



(22) Date de dépôt/Filing Date: 2015/07/27
(41) Mise à la disp. pub./Open to Public Insp.: 2016/02/04
(45) Date de délivrance/Issue Date: 2018/02/20
(30) Priorité/Priority: 2014/08/04 (US14/451380)

(51) Cl.Int./Int.Cl. *C09B 67/46* (2006.01),
C08J 3/20 (2006.01), *C08L 75/04* (2006.01),
C09D 11/328 (2014.01), *C09K 11/02* (2006.01),
C09K 9/02 (2006.01)

(72) Inventeurs/Inventors:
BANNING, JEFFERY H., US;
YAO, JIAN, US;
MOORE, KELLEY A., US;
THOMAS, JULE W., JR., US;
MEINHARDT, MICHAEL B., US;
LUCAS, PAUL C., US;
...

(73) Propriétaire/Owner:

(54) Titre : DISPERSION DE POLYURETHANE COLORANT FLUORESCENT ET PHOTOCHROMIQUE ENCAPSULE
(54) Title: ENCAPSULATED FLUORESCENT AND PHOTOCHROMIC DYE POLYURETHANE DISPERSION

(57) **Abrégé/Abstract:**

The present disclosure provides an encapsulated dye dispersion and an inkjet ink comprising an ink vehicle and an encapsulated dye dispersion thereof. In particular, the encapsulated dye dispersion includes a fluorescent and / or photochromic dye. The present disclosure also provides a process for producing the encapsulated dye dispersion.

(72) Inventeurs(suite)/Inventors(continued): GONZALEZ, JESUS, JR., US; IFTIME, GABRIEL, CA; WU, BO, US

(73) Propriétaires(suite)/Owners(continued): XEROX CORPORATION, US

(74) Agent: AIRD & MCBURNEY LP

ABSTRACT

5 The present disclosure provides an encapsulated dye dispersion and an inkjet ink comprising an ink vehicle and an encapsulated dye dispersion thereof. In particular, the encapsulated dye dispersion includes a fluorescent and / or photochromic dye. The present disclosure also provides a process for producing the encapsulated dye dispersion.

ENCAPSULATED FLUORESCENT AND PHOTOCHROMIC DYE POLYURETHANE DISPERSION

INTRODUCTION

[0001] Polyurethane dispersions have been employed as carriers in aqueous ink jet inks, for
5 example, U.S. Patent No. 5,700,851, and aqueous writing inks, for example, U.S. Patent No.
5,637,638. The dispersions described in these patents employed reactive polymeric colorants
that are built into the polyurethane backbone of the molecule by covalent bonding, and act as the
source of coloration of the final ink.

[0002] Inks with fluorescent or photochromic dyes (sometimes referred to as optically variable
10 inks) are typically used to provide latent images as a security feature. Fluorescent and
photochromic dyes are preferably colorless or substantially colorless so the resulting image is
invisible or substantially invisible in daylight. Upon irradiation of ultraviolet light, fluorescent
dyes produce visible fluorescence (of different colors), rendering the image visible. Similarly,
photochromic dyes are colorless in their normal state and become colored on exposure to
15 activating radiation, such as ultraviolet light. The color formation generally includes a ring
closure or ring opening in the photochromic dye molecule with the formation of conjugated
double bonds. Fluorescent and photochromic dyes are highly sought after for ink and coating
applications. However, encapsulating or incorporating fluorescent and photochromic dyes into a
latex, made via an emulsion polymerization, is not a trivial endeavor. This is because, during an
20 emulsion polymerization, the fluorescent and photochromic dyes must satisfy the following
requirements (1) be soluble in the monomers used in the emulsion polymerization, (2) be
captured in a monomer micelle as polymerization takes place inside the micelle, and (3) be stable
to the free radical polymerization environment. Many organic fluorescent and photochromic
dyes are not stable to such environments and their colors are subsequently destroyed. Typically,
25 even if the encapsulated fluorescent and/or photochromic dye survives the entire polymerization
process, it is often not stable to the free radical environment at the end of the process when all
the excess monomers are destroyed under oxidative or reductive conditions. The encapsulation
of a fluorescent and/or photochromic dye into a polyurethane dispersion circumvents all of these
problems.

[0003] It is important that ink compositions comprising dye dispersion remain stable, not only in storage but also over repeated jetting cycles. Therefore, a need exists for a method to encapsulate photochromic and/or fluorescent dyes into the latex, and to provide a highly stable dye polyurethane dispersion, which may be used for ink-jet applications.

5

BRIEF DESCRIPTION OF THE FIGURES

[0004] FIG. 1 shows a water-in-oil dispersion of a mixture of water and a neutralized prepolymer containing a visible dye according to certain embodiments of the present disclosure.

10 [0005] FIG. 2 shows an oil-in-aqueous dispersion of a mixture of water and a neutralized prepolymer containing a visible dye after high speed spinning according to certain embodiments of the present disclosure.

[0006] FIG. 3 shows a close up view of a single visible dye dispersion particle in water according to certain embodiments of the present disclosure.

15 [0007] FIG. 4 shows a close up view of a single visible dye dispersion particle after the addition of a chain extender dispersion according to certain embodiments of the present disclosure.

SUMMARY OF THE INVENTION

[0008] The disclosure provides an encapsulated dye dispersion comprising a polyurethane dispersion that is the reaction product of: (a) a urethane prepolymer, the urethane prepolymer being
20 the catalyzed reaction product of: (i) a polyol; (ii) a polyisocyanate; and (iii) an internal surfactant; (b) a neutralizing agent; and (c) a chain extender; and a dye selected from the group consisting of fluorescent dye, photochromic dye, and mixtures thereof, wherein the dye is not reactive towards the polyisocyanate.

[0009] In embodiments, the disclosure provides an encapsulated dye dispersion comprising a
25 polyurethane dispersion that is the reaction product of: (a) a urethane prepolymer that is the catalyzed reaction product of: (i) a polyol; (ii) a polyisocyanate; and (iii) an internal surfactant; wherein the stoichiometric equivalent molar ratio of internal surfactant to polyol is from about 0.5 to about 2 and the stoichiometric equivalent molar ratio of NCO groups to total OH groups in the prepolymer is from about 1.0 to about 3.0; (b) a neutralizing agent; and (c) a chain extender; and an aqueous dye
30 dispersion comprising a dye that is not reactive towards the polyisocyanate, wherein the dye is encapsulated in the polyurethane dispersion; further wherein the encapsulated dye dispersion has an average particle size of from about 20 nm to about 900 nm, a viscosity of from about 2 to

602325552v1

about 150 cps at room temperature, and a surface tension of from about 15 to about 65 dyn at room temperature.

[0010] The disclosure also provides an ink jet ink composition comprising an encapsulated dye dispersion comprising a polyurethane dispersion that is the reaction product of: (a) a urethane prepolymer that is the catalyzed reaction product of: (i) a polyol; (ii) a polyisocyanate; and (iii) an internal surfactant; (b) a neutralizing agent; and (c) a chain extender; and a dye selected from the group consisting of fluorescent dye, photochromic dye, and mixtures thereof, wherein the dye is not reactive towards the polyisocyanate.

[0010a] In accordance with an aspect, there is provided an encapsulated dye dispersion consisting essentially of:

a polyurethane dispersion that is the reaction product of:

(a) a urethane prepolymer having an average weight molecular weight of from about 1,000 to about 20,000, the urethane prepolymer being the catalyzed reaction product of:

(i) a polyol;

(ii) a polyisocyanate; and

(iii) an internal surfactant;

(b) a neutralizing agent; and

(c) a chain extender selected from the group consisting of ethylenediamine, 1,2-propanediamine, 1,6-hexamethylenediamine, piperazine, 2,5-dimethylpiperazine, isophoronediamine, 4,4'-dicyclohexylmethanediamine, 3,3'-dimethyl-4,4'-dicyclohexylmethanediamine, N-hydroxymethylaminoethylamine, N-hydroxyethylaminoethylamine, N-hydroxypropylaminopropylamine, N-ethylaminoethylamine, diethylenetriamine, dipropylenetriamine, and triethylenetetramine and N-methylaminopropylamine, ethylene diamine and combinations thereof; and

a dye selected from the group consisting of fluorescent dye, photochromic dye, and mixtures thereof, wherein the dye is not reactive towards the polyisocyanate;

wherein the encapsulated dye dispersion is obtained by a process comprising:

providing the urethane prepolymer;

reacting the urethane prepolymer with the neutralizing agent to form a neutralized

prepolymer;

adding the dye to the neutralized prepolymer;

adding water to the neutralized prepolymer to form an aqueous dispersion of the neutralized prepolymer; and

reacting the aqueous dispersion of the neutralized prepolymer with the chain extender thereby producing the encapsulated dye dispersion.

