

19



Europäisches Patentamt
European Patent Office
Office européen des brevets



11 Publication number: **0 364 629 B1**

12

EUROPEAN PATENT SPECIFICATION

- 45 Date of publication of patent specification: **23.02.94** 51 Int. Cl.⁵: **D21H 21/14, //D21H17:35, D21H17:43**
- 21 Application number: **88202356.7**
- 22 Date of filing: **21.10.88**

54 **Paper product prepared with structured latex particles having reinforcing and opacity characteristics and process for preparing the same.**

43 Date of publication of application:
25.04.90 Bulletin 90/17

45 Publication of the grant of the patent:
23.02.94 Bulletin 94/08

84 Designated Contracting States:
AT BE CH DE ES FR GB IT LI SE

56 References cited:
US-A- 3 897 300
US-A- 4 282 060
US-A- 4 613 633

TAPPI, vol. 64, no. 4, April 1981, Atlanta, GA (US); B. ALINCE et al., pp. 135-136&NUM;

73 Proprietor: **THE DOW CHEMICAL COMPANY**
2030 Dow Center
Abbott Road
P.O. Box 1967
Midland Michigan 48640-1967(US)

72 Inventor: **Monzon, Medardo**
3910 Applewood Road
Midland, MI 48640(US)
Inventor: **Lock, Michele Renee**
340 Undercliff Ave.,
Apt. 10B
Edgewater, NJ 07020(US)
Inventor: **Galloway, James G.**
3195 Bullock Creek Drive
Midland, MI 48640(US)

74 Representative: **Smulders, Theodorus A.H.J.,**
Ir. et al
Vereenigde Octrooibureaux
Nieuwe Parklaan 97
NL-2587 BN 's-Gravenhage (NL)

EP 0 364 629 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

Generally, this invention is directed toward a method for preparing high quality lightweight paper having increased opacity. The method employs a structured latex having both reinforcing and opacifying characteristics.

In the manufacture of papers, especially lightweight paper, a major concern is the opacity of the paper. Generally, opacity is provided by conventional fillers such as clay, calcium carbonate and titanium dioxide. Unfortunately, these fillers can adversely affect the mechanical properties of the paper if too much filler is attempted to be incorporated to obtain the desired opacity.

Attempts have been made to offset the reduction in mechanical properties through the use of various formulations of latexes having increased strength. However, improved methods of obtaining good opacity or light scattering characteristics without reducing mechanical properties are continually being sought. The problem is difficult to solve because opacity and strength are generally inversely proportional characteristics. The problem is particularly acute in lightweight papers where the amount of material that can be employed to form the paper is minimal.

US-A-3,897,300 describes a paper filled with a blushed particulate polystyrene pigment filler. This filler consists essentially of spherical particles having an air-containing microporous structure. It is capable of increasing the opacity of a sheet of paper.

Further, it is known to add structured latex particles in a paper coating, which are intended to be applied on the surface of a paper product.

US-A-4,134,872 relates to a paper product, which is coated with a layer comprising structured latex particles as a binder. These coating layers provide coated paper products having better gloss, ink receptivity, smoothness, wet binding strength, and dry binding strength.

US-A-4,613,633 relates to a copolymer latex comprising heterogeneous polymer particles having a hard and a soft polymer domain. These particles are used in paper coating layers.

It has been discovered that by specifically engineering a structured latex particle having a core/shell morphology that both characteristics of opacity and mechanical strength can be satisfied. This is accomplished by preparing the latex particle such that it not only reinforces or binds the constituents of the paper but also scatters light to provide its own measure of opacity to the paper.

The present invention provides for a structured latex particle suitable for use in the preparation of latex-containing products to increase opacity and strength comprising a core portion having a light scattering characteristic and a T_g of 80 °C or greater, and a shell portion having a T_g of 25 °C or lower. The structured latex particles have a particle size of 1,400 to 4,000 angstroms (140 to 400 nm). In one embodiment the structured latex particle has a homopolymer core portion of styrene and a shell region of styrene/butadiene/acrylic acid.

The present invention further provides for a paper product prepared with the structured latex particle as described above as a filler in the bulk. Most advantageously the latex particle is employed in the preparation of light weight paper where good opacity and mechanical strength are desired. The subject structured latex particle characteristically provides opacity and reinforcement which allows for the reduction of fillers, such as TiO_2 , in the article of manufacture. That is, the structured latex particle allows for the reduction or elimination of expensive opacifying fillers in products without a corresponding loss of opacity.

