



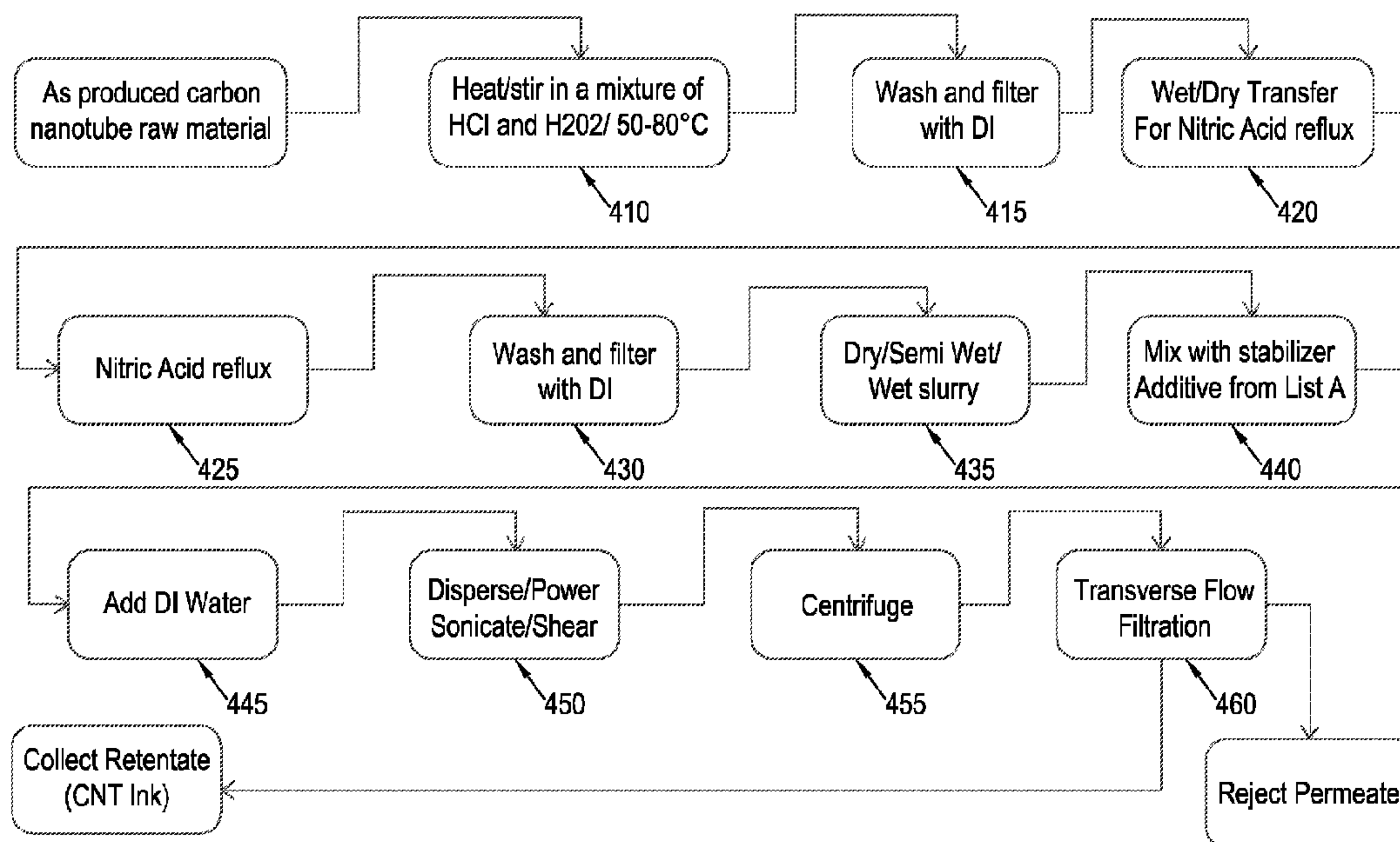
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(54) **Titre : ENCRE DE NANOTUBES DE CARBONE A BASE DE SOLVANT ET A BASE D'EAU COMPRENANT DES ADDITIFS
 POUVANT ETRE ELIMINES**
 (54) **Title: SOLVENT-BASED AND WATER-BASED CARBON NANOTUBE INKS WITH REMOVABLE ADDITIVES**

400

Sequence of Unit Operations in ink processing - Scheme 1 Water base ink



(57) **Abrégé/Abstract:**

In accordance with some embodiments, compositions and methods for forming solvent-based and water-based carbon nanotubes inks with removable additives are provided. In some embodiments, the ink composition comprises one or more carbon nanotubes, a solvent, and a removable additive, which may function as a stabilizing agent, a viscosity adjustment agent, or any suitable combination thereof. The removable additive may be removed from articles derived from the ink composition by means of thermal annealing.

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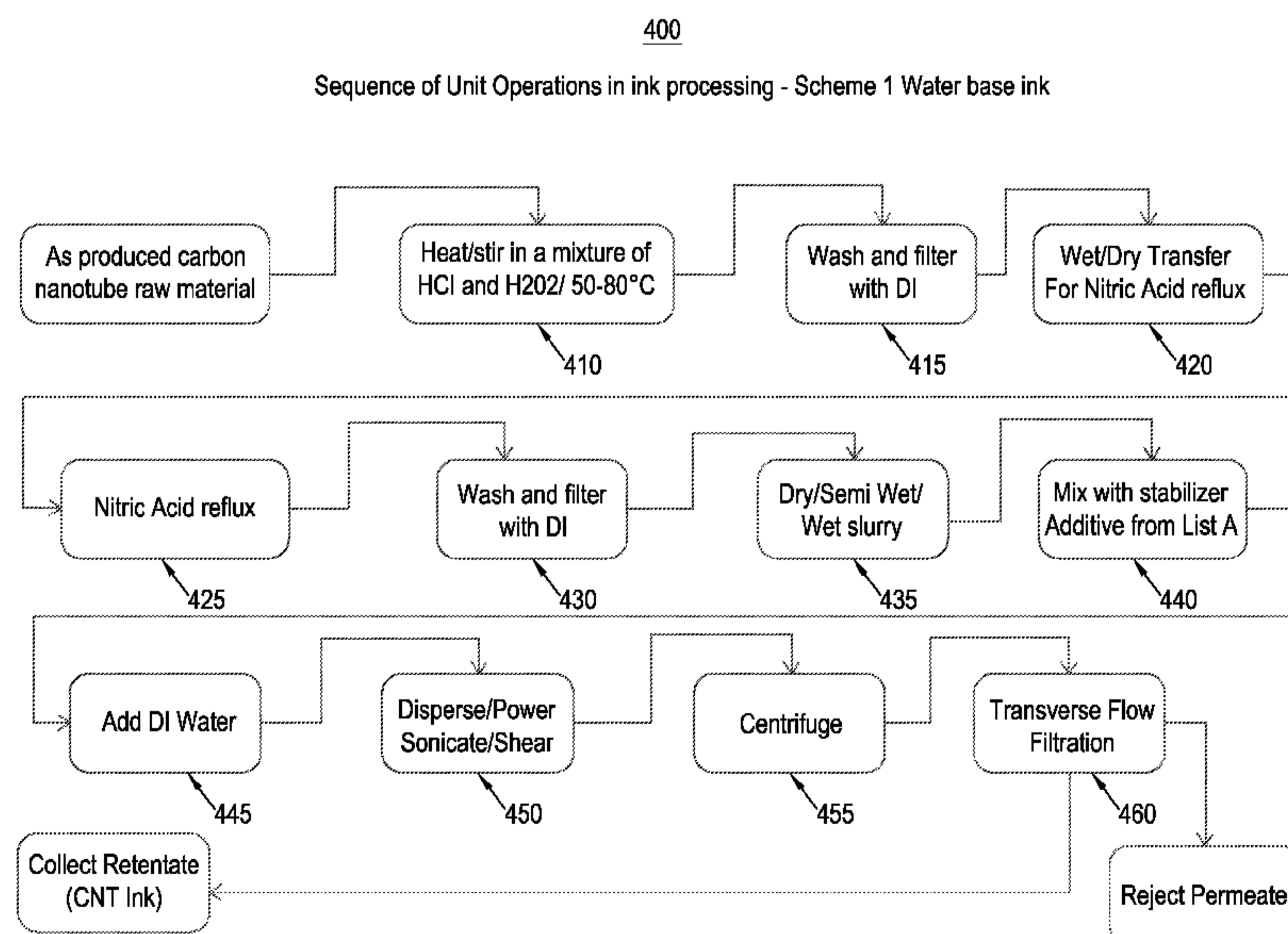
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FIG. 4

(57) **Abstract:** In accordance with some embodiments, compositions and methods for forming solvent-based and water-based carbon nanotubes inks with removable additives are provided. In some embodiments, the ink composition comprises one or more carbon nanotubes, a solvent, and a removable additive, which may function as a stabilizing agent, a viscosity adjustment agent, or any suitable combination thereof. The removable additive may be removed from articles derived from the ink composition by means of thermal annealing.

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SOLVENT-BASED AND WATER-BASED CARBON NANOTUBE INKS WITH REMOVABLE ADDITIVES

Technical Field

[0002] The disclosed subject matter relates to the formation of dispersions or inks of carbon nanotubes. More particularly, the disclosed subject matter relates to the formation of carbon nanotube inks in water and solvent media obtained with the use of removable additives.

Background

[0003] Most applications of single-walled carbon nanotubes (SWCNT), double-walled carbon nanotubes (DWCNT), and multi-walled carbon nanotubes (MWCNT) often require that they are available in the form of dispersions in a purified form in a suitable solvent system. These types of carbon nanotubes are generically described as carbon nanotubes (CNT) unless otherwise indicated.

[0004] As produced raw carbon nanotube soots generally include material impurities (extraneous impurities), such as transition metal catalysts, graphitic carbons, amorphous carbon nanoparticles, fullerenes, carbon onions, polycyclic aromatic hydrocarbons along with the desired carbon nanotube products. The nature and degree of the electronic impurities in a given raw material can depend on the method of synthesis, such as, for example, laser, arc, High-Pressure Carbon Monoxide Conversion (HiPco), chemical vapor deposition (CVD), or combustion.

[0005] Known purification protocols generally involve steps of generic unit operations like pre-oxidation, acid reflux, mechanical mixing, ultrasonication, filtration, neutralization, and centrifugation. Selecting a suitable combination depends upon the method of production of the carbon nanotubes and the specific impurity targeted. As shown below, Table 1 provides an exemplary list of the dominant impurities in different nanotube samples and unit operations

employed in their purification.

TABLE I

SI No	Tube Type	Catalyst metal impurities	Dominant carbon impurities	Unit Operations Employed	Year	Reference
1	Laser	Co, Ni	Graphitic	HNO ₃ reflux, neutralization, centrifugation, cross flow filtration	1998	Rinzler et al., Appl. Phys. A 67, 29-37 (1998)
2	Laser	Co, Ni	Graphitic	gas oxidation, HCl washing	2001	Chiang et al., J. Phys. Chem. B 105, 8297 (2001)
3	Arc	Ni, Y	Graphitic	microwave exposure, HCl washing	2002	Harutyunyan et al., J. Phys. Chem. B 106, 8671 (2002)
4	CVD	Co, Fe, Ni supported on zeolites	Amorphous	air oxidation, HF washing	1999	Colomer et al., Synthetic Metals 103, 2482 (1999)
5	HiPCO	Fe	Fullerenes, Amorphous	wet air oxidation, HCl washing and fluorinated extraction of fullerene impurities	2002	Sivarajan et al., J. Phys. Chem. B 107, 1361 (2003)
6	HiPCO	Fe	Fullerenes, Amorphous	H ₂ SO ₄ +HNO ₃ sonication	2004	Wiltshire et al., Chemical Physics Letters 386, 239 (2004)
7	HiPCO	Fe	Fullerenes, Amorphous	one pot HCl+H ₂ O ₂ washing	2007	Wang et al., J. Phys. Chem. B 111, 1249-1252 (2007)

[0006] A. G. Rinzler et al., "Large-scale purification of single-walled carbon nanotubes: process, product, and characterization," Appl. Phys. A 67, 29-37 (1998) describes a large-scale purification approach for purifying carbon nanotubes employing a sequence of steps including,

for example, nitric acid reflux, neutralization, centrifugation, and cross-flow filtration as essential steps to purify single-walled carbon nanotubes.

