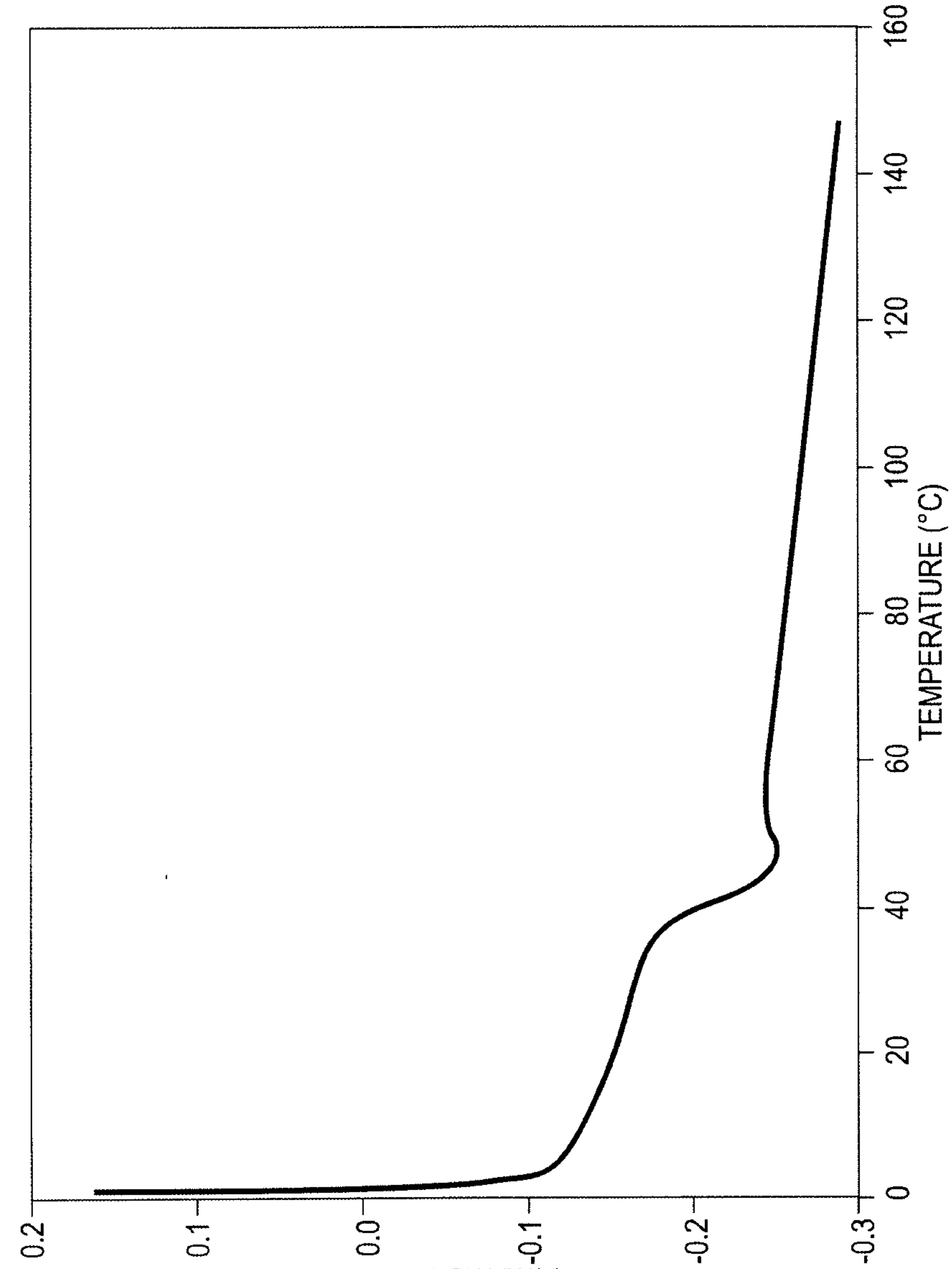


FIG. 4


HEAT FLOW (W/g)
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0.0
-0.1
-0.2
-0.3
TEMPERATURE (°C)
0
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40
60
80
100
120
140
160