Preparation of the products of the present invention requires a starting latex comprising a structured latex particle having a core/shell morphology wherein the core region has a second order transition temperature (T_g) of 80 °C or greater and the shell region has a T_g of 25 °C or lower. These structured latex particles are suitable for use in the preparation of paper products having good opacity and mechanical strength characteristics. Preferably and most advantageously, the subject latex is employed in the preparation of light weight papers where good opacity and mechanical strength are desired.

The term "opaque" is meant to define that quality of resisting the passage of light by being neither transparent nor translucent. The opaque characteristic is measurable by measuring the brightness of reflected light, light scattering or reflectance, and opacity (TAPPI standard T-425 om 81). By "mechanical strength" is meant the quality of tensile strength, modulus, tear strength, and other physical properties generally recognized in the art as contributing to mechanical strength.

The preparation of structured latexes are well documented and do not form a part of this invention except as modified by the compositional requirements of the invention. Generally, particles of a starting latex are encapsulated with additional monomers polymerized therewith. This can be conveniently accomplished by emulsion polymerizing the desired shell portion monomers in the presence of an existing latex which has the desired core composition. Thus, the polymerization is a conventional emulsion polymerization of a latex but for the polymerization of the shell monomer portion being conducted in the presence of a

preexisting latex particle which represents the core region of the final latex product.

Emulsion polymerization techniques such as staged or continuous addition of monomer feeds are typically employed. Examples of such techniques are further described in U.S. Patent Nos. 4,156,669 and 4,017,442.

5 The structured latex particle of the subject invention requires a core region which has light scattering properties. Generally, this light scattering characteristic is provided by a polymer or copolymer of ethylenically unsaturated monomers having a T_g of 80 °C or greater. The T_g of the core region is important in maintaining the identity, i.e., size and distribution, of the core which thereby contributes to the light scattering characteristic of the latex. Contrarily a lower T_g would allow the core region to coalesce during
10 paper making and result in a low light scattering characteristic.

Difunctional monomers, typically useful as crosslinkers, can be employed in the core region to increase the T_g of the core region. Examples of good crosslinkers would include allyl or crotyl acrylate and methacrylates and divinyl benzene. The preferred polymer core composition is a monovinyl aromatic polymer such as styrene and copolymers or derivatives thereof having a T_g of 80 °C or greater. More
15 preferably, the core region is a homopolymer of styrene.

The core portion of the structured latex particle comprises from 40 to 90 percent of the total particle. Preferably, the core/shell polymer weight ratio is from 50/50 to 90/10, respectively.

The particle size of the subject structured latex is important to the overall light scattering properties and, therefore, a particle size of from 1,400 to 4,000 angstroms (Å) (140 to 400 nm) is preferred. More
20 preferably, the average particle diameter is from 2,000 to 3,500 Å (200 to 350 nm).

The shell region of the subject structured latex particle is composed of a polymer or copolymer of ethylenically unsaturated monomers having a T_g of 25 °C or lower. Generally, the shell composition may include monomers employed in the core region. Thus, the shell compositions advantageously employed are various blends of polymerized monomers such as monovinyl aromatics, aliphatic conjugated dienes,
25 monoethylenically unsaturated carboxylic acids, vinyl or vinylidene halides or acrylates. Optionally, reactive monomers such as N-methylacrylamide and glycidylmethacrylate can be included.

The term "monovinyl aromatic monomer", as used herein, is meant to include those monomers with a radical of the formula



35 (wherein R is hydrogen or a lower alkyl such as an alkyl having from 1 to 4 carbon atoms) attached directly to an aromatic nucleus containing from 6 to 10 carbon atoms, including those wherein the aromatic nucleus is substituted with alkyl or halogen substituents. The preferred monomer is styrene.

The term "aliphatic conjugated diene", as used herein, is meant to include compounds such as 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-dimethyl- 1,3-butadiene, 2-neopentyl-1,3-butadiene, piperylene (1,3-
40 pentadiene), and other hydrocarbon analogs of 1,3-butadiene.

