(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 March 2006 (09.03.2006)

PCT

(10) International Publication Number
WO 2006/026283 A1

(51) International Patent Classification^7: **D21H 21/54**

(21) International Application Number: PCT/US2005/030039

(22) International Filing Date: 24 August 2005 (24.08.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/604,230 25 August 2004 (25.08.2004) US

(71) Applicant *(for all designated States except US)*: **DOW GLOBAL TECHNOLOGIES INC.** [US/US]; Washington Street, 1790 Building, Midland, MI 48674 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **TSAVALAS, John** [US/US]; 4815 Claremont Street, Apartment 2, Midland, MI 48642 (US). **GAUPP, Carleton, L.** [US/US]; 2568 North Arbutus Court, Midland, MI 48642 (US). **ROPER, John, A., III** [US/US]; 2805 Georgetown Drive, Midland, MI 48642 (US). **GALLOWAY, James, G.** [US/US]; 3195 Bullock Creek Drive, Midland, MI 48640 (US).

(74) Agent: HAYHURST, Paul, D.; The Dow Chemical Company, Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PAPER MANUFACTURING USING AGGLOMERATED HOLLOW PARTICLE LATEX

(57) Abstract: Agglomerated hollow particle latex is employed as a filler in the wet end of the paper-making process to provide paper with improved properties.

WO 2006/026283 A1

PAPER MANUFACTURING USING AGGLOMERATED HOLLOW PARTICLE LATEX

Background of the Invention

This invention relates to the manufacture of low density paper products.

The paper manufacturing process is very old. In recent years there has been an increasing demand for printing papers having excellent physical properties. On the other hand, there is a great demand for weight reduction in these papers for the sake of reduced cost in transportation and mailing. These demands historically have been mutually contradictory, given that higher quality papers conventionally have a higher base paper basis weight, and higher coat weight if a coating is applied. A paper with a lower basis weight may be selected in order to reduce the weight of a paper article made therefrom, but that is not an ideal solution since it will result in thinner paper and diminish the feeling of bulk expected from a paper product. It is further desired when decreasing the basis weight of a paper to maintain the stiffness of the paper at a lower sheet thickness. For these reasons, the market is presently demanding high quality paper articles that offer greater paper thickness at a given basis weight or a lower basis weight at a given paper thickness.

In the course of manufacturing paper and similar products, such as paper board, it is well known to incorporate inorganic fillers into the fibrous web in order to improve the quality of the resulting product. The fillers are important in improving the printing qualities of the paper by improving the surface characteristics, and the use of an appropriate filler vastly improves the opacity and brightness of a paper sheet. A number of inorganic materials have long been known to be effective for this purpose but despite the effectiveness of these inorganic fillers lower density replacements have been much sought after.

Modern paper manufacturers are constantly searching for a way to obtain paper having lower density while maintaining desired mechanical properties, thermal insulation and optical properties. Various approaches have been tried, including the use of various organic and inorganic materials as fillers.

The use of polymeric microspheres as a filler for paperboard is disclosed in U.S. Patent 6,379,497 B1. U.S. 2002/014632 A1 discloses the use of expandable microspheres in the manufacture of opaque tissue paper. U.S. 2001/0038893 A1 teaches that expanded microspheres can be used in the manufacture of a low density paperboard material having insulating properties. Japanese published patent applications 2000-053351, 01-210054 and

11-006466 disclose the use of a hollow polymer particle in the wet-end of the paper-making where the hollow particle is cationic in nature. Japanese published patent application 2000-160496 teaches the use in the wet-end of the paper-making process of a composite hollow particle obtained by the adsorbtion of a high molecular weight amphoteric polyelectrolyte onto the surface of a hollow particle. However, the amount of treated composite hollow particle that is retained in the paper is to low to be practical. An additive to the paper manufacture process must be retained by the sheet in order to function properly. U.S. Patent 6,139,961 discloses the incorporation of hollow sphere organic pigment into the formed wet sheet for improving the strength and opacity of the paper.

The problem of low cost manufacturing of a paper product simultaneously having high bulk and enhanced optical properties while maintaining acceptable mechanical properties has not been solved in the prior art.