[0007] Extraneous impurities, such as catalyst metal particles, fullerenic carbon, amorphous carbon, graphitic carbon, and carbon onions, are present to different degrees in as prepared raw carbon nanotube samples. Oxidative chemical treatments as part of the purification protocol and multiple acid treatments as part of the typical purification processes result in reasonably clean carbon nanotubes (< 0.5 wt % impurities). However, since the intrinsic electrical conductivity arises from the delocalized π electrons of the SWCNT for a SWCNT of a given length and diameter, an aggressive chemical purification or side-wall derivatization during the purification process drains the π electrons of the individual SWCNT. Such a loss of conductive electrons leads to a drastic fall in the single tube electrical conductance as well as the elimination of the inter-band optical transitions arising from the van Hove singularities. Accordingly, for many applications, especially applications requiring a combination of optical and electrical properties retaining the electronic structure of the CNT substantially intact is an important aspect in the formation of SWCNT inks.

[0008] There are numerous approaches that form stable dispersions of carbon nanotubes in water with the use of anionic, cationic, or non-ionic surfactants. These surfactants form a monolayer coating on the surface of the CNT in the dispersed form either as individuals or as thin bundles. There are also widely reported approaches that use ionic or neutral polymer molecules for solubilizing carbon nanotubes in a water medium. Known examples are, among others, polystyrene sulfonate, polyvinyl pyrrolidinone, polyethylene oxide (PEO), polypropylene oxide (PPO), and tri-block copolymers of PEO-PPO-PEO. However, when thin films of CNT networks are formed on solid substrates from such dispersions, most of the surfactants or the polymers remain as part of the carbon nanotube films/network as a coating on the carbon nanotubes and remain there even after treatments at elevated temperatures. Presence of such surface impurities affect the electronic properties of the carbon nanotube network – e.g., reducing the electrical conductivity of the network.

[0009] Another approach for forming carbon nanotube dispersions or inks in organic solvents is to chemically derivatize them. For example, Haddon et al., U.S. Patent No. 6,331,262, describes an approach that involves end functionalization employing carboxylation followed by acid-chloride formation followed by the formation of amide linkage by reacting with

a long chain amine. However, the resulting solutions in organic solvents did not show the characteristic absorption features in the UV-Visible range, thereby suggesting that the delocalized π electrons have been drained completely or significantly. In addition, it should be noted that the electrical properties of the functionalized carbon nanotubes were not reported.

[0010] Huang et al., U.S. Patent Publication No. 2006/0124028 A1, describes carbon nanotube ink compositions in an aqueous medium designed for inkjet printing, which were obtained by a chemical reaction involving an azo compound and carboxylated single-walled carbon nanotubes. This approach focuses on the ink-jet printability of the dispersion or ink rather than the intrinsic properties of the CNT altered by the azo-functionalization.

[0011] Carbon nanotube inks prepared, despite these prior art approaches, especially for SWCNT suffer from one or more of the following limitations:

- a) Loss of inter-band optical transitions indicating a significant modification of the electronic structure of the single walled carbon nanotubes or electronic defects; and/or
- b) Surfactant or polymeric dispersal aid residues that are not removable from the solid film when such inks are used to form carbon nanotube networks or films.

[0012] There is a need in the art for approaches that provide the formation of stable carbon nanotube inks in water or organic solvent media in which (a) the SWCNT have not lost their inter-band optical transitions signifying an intact electronic structure and (b) the dispersal aids that are used to stabilize the SWCNT do not leave non-volatile residue in the solid products such as films formed from such inks. Accordingly, it is desirable to provide solvent-based and water-based carbon nanotube inks that overcome these and other deficiencies of the prior art.

[0013] For example, in some embodiments, a dispersal aid system that is non-ionic, molecular in nature, conserves the electronic structure of the SWCNT as evidenced by the inter-band optical transitions and that uses dispersal aids that can be completely removed from the carbon nanotube network or films that are formed using the CNT ink.

Summary

[0014] Applications of single-walled carbon nanotubes (SWCNT), double-walled carbon nanotubes (DWCNT), and multi-walled carbon nanotubes (MWCNT) generally require carbon nanotubes in the form of dispersions in suitable solvent systems. Raw carbon nanotube soots generally include material impurities such as transition metal catalysts, graphitic carbons,

amorphous carbon nanoparticles, fullerenes, carbon onions, polycyclic aromatics along with the desired carbon nanotube products.

[0015] The nature and degree of the impurities in a given raw material depends on the method of synthesis, such as, for example, laser, arc, High-Pressure Carbon Monoxide Conversion (HiPco), chemical vapor deposition (CVD), or combustion methods. Currently available purification processes and systems generally involve generic unit operations, such as pre-oxidation, acid reflux, mechanical mixing, ultrasonication, filtration, neutralization, and centrifugation.

[0016] For example, single-walled carbon nanotubes (SWCNT) can be produced using a premixed combustion of carbon-containing fuels, such as hydrocarbons, including methane, natural gas, or alcohols, while a metal catalyst precursor (such as iron pentacarbonyl, ferrocene, or a metal salt solution) is added continuously to the fresh gas mixture. Characteristics of the SWCNT formed, such as length, can be controlled by process parameters (e.g., pressure, inert gas dilution, temperature, fresh gas velocity, residence time, etc.). By-products are reaction products of the catalyst precursor, for example, iron or iron oxides (particularly Fe_2O_3) and carbonaceous material other than SWCNT, such as polycyclic aromatic hydrocarbons (PAH).

[0017] It should be noted that, although the present invention is generally described in connection with the purification and dispersion of flame synthesized carbon nanotubes, this is merely illustrative. The disclosed subject matter can provide, among other possible advantages and beneficial features, methods, techniques, apparatuses, systems, and/or methods of manufacture that can be used for the purification and formation of water-based or solvent-based suspensions of carbon nanotubes of all types.

[0018] In some embodiments, small molecular additives, such as diethylenetriamine (DETA) and diisopropylethylamine (DIPEA or Hunig's base), can be used as stabilizing additives that disperse single-walled carbon nanotubes without the elimination of the inter-band optical transitions or viscosity adjustment agents.

[0019] It should be noted that Hunig's base (DIPEA) is not soluble in water. In some embodiments, the present invention describes a method for making a water-based dispersion of single-walled carbon nanotubes employing amines that are not necessarily soluble in water.

[0020] In some embodiments, the present invention describes the formation of solvent-based CNT inks. For example, solvent-based CNT inks can be formed using

N-methylpyrrolidinone (NMP) as the solvent and polypropylene carbonate oligomer as an additive that can be completely removed. It should be noted that the additive can act a stabilizing agent, a viscosity adjustment agent, or any suitable combination thereof.

[0021] In some embodiments, the additives described herein (e.g., stabilizing agents, dispersal aids, or viscosity adjustment agents) can also be used for the dispersion of other carbonaceous nanostructures, such as, for example, graphene, fullerenes like C₆₀ and C₇₀, shortened nanotubes (e.g., fullerene pipes), and nanofibers of any of these compounds in water and/or organic solvent media. In addition, these additives can be used for chemical derivatives of all carbonaceous nanostructures including, for example, single-walled carbon nanotubes, double-walled carbon nanotubes, multi-walled carbon nanotubes, graphene, fullerenes, shorted carbon nanotubes, and nanofibers.

[0022] In accordance with some embodiments of the present invention, an ink composition is provided, the ink composition comprising: a plurality of carbon nanotubes; a solvent; and a removable additive that stabilizes the plurality of carbon nanotubes in the solvent.

[0023] In some embodiments, the removable additive is selected to act as a dispersal agent and a stabilization agent.

[0024] In some embodiments, the removable additive is selected to adjust viscosity of the ink based at least in part on molecular weight of the removable additive.

[0025] In some embodiments, the solvent is water and wherein the removable additive is N,N-Diisopropylethylamine (DIPEA).

[0026] In some embodiments, the removable additive is selected from the group consisting of diethylenetriamine (DETA), diisopropylethylamine (DIPEA), triethanolamine, ethylene diamine, aminoethyl ethanolamine, triethylene tetramine (TETA), tetraethylene pentamine (TEPA), pentaethylene hexamine (PEHA), and mixtures thereof.

[0027] In some embodiments, the solvent is an organic solvent selected from the group consisting of N-methylpyrrolidinone (NMP), propylene glycol monomethyl ether acetate (PGMEA), cyclohexanone, methyl ethyl ketone (MEK), and methyl isopropyl ketone, and wherein the additive is polypropylene carbonate.

[0028] In some embodiments, the removable additive is selected such that the removable additive can be removed from the ink composition by at least 90% by thermal annealing at a temperature lower than about 250°C. In other embodiments, at least 90% of the removable

additive can be removed by thermal annealing at a temperature lower than about 200°C. Alternatively, at least 90% of the removable additive can be removed by thermal annealing at a temperature lower than about 300°C.

[0029] In some embodiments, the plurality of carbon nanotubes are one or more of: single-walled carbon nanotubes, double-walled carbon nanotubes, and multi-walled carbon nanotubes. In some embodiments, at least 90% of the plurality of carbon nanotubes are single-walled carbon nanotubes. In other embodiments, at least 90% of the plurality of carbon nanotubes are double-walled carbon nanotubes. Alternatively, at least 90% of the plurality of carbon nanotubes are multi-walled carbon nanotubes.

[0030] In some embodiments, the plurality of carbon nanotubes dispersed within the solvent can be separated between functionalized and unfunctionalized carbon nanotubes (e.g., using density gradient centrifugation or electrophoresis). In addition, in some embodiments, the plurality of carbon nanotubes dispersed within the solvent can be separated between metallic and semiconducting carbon nanotubes (e.g., using chemical or electrophoresis approaches) with or without prior functionalization. For example, in some embodiments, the plurality of carbon nanotubes can be separated such that at least 80% of the plurality of carbon nanotubes are semiconducting single-walled carbon nanotubes. In some embodiments, the carbon nanotube ink described herein can be enriched in either semiconducting or metallic single-walled carbon nanotubes in comparison to their initial abundance in the as-produced material (e.g., often approximately a 2:1 ratio of semiconducting vs. metallic corresponding to the ensemble of all theoretically existing chiralities).

[0031] In some embodiments, a method of preparing an ink composition is provided, the method comprising: providing a plurality of carbon nanotubes; providing a removable additive to the plurality of carbon nanotubes; providing a solvent to the plurality of carbon nanotubes and the removable additive, wherein the plurality of carbon nanotubes are dispersed within the solvent and wherein the removable additive stabilizes the plurality of carbon nanotubes that are suspended in the solvent; and removing a substantial portion of the removable additive by thermal annealing.

[0032] In some embodiments, the method further comprises applying the ink composition to a substrate. The substrate can be a glass substrate, a plastic substrate, and/or a sapphire substrate.

[0033] In some embodiments, the removable additive is removable after applying the ink composition to the substrate. The removable additive is selected such that the removable additive can be removed from the ink composition by at least 90% by thermal annealing at a temperature lower than about 250°C.

[0034] In some embodiments, the method further comprises stabilizing the plurality of carbon nanotubes by applying the removable additive to the plurality of carbon nanotubes prior to dispersing the plurality of carbon nanotubes in the solvent.

[0035] In some embodiments, the method further comprises mixing the solvent with the removable additive prior to dispersing the plurality of carbon nanotubes in the solvent.

[0036] The details of one or more embodiments of the subject matter described herein are set forth in the accompanying drawings and the description below. Other features and advantages of the subject matter described herein will be apparent from the description and drawings, and from the claims.

Brief Description of the Drawings

[0037] FIG. 1 is a chart showing a Raman spectrum of as produced carbon nanotube material in accordance with some embodiments of the present invention.

[0038] FIG. 2 is a chart showing an example of a thermogravimetric analysis of a raw carbon nanotube material containing about 50% of a catalyst metal impurity that takes into account the oxidation of initially present iron to iron oxide in accordance with some embodiments of the present invention.