The term "monoethylenically unsaturated carboxylic acid monomer", as used herein, is meant to include those monocarboxylic monomers such as acrylic acid, and methacrylic acid; dicarboxylic monomers such as itaconic acid, fumaric acid, maleic acid, and their monoesters. The preferred acid monomer is acrylic acid.

45 Vinylidene halides and vinyl halides suitable for this invention include vinylidene chloride and vinyl chloride, which are preferred. Vinylidene bromides and vinyl bromide can also be employed.

The term "acrylate", as used herein, is meant to include monomers of the acrylate or methacrylate type. Additionally, the acrylates can include acids, esters, amides and substituted derivatives thereof. Generally, the preferred acrylates are C₁-C₈ alkyl acrylates or methacrylates. Examples of such acrylates
50 include butyl acrylate, 4-biphenyl acrylate, hexyl acrylate, sec-butyl acrylate, tert-butyl acrylate, methylmethacrylate, butylmethacrylate, lauryl methacrylate, hexylmethacrylate, isobutylmethacrylate, and isopropylmethacrylate.

The shell region is preferably composed of a polymer blend comprising styrene, butadiene and acrylic acid. This particular blend has been found to yield desirable physical properties and compatibility with the
55 preferred core composition of styrene. Generally, the shell composition has the following styrene/butadiene/acrylic acid ratios of 49/49/2 to 47/47/6; 49/49/2 to 69/29/2; and 69/29/2 to 67/27/6, respectively.

Structured latex particles prepared in the foregoing manner are advantageously employed as paper coatings or fillers where good opacity and mechanical properties are desirable. More particularly, paper products prepared with the subject structured particle latex will have increased opacity and strength over a similar paper prepared in the absence of the structured particle latex. While not limited to paper applications, the subject latex can also be employed as a filler or component in other areas where latexes may be employed such as in protective or decorative coatings, e.g., paints, etc. More advantageously, the subject structured latexes are employed as a latex binder or as a partial substitute for the latex binder in the preparation of high quality lightweight or fine papers. Lightweight papers are generally defined as those papers having less than 34 pounds/3300 sq.ft. or approximately 50 g/sq.meter.

These and other advantages will be readily apparent in view of the following examples.

Example 1

A structured latex was prepared in the following manner. To 80 parts by weight per 100 parts comonomer charge of an aqueous medium containing .01 part by weight of a pentasodium salt of diethylenetriaminepentacetic acid and 0.52 part by weight of a 97/3 weight ratio styrene/acrylic acid copolymer seed latex was continuously added 100 parts by weight of a styrene monomer feed with stirring over a period of 2.8 hours. An aqueous stream containing 40 parts deionized water, 1.0 part by weight of sodium dodecylphenyl ether disulfonate, 0.5 part by weight of sodium persulfate and 0.1 part by weight of sodium hydroxide was added with said styrene feed for a period of 4.5 hours at 90 °C. Following the addition of the styrene feed a 49/49/2 weight ratio of styrene/butadiene/acrylic acid comonomer feed was continuously added with stirring over a 1.2 hour period. In addition, the comonomer feed also contained 0.15 part by weight of tertiary dodecylmercaptan.

Upon completion, the resulting latex had a total solids content of about 43 percent, a pH of 3, and the structured latex particles had an average particle diameter of 1550 Å (155 nm), and a polystyrene core (T_g approximately 100 °C) to styrene/butadiene/acrylic acid shell (T_g lower than 25 °C) ratio of 70/30.

Example 2

A structured latex particle was prepared as in Example 1 except that the core/shell ratio was 50/50.

Example 3

Paper compositions employing the latexes prepared in Examples 1 and 2 as reinforcing opacifiers were prepared. Seven and one-half parts (polymer solids basis) of the latexes from Examples 1 and 2 were admixed with individual samples of an aqueous paper composition. The paper composition consisted of 6,424 parts of an aqueous suspension containing 92.5 parts (dry weight basis) of bleached kraft wood fibers (50/50 dry weight ratio of hardwood/softwood), 100 parts of a 2 percent by weight aqueous solution of aluminum sulfate octadecahydrate, and 3.5 parts of 0.1 percent by weight aqueous solution of a high molecular weight polyacrylamide.

The suspensions described above were used to form paper handsheets having a basis weight of 40 lbs./3300 sq.ft. (59.2 g/m²) on a Noble and Wood paper machine. The structured particle latex content of each paper was measured by pyrolysis-gas chromatography. The opacity, brightness, tensile strength and elongation of the handsheets were measured and are shown below with a comparative paper example prepared as above except in the absence of the structured latex particles of this invention.