Summary of the Invention

The present invention involves a process for making a paper material, the process comprising forming an aqueous slurry comprising a predominantly cellulosic fiber pulp, forming a wet sheet from the slurry, and drying the sheet, the improvement comprising using an agglomerated hollow particle latex in the slurry. The invention also includes a composition comprising an agglomerated hollow particle latex, as well as paper materials made by the process of the invention. Surprisingly, the invention provides paper materials having a good combination of optical and mechanical properties, tactile properties, smoothness, and bulk.

Brief Description of the Drawings

Figures 1 and 2 are electron micrographs of agglomerated hollow particle latex.

Figure 3 contains plots of particle size distribution for a hollow particle latex and for an agglomerated hollow particle latex.

Figure 4 is a line graph of paper bulk vs. percent filler loading.

Figure 5 is a line graph of TAPPI paper opacity vs. percent filler loading.

Detailed Description of the Invention

The paper-making process of the invention employs agglomerated hollow particle latex, which can be prepared from a hollow particle latex.

Hollow particle latexes are well-known and are commercially available. The hollow particle latex employed in the preparation of agglomerates can be prepared by any suitable process. Many such processes are known to those skilled in the art. See, for example, U.S. Patents 4,427,836, 4,594,363 and 5,157,084 . The hollow particle latexes can have an acid-containing core or an acid-free core. Examples of hollow particle latexes include HS 3000 brand latex available from The Dow Chemical Company, and Rhopaque HP 1055 brand latex available from Rohm and Haas Company. Advantageously, the hollow particle latex employed in the agglomeration process has an average particle size of from 0.1 to 10 microns. The particle size distribution of the hollow particle latex employed in the agglomeration process is not critical to performance of the agglomerated hollow particle as a filler in paper coatings.

Most commercially available hollow particle latexes have from 20 to 40 weight percent solids. A wide range of possible void volumes for the hollow particle latex enables a wide range of filler density. The range of void volume for the hollow particle latex preferably is from 10 to about 70 volume percent, more preferably is from 30 to about 60 volume percent, and most preferably is from to about 40 to about 55 volume percent. Mixtures of hollow particle latexes can be employed. In one embodiment of the invention, agglomerates can be prepared from a mixture of a hollow particle latex and another filler.

An agglomerating agent is employed to agglomerate the particles of the hollow particle latex. The choice of the agglomerating agent is determined by the desired charge or zeta potential of the agglomerated hollow particle latex. Suitable agglomerating agents include, for example: cationic surfactants such as cetyl pyridinium chloride, quaternary ammonium salts, and ethoxylated quaternary ammonium salts; positively or negatively or amphotertically charged polyelectrolytes such as cationic starch, cationic polyacrylamide, polyethyleneimine (PEI), polyacrylamide-co-acrylic acid, poly(diallyldimethylammonium chloride), (PDADMAC), and the like; neutral water-soluble polymers such as, for example, polyethylene oxide, (PEO), and partially hydrolyzed polyvinyl acetate; and agglomerating salts such as, for example, calcium chloride, zinc chloride, aluminum chloride, and ammonium sulfate. A colloidally stabilized particle to which the hollow particles adhere is also a suitable agglomerating agent. Examples of preferred agglomerating agents include cetyl pyridinium chloride and poly(diallyldimethylammonium chloride). Mixtures of agglomerating agents can be employed. The agglomerating agent is employed in an amount sufficient to form an agglomerated particle with an average particle diameter that is larger than the average particle size of the non-agglomerated latex. The amount of agglomerating agent advantageously is sufficient to convert at least about 30 weight % of the solids of the hollow particle latex to agglomerates, preferably at least about 50 weight %, more preferably at least about 75 weight % and most preferably at least about 90%. Preferably, from about 0.01 to about 1.0 grams of agglomerating agent is employed per gram of solids of the hollow particle latex, and more preferably from about 0.03 to about 0.5 grams of agglomerating agent is employed per gram of solids of the hollow particle latex.

The agglomeration is accomplished by contacting the agglomerating agent with the hollow particle latex under conditions sufficient to agglomerate the hollow particle latex. The contacting of the agglomerating agent with the hollow particle latex preferably is done at about room temperature and atmospheric pressure with agitation. It may be advantageous to adjust the solids of the hollow particle latex for the agglomeration process in order to achieve the desired agglomerate density. It is possible to agglomerate the hollow particle latex at the paper producing site.