FIG. 5

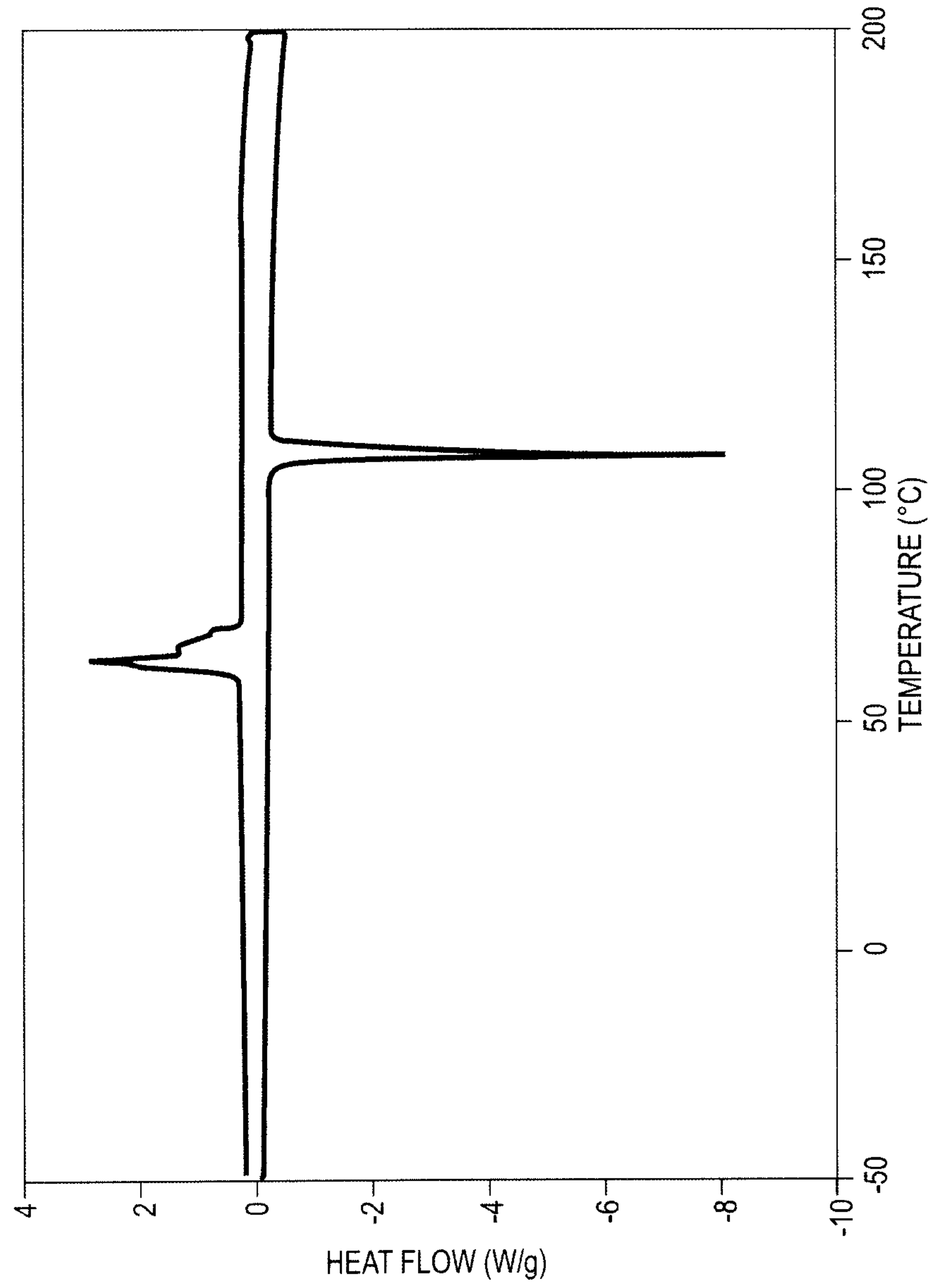


FIG. 6