50

55

	Latex		
	None 1	Example 1	Example 2
Core/Shell Ratio	--	70/30	50/50
Percent Latex	0	3.9	4.87
Opacity ²	73.4	76.6	74.3
Brightness ³	77.4	79.9	78.4
Tensile (psi)	3373	3566	3579
Elongation (%)	2.6	2.7	2.8
Scattering ⁴ (cm/g)	302	1491	544

¹Not an example of the invention; conventional paper sheet
Opacity is TAPPI standard T-425 om 81

Brightness is TAPPI standard T-452 om 83

⁴Scattering coefficients obtained from reflectance measurements
(Kubelka-Munk equation).

The results indicate that just a small addition of the subject structured latex particle increased the opacity without a reduction in strength, in fact increasing the strength, of the paper sheet over the comparative paper sheet containing no structured latex particle. This result is significant inasmuch as opacity and strength are generally inversely proportional characteristics. It is indicated that further improvement in properties would be observed at higher levels of the subject latex inclusion; however, this would tend to increase the overall cost of the paper. Generally, the subject latex can comprise from 1 to 20 percent by dry weight basis of the paper composition. Preferably, the latex content of the paper is from 2 to 10 percent by weight.

Claims

1. A lightweight paper product containing a structured latex particle comprising:
 - (1) a core portion having a light scattering characteristic and a T_g of 80 ° C or greater; and
 - (2) a shell portion having a T_g of 25 ° C or lower;
 whereby the opacity and strength of said paper is increased over a paper product prepared in the absence of said structured latex particle.
2. A paper product as claimed in Claim 1 wherein the structured latex particle comprises from 1 to 20 percent by dry weight of said paper.
3. A paper product as claimed in Claim 1 wherein said core portion comprises a monovinyl aromatic polymer, copolymer or derivative thereof.
4. A paper product as claimed in Claim 3 wherein said monovinyl aromatic polymer is styrene.
5. A paper product as claimed in Claim 1 wherein said structured particle latex has a homopolymer core region of styrene.
6. A paper product as claimed in claim 3 wherein said core portion additionally contains difunctional monomers which contribute to increasing the T_g of said core.
7. A paper product as claimed in claim 6 wherein said difunctional monomer comprises allyl or crotyl acrylates, and/or methacrylates, or divinyl benzene.
8. A paper product of claim 1 wherein said structured particle latex has a shell region comprising a polymer blend of styrene/butadiene/acrylic acid.
9. A paper product as claimed in claim 8 wherein the ratio of said styrene/butadiene/acrylic acid is 49/49/2 to 47/47/6; 49/49/2 to 69/29/2; and 69/29/2 to 67/27/6, respectively.

10. A process for preparing a lightweight paper product containing as a filler in the bulk a structured latex particle which comprises

- (a) providing a structural latex particle comprising:
 (1) a core portion having a light scattering characteristic and a T_g of 80 ° C or greater; and
 (2) a shell portion having a T_g of 25 ° C or lower;
 (b) admixing said structured latex particle with an aqueous paper composition; and
 (c) forming the mixture into a paper product.

Patentansprüche

1. Leichtgewichtiges Papierprodukt, enthaltend als Füllstoff in der Masse ein strukturiertes Latexteilchen, umfassend:

- (1) einen Kernanteil mit einer Lichtstreuungseigenschaft und einem T_g von 80 ° C oder größer; und
 (2) einen Mantelanteil mit einem T_g von 25 ° C oder niedriger;

wodurch die Opazität und Festigkeit dieses Papiers gegenüber einem bei Abwesenheit dieses strukturierten Latexteilchens hergestellten Papierproduktes erhöht ist.

2. Papierprodukt nach Anspruch 1, worin das strukturierte Latexteilchen von 1 bis 20 % Trockengewicht dieses Papiers ausmacht.

3. Papierprodukt nach Anspruch 1, worin dieser Kernanteil ein monovinylaromatisches Polymeres, Copolymeres oder Derivat hiervon umfaßt.