After formation, the agglomerated hollow particle latex may be further modified with the addition of a stabilizing agent. The purpose of the stabilizing agent is to prevent a further particle size increase by a ripening process, or further agglomeration due to high shear coagulation. Examples of suitable stabilizing agents include water-soluble polymers such as, for example, polyvinyl alcohol, carboxymethylcellulose, and starch. The preferred stabilizing agent is polyvinyl alcohol. Mixtures of stabilizing agents can be employed. The amount of stabilizer advantageously is from 0 to about 40% weight percent based on the weight of dry solids in the hollow latex.

The agglomerates employed in the invention are agglomerates of hollow particles of the hollow particle latex. The agglomerated particles typically are irregular and bumpy. The agglomerated particle latex preferably has a solids content of from about 1 to about 30% solids. As with the hollow particle latex, the solids for the agglomerated hollow particle latex employed in the wet-end of the paper-making process is not particularly critical due to the large dilution the agglomerated hollow particle latex undergoes when used as a filler in the wet-end. In one embodiment, the agglomerated hollow particles can be employed in the form of a dried, redispersible powder. The agglomerated hollow particle latex can be lower in density and higher in particle size than latexes that can be prepared using standard emulsion polymerization techniques. The larger particle size of the agglomerated hollow particle is advantageous in that the aggregates are more readily retained in the sheet during the paper-making process.

Advantageously, in one embodiment of the invention the agglomerates can be employed directly in existing paper formulations without the use of additional adjuvants, such as retention aids, and without modification of the surface of the particle. In another embodiment of the invention, additional adjuvants can be employed if desired. If the agglomerates are not retained, build up of filler in the aqueous make-up of the fiber dilution system of the paper-making process will eventually have a negative effect on the performance of the filler. Advantageously, the amount of agglomerated hollow partcle latex retained in the paper product is at least about 80 weight percent based on the weight of agglomerated hollow particle latex added to the paper-making process. In various embodiments of the invention, the amount retained is at least about 85 weight percent based on the weight of agglomerated hollow particle latex added to the paper-making process, at least about 90%, or at least about 95%.

Retention aids may be added to enhance retention of the agglomerated hollow. Cationic retention aids are preferred but anionic ones my be used. Suitable retention aids are well known to those skilled in the art, and include materials such as, for example, polyacrylamide, and water soluble polymeric reaction products of epihalohydrins. Suitable materials of this type are commercially available under trademarks PERCOL, KYMENE or CASCAMID.

The agglomerated hollow particle latex preferably has an average particle size of from about 3 to about 100 microns, more preferably from about 5 to about 80 microns and most preferably from about 5 to about 50 microns. The stability of the agglomerate is determined by monitoring light scattering particle size distribution after shearing the agglomerate in a high speed blender for one minute. It is preferred that the agglomerate particle size and particle size distribution is substantially unchanged by the blender. Mixtures of agglomerated hollow particle latexes can be employed.

The void volume of the hollow particle latex along with the interstitial void in the aggregate allows the density of the agglomerated hollow particle latex to be adjusted to the specific filler need of the paper product. The total void volume in the aggregate preferably is from about 30 to about 90 volume percent, and more preferably is from about 40 to about 80 volume percent.

The agglomerated hollow particle latex can be stabilized with surfactant or a water-soluble polymer that interacts with the surface of the agglomerate. The net surface charge of the agglomerated hollow particle latex can be either negative or positive. The agglomerated hollow particle latex particle can be further characterized as having a positive, neutral or negative zeta potential.

The paper-making process is well known to those skilled in the art. The agglomerated hollow particle latex advantageously is employed as a filler in the wet end of the paper-making process. The addition of wet-end chemicals and filler can be accomplished through a variety of means. The agglomerated hollow particle latex can be added in the wet end anywhere, such as in the wet formed web, in the fan pump, in the thick stock loop, or elsewhere in the paper machine, or in any combination of these. It is prefered to add the agglomerated latex in an area of the process where the stock is diluted, such as the mix tank, the fan pump or before the head box. An alternative is to add the agglomerated latex in a location where fiber concentration is high such as, for example, the thick stock loop or the blend chest.