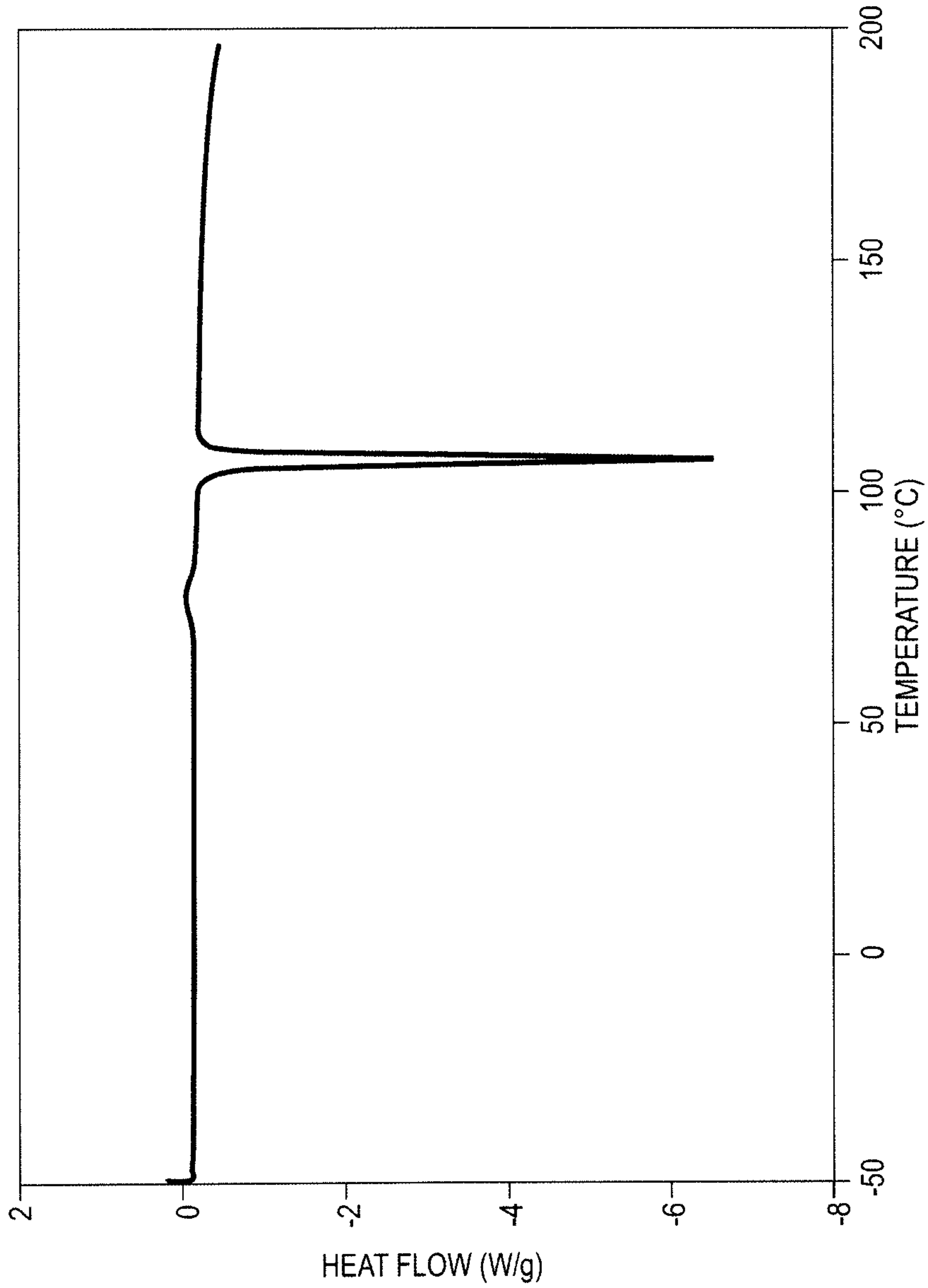
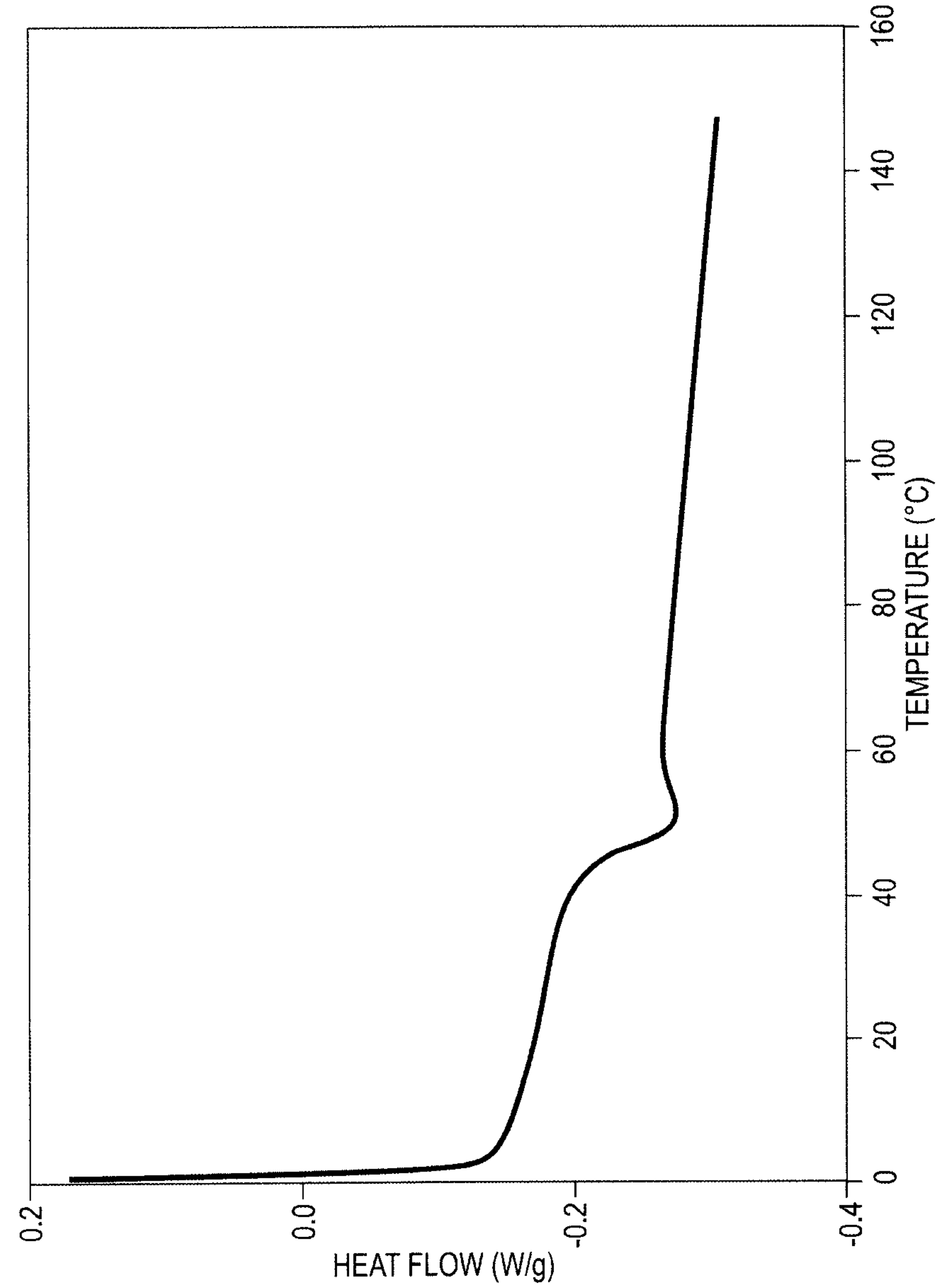