[0039] FIG. 3 is chart showing an example of a thermogravimetric analysis of a purified carbon nanotube material in accordance with some embodiments of the present invention.

[0040] FIG. 4 is a process flow chart showing a method for preparing aqueous-based carbon nanotube inks in accordance with some embodiments of the present invention.

[0041] FIG. 5 is a chart showing an ultraviolet-visible absorption spectrum of a carbon nanotube based ink as a final product in a water-based employing DIPEA as the stabilizing agent, where the interband optical transitions indicative of an intact electronic structure of the SWCNT are marked with black arrows, in accordance with some embodiments of the present invention.

[0042] FIG. 6 is a chart showing an ultraviolet-visible absorption spectrum of a carbon

nanotube film deposited from the water-based ink on a 6" x 4" glass substrate, where the interband optical transitions arising from the first van Hove transitions are shown with white arrows and the second van Hove transitions are shown with black arrows, in accordance with some embodiments of the present invention.

[0043] FIG. 7 is a scanning electron microscope (SEM) image of a dense carbon nanotube network deposited on a sapphire substrate in accordance with some embodiments of the present invention.

[0044] FIG. 8 is an exemplary schematic diagram showing the decomposable polypropylene carbonate molecules wrap around the carbon nanotubes to suspend them in the organic solvent in accordance with some embodiments of the present invention.

[0045] FIG. 9 shows a thermogravimetric analysis (TGA) plot and its first derivative of polypropylene carbonate (PPC) showing the sharp decomposition of the polymer in accordance with some embodiments of the present invention.

[0046] FIG. 10 is a process flow chart showing a method for preparing solvent-based carbon nanotube inks in accordance with some embodiments of the present invention.

[0047] FIG. 11 is a scanning electron micrograph (SEM) image of plastic beads coated with carbon nanotubes in accordance with some embodiments of the present invention.

Detailed Description

ANALYSIS OF AS PRODUCED CARBON NANOTUBES

[0048] Carbon nanotubes such as those produced using the disclosed subject matter can be analyzed and characterized using, among other possible options, Raman spectroscopy and/or thermogravimetric analysis (TGA).

[0049] Resonance Raman spectroscopy provides a fast and selective method for the identification and first characterization of SWCNTs. Major identifiable absorption features include the radial breathing mode (RBM), the tangential mode (G-band), and the disorder-induced band (D-band). RBM, which usually appears between $120 \text{ cm}^{-1} < \omega^{\text{RBM}} < 270 \text{ cm}^{-1}$, generally corresponds to the atomic vibration of the carbon atoms in the radial direction. Direct correlations with SWCNT diameters have been generally established. The tangential mode or G-band, a characteristic multi-peak feature typically occurring around 1580 cm^{-1} , corresponds to atomic displacements along the tube axis as well as the circumferential direction. Simultaneous

observation of RBM and G-band provides strong evidence for the presence of SWCNT. The D-band, occurring around 1350 cm^{-1} , reflects the presence of impurities or other symmetry-breaking defects, such as amorphous carbon.

[0050] For the example described below, material synthesized and collected under well defined conditions was investigated with a Dimension-P2 Raman system (Lambda Solutions, Waltham, MA) using an exciting wavelength of 784.87 nm and approximately 10 mW power. A laser beam with a diameter of about 200 micrometers was directed without microscope to the samples from a distance of about 1 cm. Generally, a 5 second exposure time and integration over 5 spectra were applied. Peak heights of the RBM and G-bands were optimized by fine-tuning the distance between the laser probe and the samples. Samples with strong RBM and weak D-bands as well as high G- to D-band ratios have been considered as being at or close to the optimized conditions and submitted to further analysis, such as scanning electron microscopy (SEM) and TGA, the latter allowing for a quantitative assessment of SWCNT abundance in given samples.

[0051] As shown in the Raman spectrum of FIG. 1, the D-band was found to be barely detectable while RBM peaks at 229.6 cm^{-1} and 265.5 cm^{-1} were identified. Using the relationship $\omega^{\text{RBM}} = 234/d_t + 10\text{ cm}^{-1}$, as suggested by Milnera et al., "Periodic Resonance Excitation and Intertube Interaction from Quasicontinuous Distributed Helicities in Single-Wall Carbon Nanotubes," Phys. Rev. Lett. 84, 1324-1327 (2000), for bundles of SWCNT, these peaks correspond to diameters of about 1.07 and about 0.92 nm, respectively. However, due to the strong dependence of Raman intensities on the resonance energies of the SWCNT present, such a diameter distribution generally reflects only SWCNT resonating at 784.87 nm and may not be representative for the investigated sample. For example, a Raman spectrum of similar material measured at 647 nm gives a significantly different picture: RBM peaks corresponding to 1.30, 0.98 and 0.87 nm have also been identified.

[0052] It should be noted that, as shown in FIG. 1, the shape of the G-band occurring in the $1500\text{-}1605\text{ cm}^{-1}$ range corresponds to tangential vibrations indicating the presence of both conducting SWCNTs and semi-conducting SWCNTs. It should further be noted that, as also shown in FIG. 1, the weakness of the peak near 1350 cm^{-1} indicates that an insignificant low level of impurities or other symmetry-breaking defects is present.

[0053] The purity of bulk SWCNT samples can be determined using thermogravimetric analysis (TGA) under air, for example, using a TGA i 1000 instrument (available from Instrument Specialists, Twin Lakes, WI). Heating rates of, for example, 5 or 7.5 K/min from room temperature to 900 °C were applied. A typical TGA plot of raw, unpurified SWCNT is shown in FIG. 2. FIG. 2 is a chart showing an example of a thermogravimetric analysis of a raw carbon nanotube material containing about 50% of a catalyst metal impurity in accordance with some embodiments of the present invention. This chart takes into account the oxidation of initially present iron to iron oxide. FIG. 3 is a chart showing an example of a thermogravimetric analysis of a purified carbon nanotube material in accordance with some embodiments of the present invention.

[0054] Analysis of multiple batches produced at identical process conditions using the disclosed subject matter led to very similar, nearly overlapping TGA plots, indicating a high degree of reproducibility of purity assessment. Quantification of the composition of a carbonaceous material requires the knowledge of the composition of the metal phase in the initial sample in order to account for increase of mass by oxidation of elemental iron.

[0055] Quantitative characterization of the metal phase can be conducted using wide-angle X-Ray Diffraction (XRD) (e.g., using a Rigaku RU300 X-ray generator). Silicon (Si) can be added as an internal standard and XRD patterns measured. Both maghemite (Fe_2O_3) and elemental iron (Fe) can be identified in the as-produced material, whereas only some elemental iron (Fe) is typically found to remain in SWCNT that are purified according to the disclosed subject matter. Using an internal standard, analysis of XRD spectra allows for the quantitative determination of Fe-to- Fe_2O_3 weight ratios. Assuming complete oxidation of elemental iron to Fe_2O_3 during the TGA run, weight fractions for Fe, Fe_2O_3 , and carbonaceous material were determined. The trace metal contents of the purified CNT material were analyzed by TGA employing the same procedures described above.

GENERAL DESCRIPTION OF INK FORMATION: WATER-BASED INK

[0056] FIG. 4 is a process flow chart showing a method 400 for preparing aqueous-based carbon nanotube inks in accordance with some embodiments of the present invention. The detailed flow chart shows the sequence of unit operations in the processing of a water-based carbon nanotube ink formulation. It should be noted that, in the process flow chart of FIG. 4 and

other process flow charts described herein, some steps can be added, some steps may be omitted, the order of the steps may be re-arranged, and/or some steps may be performed simultaneously.

[0057] As shown, as produced carbon nanotube raw material is heated on a stir-hot plate in a mixture of hydrochloric acid (HCl) and hydrogen peroxide (H₂O₂) at 410. The concentration of hydrochloric acid can generally be between about 0.5N to about 10N and the concentration of hydrogen peroxide can generally be between about 5% to about 30%. The ratio of HCl to H₂O₂ can be kept between about 3:1 to about 1:1. It should also be noted that the temperature at which stirring takes place can generally be between about 50°C to about 80°C.

[0058] It should be noted that as produced carbon nanotube raw material, purified carbon nanotube materials, fullerenes, and/or any other fullerenic materials can be synthesized and/or processed by the approaches described, for example, in Howard et al., U.S. Patent No. 5,273,729, filed May 24, 1991, Howard et al., U.S. Patent No. 5,985,232, filed September 11, 1996, Height et al., U.S. Patent No. 7,335,344, filed March 14, 2003, Kronholm et al. U.S. Patent No. 7,435,403, filed July 3, 2003, and Howard et al., U.S. Patent No. 7,396,520, filed January 21, 2005.

[0059] It should also be noted that the carbon nanotubes in these carbon nanotube-based inks can be synthesized such that any suitable percentage of a particular type of carbon nanotube is included in the carbon nanotube-based ink. For example, in some embodiments, at least 90% of the plurality of carbon nanotubes are single-walled carbon nanotubes. In other embodiments, at least 90% of the plurality of carbon nanotubes are double-walled carbon nanotubes. Alternatively, at least 90% of the plurality of carbon nanotubes are multi-walled carbon nanotubes.

[0060] In one embodiment, the hydrogen peroxide can be slowly added to the carbon nanotube acid mixture by, for example, using a syringe pump. Alternatively, the hydrogen peroxide needed for the reaction can be generated in in-situ reactions.

[0061] The duration of the stirring/heating can range from about 1 hour to about 48 hours. The CNT/acid/peroxide mixture on heating/stirring can be washed with deionized (DI) water repeatedly in a filtration funnel or Nutsche-type filter for large scale operations (see, e.g., 415-430 of FIG. 4). The CNT-acid slurry is washed until it is neutral to pH paper and colorless.

[0062] The HCl/H₂O₂ slurry after repeated washings can be completely dried (e.g., less than 1 wt % of water), partially dried (e.g., less than 50 wt% of water), or wet (e.g., the weight of CNT is less than the weight of water) at 435. Accordingly, the HCl/H₂O₂ slurry can be used in the form of a powder, partially dried paste, or a wet paste in downstream applications.

[0063] In some embodiments, the CNT powder or pastes as described above can be mixed with a non-ionic additive acting as a stabilizing agent at 440, such as diethylenetriamine (DETA), diisopropylethylamine (DIPEA or Hunig's base), or triethanolamine. Other possible amines that can be used are, for example, ethylene diamine, aminoethyl ethanolamine, triethylene tetramine (TETA), tetraethylene pentamine (TEPA), and pentaethylene hexamine (PEHA). It should be noted that small molecular additives can be used as stabilizing agents that disperse single-walled carbon nanotubes without the elimination of the inter-band optical transitions.

[0064] In some embodiments, the CNT powder or pastes can also be mixed with composition of amines consisting one or more of the following amines: diethylenetriamine (DETA), diisopropylamine (DIPEA or Hunig's base), triethanolamine, ethylene diamine, aminoethyl ethanolamine, triethylene tetramine (TETA), tetraethylene pentamine (TEPA), and/or pentaethylene hexamine (PEHA) in different proportions.

[0065] The mixture of CNT powder or pastes with the inclusion of one or more of the above-mentioned additives can then be agitated in deionized water, sonicated in deionized water, power sonicated in deionized water, or dispersed in water using a high-shear mixer at 445 and 450.

[0066] The CNT-water-stabilizer suspension or dispersion thus obtained can then be filtered through a coarse filter (e.g., a filter having openings greater than about 10 micrometers) to eliminate larger suspended particles.

[0067] At 455, the resulting filtered solution can be centrifuged in an ultracentrifuge that subjects a centrifugal force of greater than about 5,000g to about 200,000g. The centrifuge used can be, for example, a static batch rotor type centrifuge, a continuous flow type centrifuge, or a tubular flow type centrifuge. It should also be noted that volumes of CNT dispersions handled in a batch system can be about a few cc to several hundreds of cc. The volumes handled by the flow system can range from about a few cc/minutes to several gallons/hr.

[0068] At 460, the centrifuged solution obtained can be filtered in a tangential flow filtration assembly to remove extraneous carbon nanoparticles that are below a certain cut-off limit. It should be noted that the filtration assembly can handle volumes ranging from about a few cc/minutes to several gallons/hr.