The amount of agglomerated particles employed in the paper-making process is dependent on the grade of paper being made and is limited by the volume of the low density filler material. Preferably, the level of usage is from about 0.5 to about 50 parts of agglomerated hollow particles per 100 weight parts of fiber, more preferably from about 0.75 to 25 parts, and most preferably from about 1 to about 20 parts. The agglomerated hollow particle latex can be employed as the sole filler or can be employed with other fillers, such as synthetic magadiite kaolin, titanium dioxide, ground calcium carbonate, precipitated calcium carbonate, and including low density materials such as, for example, hollow particle latex, hollow calcium carbonate or calcined kaolin clay. In various embodiments of the invention, the agglomerated hollow particle latex comprises at least about 10% of the total filler by weight, at least about 20% of the total filler by weight, at least about 50% of the total filler by weight, or at least about 80% of the total filler by weight.

The use of agglomerated hollow particle latex surprisingly can result in paper having a unique combination of properties, such as bulk, opacity and brightness, compared to paper produced using only mineral pigments or solid polymer pigments.

Specific Embodiment of the Invention

The following examples are included to illustrate the invention, and do not limit the scope of the claims. All parts and percentages are by weight unless otherwise stated.

Example 1: Preparation of Agglomerated Hollow Particle Latex

Starting Materials:

HS3000 (CAS#214154-63-9) from The Dow Chemical Company.

Cetylpyridinium Chloride Monohydrate (CPC) (CAS#6004-24-6) from Sigma Aldrich, St. Louis, MO, USA.

Polyvinyl Alcohol (PVOH) (CAS#9002-89-5) from Sigma Aldrich.

De-ionized Water (CAS#007732-18-5)

An 8.7% solids PVOH stock solution is prepared. The PVOH solution is heated and stirred before use to ensure good solubilization and homogeneous mixing, and the solution is allowed to cool to room temperature before being added to the latex agglomerates.

HS3000 (10% solids, 400g) is added to a 900ml container (3.5" O.D., 7.0" height). The latex is mechanically mixed at 400 rpm (impeller blade 1.5" O.D. with alternating rectangular 1"x 0.4" teeth parallel to the stir shaft) while CPC (0.28 M, 80 mL) is added over the course of about 20 minutes. The latex mixture is stirred at room temperature for 4 hours after complete addition of the CPC in order to prepare an agglomerated latex. Then, 120g of the PVOH stock solution is added with continued stirring over the course of about 3 to 5 minutes. The mixture (now agglomerated) is allowed to continue to stir at room temperature for about 40 minutes. Upon completion of stirring, agglomerate sizes in the wet state are measured by dynamic light scattering. Alternatively, electron microscopy is used to determine the agglomerated particle size of the dry particle and can also be used to determine the dry agglomerated particle morphology.

Scanning electron microscopy (SEM) is performed with an Armray 1810 SEM instrument at an acceleration voltage of 20kV. Diluted samples are prepared for analysis by adding 2 drops of the agglomerated hollow particle latex prepared above to 20 mL of deionized water. The diluted samples are then added dropwise to an SEM stub, are allowed to dry at room temperature overnight, and are plasma sputtered with a thin layer of gold to enhance the conductivity and contrast of the polymer sample under the electron beam.

Figures 1 and 2 offer a direct view of the morphologies present in the aggregated sample while also giving an indication of the distribution of agglomerate size. Figure 2 shows the dense packing of the agglomerate morphology and roughly a 10μm circular diameter for the particular agglomerate particle shown.

In Figure 3, dynamic light scattering (Particle Sizing Systems, Inc. Model 770 Accusizer) is used to analyze the particle size, distribution, and percent conversion of the hollow particle latex into the agglomerated hollow particle latex. Samples are prepared for analysis by adding 1 drop of the agglomerated hollow particle latex described above to 20 mL of deionized water. Data is recorded by a computer for both the number and volume weighted particle size distributions. The number distribution profile suggests that a small percentage of un-agglomerated primary particles remain; however, the amount of un-agglomerated primary particles is quite low. To better exemplify the increase in overall particle size upon agglomeration, the volume weighted size distribution is shown in Figure 3 for both the un-agglomerated and agglomerated sample. It is clear that the primary particles are converted to aggregates of between 10 to 30μm (assuming circular diameter). These results are in agreement with that observed by SEM in Figure 1.