FIG. 7



HEAT FLOW (W/g)
0.2
0.0
-0.2
-0.4
TEMPERATURE (°C)
0
20
40
60
80
100
120
140
160

FIG. 8

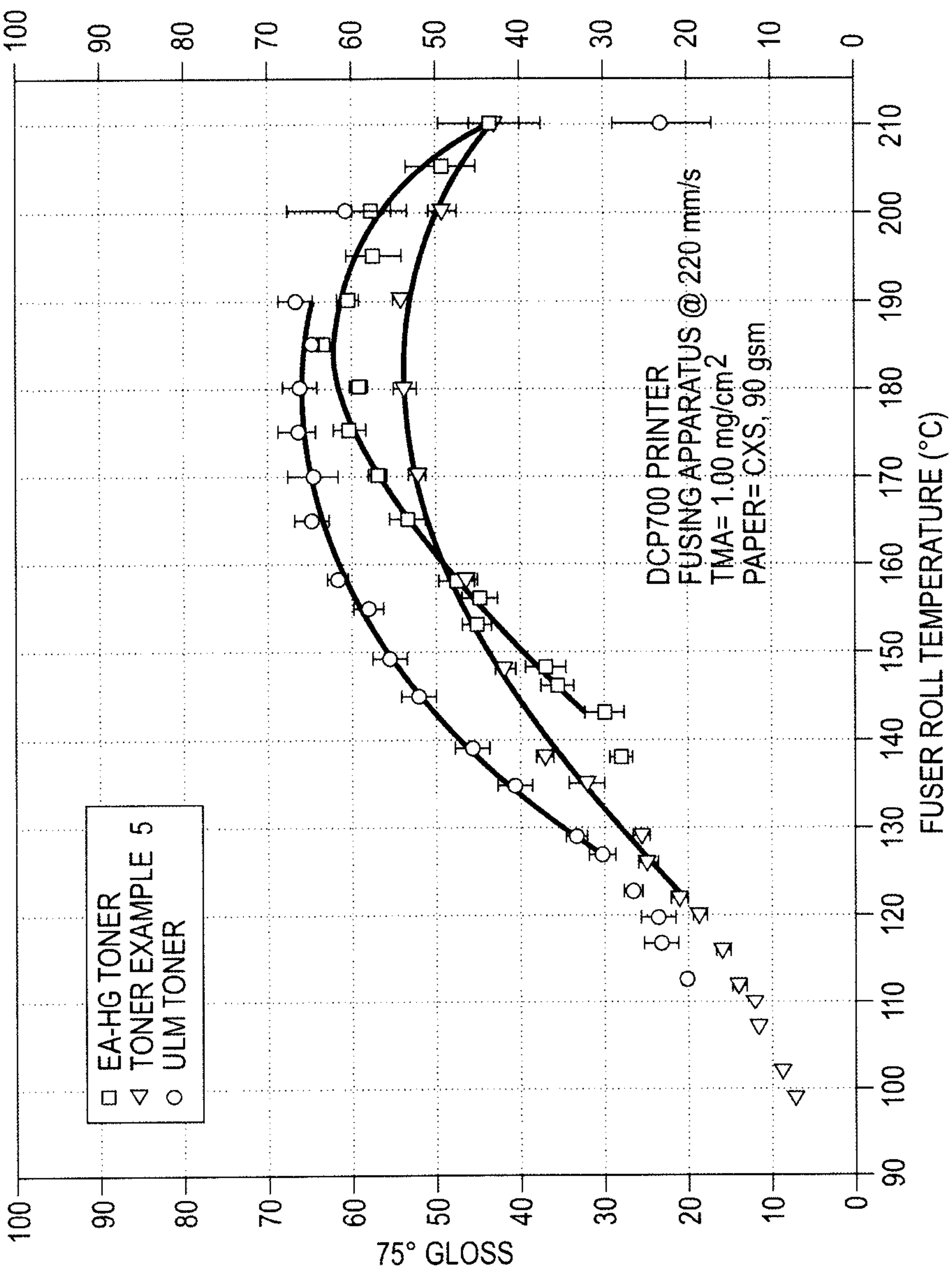

EA-HG TONER
TONER EXAMPLE 5
ULM TONER
DCP700 PRINTER
FUSING APPARATUS @ 220 mm/s
TMA= 1.00 mg/cm2
PAPER= CXS, 90 gsm
75° GLOSS
FUSER ROLL TEMPERATURE (°C)
0
10
20
30
40
50
60
70
80
90
100
90
100
110
120
130
140
150
160
170
180
190
200
210