[0069] A single walled carbon nanotube (SWCNT) can be viewed as a rolled-up graphene sheet within certain allowed chiralities. Based on this geometric constraint, SWCNT produced by any method statistically is made up of about one-third with metal-like electrical conduction and about two-thirds showing a semiconducting behavior. Various chemical and electrophoretic methods have demonstrated the separation of the carbon nanotubes by types, falling into the metallic and semiconducting ones.

[0070] In some embodiments, carbon nanotubes thus separated into metallic and semiconducting carbon nanotubes at various degrees of separation or enrichment can be made into the formation of carbon nanotube inks employing a combination of steps described herein. For example, in some embodiments, the plurality of carbon nanotubes dispersed in the solvent can be separated such that at least 80% of the plurality of carbon nanotubes are semiconducting single-walled carbon nanotubes. In some embodiments, the plurality of carbon nanotubes can be enriched in either semiconducting or metallic single-walled carbon nanotubes, for example, in comparison to their initial abundance in the as-produced carbon nanotube materials (e.g., often approximately a 2:1 ratio of semiconducting vs. metallic corresponding to the ensemble of all theoretically existing chiralities).

[0071] FIG. 5 is a chart showing an ultraviolet-visible absorption spectrum of a carbon nanotube-based ink as a final product in a water-based employing DIPEA as the stabilizing agent. The interband optical transitions indicative of an intact electronic structure of the SWCNT are indicated with black arrows.

[0072] FIG. 6 is a chart showing an ultraviolet-visible absorption spectrum of a carbon nanotube film deposited from the water-based ink on a 6" x 4" glass substrate. The interband optical transitions arising from the first van Hove transitions are indicated with white arrows and the second van Hove transitions are indicated with black arrows.

[0073] FIG. 7 is a scanning electron microscope (SEM) image of a dense carbon nanotube network deposited on a sapphire substrate in accordance with some embodiments of the present invention.

GENERAL DESCRIPTION OF INK FORMATION: SOLVENT-BASED INK

[0074] FIG. 8 is an exemplary schematic diagram showing the mechanisms for creating a solvent-based ink. In some embodiments, the decomposable polypropylene carbonate molecules wrap around the carbon nanotubes, as shown in FIG. 8, to help them stabilize in the chosen organic solvent. Alternatively, the polymer molecules may co-dissolve and function as viscosity adjustment agents, thereby aiding to control the rheological properties of the CNT-solvent ink. In either embodiment, a CNT film that is deposited on a solid substrate will still have the polymer molecules. The polymer molecules decompose on thermal annealing in air into 100% non-toxic gaseous products. In addition, more than about 90% of the polymer loss occurs below 200°C at which temperature carbon nanotubes are very stable even in air. The resulting final product is a neat carbon nanotube film.

[0075] For example, FIG. 9 is a chart showing a thermogravimetric analysis (TGA) plot of polypropylene carbonate (PPC) and the sharp decomposition of the polymer. As shown, more than 95% of the polymer loss occurs below 200°C at which temperature carbon nanotubes are very stable even in air. The derivative plot shows the sharp and rapid decomposition. It should be noted that approximately 0.5 wt% residue shown in FIG. 9 arises from extraneous impurities.

[0076] Referring to FIG. 10, FIG. 10 is a process flow chart showing one of the methods 1000 for preparing solvent-based carbon nanotube inks in accordance with some embodiments of the present invention. The detailed flow chart shows the sequence of unit operations in the processing of a solvent-based carbon nanotube ink formulation. It should be noted that, in the process flow chart of FIG. 10 and other process flow charts described herein, some steps can be added, some steps may be omitted, the order of the steps may be re-arranged, and/or some steps may be performed simultaneously.

[0077] Similar to FIG. 4, method 1000 begins with heating as produced carbon nanotube raw material on a stir-hot plate in a mixture of hydrochloric acid (HCl) and hydrogen peroxide (H₂O₂). The concentration of hydrochloric acid can generally be between about 0.5N to about 10N and the concentration of hydrogen peroxide can generally be between about 5% to about 30%. The ratio of HCl to H₂O₂ can be kept between about 3:1 to about 1:1. It should also be noted that the temperature at which stirring takes place can generally be between about 50°C to about 80°C.

[0078] As described above, in one embodiment, the hydrogen peroxide can be slowly added to the carbon nanotube acid mixture by, for example, using a syringe pump. Alternatively, the hydrogen peroxide needed for the reaction can be generated in in-situ reactions.

[0079] The duration of the stirring/heating can range from about 1 hour to about 48 hours. The CNT/acid/peroxide mixture on heating/stirring can be washed with deionized (DI) water repeatedly in a filtration funnel or Nutsche-type filter for large scale operations (see, e.g., 115-130). The CNT-acid slurry is washed until it is neutral to pH paper and colorless.

[0080] The HCl/H₂O₂ slurry after repeated washings can be completely dried (e.g., less than 1 wt % of water), partially dried (e.g., less than 50 wt% of water), or wet (e.g., the weight of CNT is less than the weight of water). Accordingly, the HCl/H₂O₂ slurry can be used in the form of a powder, partially dried paste, or a wet paste in downstream applications.

[0081] As shown in FIG. 10, a solvent mixture is prepared by mixing an organic solvent with a stabilizing additive at 1010. For example, a solvent mixture can be prepared by dissolving an accurately weighed quantity of a stabilizer in the range of about 0.1 to about 5 wt% of polypropylene carbonate in a suitable organic solvent, preferably N-methylpyrrolidinone (NMP).

[0082] Other suitable solvents that can also be used may include, for example, propylene glycol monomethyl ether acetate (PGMEA), cyclohexanone, Methyl ethyl ketone (MEK), methyl isopropyl ketone, etc.

[0083] It should be noted that polypropylene carbonates of different molecular weights can also be used as a viscosity adjusting agent instead of or in addition to a stabilizing additive in solvents such as N-methylpyrrolidinone (NMP), propylene glycol monomethyl ether acetate (PGMEA), cyclohexanone, Methyl ethyl ketone (MEK), methyl isopropyl ketone, etc.

[0084] Referring back to FIG. 10, at 1020, as prepared raw carbon nanotubes, semi-purified carbon nanotubes, purified carbon nanotube powder, or purified carbon nanotube pastes as described above can be mixed with the solvent mixture at a concentration of about 0.1 to about 5 wt% and then agitated, sonicated, power sonicated, or dispersed using a high-shear mixer.

[0085] The CNT-polymer-solvent suspension or dispersion can be filtered through a coarse filter (e.g., a filter having openings greater than about 10 micrometers) to eliminate larger suspended particles.

[0086] The resulting filtered solutions/dispersions can be centrifuged in an ultracentrifuge that subjects a centrifugal force of greater than about 5,000g to about 200,000g. The centrifuge used can be, for example, a static batch rotor type centrifuge, a continuous flow type centrifuge, or a tubular flow type centrifuge. It should also be noted that volumes of CNT dispersions handled in a batch system can be about a few cc to several hundreds of cc. The volumes handled by the flow system can range from about a few cc/minutes to several gallons/hr.

EXAMPLES

[0087] The following examples further illustrate some embodiments of the present invention, but should not be construed as in any way limiting the scope.

EXAMPLE 1

[0088] Raw carbon nanotubes were produced in a combustion method employing methane as the feed stock and iron nanoparticles formed in-situ by the decomposition of iron pentacarbonyl. Approximately 970 mg of raw carbon nanotubes prepared by combustion of methane were added to 200 ml of DI water in a 500 ml round bottom flask. To this mixture, 75 ml of 36% hydrochloric acid was added slowly with stirring followed by the slow addition of 75 ml of ice cold, 30% hydrogen peroxide in drops. This mixture was allowed to stir over a magnetic hot plate stirrer overnight at a temperature of about 60°C. The mixture was then allowed to cool to room temperature without stirring. A black sediment of carbon nanotubes settled at the bottom while the supernatant liquid was deep yellow/brown and transparent due to the presence of iron ions. The supernatant liquid was decanted into a larger flask. About 100 ml of DI water was added to the solid contents, which was hand stirred and allowed to settle over few minutes. The new supernatant liquid turned pale and was decanted as described before. This procedure was repeated until the supernatant liquid was colorless and clear. At this point the decanted liquid was filtered through a 90 mm diameter Whatman filter paper (#50, hardened) in a ceramic Büchner funnel. This first stage wet CNT slurry collected on the filter paper was washed until the washings were no different in pH compared to DI water as tested by a pH paper. A small portion of this wet CNT slurry was dried in the Büchner funnel by drawing air through it

by applying vacuum at the flask. The vacuum was applied with a simple rotary pump (10 mm of mercury) until the powder peeled off from the filter paper and was collected in a bottle.

EXAMPLE 2

[0089] A first stage wet CNT slurry prepared as described in Example 1 was transferred back to a clean 500 ml round bottom (RB) flask from the filter paper by washing with approximately 50 ml of DI water. To this slurry, 100 ml of DI water and 50 ml of 6N nitric acid was added. The nitric acid was added dropwise. The flask was fitted with a reflux condenser cooled with running cold water and the mixture in the RB flask was stir heated on a hot plate to reflux. After refluxing for about 3 hours, this mixture was allowed to cool to room temperature without stirring. A black sediment of carbon nanotubes settled at the bottom of the RB flask while the supernatant liquid was very pale yellow. The supernatant liquid was decanted into a larger flask. About 100 ml of DI water was added to the solid contents in the RB flask and was hand stirred before being allowed to settle over few minutes. The supernatant liquid in the RB flask turned colorless and clear and was decanted. The decanted liquid was filtered through a 90 mm diameter Whatman filter paper (#50, hardened) in a ceramic Büchner funnel. The wet carbon nanotube slurry was washed until the washings were no different in pH compared to DI water as tested by a pH paper. This resultant, second stage wet CNT slurry was dried in the Büchner funnel by drawing air through it under vacuum. The vacuum was applied with a simple rotary pump (10 mm of mercury) until the powder peeled off from the filter paper for collection in a bottle. Some of the second stage wet slurry was only partially dried and stored as a purified CNT paste.

EXAMPLE 3

[0090] In yet another purification method, as prepared raw carbon nanotube samples were pre-washed in neutral DI water prior to acid treatment as described below. An accurately weighed amount of raw carbon nanotubes (e.g., less than about one gram) is placed in a thick walled glass tube and sonicated with a power sonicator horn for 15 minutes. The resulting dark suspension was filtered through a cellulose filter (2-5 microns) for the removal of finer particles. The CNT water paste collected over the filter paper was used in the further purification process in the place of as prepared CNT.

EXAMPLE 4

[0091] In yet another acid purification process, approximately one gram of the CNT water paste collected as described in Example 3 was transferred to a 2 liter round bottom flask and DI water was added to make up the volume to 1000ml. To this mixture, 100 ml of 36% HCl and 50 ml of 30% hydrogen peroxide were added and allowed to stir on a hot plate at room temperature overnight. The CNT acid slurry was washed with DI water as described in Examples 1 and 2. The purified wet CNT slurry was transferred to a 500 ml round bottom flask to which 100 ml of 6N nitric acid and 250 ml of DI water were added. The CNT acid mixture was refluxed for 3 hours and allowed to cool. The nitric acid water slurry was filtered and washed through a filter paper and allowed to dry partially. The partially dried CNT was further used in the preparation of a water-based CNT ink as described herein.

EXAMPLE 5

[0092] In yet another example, about 500 mg of the partially dried CNT paste as described in Example 4 was placed in a ceramic cup to which 2 ml of N,N-diisopropylethylamine (DIPEA) was added and mixed well manually with a ceramic paddle. The mixture was allowed to sit overnight. The CNT-DIPEA paste was transferred to a 1L conical flask to which 750 ml of DI water was added. The mixture was sonicated for about 1 hour in a Branson bath sonicator and allowed to stand for about an hour. It was resonicated for one more hour and the resulting suspension was centrifuged at 15,000 RPM at 10°C for 1 hour. The supernatant liquid was collected as a stable, water-based CNT ink.

