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[54] PROCESS FOR FILM-COATING ARTICLES

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[58] **Field of Search**.............. 117/36.2, 36.8, 155 R, 117/155 UA, 155 L; 252/316; 162/175

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[57] ABSTRACT

A coating process wherein there is provided a wettable surface, particularly a paper sheet surface, and a coating solution of coacervate-forming materials in a state of incipient coacervation, wherein said coacervate-forming materials are capable of interacting to give a film-forming coacervate phase under the conditions that prevail at the surface to be coated and wherein said surface is contacted with said coating solution to cause the emergence from solution of the film-forming coacervate phase at said surface.

16 Claims, No Drawings

PROCESS FOR FILM-COATING ARTICLES

This invention relates to a process (and the product thereof) for coating a wettable surface, particularly a fibrous web, such as paper sheet material, by contacting said surface with a liquid solution comprising a liquid vehicle having dissolved therein at least two coacervate-precursor materials, wherein at least one of said coacervate-precursor materials must be a coacervatable film-forming material, wherein a second coacervate-precursor material must be a coacervating agent for said film-forming first coacervate-precursor material, and wherein said liquid solution is maintained in such a condition that coacervation does not take place until said liquid solution contacts said surface of said fibrous web or other wettable surface chosen for treatment. Said second coacervate-precursor material may, but need not be a film-forming material. Said liquid solution may optionally include other materials not soluble therein but suspended therein such as clay particles, air or other gaseous bubbles, microcapsules, pigment particles or insoluble liquid droplets, in which case the film-forming material, which is caused to coacervate, that is to emerge from solution as a viscous, film-forming liquid phase, at the moment it comes in contact with the fibrous web, will serve as a binder material for the suspended particles, binding said particles at or near the surface of said fibrous web. If a fibrous web is treated by the process of this invention after it is fully formed, the emergent film-forming material will bind any included particles on the surface of said web, but if the fibrous web is contacted with the liquid solution of this invention while still in a formative state on the wet end of a paper-making machine said optionally included particles will penetrate the fibrous web to some degree before said particles are bound to the neighboring fibers by the emergent coacervate material.

When the polymeric film-forming material chosen for incorporation in the liquid solution as part of the potential coacervate material is an anionic polymer or a polymer which is potentially anionic, the coacervating agent included therewith may be a salt having multivalent cations or a second polymeric material which is cationic or potentially so. Conversely, when the chosen polymeric film-forming material is cationic or potentially so, the coacervating agent included therewith may be a salt having multi-valent anions or a second polymeric material which is anionic or potentially so. It is a requirement of the method of this invention that the charged or potentially charged species chosen to be said first and second coacervate-precursor materials, must be capable of existing as oppositely charged species under some experimentally determinable set of conditions. For instance, if acidity is chosen as the critical and variable condition in the treatment system, the chosen materials must bear charges of opposite sign at some particular pH range in the selected system.

In the process of this invention, the film-forming material and the coacervating agent (which are maintained together in the liquid solution prior to use) are caused to effectively interact to give an emergent coacervate phase at the time and point of contact with the fibrous web material by a change in the condition of the solution induced by contact with the fibers of said web. The condition found to be most conveniently and effectively varied so as to maintain said first and second interacting coacervate-precursor materials in solution together prior to use and to then bring about the desired coacervation when the web fibers are contacted is the degree of acidity or basicity, that is the pH of the liquid solution.

Complex coacervation, that is liquid-liquid phase separation which is brought about by charge neutralization between two oppositely charged species in solution (at least one of which is commonly a film former), is more readily effected by changing the pH of the medium than is simple coacervation or Dobry-type phase separation. Both simple coacervation and Dobry-type phase separation are solvent-robbing phenomena largely dependent on the competition of two species for the vehicle solvent. In simple coacervation, one of the species is a film former and a second species is an inorganic ion. In the Dobry-type phase separation the two competing species are both polymeric materials, generally film formers. In both the latter cases, the two competing species are separated from each other by the phase separation, one of the species being almost entirely in one of the liquid phases and the other of the species being almost entirely in the second liquid phase. This separation of the two species, distinguishes over complex coacervation where both species are charged, oppositely charged, and both end up almost entirely in one of the two liquid phases after coacervation or liquid-liquid phase separation. Complex coacervation is greatly dependent on pH and is therefore the type of liquid-liquid phase separation most readily brought about by the practice of this invention.