FIG. 9

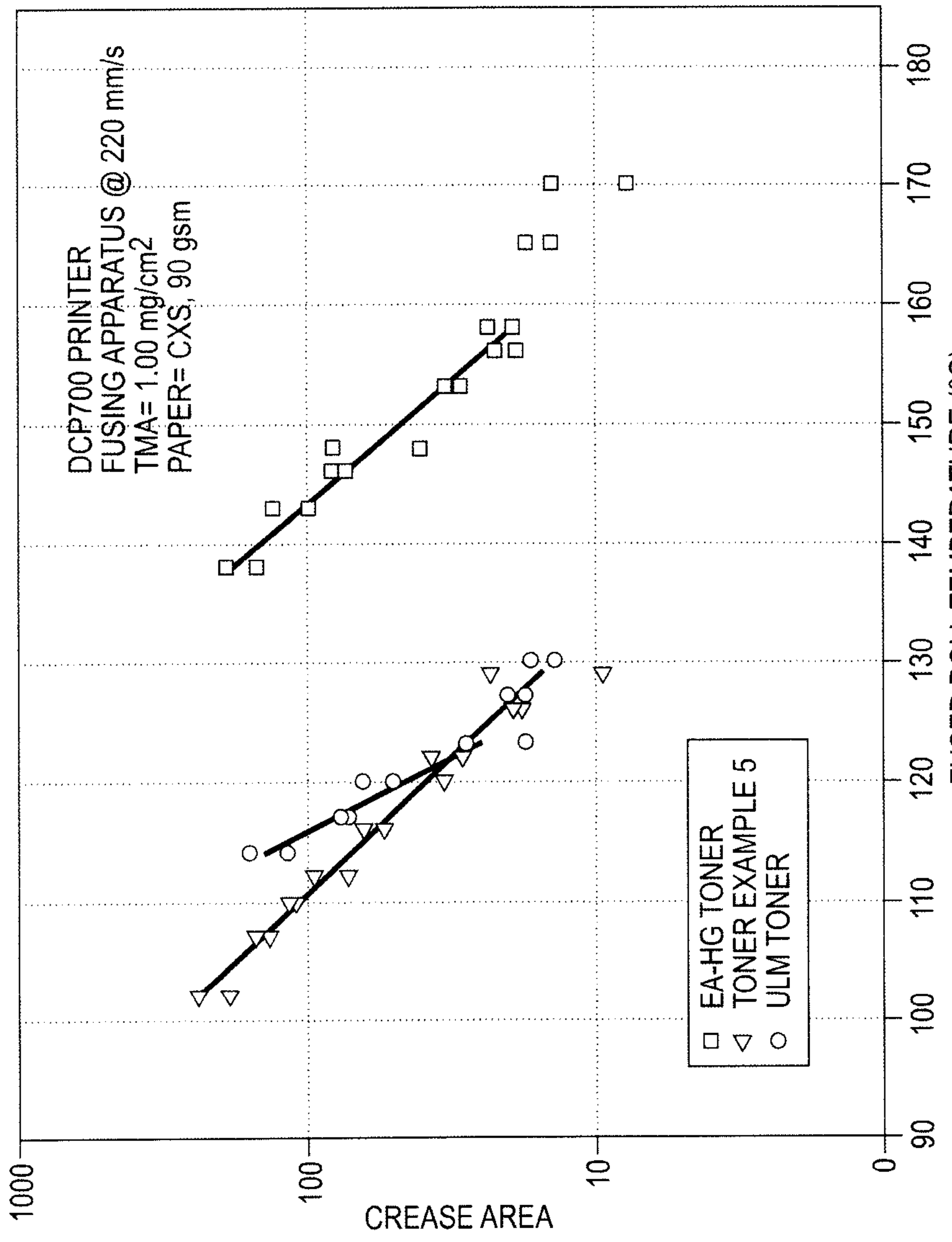

DCP700 PRINTER
FUSING APPARATUS @ 220 mm/s
TMA= 1.00 mg/cm2
PAPER= CXS, 90 gsm
EA-HG TONER
TONER EXAMPLE 5
ULM TONER
CREASE AREA
FUSER ROLL TEMPERATURE (°C)
1000
100
10
0
90
100
110
120
130
140
150
160
170
180