EXAMPLE 6

[0093] In yet another acid purification process of the raw carbon nanotubes, two grams of the raw carbon nanotubes in a one liter round bottom flask, 500 ml of DI water, 100 ml of 36% HCl and 100 ml of ice cold hydrogen peroxide were added and set for stirring at approximately 60°C overnight. The CNT acid slurry was washed with DI water as described in Examples 1 and 2. The purified wet CNT slurry was transferred to a 500 ml round bottom flask to which 100 ml of 6N nitric acid and 250 ml of DI water were added. The CNT acid mixture was refluxed for 3h and allowed to cool. The nitric acid water slurry was filtered through a #50

Whatman filter paper in a Buchner funnel and allowed to dry partially. The partially dried CNT was further used in the preparation of a solvent-based CNT ink as described below in Example 7.

EXAMPLE 7

[0094] A solution of polypropylene carbonate (PPG) (a commercial sample from Novomer Inc.) was prepared by dissolving PPG in 20 ml of N-methylpyrrolidinone (NMP) to a concentration of 2 mg/mL. To this solution, 20 mg of the partially dry CNT prepared as described in Example 6 was added and sonicated in a bath sonicator for 1 hour. The solution in the test tube was transferred to a conical flask. 80 ml of NMP was added to the mixture to make up the total volume to 100 ml. The solution was sonicated 90 minutes and centrifuged at 10,000 RPM for 1 hour at 10°C. A very stable dark solvent-based CNT ink was obtained and bottled.

APPLICATIONS

[0095] The resulting ink composition can be coated on any suitable substrate (e.g., a glass substrate, a plastic substrate, a sapphire substrate, etc.) using a number of techniques, including inkjet printing, spin coating, spray coating, etc. In addition, the resulting ink composition can be used in numerous applications ranging from liquid crystal displays (LCDs), antistatic coatings, electrodes, touchscreens, and numerous other applications.

[0096] For example, in one embodiment, an ink with extensive bundling of SWCNT and, thus, limited suspendability can be used for applications, such as battery electrodes or capacitors. In another embodiment, an ink with individually suspended SWCNTs can be used for applications, such as transparent conductive coatings.

[0097] In another suitable embodiment, an ink prepared as described herein can be coated onto plastic beads ranging in size from about 10 nanometers to several hundred micrometers (μm). Alternatively or additionally, the ink can be coated onto plastic fibers, glass fibers, or ceramic fibers having diameters ranging from 10 nanometers to several hundred micrometers (μm) and having aspect ratios ranging from 10 to 10^6 . In a more particular example, a scanning electronic microscope (SEM) image of plastic beads coated with carbon nanotubes using the above-described ink is shown in FIG. 11.

[0098] It should be noted that the coating of plastic, glass, ceramic, and/or other suitable substrates and materials can be used to enhance electric and/or thermal conductivity.

Accordingly, this can be used for electrically conducting films or electrostatic dissipation applications.

[0099] It should further be noted that the inks prepared as described herein can be used as a medium for chemical functionalization of carbon nanotubes with, for example, but not limited to, reactions with diazonium salts, Diels-Alder reagents, cycloadditions, halogenations, nucleophilic or radical additions (see, e.g., Tasis et al., Chem. Rev. 2006, 106, 1105-1136; and Zhang et al., J. Am. Chem. Soc. 2009, 131, 8446-8454). Such functionalization may selectively occur with metallic or semi-conducting carbon nanotubes.

[0100] Mixtures between functionalized and unfunctionalized carbon nanotubes dispersed in the above-mentioned inks can be separated by density gradient centrifugation or electrophoresis.

[0101] Carbon nanotubes that are functionalized in other reaction media, such as organic solvents (e.g., o-dichlorobenzene, tetrahydrofuran (THF), etc.) or water in the presence or not of ionic surfactants, are redissolved in the above-mentioned inks.

[0102] Accordingly, solvent-based and water-based carbon nanotube inks with removable additives are provided.

[0103] Although the invention has been described and illustrated in the foregoing illustrative embodiments, it is understood that the present disclosure has been made only by way of example, and that numerous changes in the details of implementation of the invention can be made without departing from the spirit and scope of the invention. Features of the disclosed embodiments can be combined and rearranged in various ways.

What is claimed is:

1. An ink composition comprising:
 - a plurality of carbon nanotubes;
 - a solvent; and
 - a removable additive that stabilizes the plurality of carbon nanotubes in the solvent,wherein the solvent is an organic solvent selected from the group consisting of N-methylpyrrolidinone (NMP), propylene glycol monomethyl ether acetate (PGMEA), methyl ethyl ketone (MEK), and methyl isopropyl ketone;
 - wherein the removable additive is polypropylene carbonate; and
 - wherein the removable additive is removed from the ink composition by at least 90% by thermal annealing at a temperature lower than about 200°C.
2. The ink composition of claim 1, wherein the removable additive acts as a dispersal agent and a stabilization agent.
3. The ink composition of claim 1, wherein the removable additive adjusts viscosity of the ink based at least in part on molecular weight of the removable additive.
4. The ink composition of any one of claims 1-3, wherein at least 90% of the plurality of carbon nanotubes are single-walled carbon nanotubes.
5. The ink composition of claim 4, wherein the single-walled carbon nanotubes dispersed in the solvent are enriched in semiconducting or metallic carbon nanotubes in comparison to its distribution in initial as-produced single-walled carbon nanotube materials.
6. The ink composition of any one of claims 1-3, wherein at least 90% of the plurality of carbon nanotubes are double-walled carbon nanotubes.
7. The ink composition of any one of claims 1-3, wherein at least 90% of the plurality of carbon nanotubes are multi-walled carbon nanotubes.

8. The ink composition of claim 7, wherein the plurality of carbon nanotubes are functionalized.
9. The ink composition of any one of claims 1-8, wherein the solvent is N-methylpyrrolidinone (NMP).
10. A method of preparing an ink composition, the method comprising:
 - providing a plurality of carbon nanotubes;
 - providing a removable additive to the plurality of carbon nanotubes;
 - providing a solvent to the plurality of carbon nanotubes and the removable additive, wherein the plurality of carbon nanotubes are dispersed within the solvent and wherein the removable additive stabilizes the plurality of carbon nanotubes that are suspended in the solvent; and
 - removing a substantial portion of the removable additive by thermal annealing,wherein the solvent is an organic solvent selected from the group consisting of N-methylpyrrolidinone (NMP), propylene glycol monomethyl ether acetate (PGMEA), methyl ethyl ketone (MEK), and methyl isopropyl ketone; wherein the removable additive is polypropylene carbonate; and wherein the removable additive is removed from the ink composition by at least 90% by thermal annealing at a temperature lower than about 200°C.
11. The method of claim 10, further comprising applying the ink composition to a substrate.
12. The method of claim 11, wherein the removable additive is removed after applying the ink composition to the substrate.
13. The method of claim 11 or 12, wherein the substrate is one of a glass substrate, a plastic substrate, and a sapphire substrate.
14. The method of any one of claims 10-13, wherein the removable additive acts as a dispersal agent and a stabilization agent.

15. The method of any one of claims 10-13, wherein the removable additive adjusts viscosity of the ink based at least in part on molecular weight of the removable additive.
16. The method of any one of claims 10-15, further comprising mixing the solvent with the removable additive prior to dispersing the plurality of carbon nanotubes in the solvent.
17. The method of any one of claims 10-16, wherein the plurality of carbon nanotubes are individually suspended within the solvent.
18. The method of any one of claims 10-17, wherein the plurality of carbon nanotubes are substantially bundled within the solvent.
19. The method of any one of claims 10-18, further comprising depositing the ink composition onto a surface, wherein the ink composition forms an antistatic thin film on the surface.
20. The method of any one of claims 10-19, wherein the solvent is N-methylpyrrolidinone (NMP).