Variable factors (other than the degree of acidity) which can be used to trigger a useful coacervate formation are materials concentrations and temperature. Illustrative of processes of this invention which make use of materials concentration variations are the following: (1) providing as a coating solution a liquid vehicle solution of two or more interacting coacervate-precursor materials at the point of incipient coacervation, together with a surface that has an additional amount of one of the coacervate-precursor materials present and bringing the coating solution and the surface into contact to bring about coacervation at and on the surface due to an increase in the concentration of one of the coacervate-precursor agents; (2) providing as a coating solution a liquid vehicle solution of two or more interacting coacervate-precursor materials at the point of incipient coacervation, together with a surface that has an additional amount of said liquid vehicle and bringing the coating solution and the surface into contact to bring about coacervation at and on the surface due to the decrease in concentration of all of the coacervate-precursor agents. Illustrative of processes of this invention which make use of temperature variations are the following: (3) providing as a coating solution a liquid-vehicle solution of two or more interacting coacervate-precursor materials at a temperature where the solution is at the point of incipient coacervation together with a surface that is at a higher temperature than the coating solution (in cases where coacervate-precursor and liquid vehicle materials have been chosen that yield a coacervate phase as a result of a temperature increase) or a lower temperature than the coating solution (in cases when the aforesaid materials have been chosen that yield a coacervate phase as a result of a temperature decrease) and bringing the coating solution and the surface into contact to bring about coacervation at and on the surface due to the increase or decrease in temperature of the coating solution at the surface.

Coating solutions which contain all of the coacervate-precursor materials necessary for coacervate formation, and which are maintained on the verge of coacervating, a state which may also be described as incipient coacervation, have not been taught in the art. For instance Sandberg, Brockett and Clark in U.S. Pat. No. 3,384,536, teach the application of a coating solution, containing one coacervate-precursor material, to a surface containing a second coacervate-precursor material which interacts with the first coacervate-precursor material to given an emergent coacervate phase. In the instant invention, which is an improvement of the aforementioned Sandberg, Brockett and Clark invention, the presence of all of the necessary coacervate-precursor materials in the coating solution before said solution contacts the surface to be coated, allows for improved control of the depth of penetration when application is made to a surface of a porous or absorbent material such as paper. This is because, in the instant invention, the coating solution is in a state of incipient coacervation, and the coacervation is therefore readily, indeed instantly if it is so-desired, initiated by relatively minute changes in materials concentration, temperature or acidity at the time of contacting the surface to be coated. In the older art, where the coating solution is a solution of a single coacervate-precursor material, the coating solution will not give complete coacervation until the coating solution has soaked through sufficient thickness to encounter an equivalent weight of already-present, interacting, coacervate-precursor material. In the instant invention soak-in prior to coacervation can be practically eliminated, and the extent of soak-in-depth (down to and including complete soak-through, prior to complete coacervation) can be easily controlled by controlling the degree of coacervation incipiency in the provided coating solution. The coating solutions in the state closest to coacervation will give the least penetration prior to complete coacervation.

In the previously mentioned U.S. Pat. No. 3,384,536 (Sandberg, et al.) various film-forming materials are set out in Table III as couplet combinations that form coacervate films on a web surface when one of the film formers is in a solution in or on the web and the other is added in a second solution to the surface. It is here taught as a chief embodiment of this invention that any and all of the referred-to Sandberg couplet combinations can be included (at the stated concentrations) in a single solution and kept in solution by proper adjustment of the pH. Further the chosen film-forming materials can be caused to yield a viscous coacervate phase at the web surface if the pH is adjusted into the coacervate range by contact of the solution with the web surface.

The needed pH adjustments are readily determined by means of a simple test-tube experiment: (1) The chosen film-forming couplet combination materials are mixed in water at the desired concentrations. The mixing of materials will give either a two phase mixture or a one-phase solution. In either case, mixing is continued while the sample is (2) titrated with aqueous acid and/or aqueous base until a phase change is observed—either the disappearance of the viscous phase if the sample was originally biphasic or the appearance of a viscous second phase if the sample was originally monophasic. (3) The pH of the sample at the point of phase change is then determined and used to make up the film-forming agent solution for use therein. The solution is made up to be at a pH very near the pH of phase change, but just slightly in the direction of the monophasic pH range. A very slight change in pH toward the biphasic pH range will then cause emergence of the desired coacervate phase at a time and point where film-forming and/or binding action is desired. Actually rather sizable pH changes can be effected at a web surface by use of acidic or alkaline furnish water, but, by proper adjustment of the pH of the added solution so that it is just outside the coacervate range, the need for large pH changes can be obviated.