FIG. 10

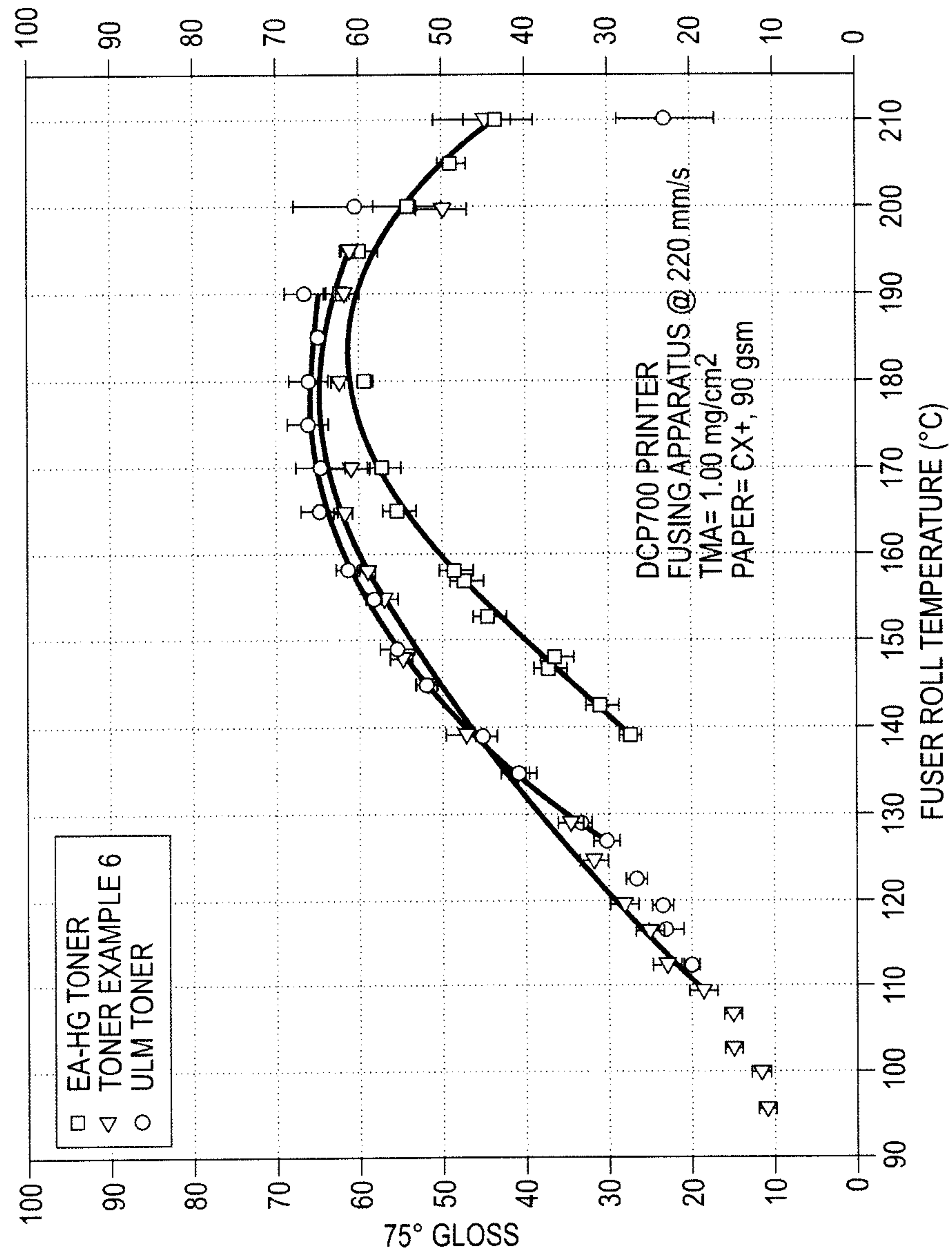

EA-HG TONER
TONER EXAMPLE 6
ULM TONER
DCP700 PRINTER
FUSING APPARATUS @ 220 mm/s
TMA= 1.00 mg/cm2
PAPER= CX+, 90 gsm
75° GLOSS
FUSER ROLL TEMPERATURE (°C)
0
10
20
30
40
50
60
70
80
90
100
90
100
110
120
130
140
150
160
170
180
190
200
210