4. Papierprodukt nach Anspruch 1, worin dieses monovinylaromatische Polymere Styrol ist.

5. Papierprodukt nach Anspruch 1, worin dieses strukturierte Latexteilchen einen Homopolymer-Kernbereich aus Styrol hat.

6. Papierprodukt nach Anspruch 3, worin dieser Kernanteil zusätzlich difunktionelle Monomere, welche zur Erhöhung des T_g dieses Kernes beitragen, enthält.

7. Papierprodukt nach Anspruch 6, worin dieses difunktionelle Monomere Allyl- oder Crotylacrylate und /oder -methacrylate oder Divinylbenzol umfaßt.

8. Papierprodukt nach Anspruch 1, worin dieser strukturierte Teilchenlatex einen Mantelbereich hat, der eine Polymermischung aus Styrol/Butadien/Acrylsäure umfaßt.

9. Papierprodukt nach Anspruch 8, worin das Verhältnis von diesen Styrol/Butadien/Acrylsäure 49/49/2 bis 47/47/6; 49/49/2 bis 69/29/2 bzw. 69/29/2 bis 67/27/6 beträgt.

10. Verfahren zur Herstellung eines leichtgewichtigen, als Füllstoff in der Masse ein strukturiertes Latexteilchen enthaltenden Papierproduktes, welches umfaßt:

- (a) Bereitstellung eines Strukturlatexteilchens, umfassend:
 (1) einen Kernanteil mit einer Lichtstreuungseigenschaft und einem T_g von 80 ° C oder größer; und
 (2) einen Mantelanteil mit einem T_g von 25 ° C oder niedriger;
 (b) Zusammenmischen dieses strukturierten Latexteilchens mit einer wässrigen Papiermasse; und
 (c) Umwandeln der Mischung in ein Papierprodukt.

Revendications

1. Produit à base de papier, de faible poids, contenant, comme charge dans la masse, des particules de latex structurées, comprenant :

(1) une partie coeur ayant des propriétés de diffusion de la lumière et une T_g supérieure ou égale à 80 ° C, et

(2) une partie enveloppe ayant une T_g inférieure ou égale à 25 ° C,

grâce à quoi l'opacité et la résistance dudit papier sont augmentées par rapport à celles d'un produit à base de papier, préparé en l'absence desdites particules de latex structurées.

2. Produit à base de papier selon la revendication 1, dans lequel les particules de latex structurées représentent de 1 à 20 % en poids à l'état sec dudit papier.
- 5 3. Produit à base de papier selon la revendication 1, pour lequel ladite partie coeur comprend un polymère aromatique monovinyle, un copolymère ou un dérivé des précédents.
4. Produit à base de papier selon la revendication 3, pour lequel ledit polymère aromatique monovinyle est un polymère de styrène.
- 10 5. Produit à base de papier selon la revendication 1, dans lequel lesdites particules de latex structurées présentent une région coeur, constituée d'un homopolymère de styrène.
6. Produit à base de papier selon la revendication 3, pour lequel ladite partie coeur renferme en plus des monomères bifonctionnels qui contribuent à l'augmentation de la T_g dudit coeur.
- 15 7. Produit à base de papier selon la revendication 6, pour lequel ledit monomère bifonctionnel comprend les acrylates et/ou méthacrylates d'allyle ou de crotyle, ou le divinylbenzène.
- 20 8. Produit à base de papier selon la revendication 1, dans lequel lesdites particules de latex structurées présentent une région enveloppe comprenant un mélange polymère de styrène/butadiène/acide acrylique.
- 25 9. Produit à base de papier selon la revendication 8, pour lequel le rapport styrène/butadiène/acide acrylique dudit mélange polymère est 49/49/2 à 47/47/6, 49/49/2 à 69/29/2, et 69/29/2 à 67/27/6, respectivement.
- 30 10. Procédé de préparation d'un produit à base de papier, de faible poids, contenant, comme charge dans la masse, des particules de latex structurées, qui comprend :
- (a) la fourniture de particules de latex structurées, comprenant :
- (1) une partie coeur ayant des propriétés de diffusion de la lumière et une T_g supérieure ou égale à 80 °C, et
- (2) une partie enveloppe ayant une T_g inférieure ou égale à 25 °C,
- (b) le mélange desdites particules de latex structurées avec une composition aqueuse de papier, et
- (c) la mise du mélange sous la forme d'un papier.
- 35
- 40
- 45
- 50
- 55