Example 2: Preparation of Handsheets from Agglomerated Hollow Particle Latex

Paper handsheets are prepared using a British Standard Semiautomatic Handsheet Mold according to the method TAPPI T-205 sp-95 in order to test the performance of the agglomerated hollow particle latex. Precipitated calcium carbonate, an industry standard, is used as a control filler. A blank handsheet (i.e. no filler added) is also prepared to compare the performance of the fillers versus loading.

The sheets for this example are labeled as follows:

AGG – Agglomerated hollow particle latex from Example 1

$CaCO_3$ - (Control Filler: PCC, Albacar®, a scalenohedral-shaped mineral filler from Specialty Minerals)

Blank - (no filler, this sample is shown on plots as the 0% filler data point)

Each sample is run at three different filler loadings (6%, 10%, and 15%, based on the weight of the filled paper). All fillers are added on a dry weight basis. A weight of 80 lbs/3300 ft^2 or 118 grams/m^2 is used as a target for the basis weight of the paper.

The base furnish used to make the paper is a 50/50 blend of hardwood and softwood refined to a Canadian Standard Freeness of 420. All handsheets in this example are made from the same batch of refined pulp. Approximately 20 liters of pulp at 0.5% consistency are mixed and the amount needed for each set of handsheets is drawn from this sample. Consistency pads are made in duplicate for each of the base furnishes to determine the amount needed for each sample.

Mixtures of fiber and filler are prepared for each filler loading. For the PCC control, $CaCO_3$ filler is weighed and placed in a blender for 1 minute with 700 ml of dilution water. For the agglomerated hollow particle latex , the filler is weighed, diluted, and placed in a blender for 1 minute along with an anti-foaming agent (Dow Corning ANTIFOAM 1410) to control potential foaming upon mixing. The filler is then added to the fiber furnish and diluted to 8.0 liters.

A 500 ml sample of each fiber/filler mixture is then measured and placed on a magnetic stirrer. One lb. of PERCOL 292 Cationic Retention Aid per ton of fiber/filler mixture is added to the mixture and mixed for 30 seconds. The British Standard Semi-Automatic Handsheet Mold is then started, and the fiber/filler/retention aid mixture is poured into the handsheet mold. The handsheet mold is filled to the correct height, allowed to mix, followed with a settling stage, and allowed to drain. The sheet is then removed from the wire. Twelve sheets are stacked and pressed simultaneously to form the hand sheets.

Percentage retention of the agglomerated hollow particle filler in a handsheet is determined by pyrolysis of the solid residue remaining in the water after the handsheets are pressed. The solids in the water remaining from a particular sample is dried and the percent solids is determined. A 1 mg sample of that residue is then pyrolyzed at 700°C. The amount of latex present is determined by comparing the styrene peak areas of the residue samples to that of the latex used in the experiment. The water samples are found to have less than 3 ppm of latex in their residue. The starting level of latex in the water was 100 ppm, which indicates that greater than 97% of the agglomerated hollow latex was retained in the paper handsheets.

<u>Evaluation of End-Use Performance in Paper</u>

A comparative analysis of the fillers is performed using the handsheets prepared. The following data exemplify the superior performance of the agglomerated hollow particle latex filler as compared to precipitated calcium carbonate filler, specifically in terms of bulking ability and optical properties. Twelve handsheets are prepared for each type of sample and the properties reported are the averages of 10 sheets based on multiple readings on each sheet.

The bulk of a sheet is measured as the quotient of its caliper to basis weight. Caliper is measured in mils, and basis weight is determined by weighing the sheet in grams and dividing by the area of the sheet in square meters. Bulk is then calculated by dividing caliper by basis weight and multiplying by 25.4 to convert to specific volume units of cm^3/gram. The effects of filler loading on bulk are depicted graphically in Figure 4. The superior bulking ability of the agglomerated hollow particle latex is apparent.

Opacity is measured on the handsheets by TAPPI Method T519. The results are depicted In Figure 5, which shows that the agglomerated hollow particle latex outperforms the blank and precipitated calcium carbonate for all filler loadings.

Brightness is measured on the handsheets by TAPPI Method T452. The results are shown in Figure 6 (TAPPI brightness versus filler loading), which shows that the agglomerated hollow particle latex filler outperforms precipitated calcium carbonate, and the blank sheet, in brightness at all concentrations.

When the agglomerated hollow is substituted for a portion of the mineral filler the handsheets are found to be smoother and feel softer to the touch (velvet like).