5 1. **[0010b]** In accordance with an aspect, there is provided an encapsulated dye dispersion consisting essentially of:

a polyurethane dispersion that is the reaction product of:

(a) a urethane prepolymer having an average weight molecular weight of from about 1,000 to about 20,000, that is the catalyzed reaction product of:

- 10 (i) a polyol;
 (ii) a polyisocyanate; and
 (iii) an internal surfactant;

wherein the stoichiometric equivalent molar ratio of internal surfactant to polyol is from about 0.5 to about 2 and the stoichiometric equivalent molar ratio of NCO groups to total
 15 OH groups in the prepolymer is from about 1.0 to about 3.0;

(b) a neutralizing agent; and

(c) a chain extender selected from the group consisting of ethylenediamine, 1,2-propanediamine, 1,6-hexamethylenediamine, piperazine, 2,5-dimethylpiperazine, isophoronediamine, 4,4'-dicyclohexylmethanediamine, 3,3'-dimethyl-
 20 4,4'dicyclohexylmethanediamine, N-hydroxymethylaminoethylamine, N-hydroxyethylaminoethylamine, N-hydroxypropylaminopropylamine, N-ethylaminoethylamine, diethylenetriamine, dipropylenetriamine, and triethylenetetramine and N-methylaminopropylamine, ethylene diamine, and combinations thereof; and

an aqueous dye dispersion comprising a dye that is not reactive towards the polyisocyanate,
 25 wherein the dye is encapsulated in the polyurethane dispersion;

further wherein the encapsulated dye dispersion has an average particle size of from about 20 nm to about 900 nm, a viscosity of from about 2 to about 150 cps at room temperature, and a surface tension of from about 15 to about 65 dyn at room temperature;

wherein the encapsulated dye dispersion is obtained by a process comprising:

30 providing the urethane prepolymer;

reacting the urethane prepolymer with the neutralizing agent to form a neutralized prepolymer;

adding the dye to the neutralized prepolymer;

adding water to the neutralized prepolymer to form an aqueous dispersion of the

5 neutralized prepolymer; and

reacting the aqueous dispersion of the neutralized prepolymer with the chain extender thereby producing the encapsulated dye dispersion.

2. **[0010c]** In accordance with an aspect, there is provided an ink jet ink composition comprising an encapsulated dye dispersion comprising:

10 a polyurethane dispersion that is the reaction product of:

(a) a urethane prepolymer that is the catalyzed reaction product of:

(i) a polyol;

(ii) a polyisocyanate; and

(iii) an internal surfactant;

15 (b) a neutralizing agent; and

(c) a chain extender selected from the group consisting of ethylenediamine, 1,2-propanediamine, 1,6-hexamethylenediamine, piperazine, 2,5-dimethylpiperazine, isophoronediamine, 4,4' -dicyclohexylmethanediamine, 3,3 '-dimethyl-

20 4,4'dicyclohexylmethanediamine, N-hydroxymethylaminoethylamine, N-hydroxyethylaminoethylamine, N-hydroxypropylaminopropylamine, N-ethylaminoethylamine, diethylenetriamine, dipropylenetriamine, and triethylenetetramine and N-methylaminopropylamine, ethylene diamine, and combinations thereof; and a dye selected from the group consisting of fluorescent dye, photochromic dye, and mixtures thereof, wherein the dye is not reactive towards the polyisocyanate;

25 wherein the encapsulated dye dispersion is obtained by a process comprising:
providing the urethane prepolymer;

reacting the urethane prepolymer with the neutralizing agent to form a neutralized prepolymer;

adding the dye to the neutralized prepolymer;

30 adding water to the neutralized prepolymer to form an aqueous dispersion of the neutralized prepolymer; and

reacting the aqueous dispersion of the neutralized prepolymer with the chain extender thereby producing the encapsulated dye dispersion.

DETAILED DESCRIPTION

5 [0011] As used herein, the term "dispersion" means a two phase system where one phase consists of finely divided particles (often in the colloidal size range) distributed throughout a bulk substance, the particles being the dispersed or internal phase and the bulk substance the continuous or external phase. The bulk system is often an aqueous system.

[0012] As used herein, the term "PUD" means the polyurethanes dispersions described herein.

10 [0013] As used herein, the term "DMPA" means dimethylol propionic acid.

[0014] Disclosure provides an encapsulated dye dispersion including a polyurethane dispersion and an aqueous dye dispersion including a dye selected from, fluorescent dye, photochromic dye, and mixtures thereof that is unreactive towards any reagent / or precursor of the urethane prepolymer (*i.e.*, the polyol, the polyisocyanate, and/or the internal surfactant). The polyurethane dispersion of the disclosure is a reaction product of (a) a urethane prepolymer, (b) a neutralizing agent, and (c) a chain extender, where the urethane prepolymer is prepared from (i) a polyol, (ii) a polyisocyanate, and (iii) an internal surfactant. The reaction to form the polyurethane dispersion of the present disclosure is not a free radical reaction.

20 [0015] When preparing the encapsulated dye dispersion of the present disclosure, the dye may be incorporated, or encapsulated, into the polyurethane dispersion by adding the dye during the formation of the polyurethane dispersion, such as prior to the addition of a neutralizing agent.

[0016] The preparation of encapsulated fluorescent and/or photochromic dye dispersion requires a viscous prepolymer being first formed, and then the fluorescent and/or photochromic dye being added after the pre-polymer has been formed. The fluorescent and photochromic dyes of the disclosure are immiscible in water. Therefore, if such dyes are added to the polyurethanes

dispersions after they have been made, the dyes would simply “float” in the water portion of the latex. In the present disclosure, the dyes are added to the prepolymer or the components that are reacted to make the prepolymer (i.e., polyisocyanate, polyol & internal surfactant), as the dyes are soluble in these organics.

5 **[0017]** In certain embodiments, the encapsulated dye dispersion may be prepared by a process including preparing a urethane prepolymer; reacting the urethane prepolymer with a neutralizing agent; adding water to the neutralized prepolymer to form an aqueous dispersion of the neutralized prepolymer; and reacting the aqueous dispersion of the neutralized prepolymer with a chain extender thereby producing an encapsulated dye dispersion, wherein the step of preparing a
10 urethane prepolymer include adding a fluorescent or photochromic dye to the reaction mixture. For example, the dye may be added to the mixture of polyol, polyisocyanate, and internal surfactant in the presence of a catalyst.

[0018] In certain embodiments, the encapsulated dye dispersion may be prepared by a process including preparing a urethane prepolymer; adding a dye to the urethane prepolymer; reacting
15 the urethane prepolymer with a neutralizing agent to form a neutralized prepolymer; adding water to the neutralized prepolymer to form an aqueous dispersion of the neutralized prepolymer; and reacting the aqueous dispersion of the neutralized prepolymer with a chain extender thereby producing an encapsulated dye dispersion.

[0019] In certain embodiments, the encapsulated dye dispersion may be prepared by a process
20 including preparing a urethane prepolymer; reacting the urethane prepolymer with a neutralizing agent to form a neutralized prepolymer; adding a dye to the neutralized prepolymer; water to the neutralized prepolymer to form an aqueous dispersion of the neutralized prepolymer; and reacting the aqueous dispersion of the neutralized prepolymer with a chain extender thereby producing an encapsulated dye dispersion.

25 **[0020]** The urethane prepolymer can be prepared by reacting a polyol, a polyisocyanate, and an internal surfactant in the presence of a catalyst.

[0021] The internal surfactant may be dissolved in an organic solvent, such as NMP, DMF, or other polar aprotic solvents, prior to the addition to the polyol and polyisocyanate.