FIG. 11

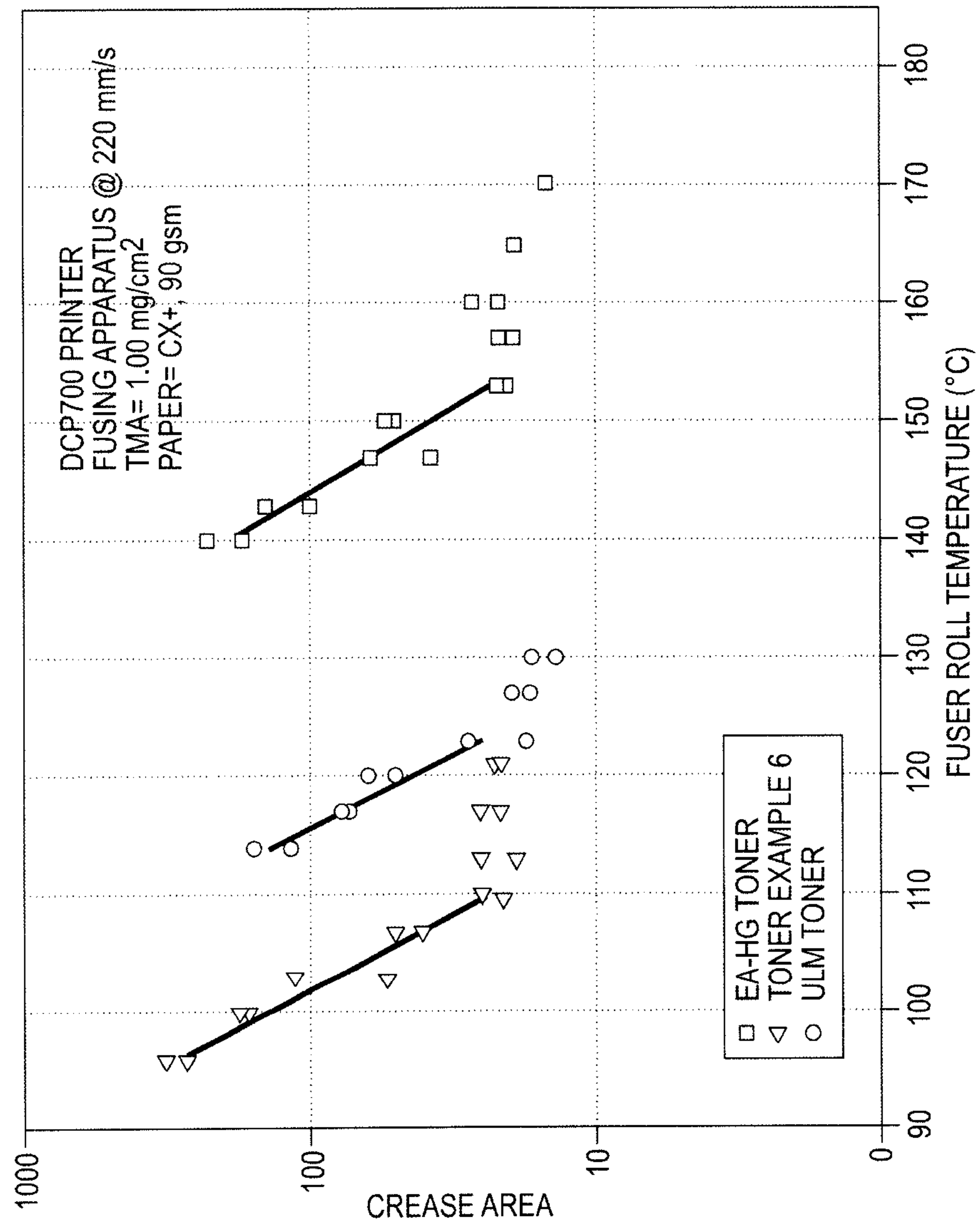

DCP700 PRINTER
FUSING APPARATUS @ 220 mm/s
TMA= 1.00 mg/cm2
PAPER= CX+, 90 gsm
EA-HG TONER
TONER EXAMPLE 6
ULM TONER
CREASE AREA
1000
100
10
0
FUSER ROLL TEMPERATURE (°C)
90
100
110
120
130
140
150
160
170
180