If solid, gaseous or liquid droplet material is to be enveloped and/or bound to the fibrous web by the emergent coacervate, it is advantageous to add a corresponding amount of said material to the test samples after pH adjustment to be sure the sample solution remains monophasic in the presence of the added material. If such is not the case, that is if a coacervate phase emerges in the presence of the added material, it is a simple matter to readjust the pH to made the sample again monophasic (monophasic, exclusive of the added material).

When a suitable amount of liquid solution has been prepared, with or without added material to be enveloped or bound to a surface, according to the method and conditions determined above for the test sample, the liquid solution may be applied to a surface, particularly a paper surface by a number of methods well-known in the paper-coating and paper-making arts. Depending largely on the consistency and materials of the liquid to be coated on a paper surface, a coating method may be selected from the methods which make use of coaters and printers such as dandy roll coaters, air knife coaters, curtain coaters, reverse-roll coaters, flexographic roll printers and other well-known coaters and printers. A particularly useful coating method for coating on the wet-end of a paper-making machine is the curtain coater; air knife coaters are particularly good for conversion coating.

In addition to the coacervate-forming material couples set out in Table III of the Sandberg, et al. patent, additional coacervate precursor couples may be made up by selecting materials from the lists below. A solution of coacervate precursor materials may be made up (which will yield a separate coacervate phase at a readily determined pH) by choosing at least one cationic material for use with at least one anionic material or by choosing at least one amphoteric material for use with at least one material selected from either the cationic or the anionic list of materials, provided that in all cases at least one of the selected materials is a film-forming material.

CATIONIC MATERIALS

diallyldimethylammonium chloride-diacetone acrylamide copolymer

diallyldodecylmethylammonium chloride-diallyldimethylammonium chloride copolymer
poly(diallyldimethylammonium chloride)
colloidal zirconium oxide[1]
cationic starch
colloidal alumina[1]
galactomannan colloid (mixture

mixed polymers of pentaethylenehexamine, ethylene dichloride, and epichlorohydrin

pentaethylenehexamine-ethylene dichloride copolymer
cationic guar gum

multivalent cations[1]
zinc naphthenate[1]
copper naphthenate[1]

of guar, locust bean and other natural gums treated to have cationic substituents).

[1] Not film-forming

ANIONIC MATERIALS

polyacrylamide
partially hydrolyzed polyacrylamide
sodium polystyrene sulfonate
deacetylated karaya gum
partially hydrolyzed poly(methylvinylether/maleic anhydride)
locust bean gum
guar gum
gum arabic
carboxymethyl cellulose
partially hydrolyzed ethylmaleic anhydride
starch
colloidal silica
poly(vinyl alcohol)
methyl cellulose
gum tragacanth
sodium polyacrylate
sodium cellulose sulfate
polysaccharide xanthan gum
sodium alginate
multivalent anions[1]

[1] Not film-forming

AMPHOTERIC MATERIALS

1:1 acrylic acid-diallyldimethylammonium chloride copolymer
1:1 partially hydrolyzed acrylamide-diallyldimethylammonium chloride copolymer
gelatin
poly-N-(2 hydroxyethyl) aziridine
poly-N-(2-hydroxypropyl) aziridine
ethylenediamine pectinate
casein
poly-N-[N,N-dimethylamino)methyl] acrylamide (i.e. the dimethyl-amine-formaldehyde Mannich Reaction derivative of polyacryl-amide; other (di-lower alkyl-amine)-formaldehyde derivatives of polyacrylamide are known and useful.)

The preceding lists of useful coacervate-precursor materials are intended not to be limiting but rather to be illustrative of the classes of useful materials. The following specific examples will illustrate methods of using selected materials. In the following examples all percents and parts are weight percents and parts by weight unless otherwise stated.

EXAMPLE 1

A solution of a coacervate-precursor couple was prepared by combining (*a*) 100 grams of a 10 percent solution of poly-ethylenimine (mol. wt., 20,000–30,000) in water, adjusted to pH 12.0 with 20 percent aqueous sodium hydroxide, with (*b*) 50 grams of a one percent solution of deacetylated karaya gum in water, also at pH 12.0. The pH of the resulting solution was adjusted to pH 10.0 with acetic acid. The solution at pH 10.0 was coated onto a sheet of paper sized with rosin and alum. The acidity of the rosin-alum sizing was such that the pH of the coating solution was sufficiently lowered to bring about emergence of the coacervate phase when and where the coating solution contacted the paper surface. On drying, the coacervate phase became a tough and flexible film which adhered well to the paper stock. The film-coated paper was quite smooth and resistant to the passage of water vapor.