[0022] Generally, the stoichiometric equivalent molar ratio of internal surfactant to polyol may
30 be from about 0.5 to about 2, from about 0.75 to about 1.75 to about 1 to about 1.5, the stoichiometric equivalent molar ratio of NCO groups to total OH groups in the prepolymer may

be from about 1.0 to about 3.0, from about 1.25 to about 2.5, or from about 1.5 to about 2.0 . It is desired to have a high internal surfactant to polyol ratio and a low NCO group to OH group ratio. Typically, the urethane prepolymer reaction is carried out at about 70 °C to about 100 °C for about 1 to about 5 hours until the theoretical isocyanate content, which can be determined by, *e.g.*, the di-n-butylamine titration method, is reached to form an urethane prepolymer (isocyanate-terminated) containing an internal surfactant therein.

[0023] The urethane prepolymer (isocyanate terminated prepolymer containing an internal surfactant therein) can be neutralized with a neutralizing agent, such as a trialkylamine, *e.g.*, triethylamine. The amount of neutralizing agent used may be dependent upon the amount of internal surfactant present in the urethane prepolymer, and ranges from about 50 % to about 110 %, or from about 90 % to about 105 % of the quantity of internal surfactant. This neutralization step allows the urethane prepolymer to be dispersible by neutralizing the functional groups of the urethane prepolymer. In one embodiment, the carboxylic acid sites on the internal surfactants may be neutralized thereby forming a salt, such as $\text{--CO}_2^- \text{HN}^+ \text{R}_3$, where R is a lower alkyl group.

[0024] The neutralized prepolymer, typically, has an average weight molecular weight (MW) of from about 5,000 to about 10,000, from about 1,000 to about 20,000, from about 3,000 to about 15,000, or from about 5,000 to about 10,000.

[0025] Water 1, *e.g.*, deionized (DI) water, can be added to the neutralized prepolymer 3 which contains dye 2 which can be added during the formation of the prepolymer or after the formation of the prepolymer but prior to the addition of the neutralizing agent. The amount of water in the aqueous dispersion is based on the desired percentage of solids in the final polyurethane dispersion, which may be in amount of from about 1.0 to about 99 percent, from about 20 to about 80 or from about 35 to about 60 percent based on the total weight of the aqueous dispersion. The aqueous dispersion usually starts out as a “water-in-oil” dispersion the moment the water is added under dispersion conditions. **FIG. 1** shows a “water-in-oil” dispersion when water is first added to the neutralized prepolymer 3. During the dispersion process, the mixture (*i.e.*, water and the neutralized prepolymer 3) may be spinned at high speed (*e.g.*, 5,000-10,000 rpms) and the “water-in-oil” dispersion may be converted to an “oil-in-water” dispersion. The dispersion can be accomplished by spinning a blade, such as a dispersion blade 4. The effect of employing a dispersion blade at high speed imparts energy into the system to disperse rather than

to mix. At this point, the particle size of the final encapsulated dye dispersion may be determined. **FIG. 2** shows an “oil-in-water” dispersion, where the neutralized prepolymer **3** is suspended in the water. Inside a droplet of the neutralized prepolymer **3**, the terminals (i.e., free – NCO groups) of the neutralized prepolymer are at the inside surface of the droplet. In one
5 embodiment of the disclosure, **FIG. 3** shows a close up view of a single dispersion particle in water, where DMPA is employed as the the internal surfactant.

[0026] A chain extender such as a suitable diamine, triamine, diol or a triol, may be then added to increase the average weight molecular weight of the polyurethane dispersion by using an amount stoichiometrically equivalent to from about 60 to about 100 percent of the amount of
10 prepolymer, or from about 85 to about 95 percent of the amount of the prepolymer. The average weight molecular weight of the polyol employed and the particular chain extender used can impact the adhesion of the ink to the final receiving substrate.

[0027] The chain extender may diffuse or migrate into the particles of the dispersion and react with the terminated free isocyanate groups of the neutralized prepolymer, and thus extend the
15 molecular weight of the polyurethane polymer and form ureas in the process. In one embodiment of the disclosure, **FIG. 4** shows a close up view of a single dispersion particle after the addition of a chain extender, e.g., ethylene diamine in water, where DMPA is employed as the the internal surfactant.

[0028] Examples of the chain extender suitable for use in the present disclosure include diamines
20 such as ethylenediamine, 1,2-propanediamine, 1,6-hexamethylenediamine, piperazine, 2,5-dimethylpiperazine, isophoronediamine, 4,4'-dicyclohexylmethanediamine, 3,3'-dimethyl-4,4'-dicyclohexylmethanediamine, and 1,4-cyclohexanediamine; diamines containing one primary amino group and one secondary amino group such as N-hydroxymethylaminoethylamine, N-hydroxyethylaminoethylamine, N-hydroxypropylaminopropylamine, N-ethylaminoethylamine,
25 and N-methylaminopropylamine; polyamines such as diethylenetriamine, dipropylenetriamine, and triethylenetetramine. In one embodiment, the chain extender includes ethylene diamine.

[0029] Any suitable amounts of prepolymer, neutralizing agent, water and chain extender may be added to the urethane prepolymer as long as a stable polyurethane dispersion is formed.

[0030] As a stirring/dispersing device for dispersing pigments, for example, various known
30 dispensers such as a high speed impeller disc, an ultrasonic homogenizer, a high-pressure

homogenizer, a paint shaker, a ball mill, a roll mill, a sand mill, a sand grinder, a dyno mill, dispermat, an SC mill, a nanomizer, or the like can be used.

[0031] The encapsulated dye polyurethane dispersion is then combined with an aqueous medium, at least one humectant, and optionally at least one plasticizer.

5 [0032] The encapsulated dye dispersion of the present disclosure may have an average dispersion particle size (*i.e.*, particle diameter) of from about 20 nm to about 900 nm, from about 30 nm to about 600 nm, or from about 50 nm to about 100 nm. This size range permits the particles and the resultant ink in which they are dispersed to overcome settling and stability/dispersing problems. The average particle diameter can be measured by various
10 methods, for example, they can be measured using a particle analyzer UPA 150 manufactured by Nikkiso Co., Ltd.

[0033] The encapsulated fluorescent and photochromic dye dispersion of the present disclosure may have a viscosity of from about 2 to about 150 cps, from about 10 to about 100 cps, or from about 20 to about 80 cps at room temperature. The encapsulated dye dispersion of the present
15 disclosure may have a surface tension of from about 15 to about 65 dyn, from about 25 to about 60 dyn, or from about 35 to about 55 dynes, at room temperature.

[0034] The dye content of the encapsulated dye dispersion of the present disclosure may be in the range of from 0.1 to about 30 percent, from about 1.0 to about 15 percent, or from about 2.0 to about 5.0 percent by weight of the encapsulated dye dispersion.

20 [0035] The fluorescent and photochromic dyes of the present disclosure are unreactive towards any reagent / or precursor of the urethane prepolymer (*i.e.*, the polyol, the polyisocyanate, and the internal surfactant). Particularly, the dyes do not contain any non-phenolic hydroxyl group or aliphatic primary or secondary amines, but may include a phenolic hydroxyl group and/or a tertiary amine in which one of the substituents is an aromatic ring.

25 [0036] The dyes used in the present disclosure may contain fluorescent dye, and/or photochromic dye, or mixtures thereof.