WHAT IS CLAIMED IS:

1. In a process for making a paper material, the process comprising forming an aqueous slurry comprising a predominantly cellulosic fiber pulp, forming a wet sheet from the slurry, and drying the sheet, the improvement comprising using an agglomerated hollow particle latex in the slurry.

2. The process of Claim 1 wherein the agglomerated hollow particles have an average particle size of from about 3 to about 100 microns.

3. The process of Claim 1 wherein the agglomerated hollow particles have a cationic surface charge.

4. The process of Claim 1 wherein the agglomerated hollow particles have an anionic surface charge.

5. The process of Claim 1 wherein the agglomerated hollow particles have a neutral surface charge.

6. The process of Claim 1 wherein an additional filler is employed, and the agglomerated hollow particles comprise at least 10 weight percent of the total filler employed.

7. The process of Claim 1 wherein the agglomerated hollow particles are prepared from hollow latex particles with an interior void in the range of 10-70 percent of the volume of the latex particle.

8. The process of Claim 1 wherein the agglomerated hollow particles have a total void volume in the range of 30-90 percent.

9. The process of Claim 1 wherein the agglomerated hollow particle latex is modified with the addition of a stabilizing agent.

10. A paper material prepared by the process of Claim 1.

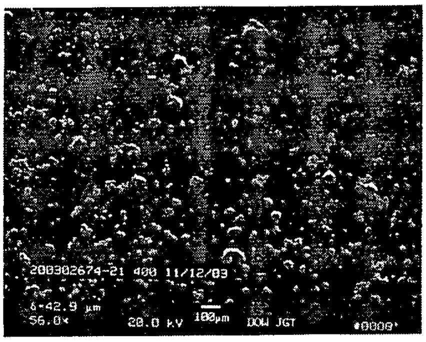


Fig. 1

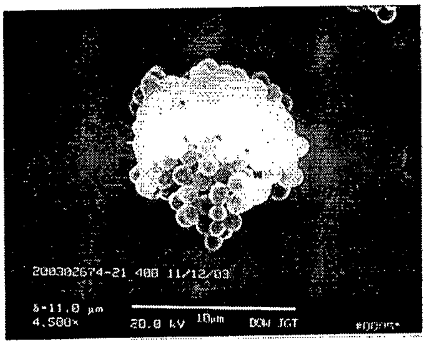
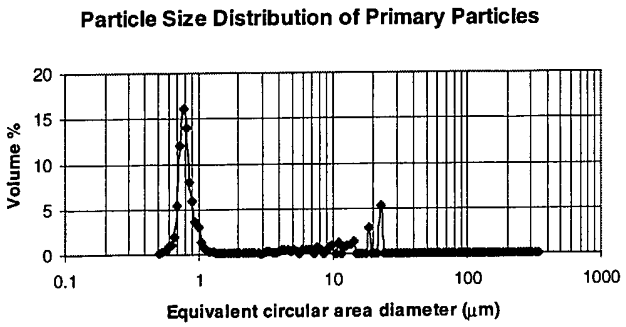


Fig. 2


Particle Size Distribution of Primary Particles
Volume %
20
15
10
5
0
0.1
1
10
100
1000
Equivalent circular area diameter (μm)

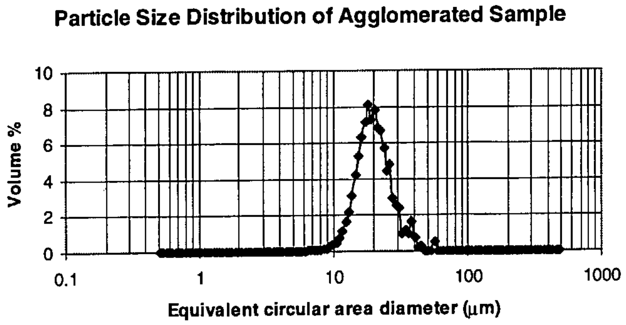

Particle Size Distribution of Agglomerated Sample
Volume %
10
8
6
4
2
0
0.1
1
10
100
1000
Equivalent circular area diameter (μm)