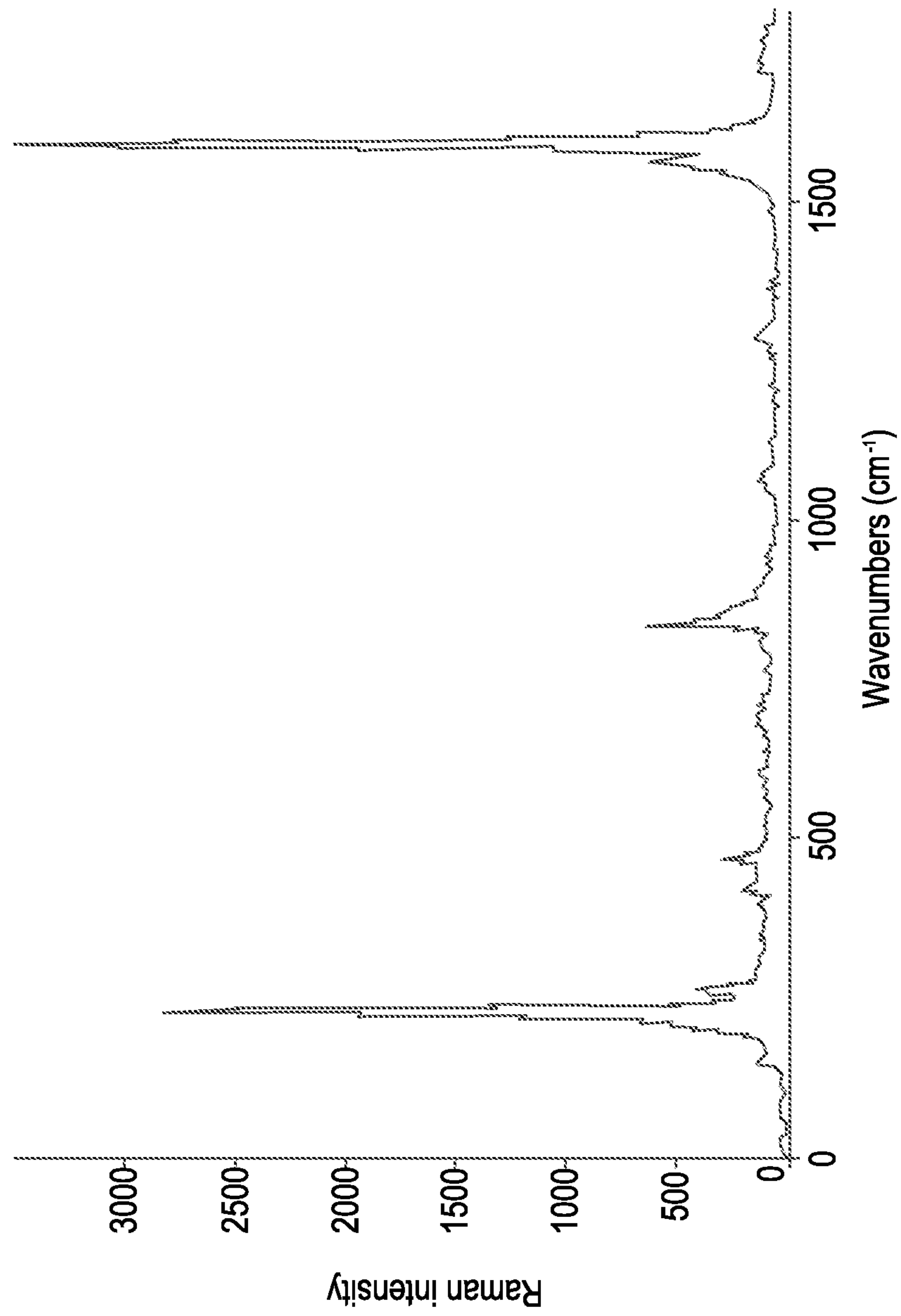


FIG. 1

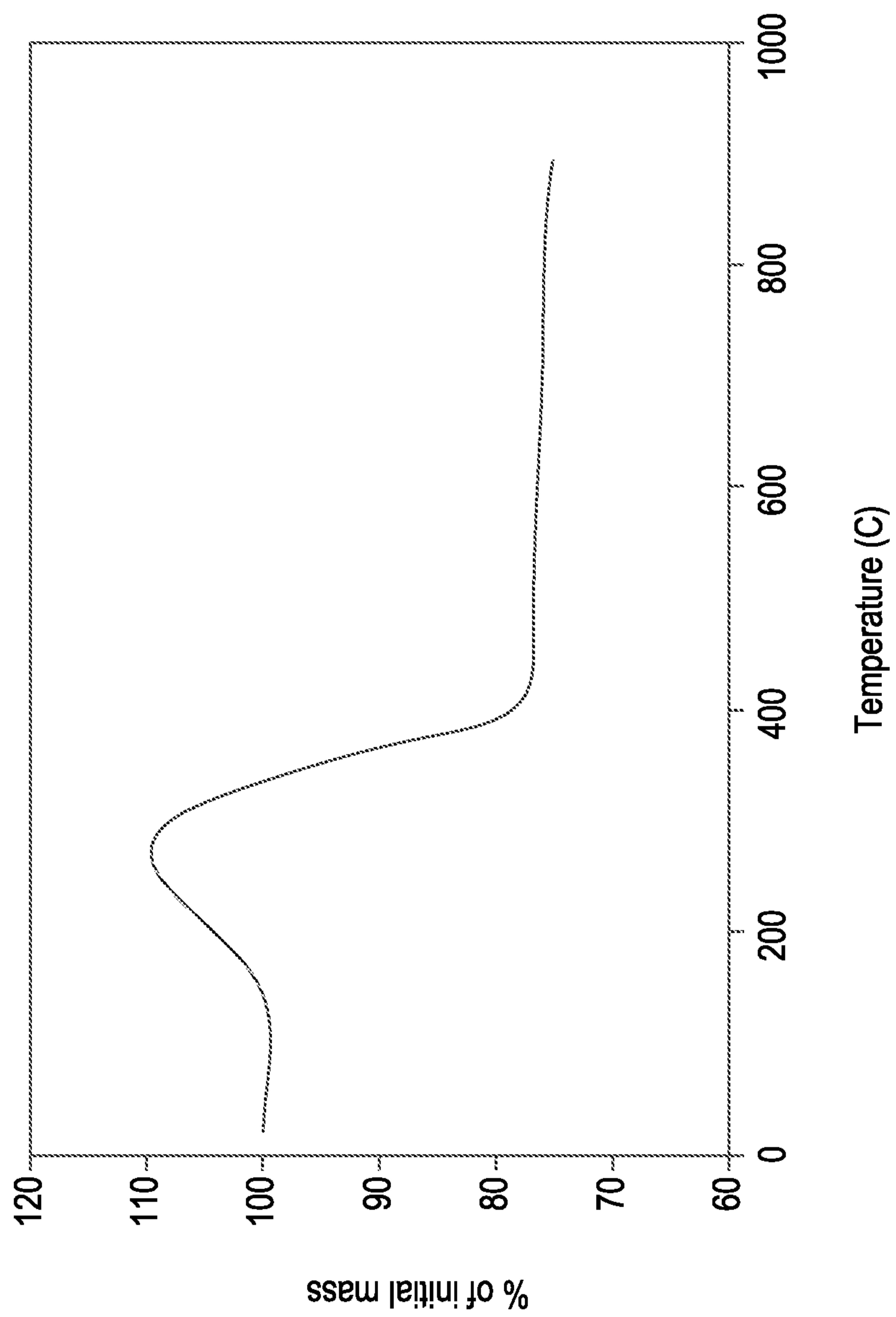


FIG. 2

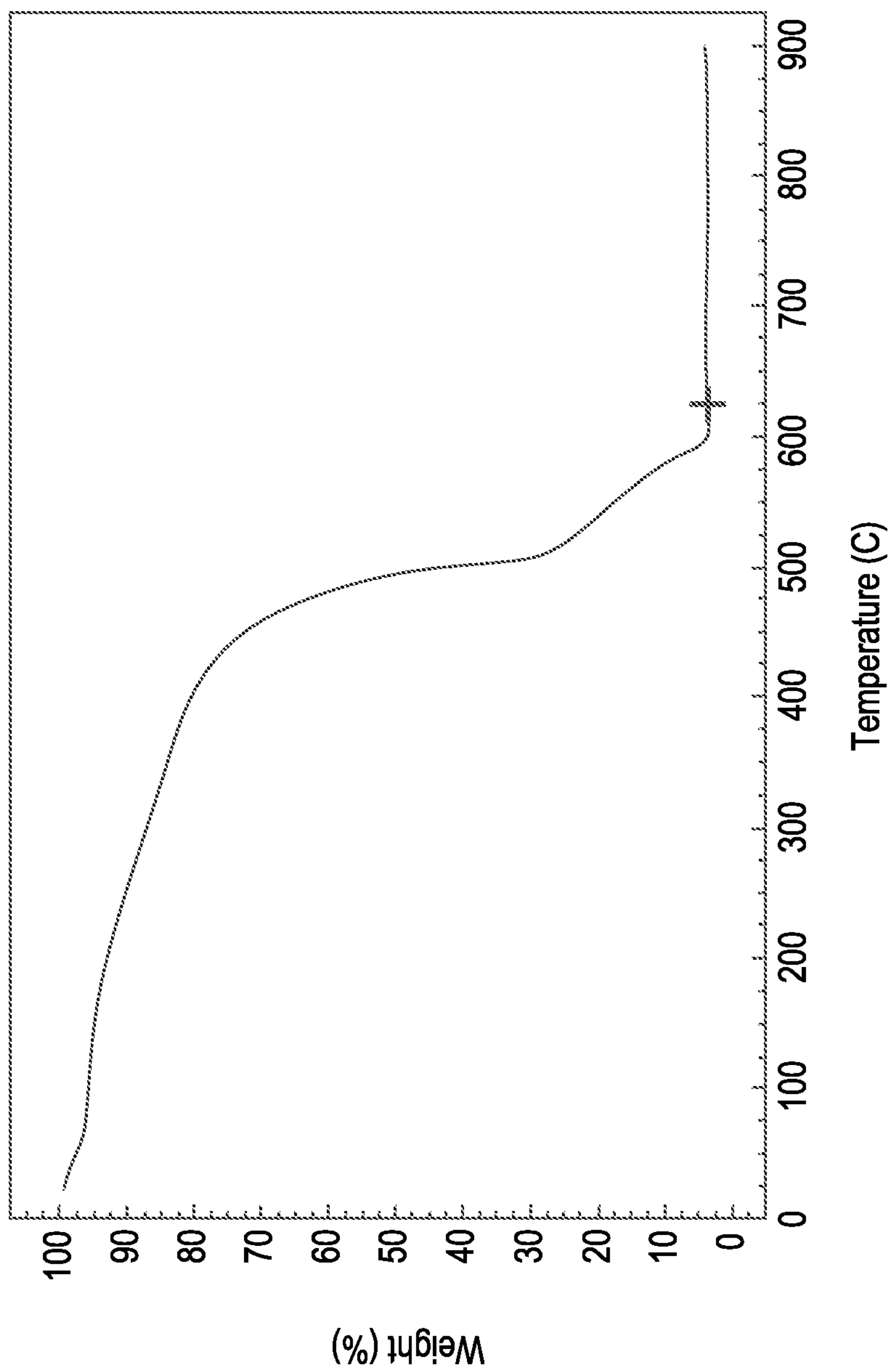


FIG. 3

400

Sequence of Unit Operations in ink processing - Scheme 1 Water base ink

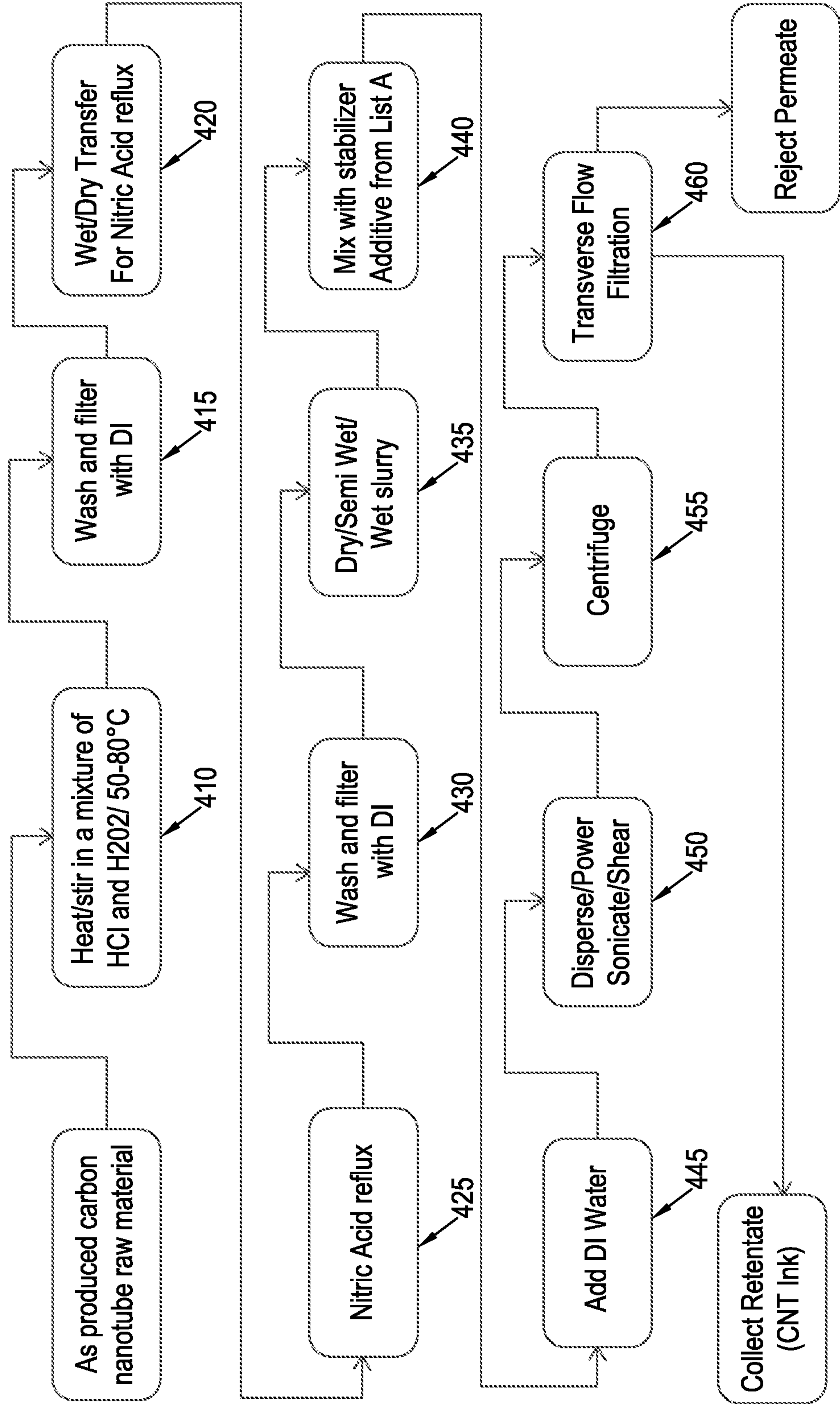