[0037] Suitable fluorescent dyes include organic and inorganic dyes that are soluble in organic solvents and also in water, as well as other solvent systems. Specific examples include, but are not limited to, zinc or cadmium based quantum dots and nanocrystals, stilbene derivatives, fluorescent
30 brighteners, 2,5-Bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene, 4,4'-Bis(2-benzoxazolyl)stilbene, 4,4'-Diamino-2,2'-stilbenedisulfonic acid, fluorescent brightener 28, TinopalTM UNPA-GX, 2-(2-

Hydroxyphenyl)benzothiazole, Tris [1-phenyl Isoquinolinato C2,N] iridium (III), Tris[2-phenyl pyridinato C2, N] iridium (III) and Tris [2-(4,6-difluorophenyl) 1pyridinato C2,N] iridium (III) xanthene derivatives, cyanine derivatives, naphthalene derivatives, coumarin derivatives, oxadiazole derivatives, pyrene derivatives, oxazine derivatives, acridine derivatives, arylmethine derivatives, tetrapyrrole derivatives. Suitable photochromic dye can be found in both organic compounds, such as anils, disulfoxides, hydrazones, osazones, semicarbazones, stilbene derivatives, o-nitrobenzyl derivatives, spiro compounds [spiropyrans and spirooxazine compounds], and the like; and in inorganic compounds, such as metal oxides; alkaline earth metal sulfides; titanates; mercury compounds; copper compounds; minerals; transition metal compounds such as carbonyls, and the like. Specific examples of photochromic dye include 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran, 1,3,3-Trimethylindolinobenzopyrylospiran, 1,3,3-Trimethylindolino-6'-nitrobenzopyrylospiran, 1,3,3-Trimethylindolino-6'-bromobenzopyrylospiran, 1,3,3-Trimethylindolino-8'-methoxybenzopyrylospiran, 1,3,3-Trimethylindolino- β -naphthopyrylospiran, 1,3,3-Trimethylindolinonaphthospirooxazine, diarylethenes, spiropyrans, spiroperimidines, and viologens and azobenzene.

[0038] As used herein, the term "polyol" is intended to include materials that contain two or more hydroxyl groups, *e.g.*, diol, triol, tetraol, *etc.* The average weight molecular weight of the polyol may be in the range of from about 60 to about 10,000, from about 500 to about 5000, or from about 1000 to about 2000. Polyols for use in the polyurethane polymerization of the present disclosure could be selected to enhance the solubility of a specific fluorescent or photochromic dye. Non-limiting examples of polyols include diols, triols, polyether polyols, polyacrylate polyols, polyester polyols, polycarbonate polyols, and combinations thereof. Suitable polyether polyol include, but are not limited to, polytetramethylene ether glycol (PTMEG), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. Suitable polyacrylate polyols include, but are not limited to, glycerol 1,3-diglycerolate diacrylate. Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol; polybutylene adipate glycol; polyethylene propylene adipate glycol; o-phthalate-1,6-hexanediol; poly(hexamethylene adipate) glycol; and mixtures thereof. Suitable polycarbonate polyols include, but are not limited to, poly(polyTHFcarbonate)diol.

[0039] As used herein, the term "polyisocyanate" is intended to include materials that contain two or more isocyanate groups. The average weight molecular weight of the polyisocyanate may

be in the range of from about 140 to about 1000, from about 168 to about 262, or from about 222 to about 680. Suitable polyisocyanates include diisocyanates, triisocyanates, copolymers of a diisocyanate, copolymers of a triisocyanate, polyisocyanates (having more than three isocyanate functional groups), and the like, as well as mixtures thereof. Examples of diisocyanates include isophorone diisocyanate (IPDI); toluene diisocyanate (TDI); diphenylmethane-4,4'-diisocyanate (MDI); hydrogenated diphenylmethane-4,4'-diisocyanate (H12MDI); tetra-methyl xylene diisocyanate (TMXDI); hexamethylene-1,6-diisocyanate (HDI); hexamethylene-1,6-diisocyanate; naphthylene-1,5-diisocyanate; 3,3'-dimethoxy-4,4'-biphenyldiisocyanate; 3,3'-dimethyl-4,4'-bimethyl-4,4'-biphenyldiisocyanate; phenylene diisocyanate; 4,4'-biphenyldiisocyanate; trimethylhexamethylene diisocyanate; tetramethylene xylene diisocyanate; 4,4'-methylenebis(2,6-diethylphenyl isocyanate); 1,12-diisocyanatododecane; 1,5-diisocyanato-2-methylpentane; 1,4-diisocyanatobutane; dimer diisocyanate and cyclohexylene diisocyanate and its isomers; uretidione dimers of HDI; and the like, as well as mixtures thereof. Examples of triisocyanates or their equivalents include the trimethylolpropane trimer of TDI, and the like, isocyanurate trimers of TDI, HDI, IPDI, and the like, and biuret trimers of TDI, HDI, IPDI, and the like, as well as mixtures thereof. Examples of higher isocyanate functionalities include copolymers of TDI/HDI, and the like, and MDI oligomers, as well as mixtures thereof.

[0040] Suitable internal surfactants include both anionic and cationic internal surfactants. These include sulfonate diamines and diols, and dihydroxy carboxylic acids. In one embodiment, the internal surfactant is α,α -dimethylolpropionic acid (DMPA).

[0041] Any conventional urethane forming catalyst can be used in the prepolymer-forming reaction. Suitable urethane reaction catalyst, include, but are not limited to, dibutyl tindilaurate, bismuth tris-neodecanoate, cobalt benzoate, lithium acetate, stannous octoate, triethylamine, or the like.

[0042] The encapsulated dye dispersions of the present disclosure may be used in inkjet inks. The inkjet inks of the present invention can be prepared by diluting the encapsulated dye dispersion of the present invention with water or an aqueous solvent that contains water, and adding thereto other optional additives, *e.g.*, humectant, plasticizier, contuctibity agents, defoamers, anti-oxidants, corrosion inhibitors, bacteriocides, pH control agents, if necessary.

[0043] The ink jet ink compositions may include a humectant. Examples of humectants include, but are not limited to, alcohols, for example, glycols such as 2,2'-thiodiethanol, glycerol, 1,3-

propanediol, 1,5-pentanediol, polyethylene glycol, ethylene glycol, diethylene glycol, propylene glycol and tetraethylene glycol; pyrrolidones such as 2-pyrrolidone; N-methyl-2-pyrrolidone; N-methyl-2-oxazolidinone; and monoalcohols such as n-propanol and iso-propanol. The humectant may be present in an amount from about 2% to about 20%, or from about 4% to about 10% by weight of the ink composition.

[0044] The ink jet ink compositions may include a plasticizer. Examples of plasticizers include, but are not limited to, aliphatic polyols, phthalate esters (such as 1,6-hexane diol and dioctylphthalate), and other urethane compatible plasticizers.

[0045] The ink jet ink compositions may also include other components to impart characteristics desirable for ink jet printing applications. These optional components include conductivity agents, defoamers, anti-oxidants and corrosion inhibitors which improve ink manufacturing and printer performance; bacteriocides, which prevent bacterial attack that fouls ink manufacturing equipment and printers; and pH control agents, which insure that the components of the ink composition remain soluble throughout the operable range of water contents as well as throughout the period of storage and use.

[0046] The ink jet ink compositions of the present disclosure have a high degree of transparency and brightness. The inks of the present disclosure may have a surface tension in the range of about 20 dynes/cm to about 70 dynes/cm, or in the range 30 dynes/cm to about 50 dynes/cm; a viscosity in the range of about 1.0 to about 10.0, or about 1.0 to about 5.0 centipoise at room temperature.

[0047] The encapsulated dye dispersion particles remain stabilized or dispersed in a liquid carrying medium in the ink having a pH of from about 4 to about 10, from about 5 to about 9, or from about 6 to about 8.

EXAMPLES

[0048] The following Examples further illustrate the present invention. All parts and percentages are by weight and all temperatures are degrees Celsius unless explicitly stated otherwise.

Example 1

Preparation of Neutralized Dyed Pre-polymer

[0049] Pre-dissolved DMPA/NMP solution:

[0050] Into a 50 ml flask equipped with a Teflon coated stir magnetic was added 9.75 g of 2,2-bis(hydroxymethyl) propionic acid (DMPA, MW=134, available from Adrich Chemical of

Milwaukee, Wis.) and 15.6 g of N-methylpyrrolidone (NMP). The mixture was heated at 70°C with stirring until the DMPA was completely dissolved.

[0051] Pre-polymer Formation:

[0052] Into a 1L kettle equipped with a Trubore™ stirrer and Teflon™ stir paddle, temperature
 5 controller, 100 mL constant pressure addition funnel and N₂ inlet was charged 72.76 g pre-melted Terathane® 2000 (average Mn=2000 poly(tetrahydrofuran), available from Sigma-Aldrich). The kettle was secured in a bracket and the bottom 1/3 of the kettle was submerged in a 70°C oil bath, and the contents were stirred for 15 minutes. The pre-dissolved DMPA/NMP solution was added to the kettle. After the contents were stirred for about 15 minutes, 42.4 g of
 10 isopherone diisocyanate (IPDI, MW=222, available from Huls America, Inc. of Piscataway, N.J.) was added to the kettle drop-wise through an addition funnel over about 30 minutes. A slight exotherm was observed. The reaction mixture was continued to be heated at 70°C with stirring for about 3 hours and 45 minutes.