Fig. 3

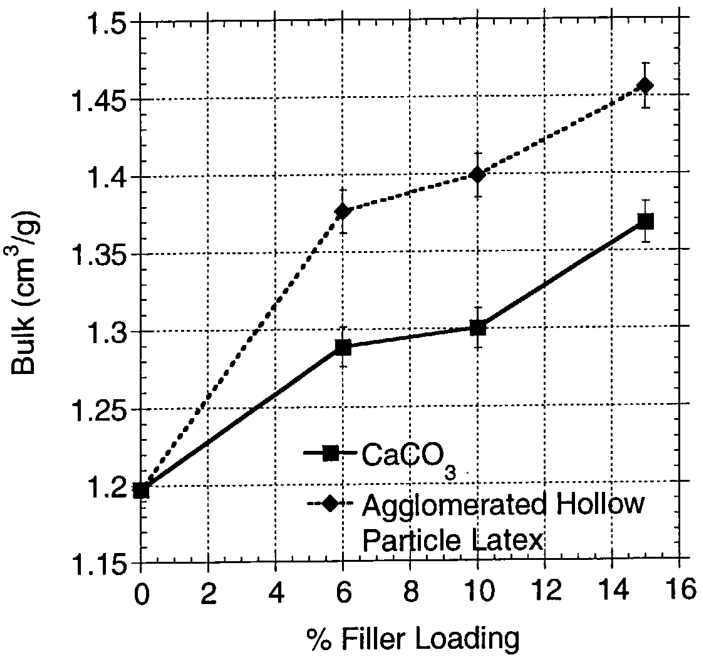

1.5
1.45
1.4
1.35
1.3
1.25
1.2
1.15
Bulk (cm³/g)
0
2
4
6
8
10
12
14
16
% Filler Loading
CaCO3
Agglomerated Hollow Particle Latex

Fig. 4

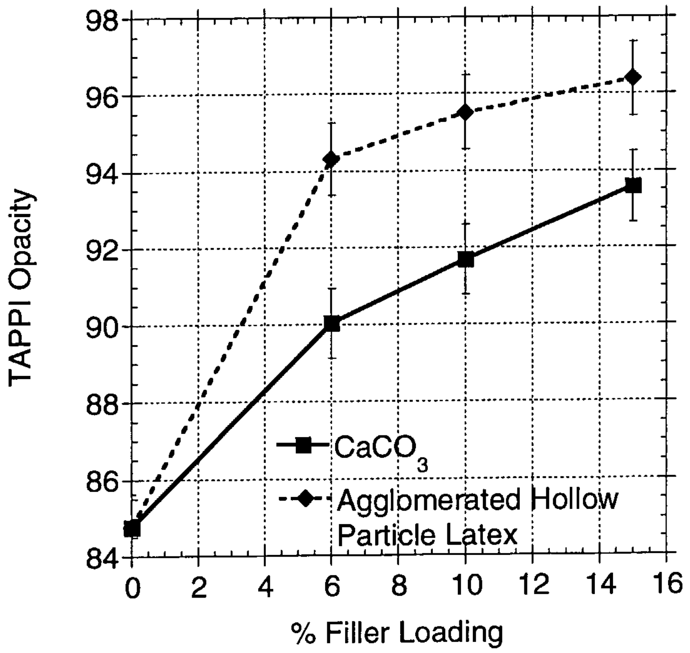

98
96
94
92
90
88
86
84
TAPPI Opacity
0
2
4
6
8
10
12
14
16
% Filler Loading
CaCO$_3$
Agglomerated Hollow Particle Latex