Similar results were obtained when starch-sized or unsized paper sheets were substituted for the rosin and alum-sized sheets when the substitute sheets were made acidic by being dipped in or coated with aqueous acetic acid just before said sheets were coated with the coacervate-precursor solution of this example.

EXAMPLE 2

A solution of a coacervate-precursor couple was prepared by combining (*a*) 100 grams of a 1.0 percent aqueous solution of N-[N,N-dimethyl(amino)methyl-]acrylamide polymer (mol. wt. 1.5–3 million) and (*b*) 100 grams of a 1.0 percent solution of sodium polystyrene sulfonate (pH 9.3). The solution was coated on a sheet of rosin/alum-sized paper. Immediately upon contact with the acid-sized sheet, the acidity of the coating solution rose to give an emergent film-forming coacervate phase. On drying, the tough flexible film exhibited organic-solvent barrier properties and had excellent clarity. On rewetting with water, the film exhibited adhesive properties.

EXAMPLE 3

In the same concentration and amount, a cationic starch solution was substituted for the sodium polystyrene sulfonate solution of Example 2. The resulting coating solution was coated on raw paper stock that had been pre-coated with a 10 percent solution of sodium hydroxide to give a viscous, emergent coacervate phase on the paper surface. On drying the resultant film was tough and flexible. A suitable cationic starch for use herein was found to be a quaternary amine starch such as Q-TAC 3891 (a trademark of Corn Products Refining Company, 17 Battery Place, New York, New York 10004, United States of America).

EXAMPLE 4

In the same concentration and amount, a solution of polyethylenimine was substituted for the cationic starch solution of Example 3. As in Example 3, the increased alkalinity gave rise to a coacervate phase of film-forming material that dried to a tough, flexible film on the paper surface.

EXAMPLE 5

A slurry of oil-containing, gelatin microcapsules in water (at 20 percent solids) was treated by having mixed therewith sufficient of the solution (pH 12.0) of Example 1 to give a 12 percent solids content to the slurry. As in Example 1, the pH of the coating liquid was adjusted to 10.1, and the coating liquid (slurry) was coated onto rosin/alum-sized paper. As in Example 1 an emergent coacervate phase resulted and gave a tough, flexible, vapor-resistant film coating but this time the film at least partly enveloped oil-containing microcapsules and bound the microcapsules to the paper surface.

EXAMPLE 6

Preferred Example

An aqueous slurry of capsules (2880 grams at 18.36 percent solids) was prepared according to the procedure of Bernard Katchen and Robert E. Miller, United States Patent No. 3,041,289, June 26, 1962. The pH of the slurry was adjusted to 12.0. To the slurry were added the following amounts of aqueous solutions:

72.0 grams of 33 percent polyethyleneimine solution, being a mixture of two equal fractions, one with mol. wt. 40–60 thousand and one with mol. wt. 50–100 thousand, and 960 grams of 0.25 percent solution of polyacrylamide (35 percent hydrolyzed, mol. wt. 2–4 million).

Dilute acetic acid was added to the slurry in such an amount and concentration that the final capsule content (by weight) of the slurry was 4.0 percent and the pH was 11.2.

The coating slurry was coated onto a wet handsheet with a curtain coater. The wet handsheet was made from rosin/alumsized pulp, and had a pH of 5.1 and a moisture content of 80 percent.

EXAMPLE 7

To 100 grams of an aqueous slurry of 20 percent solids, of oil-filled microcapsules, similar to those used in Example 6, were added:

1.00 gram of solid polyethylene microspheres
10.0 grams of a 10 percent solution of polyethyleneimine (aq.) and
Sufficient 20 percent (aq.) sodium hydroxide to give the slurry a pH of 12.0.

The above mixture was treated by addition of the second coacervate-precursor agent, 4.00 grams of a 0.25 percent solution (aq.) of polyacrylamide, the pH of which had been adjusted to 12.0 before the addition. The pH of the entire coating slurry was then coated by means of a conversion coater on rosin/alum-sized raw stock. On drying, the resulting coat included interspersed polyethylene microspheres and oil-filled microcapsules encased in a tough flexible plastic film which adhered tightly to the raw stock.