15 **Example 2**

Neutralization and Incorporation of Dye in Polyurethane Dispersion:

[0053] The resulting mixture was added:

a) a red UV-fluorescing colorless dye:

experiment 1: 1.9 g of DFSB-C7 Clear Red [available from Risk Reactor],

20 experiment 2: 2.7g of DFSB-C7 Clear Red [available from Risk Reactor],

b) a blue UV-fluorescing colorless dye: 1.0 g of fluorescent brightener 28 [available from the Aldrich Chemical Corp],

c) a blue UV-fluorescing colorless dye: 1 g of 2,5-bis(5-tert-butyl-2-benzoxazolyl)thiophene [available from the Aldrich Chemical Corp],

25 d) a blue UV-fluorescing colorless dye: 1 g of 2-(2-hydroxyphenyl)-benzothiazole [available from the Aldrich Chemical Corp], or

e) a photochromic dye: 1 g of 1,3,3-trimethylindolino-6'-nitrobenzopyrylospiran [available from the Aldrich Chemical Co.],

and stirred for several minutes, followed by addition of about 7.35 g of triethylamine (MW=101)
 30 with continuous stirring and heating at 70°C. After stirring and heating for about 15 minutes the neutralized pre-polymer was ready to be dispersion. The kettle containing the neutralized pre-

polymer was transferred to the dispersing apparatus with the dispersion blade about 0.25 inch below the surface of the neutralized pre-polymer.

[0054] To the neutralized dyed pre-polymers obtained above were each added 245 mL of chilled (~5 °C) deionized water. The resulting mixtures were dispersed at the highest speed

5 (approximately 7,500 rpms) with an IKA® Crushing Disperser for about 15 seconds. A long wood tongue depressor was employed to scrape off the un-dispersed pre-polymer stuck on the wall of the kettle. The un-dispersed pre-polymer was placed onto the bottom of the blade of the IKA® Crushing Disperser and dispersed again for about 10 seconds at the highest rpm setting. Aqueous dye dispersions of the neutralized propolymer were obtained.

10

Example 3

Chain Extension

[0055] To the aqueous dye dispersion of the neutralized propolymers obtained in Example 2 was each added dropwise an ethylene diamine solution (4.9 g ethylene diamine / 10g distilled water)

15 over about 5 minutes. After stirring for about 1 hour, the resulting mixture was transferred to a 32 oz glass jar, capped and stored for at least 72 hours. At the end of the 72 hours, four different encapsulated dye dispersions were obtained. The appearance of the final encapsulated dye PU-dispersions were observed and summarized in **Table 1**. The average particle size of the encapsulated dye PU-dispersion particles were measured on a Zetasizer and the results were also
20 summarized in **Table 1**.

Table 1

Dye	PUD Particle Size (nm)	Appearance of Encapsulated Dye PU-Dispersion of Example 3
a) DFSB-C7 Clear Red	47.7	Almost clear, colorless solution; some solids settled (appeared to be the unencapsulated uv-fluorescent dye) after about 1 week.
b) fluorescent brightener 28	52.4	Almost clear, colorless solution.
c) 2,5-bis(5-tert-butyl-2-enzoxazolyl)thiophene	48.2	Almost clear, colorless solution; some solids settled (appeared to be the unencapsulated uv-fluorescent dye) after about 1 week.
d) 2-(2-hydroxyphenyl)-benzothiazole	46.2	Almost clear, colorless solution.
e) 1,3,3-trimethylindolino-6'-nitrobenzopyrrolospiran	49.1	Almost clear, colorless solution; some solids settled (appeared to be the

602325552v1

		unencapsulated uv-fluorescent dye) after about 1 week.
--	--	-----------------------------------------------------------

Example 4

Analysis and Measurements

Approximately 20 g of each of the encapsulated dye PU-dispersions obtained in Example 3 was poured into a 100 mm x 10 cm petri dish top or bottom and allowed to dry/coalesce over a 48 hour period. The samples were peeled out of the Petri dish for future analysis. Polyurethane films were formed and the appearance of the polyurethane films were observed and summarized in **Table 2**.

Table 2

Dye	Appearance of Polyurethane Films of Example 4
a) DFSB-C7 Clear Red	Clear, colorless and transparent disc, which fluoresced red when irradiated by a UV-light.
b) fluorescent brightener 28	Clear, colorless and transparent disc (See. FIG. 5a), which fluoresced blue when irradiated by a UV-light (See. FIG. 5b).
c) 2,5-bis(5-tert-butyl-2-enzoxazoly)thiophene	Clear, colorless and transparent disc, which fluoresced blue when irradiated by a UV-light
d) 2-(2-hydroxyphenyl)-benzothiazole	Clear, colorless and transparent disc which fluoresced green when irradiated by a UV-light.
e) 1,3,3-trimethylindolino-6'-nitrobenzopyrylospiran	Clear, slightly yellowish and transparent disc, which changed to red when irradiated by a UV-light and disappeared shortly after the light was removed. This color change was repeated numerous times.

[0056] Example 5

Preparation of Aqueous Ink-Jet Inks

[0057] Into three separate 2-oz jars was each charged 10 g of a different encapsulated dye dispersion obtained from Example 4, and 2 g of 0.1M pH8 K₂HPO₄/KH₂PO₄ buffer and 8 g DI water. The contents were stirred for about 2 minutes.

[0058] The resulting inks were loaded onto four separate empty ink cartridges, and were printed out on an EPSON™ WF-3540 printer. Xerox 4200 paper was used but the images were difficult to see due to the uv-brighteners in the paper. Solid fill boxes and text of the colorless fluorescent/photochromic dye containing ink were printed on paper containing no UV-brighteners such a TESLIN™ Synthetic Printing Sheet [polyolefinic] which is a product of PPG

industries allowing the dyes to be seen when irradiated by uv-light and not masked by other brighteners.

What is claimed is:

1. An encapsulated dye dispersion consisting essentially of:

a polyurethane dispersion that is the reaction product of:

(a) a urethane prepolymer having an average weight molecular weight of from about

5 1,000 to about 20,000, the urethane prepolymer being the catalyzed reaction product of:

(i) a polyol;

(ii) a polyisocyanate; and

(iii) an internal surfactant;

(b) a neutralizing agent; and

10 (c) a chain extender selected from the group consisting of ethylenediamine, 1,2-

propanediamine, 1,6-hexamethylenediamine, piperazine, 2,5-dimethylpiperazine,

isophoronediamine, 4,4'-dicyclohexylmethanediamine, 3,3'-dimethyl-

4,4'-dicyclohexylmethanediamine, N-hydroxymethylaminoethylamine, N-

hydroxyethylaminoethylamine, N-hydroxypropylaminopropylamine, N-ethylaminoethylamine,

15 diethylenetriamine, dipropylenetriamine, and triethylenetetramine and N-

methylaminopropylamine, ethylene diamine and combinations thereof; and

a dye selected from the group consisting of fluorescent dye, photochromic dye, and mixtures thereof, wherein the dye is not reactive towards the polyisocyanate;

wherein the encapsulated dye dispersion is obtained by a process comprising:

20 providing the urethane prepolymer;

reacting the urethane prepolymer with the neutralizing agent to form a neutralized prepolymer;

adding the dye to the neutralized prepolymer;

adding water to the neutralized prepolymer to form an aqueous dispersion of the

25 neutralized prepolymer; and

reacting the aqueous dispersion of the neutralized prepolymer with the chain extender thereby producing the encapsulated dye dispersion.

2. The encapsulated dye dispersion of claim 1 having an average dispersion particle size of

30 from about 20 nm to about 900 nm.