FIG. 4

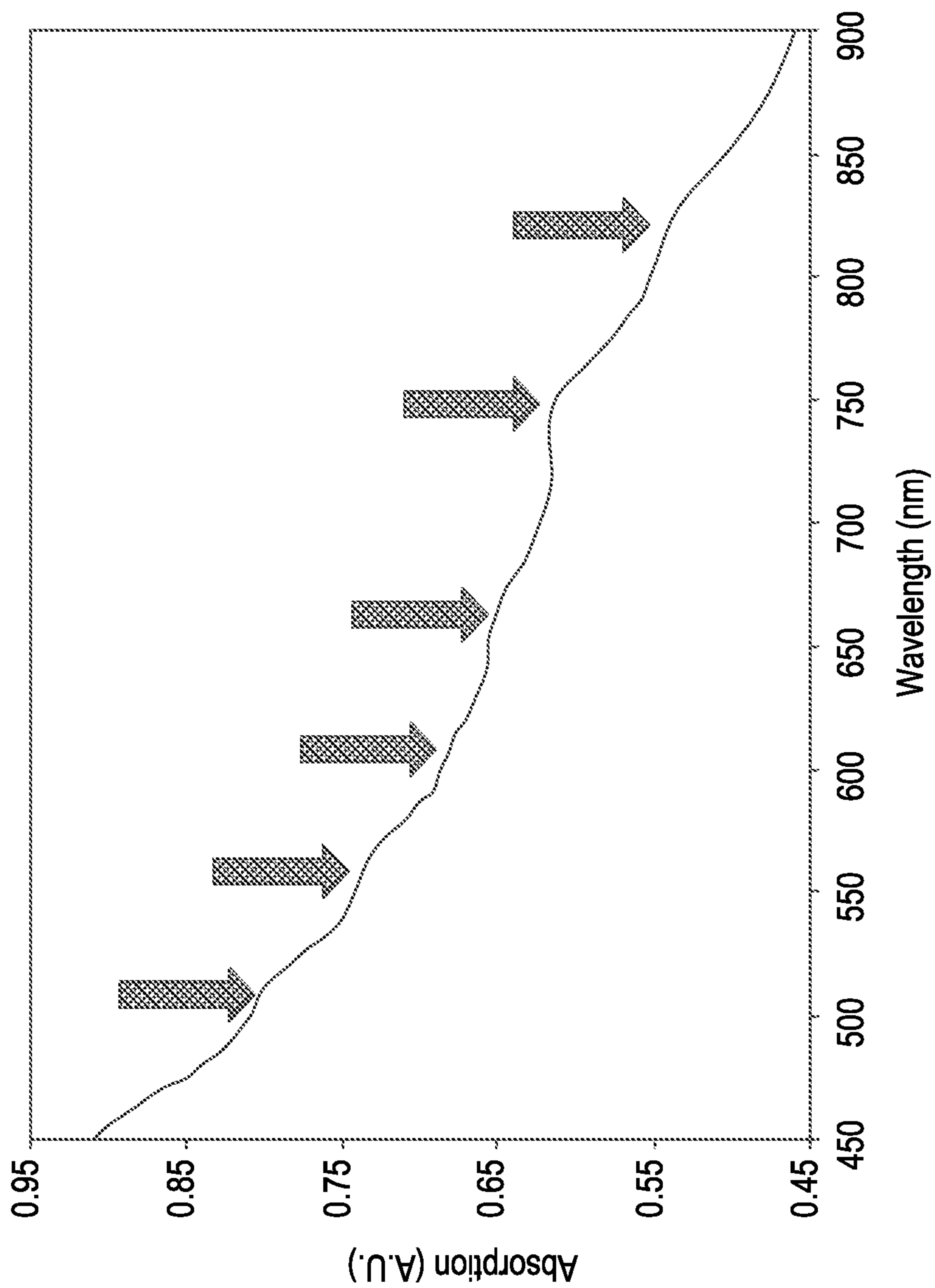


FIG. 5

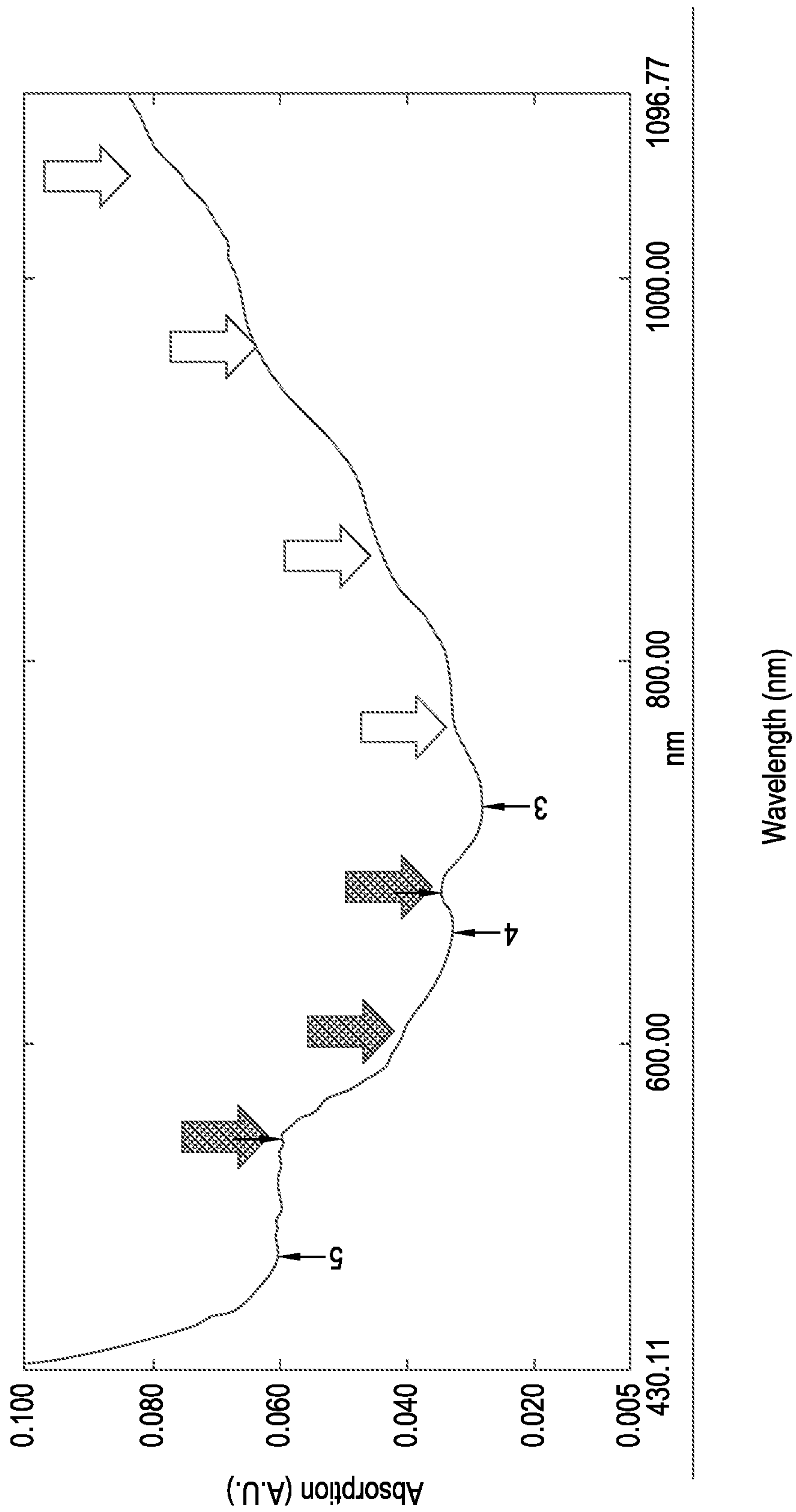


FIG. 6

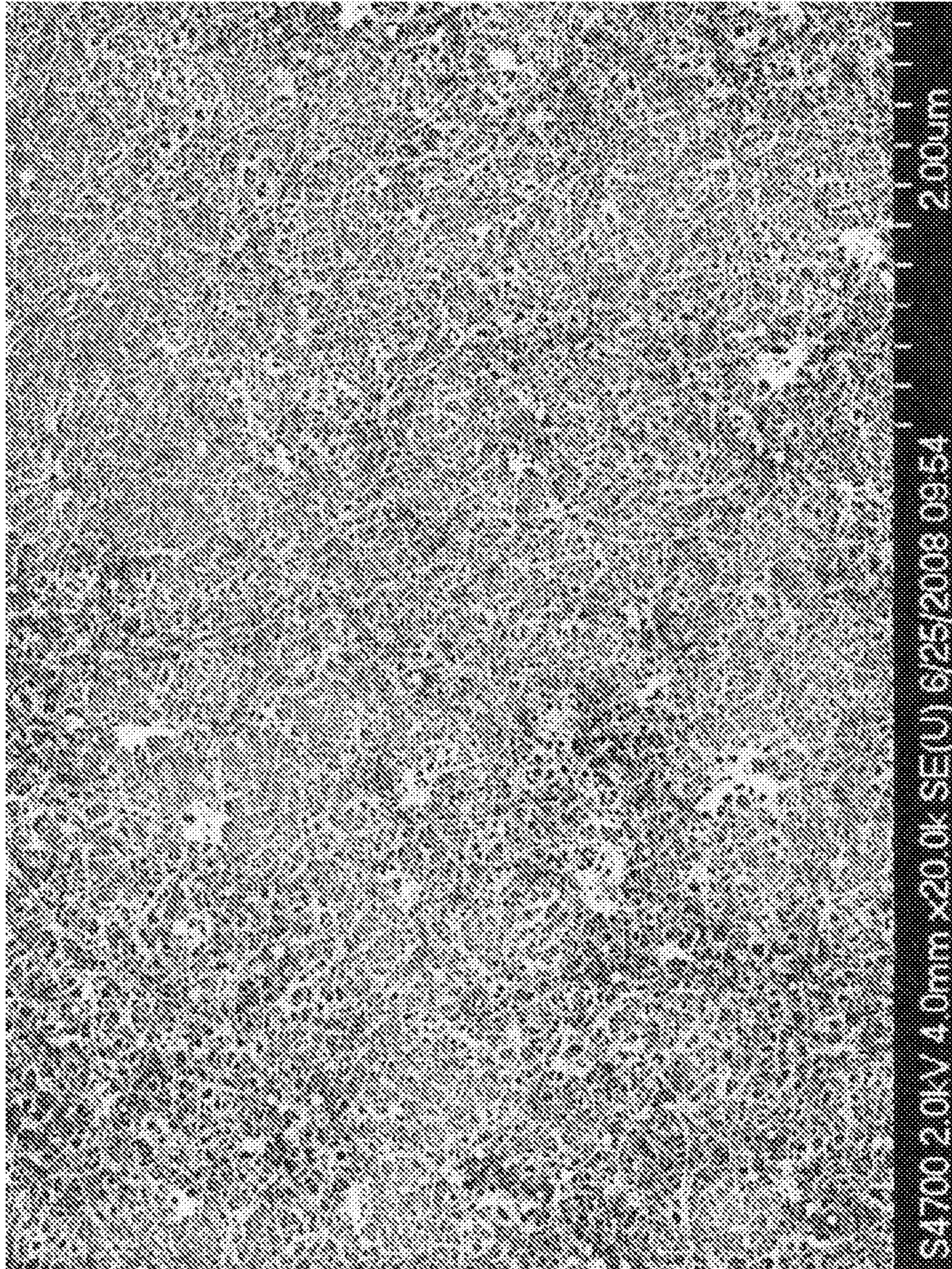


FIG. 7

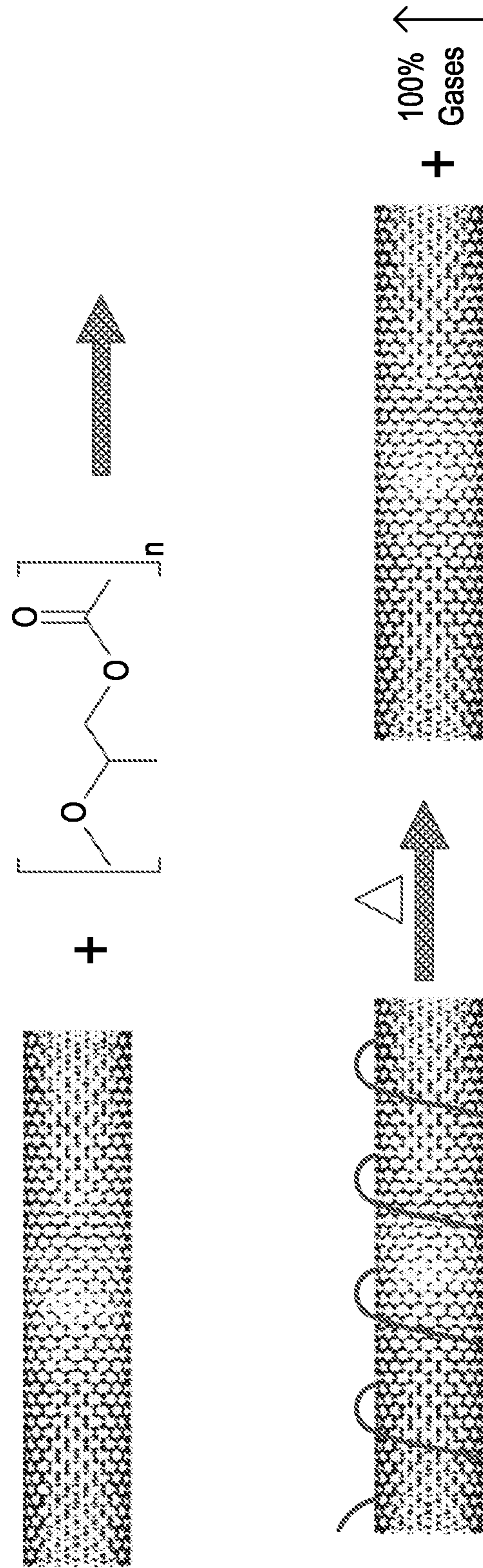


FIG. 8

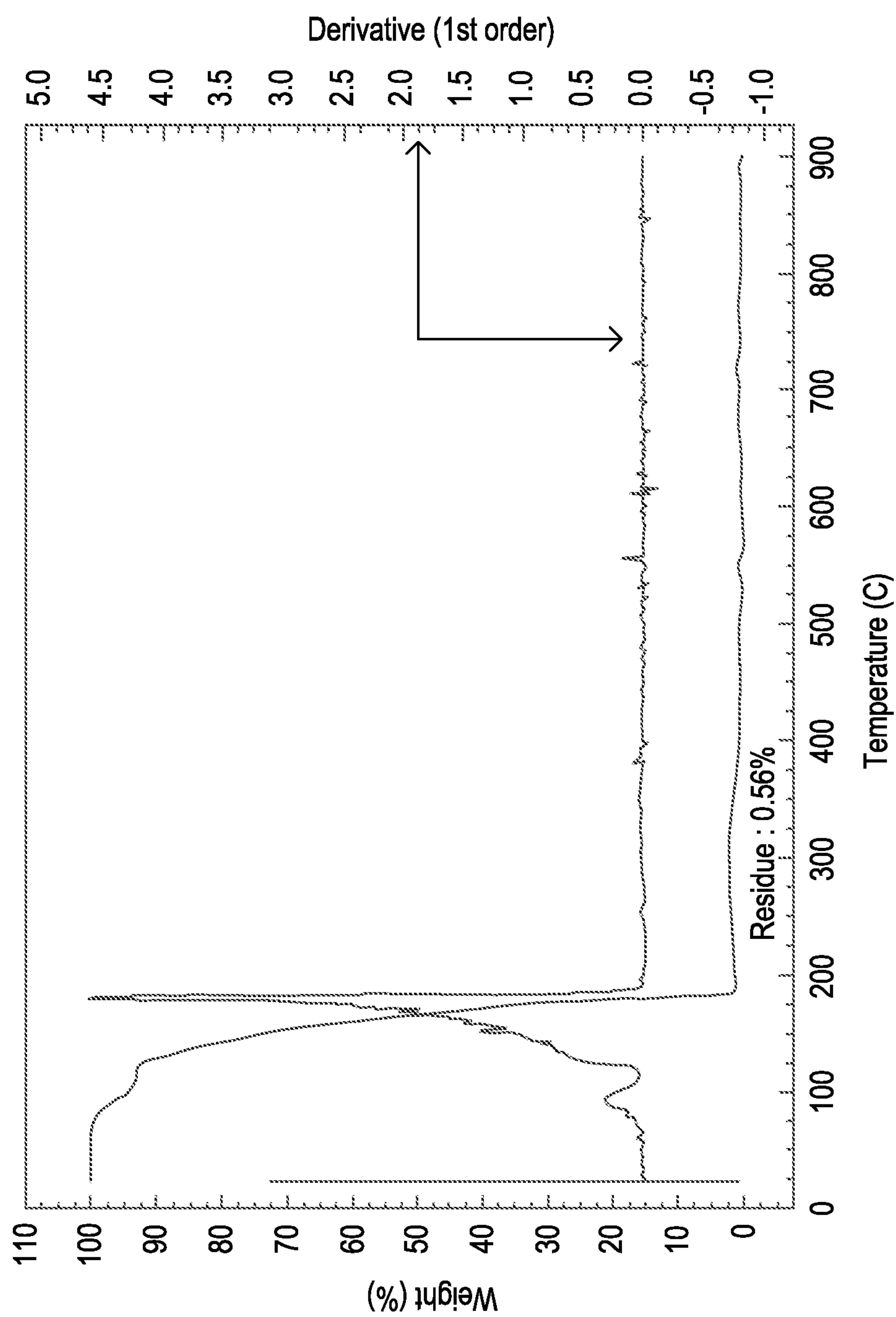