EXAMPLE 8

A coating solution of a coacervate-precursor couple was prepared by combining 10 milliliters of a 33 percent aqueous polyethyleneimine solution with 10 milliliters of an 11 percent aqueous gum arabic solution and 80 milliliters of water. The pH was adjusted to 7.0 with a 10 percent aqueous sulfuric acid solution. At this pH the coating solution showed a very faint milky color.

A base sheet of paper was prepared by coating it with 10 milliliters of an 11 percent solution of gum arabic in water (at a pH of 7.0). The so-prepared wet base sheet was then coated with 10 milliliters of the coating solution from above. A coacervate phase separated instantly and dried on the base sheet to give a tough, transparent film.

EXAMPLE 9

A coating solution for coacervation by dilution was prepared with the following amounts of coacervate-precursor materials:

10 milliliters of 33 percent polyethyleneimine solution (aqueous)
30 milliliters of 11 percent gum arabic solution (aqueous).

The pH of the above solution was adjusted to 7.5 with 10 percent sulfuric acid. The resultant clear solution was applied to a wet base sheet, having a water-content of 80 to 95 percent, at a pH of 7.5. Coacervation occurred immediately to give a polymer-rich separated phase that dried to a smooth, flexible, transparent film.

EXAMPLE 10

A coating solution for coacervation by decreasing the temperature was prepared by combining the following amount of coacervate-precursor materials:

30 milliliters of 1.0 percent aqueous solution of N-[(N,N-dimethylamino)methyl] acrylamide polymer
60 milliliters of 0.5 percent aqueous polyacrylamide (35 percent hydrolyzed, mol. wt. 2–4 million)

A solution (14 percent, aq.) of acetic acid was added to the above combination to give a pH of 5.5—6.0. The mixture was then heated to 40°–50° centigrade to give a clear coating solution. The coating solution was coated onto a series of articles which were at or below room temperature when dipped into the coating solution. When the temperature of the coating solution fell to about 30° centigrade, at the surface of the object being coated, the desired coacervate phase was deposited on the surface of the object. Among the objects so-coated in this example were a piece of polyurethane foam, an iron nail and a glass microscope slide.

What is claimed is:

1. A process for coating a film of polymeric material onto a surface comprising the steps of:

a. establishing a liquid solution which includes an aqueous liquid vehicle and at least two coacervate-precursor materials capable of interacting with each other to yield a film-forming coacervate under conditions proper for causing coacervation, at least one of which materials is a polymeric film-forming material and all of which materials are dissolved in the vehicle and are in a state of incipient coacervation;
b. providing a surface to be coated, the surface having prevailing conditions proper for causing coacervation of said coacervate-precursor materials;
c. applying the liquid solution to the surface to be coated thereby causing coacervation of the polymeric film-forming material at said surface; and
d. drying the surface to leave a dry coating of the coacervated polymeric film-forming material on said surface.

2. The process of claim **1** wherein coacervation occurs as a result of a pH change in said liquid solution, and wherein said pH change is brought about by the contact of said liquid solution with said surface.

3. The process of claim **1** wherein at least two of the coacervate-precursor materials are film-forming materials and wherein the coacervation which occurs is complex coacervation.

4. The process of claim **1** wherein the liquid solution further comprises substantially insoluble material dispersed therein.

5. The process of claim **1** wherein at least one of said coacervate-precursor materials is selected from the group consisting of polyethyleneimine, polyacrylamide, partially hydrolyzed polyacrylamide, and (diloweralkyl-amine)-formaldehyde derivatives of polyacrylamide.

6. The process of claim **3** wherein coacervation occurs as a result of a pH change in said liquid solution, and wherein said pH change is brought about by the contact of said liquid solution with said surface.

7. The process of claim **6** wherein said surface is a surface of a web of paper fibers.

8. The process of claim **7** wherein said web of paper fibers is a fully-formed sheet of paper.

9. The process of claim **7** wherein said web of paper fibers is a sheet of paper in a formative state.

10. The process of claim **7** wherein said web of paper fibers comprises rosin/alum-sizing material.

11. The process of claim **10** wherein said film-forming materials comprise polyethyleneimine.

12. The process of claim 4 wherein the substantially insoluble material is gaseous.

13. The process of claim 4 wherein the substantially insoluble material is liquid.

14. The process of claim 4 wherein the substantially insoluble material is solid.

15. The process of claim 14 wherein said solid material comprises pressure-rupturable microcapsules.

16. The process of claim 15 wherein said microcapsules have liquid core material.

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