3. The encapsulated dye dispersion of claim 1 having a viscosity of from about 2 to about 150 cps at room temperature.
4. The encapsulated dye dispersion of claim 1 having a surface tension of from about 15 to about 65 dyn at room temperature.
5. The encapsulated dye dispersion of claim 1, wherein the stoichiometric equivalent molar ratio of internal surfactant to polyol is from about 0.5 to about 2 and the stoichiometric equivalent molar ratio of NCO groups to total OH groups in the prepolymer is from about 1.0 to about 3.0.
6. The encapsulated dye dispersion of claim 1, wherein the dye is present in the amount of from about 0.1 to about 30 percent by weight of the encapsulated dye dispersion.
7. The encapsulated dye dispersion of claim 1, wherein the polyol is selected from the group consisting of polyether polyols, polyester polyols, polyacrylate polyols, polycarbonate polyols, silicone-based polyols and combinations thereof.
8. The encapsulated dye dispersion of claim 1, wherein the polyisocyanate is selected from the group consisting of aliphatic, cycloaliphatic, aromatic and heterocyclic polyisocyanates and combinations thereof.
9. The encapsulated dye dispersion of claim 1, wherein the internal surfactant is selected from the group consisting of anionic internal surfactants, cationic internal surfactants and combinations thereof.
10. The encapsulated dye dispersion of claim 1, wherein the internal surfactant comprises dimethylopropionic acid.
11. The encapsulated dye dispersion of claim 1, wherein the neutralizing agent comprises trialkylamine.

12. The encapsulated dye dispersion of claim 1, wherein the encapsulated dye dispersion is obtained by the process comprising:

preparing a urethane prepolymer;

reacting the urethane prepolymer with a neutralizing agent;

5 adding water to the neutralized prepolymer to form an aqueous dispersion of the neutralized prepolymer; and

reacting the aqueous dispersion of the neutralized prepolymer with a chain extender selected from the group consisting of ethylenediamine, 1,2-propanediamine, 1,6-hexamethylenediamine, piperazine, 2,5-dimethylpiperazine, isophoronediamine, 4,4'-dicyclohexylmethanediamine, 3,3'-dimethyl-4,4'-dicyclohexylmethanediamine, N-hydroxymethylaminoethylamine, N-hydroxyethylaminoethylamine, N-hydroxypropylaminopropylamine, N-ethylaminoethylamine, diethylenetriamine, dipropylenetriamine, and triethylenetetramine and N-methylaminopropylamine, ethylenediamine, and combination thereof, thereby producing an encapsulated dye dispersion;

15 wherein the process further includes a step of adding a dye which occurs prior to reacting the aqueous dispersion of the neutralized prepolymer with a chain extender.

13. The encapsulated dye dispersion of claim 1, wherein a step of adding a dye occurs during the step of preparing a urethane prepolymer.

20

14. The encapsulated dye dispersion of claim 1, wherein a step of adding a dye occurs after adding water to the neutralized prepolymer to form an aqueous dispersion of the neutralized prepolymer and before reacting the aqueous dispersion of the neutralized prepolymer with a chain extender.

25

15. An encapsulated dye dispersion consisting essentially of:
a polyurethane dispersion that is the reaction product of:

(a) a urethane prepolymer having an average weight molecular weight of from about 1,000 to about 20,000, that is the catalyzed reaction product of:

30

(i) a polyol;

(ii) a polyisocyanate; and

(iii) an internal surfactant;

wherein the stoichiometric equivalent molar ratio of internal surfactant to polyol is from about 0.5 to about 2 and the stoichiometric equivalent molar ratio of NCO groups to total OH groups in the prepolymer is from about 1.0 to about 3.0;

5 (b) a neutralizing agent; and

(c) a chain extender selected from the group consisting of ethylenediamine, 1,2-propanediamine, 1,6-hexamethylenediamine, piperazine, 2,5-dimethylpiperazine, isophoronediamine, 4,4' -dicyclohexylmethanediamine, 3,3' -dimethyl-4,4'dicyclohexylmethanediamine, N-hydroxymethylaminoethylamine, N-hydroxyethylaminoethylamine, N-hydroxypropylaminopropylamine, N-ethylaminoethylamine, diethylenetriamine, dipropylenetriamine, and triethylenetetramine and N-methylaminopropylamine, ethylene diamine, and combinations thereof; and an aqueous dye dispersion comprising a dye that is not reactive towards the polyisocyanate, wherein the dye is encapsulated in the polyurethane dispersion;

15 further wherein the encapsulated dye dispersion has an average particle size of from about 20 nm to about 900 nm, a viscosity of from about 2 to about 150 cps at room temperature, and a surface tension of from about 15 to about 65 dyn at room temperature;

wherein the encapsulated dye dispersion is obtained by a process comprising:
providing the urethane prepolymer;

20 reacting the urethane prepolymer with the neutralizing agent to form a neutralized prepolymer;

adding the dye to the neutralized prepolymer;

adding water to the neutralized prepolymer to form an aqueous dispersion of the neutralized prepolymer; and

25 reacting the aqueous dispersion of the neutralized prepolymer with the chain extender thereby producing the encapsulated dye dispersion.

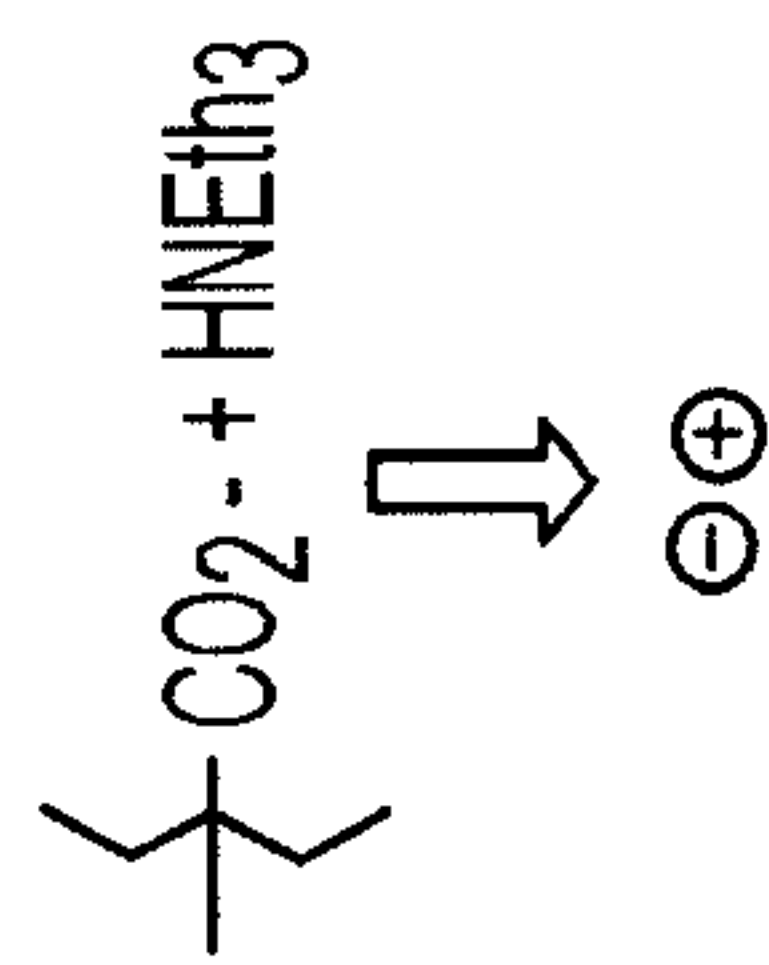
16. An ink jet ink composition comprising an encapsulated dye dispersion comprising:
a polyurethane dispersion that is the reaction product of:

30 (a) a urethane prepolymer that is the catalyzed reaction product of:

(i) a polyol;

(ii) a polyisocyanate; and
(iii) an internal surfactant;
(b) a neutralizing agent; and
(c) a chain extender selected from the group consisting of ethylenediamine, 1,2-
5 propanediamine, 1,6-hexamethylenediamine, piperazine, 2,5-dimethylpiperazine,
isophoronediamine, 4,4' -dicyclohexylmethanediamine, 3,3' -dimethyl-
4,4' dicyclohexylmethanediamine, N-hydroxymethylaminoethylamine, N-
hydroxyethylaminoethylamine, N-hydroxypropylaminopropylamine, N-ethylaminoethylamine,
diethylenetriamine, dipropylenetriamine, and triethylenetetramine and N-
10 methylaminopropylamine, ethylene diamine, and combinations thereof; and
a dye selected from the group consisting of fluorescent dye, photochromic dye, and mixtures
thereof, wherein the dye is not reactive towards the polyisocyanate;
wherein the encapsulated dye dispersion is obtained by a process comprising:
providing the urethane prepolymer;
15 reacting the urethane prepolymer with the neutralizing agent to form a neutralized
prepolymer;
adding the dye to the neutralized prepolymer;
adding water to the neutralized prepolymer to form an aqueous dispersion of the
neutralized prepolymer; and
20 reacting the aqueous dispersion of the neutralized prepolymer with the chain extender
thereby producing the encapsulated dye dispersion.

