(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 010 807 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
21.06.2000 Bulletin 2000/25

(51) Int Cl.^{7}: **D21H 23/22**, D21H 27/10
// D21H19/56

(21) Application number: **99308765.9**

(22) Date of filing: **04.11.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **16.11.1998 US 108654 P**

(71) Applicant: **ROHM AND HAAS COMPANY**
Philadelphia, Pennsylvania 19106-2399 (US)

(72) Inventors:
- **Lau, Willie**
  Ambler, Pennsylvania 19002 (US)
- **Egolf, Scott Lind**
  Lansdale, Pennsylvania 19446 (US)
- **King, Gregory Allen**
  Johnson City, Tennessee 37604 (US)

(74) Representative: **Davis, Carole Amanda et al**
Rohm and Haas (UK) Limited
European Operations Patent Dept.,
Lennig House,
2 Mason's Avenue
Croydon, Surrey CR9 3NB (GB)

(54) Polymers for use as barrier coatings

(57) The use of polymers as barrier coatings for paper applications is disclosed. The polymers provide low water absorption and water vapor transmission rates as well as repulpability.

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] This invention relates to the use of polymers as barrier coatings in paper applications. By barrier coating is meant a layer or coating that prevents the penetration of oil, water, or moisture through paper products. Barrier coatings are typically applied to cardboard, paperboard, corrugated paperboard, Kraft paper, and ream wrap.

[0002] Containers made from paper may be used to transport fruits, meats, vegetables, candy, and the like. There are several problems associated with the use of these containers. One problem is that the containers may become wet when the materials transported in the container are wet or when the container is exposed to rain or a humid environment. The paper the containers are made from generally weakens and stains as a result of exposure to water. This may lead to the container breaking open and the spilling of the contents of the container. In order to avoid this problem, containers are generally coated with a material such as wax to prevent water from contacting the paper.

[0003] One problem with wax coated containers is that although wax is effective at preventing water and oil from contacting the paper, the wax generally must be applied as a thick coating. By thick is meant a dry coating of from 55 microns to 125 microns. The thick coating adds significantly to the weight of the container. In fact, the wax may account for from 20% to 40% by weight of the coated container. Therefore, it is desirable to provide a barrier coating that is more efficient than wax so that a thinner coating may be applied without sacrificing barrier coating properties.

[0004] For economic reasons as well as the preservation of natural resources, it is desirable to recycle the containers used to transport fruits, meats, vegetables, candy, and the like. However, a second problem with wax coated containers is that the wax coating makes it difficult to recycle the paper the container is made from. The wax adheres to the paper fibers, making it difficult to re-pulp the fibers. There is a continuing need for a barrier coating that is more efficient than wax and easier to remove from paper fibers than wax.

[0005] We have surprisingly found that the use of a polymer as a barrier coating allows a reduction in the amount of coating used without sacrificing barrier coating properties, while improving the ability to re-cycle the coated paper.

[0006] U.S. Pat. No. 5,521,266 discloses a method for forming polymers from hydrophobic monomers. The disclosed method utilizes macromolecular organic compounds which have a hydrophobic cavity to complex monomers which have low water solubility. This enables the formation of polymers from low water solubility monomers by emulsion polymerization. Suitable monomers for use in the method for forming polymers include lauryl methacrylate and stearyl methacrylate. The patent does not disclose the utility of the polymers as barrier coatings.

[0007] WO 94/26513 patent application discloses recyclable paper stock coated with an emulsion containing an acrylic-styrene copolymer and a wax. The copolymers tested are limited to lower alkyl acrylic-styrene copolymers.

[0008] Despite these disclosures, there is a continuing need for a barrier coating that is more efficient than wax and easier to remove from paper fibers than wax.

[0009] As used throughout this specification, by the term (meth)acrylic is meant acrylic or methacrylic and by the term (meth)acrylate is meant acrylate or methacrylate.

[0010] The present invention provides a method of modifying paper substrates including: applying a polymer to the paper substrate wherein the polymer contains as polymerized units: a) from 1 to 100 parts by weight of at least one C_{12} to C_{40} alkyl ester of (meth)acrylic acid, b) from 0 to 99 parts by weight of at least one ethylenically unsaturated monomer, and c) from 0 to 15 parts by weight of at least one ethylenically unsaturated acid containing monomer or salts thereof.