FIG. 9

1000

Sequence of Unit Operations in ink processing - Scheme 2 Solvent base ink

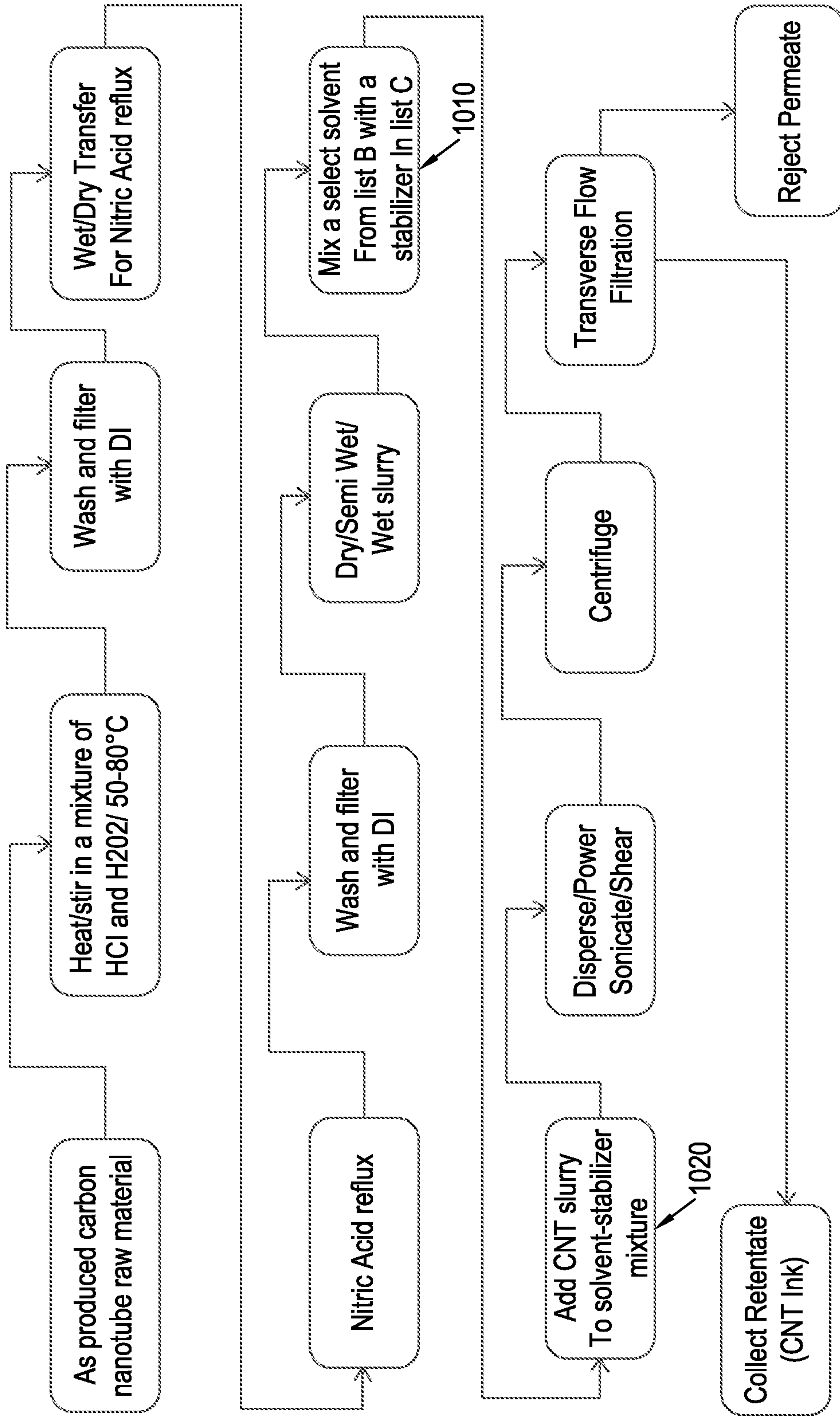


FIG. 10

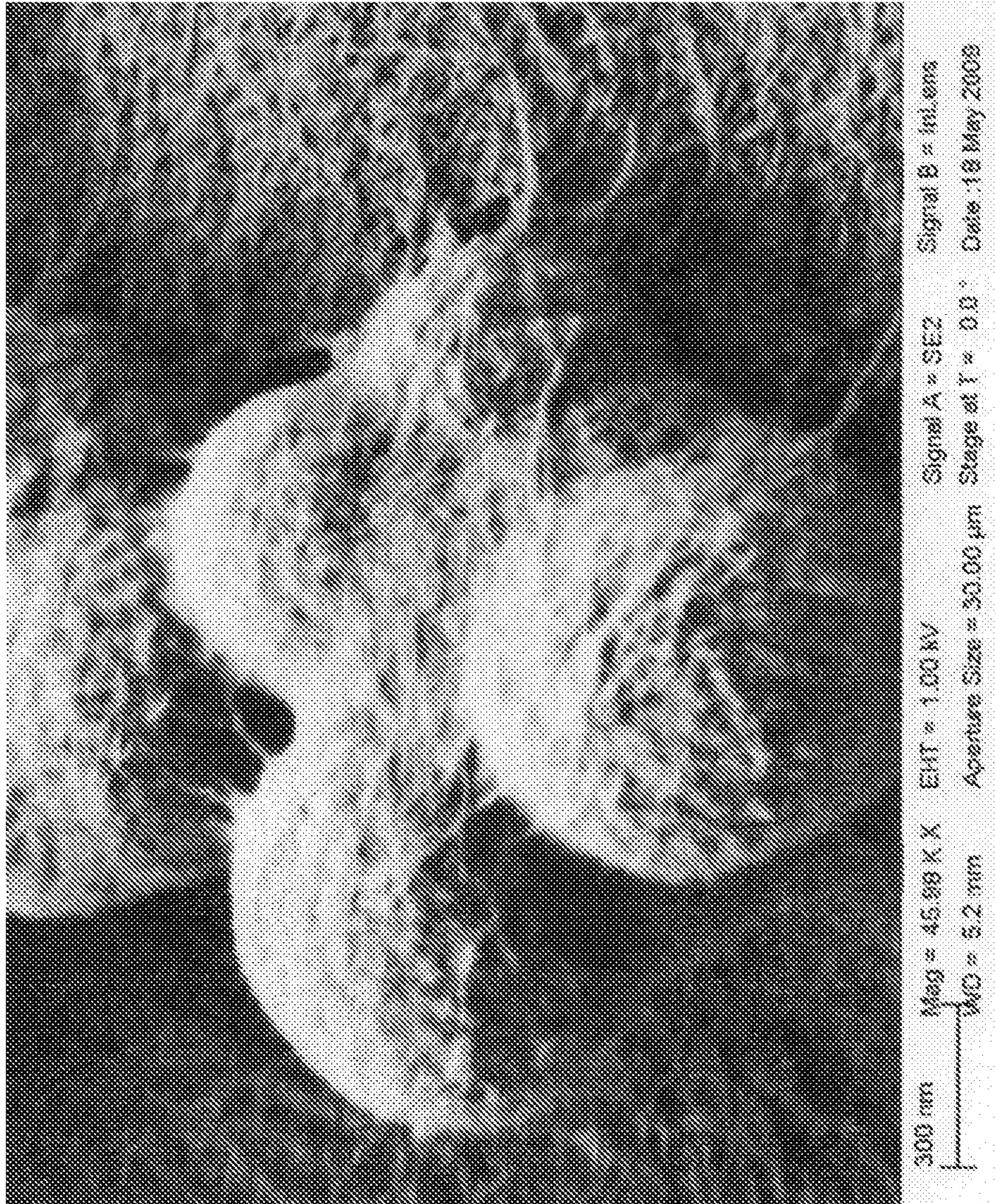


FIG. 11

Sequence of Unit Operations in ink processing - Scheme 1 Water base ink