FIG. 12

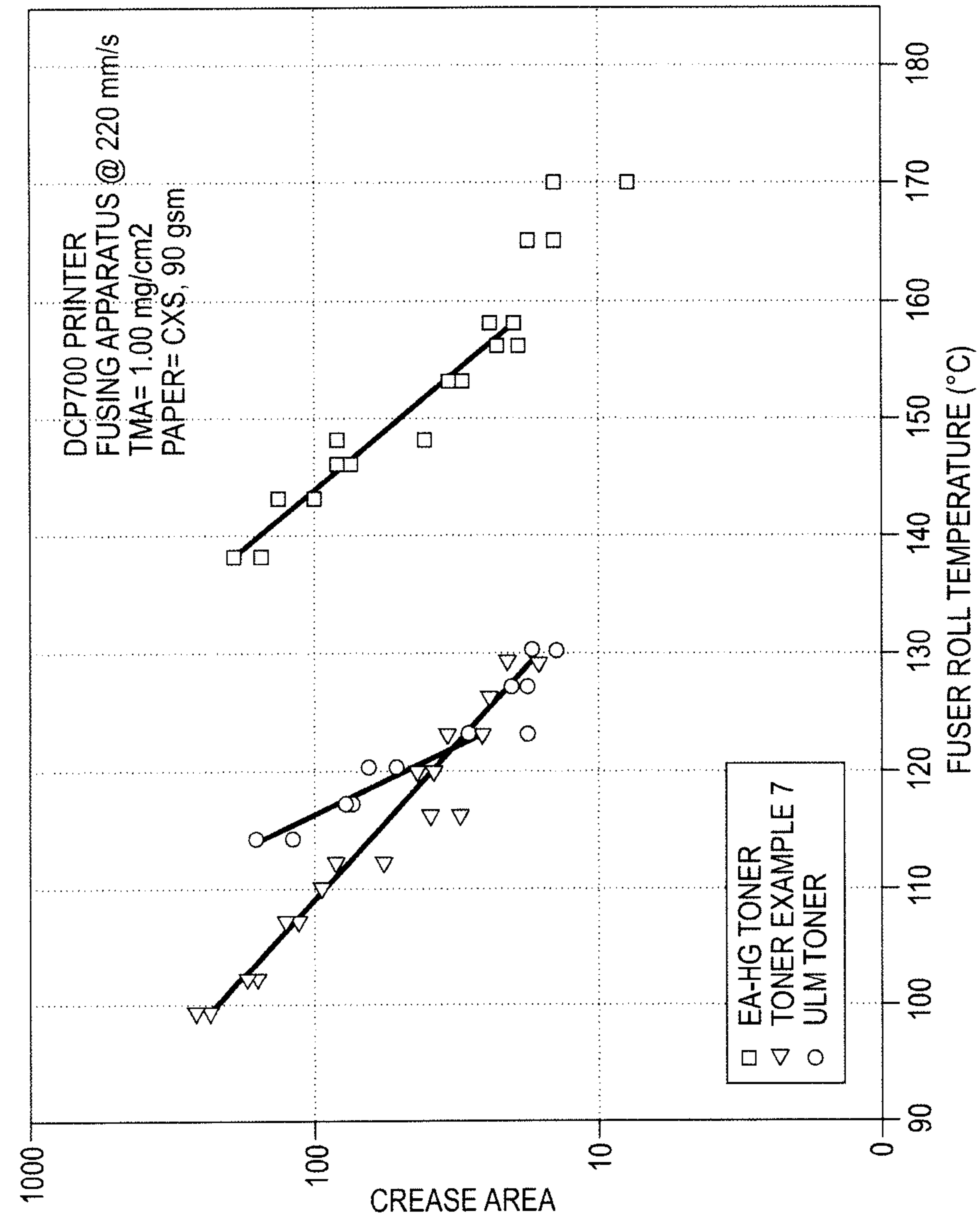

DCP700 PRINTER
FUSING APPARATUS @ 220 mm/s
TMA= 1.00 mg/cm2
PAPER= CXS, 90 gsm
EA-HG TONER
TONER EXAMPLE 7
ULM TONER
CREASE AREA
1000
100
10
0
FUSER ROLL TEMPERATURE (°C)
90
100
110
120
130
140
150
160
170
180

FIG. 13

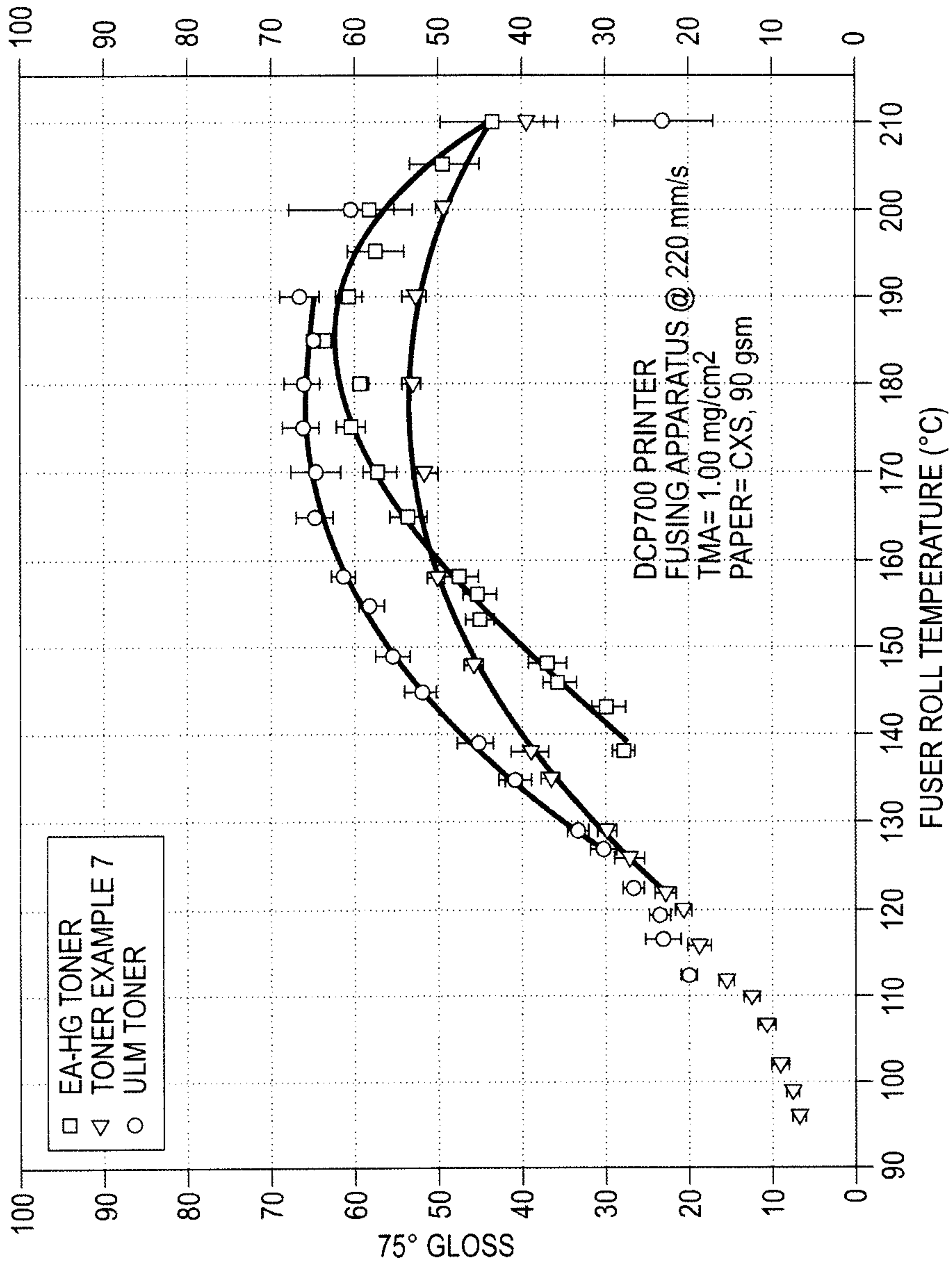

EA-HG TONER
TONER EXAMPLE 7
ULM TONER
DCP700 PRINTER
FUSING APPARATUS @ 220 mm/s
TMA= 1.00 mg/cm2
PAPER= CXS, 90 gsm
75° GLOSS
FUSER ROLL TEMPERATURE (°C)
0
10
20
30
40
50
60
70
80
90
100
90
100
110
120
130
140
150
160
170
180
190
200
210

FIG. 14