Fig. 5

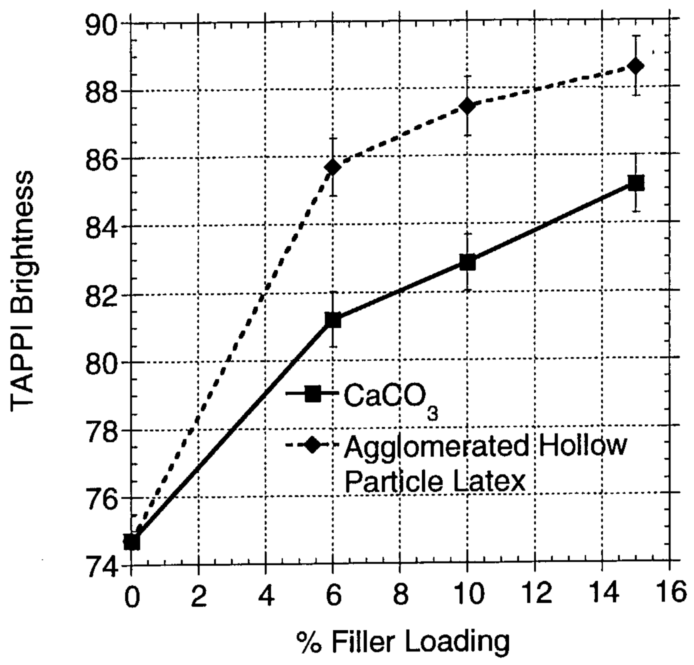

TAPPI Brightness
90
88
86
84
82
80
78
76
74
0
2
4
6
8
10
12
14
16
% Filler Loading
CaCO3
Agglomerated Hollow Particle Latex

Fig. 6

IN[illegible]RNATIONAL SEARCH REPORT

Inter[illegible]nal Application No
PCT/US2005/030039

A. CLASSIFICATION OF SUBJECT MATTER
D21H21/54

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 355 141 B1 (SIKKAR REIN ET AL) 12 March 2002 (2002-03-12) paragraphs ‘0010! - ‘0014!; claims 1-14 -----	1,10
X	US 4 087 581 A (VINCENT ET AL) 2 May 1978 (1978-05-02) claims 1-8; figure 2; examples 1,2 -----	1,10
X	US 6 221 956 B1 (CHEN HAUNN-LIN) 24 April 2001 (2001-04-24) claims 1-43 -----	1,10
A	WO 01/60510 A (NESTE CHEMICALS OY; PAVLYUCHENKO, VALERY; SKRIFVARS, MIKAEL; SOROCHINS) 23 August 2001 (2001-08-23) the whole document ----- -/--	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 6 December 2005	Date of mailing of the international search report 15/12/2005
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Karlsson, L

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/030039

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004/034147 A1 (ZAMA YOSHIAKI) 19 February 2004 (2004-02-19) the whole document	1-10
A	US 6 139 961 A (BLANKENSHIP ET AL) 31 October 2000 (2000-10-31) the whole document	1-10
A	EP 0 049 672 A (LA CELLULOSE DU PIN) 14 April 1982 (1982-04-14) the whole document	1-10
A	US 6 042 936 A (KEMPF ET AL) 28 March 2000 (2000-03-28) the whole document	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US2005/030039

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6355141 B1	12-03-2002	NONE	
US 4087581 A	02-05-1978	BE 833728 A1	16-01-1976
		BR 7506082 A	03-08-1976
		DE 2542190 A1	01-04-1976
		FI 752630 A	24-03-1976
		FR 2285174 A1	16-04-1976
		GB 1529232 A	18-10-1978
		GB 1529231 A	18-10-1978
		IT 1042747 B	30-01-1980
		JP 973453 C	28-09-1979
		JP 51076384 A	01-07-1976
		JP 54006080 B	24-03-1979
		NL 7511201 A	25-03-1976
		SE 7510597 A	24-03-1976
		US 4239646 A	16-12-1980
US 6221956 B1	24-04-2001	AT 286922 T	15-01-2005
		AU 743952 B2	07-02-2002
		AU 1299899 A	28-06-1999
		BR 9813432 A	10-10-2000
		CA 2313544 A1	17-06-1999
		CN 1281472 A	24-01-2001
		DE 69828648 D1	17-02-2005
		DE 69828648 T2	16-06-2005
		EP 1040141 A1	04-10-2000
		ID 24972 A	31-08-2000
		TW 466246 B	01-12-2001
		WO 9929745 A1	17-06-1999
		US 5985992 A	16-11-1999
		ZA 9811280 A	10-06-1999
WO 0160510 A	23-08-2001	AU 3746001 A	27-08-2001
		FI 20000367 A	18-08-2001
US 2004034147 A1	19-02-2004	NONE	
US 6139961 A	31-10-2000	NONE	
EP 0049672 A	14-04-1982	DE 3169705 D1	09-05-1985
		ES 8304245 A1	16-05-1983
		FI 813100 A	09-04-1982
		FR 2491514 A1	09-04-1982
		US 4477518 A	16-10-1984
US 6042936 A	28-03-2000	EP 1019246 A1	19-07-2000
		WO 9915331 A1	01-04-1999