17. The ink jet ink of claim 16, wherein the encapsulated dye dispersion has an average
particle size of from about 20 nm to about 900 nm, a viscosity of from about 2 to about 150 cps
25 at room temperature, and a surface tension of from about 15 to about 65 dyn at room
temperature.



DEPICTING NEUTRALIZED DMPS (INTERNAL SURFACTANT) AS (+) AND (-) CHARGES

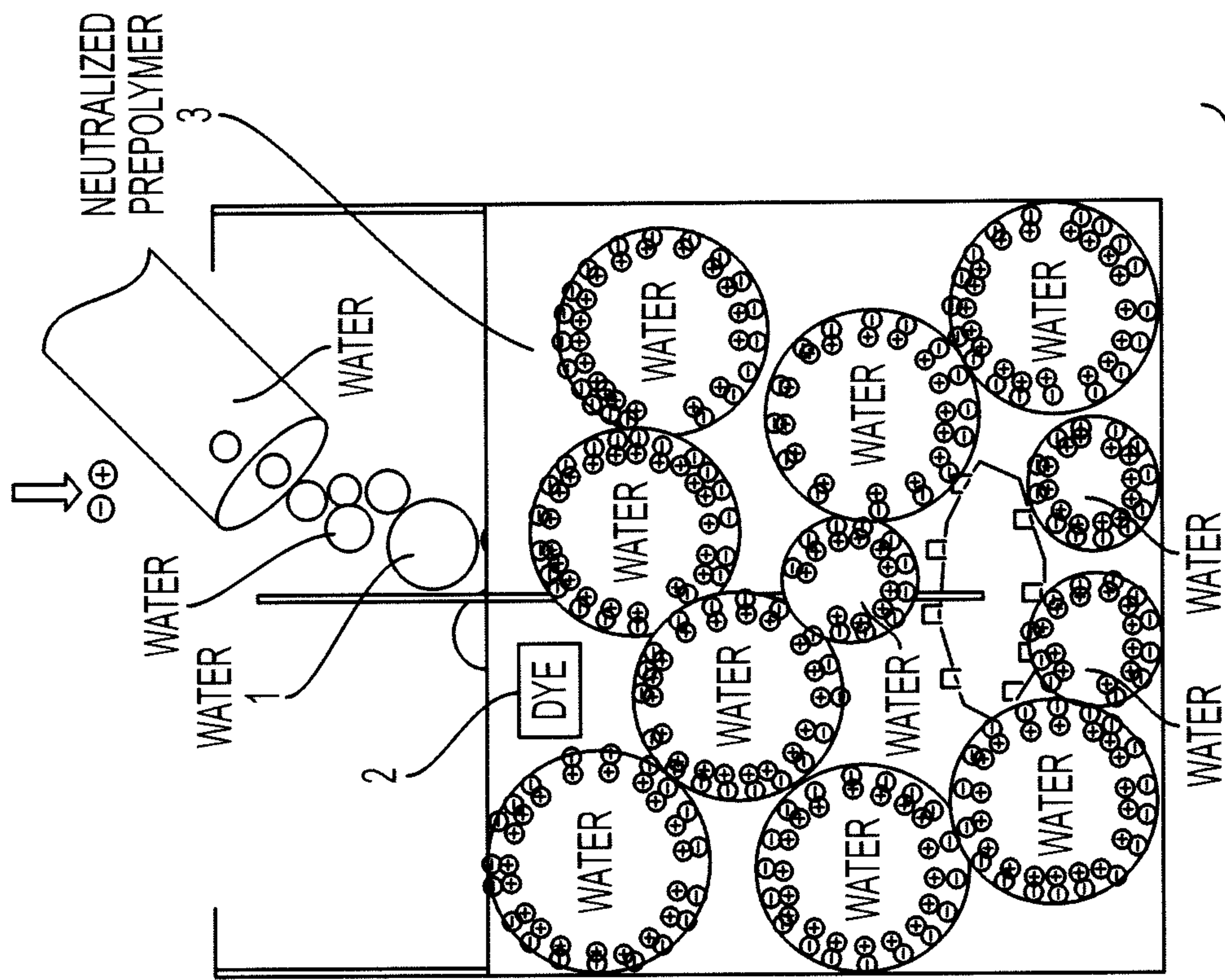


FIG. 1

2/4

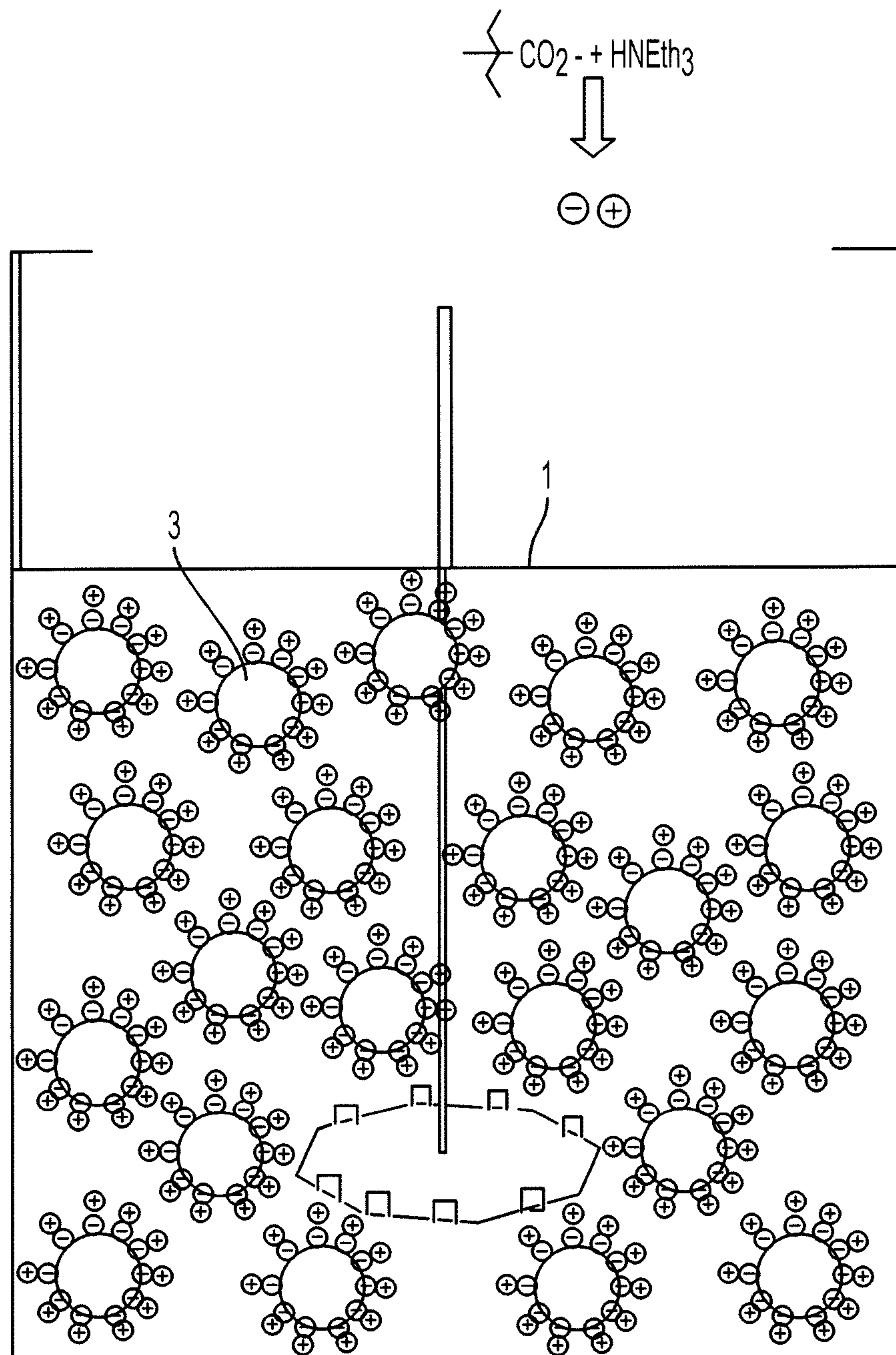


FIG. 2

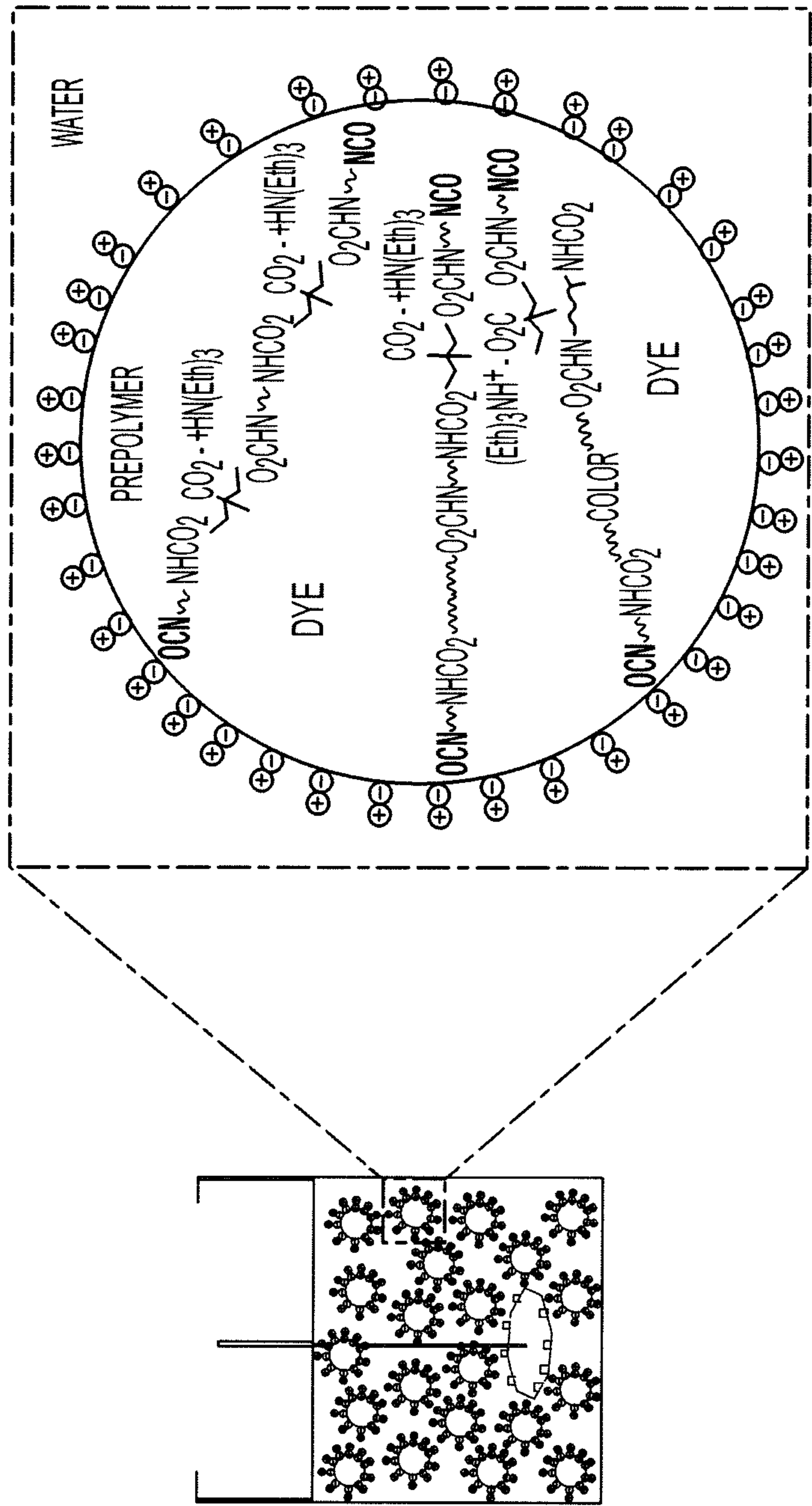


FIG. 3

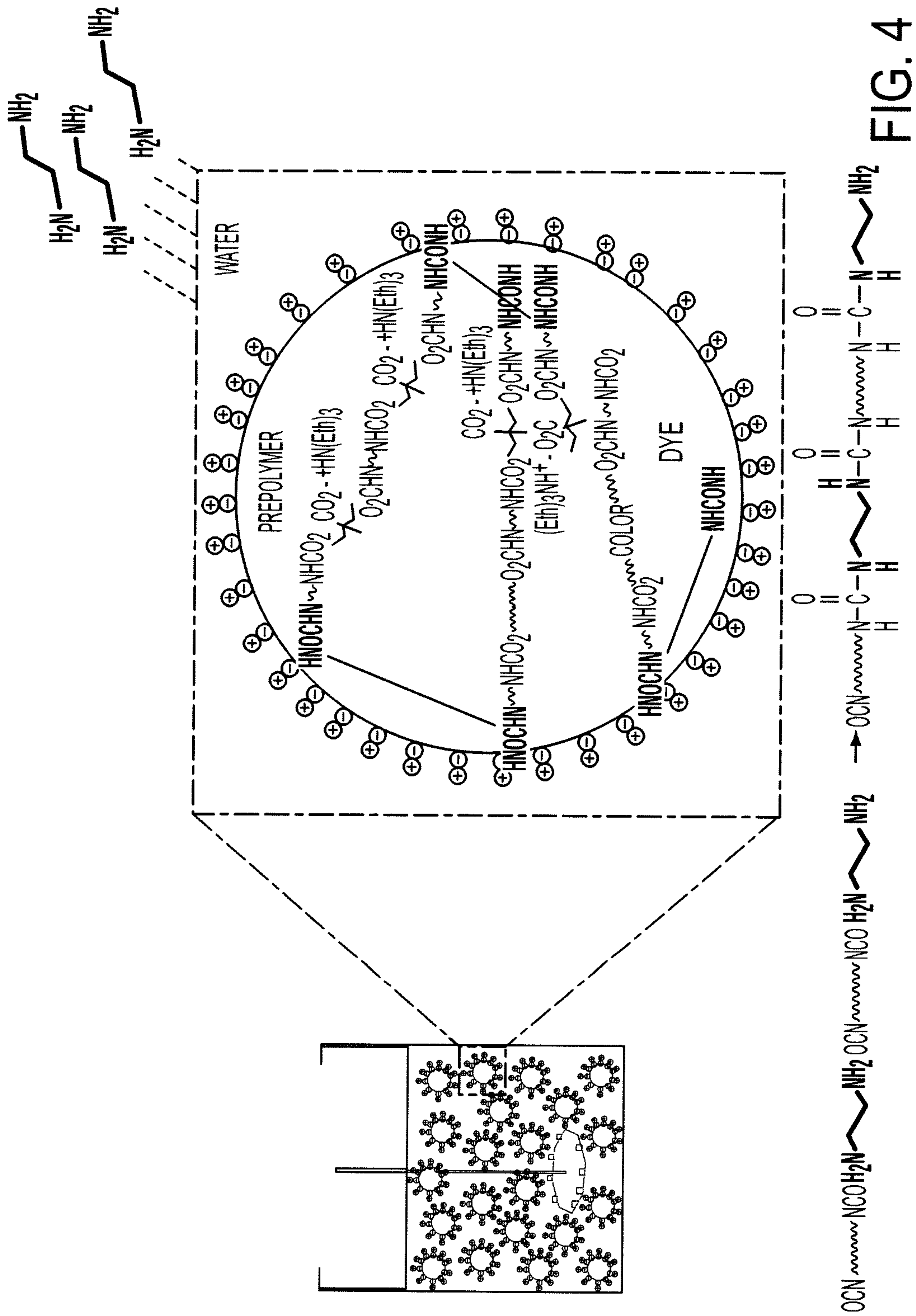


FIG. 4