[0011] The polymer may be applied as is to a paper substrate to modify the paper substrate. The modification of the paper substrate results in good barrier coating and recycle properties. Alternatively, the polymer may be used as an additive to improve barrier coating and recycle properties of latexes such as, but not limited to butyl acrylate/methyl methacrylate, butyl acrylate/styrene, styrene/butadiene, and vinyl acetate latexes.

[0012] The present invention also provides an article including a paper substrate coated with the polymer described above. An article including a paper substrate coated with the admixture described above is also within the scope of the present invention.

[0013] The polymer used in this invention may be prepared by a single stage or multi-stage process. The process may be an emulsion polymerization. See U.S. Pat. No. 5,521,266 for a detailed description of emulsion polymerization processes. The process may also be solution polymerization followed by emulsification. See U.S. Pat. No. 5,539,021 for detailed descriptions of a solution polymerization followed by mini-emulsion polymerization or micro-emulsion polymerizations. The emulsion polymerization process of U.S. Pat. No. 5,521,266 is preferred.

[0014] The morphology of the polymer utilized in this invention may be designed to optimize certain properties of the polymer. For example, the polymer may be made in a core-shell morphology wherein the core polymer is designed to have a lower glass transition temperature than the polymer that creates the shell. This type of morphology may improve barrier properties as well as blocking properties. Alternatively, the polymer that makes up the core may be designed to have a higher glass transition temperature than the polymer that makes up the shell. In this case, the core may act as a filler and the shell may bind the harder cores together to aid in film formation. The core-shell polymers may be prepared by methods well known in the art.

[0015] In the process utilized for preparing the samples within this application, a first stage was prepared by adding a monomer emulsion and sodium persulfate to a solution containing methyl-β-cyclodextrin ("CD"), deionized water, and surfactant. The first stage was reacted at 85°C. A second stage was prepared by making a second monomer emulsion and feeding the second monomer emulsion and a sodium persulfate solution to the reacted first stage. The second stage was reacted at 85°C.

[0016] The polymer used in this invention is a composition which contains as polymerized units from 1 to 100 parts by weight, preferably from 5 to 95 parts by weight, more preferably 10 to 90 parts by weight of at least one C_{12} to C_{40} alkyl ester of (meth)acrylic acid. It is further preferred that the polymer used in this invention contains as polymerized units from 20 to 80 parts by weight, preferably 30 to 70 parts by weight, more preferably 40 to 60 parts by weight of at least one C_{12} to C_{40} alkyl ester of (meth)acrylic acid. It is preferred that the alkyl ester of (meth)acrylic acid be a C_{12} to C_{30} alkyl ester of (meth)acrylic acid. It is more preferred that the alkyl ester of (meth)acrylic acid be a C_{12} to C_{18} alkyl ester of (meth)acrylic acid. Suitable alkyl esters of (meth)acrylic acid include, but are not limited to lauryl (meth) acrylate, cetyl (meth)acrylate, stearyl (meth)acrylate, behenyl (meth)acrylate, and eicosyl (meth)acrylate. Beneficial properties may be obtained by utilizing more than one C_{12} to C_{40} alkyl ester of (meth)acrylic acid.

[0017] The polymer used in this invention may also contain as polymerized units from 0 to 99 parts by weight, preferably 4 to 94 parts by weight, more preferably 9 to 89 parts by weight of at least one ethylenically unsaturated monomer. It is further preferred that the polymer used in this invention contains as polymerized units from 18 to 80 parts by weight, preferably 28 to 70 parts by weight, more preferably 38 to 60 parts by weight of at least one ethylenically unsaturated monomer. Suitable ethylenically unsaturated monomers for use in the preparation of the polymer compositions of this invention include, but are not limited to (meth)acrylic ester monomers including methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, methyl methacrylate, butyl methacrylate, hydroxyethyl methacrylate, and hydroxypropyl acrylate; acrylamide or substituted acrylamides; styrene or substituted styrene; vinyl acetate or other vinyl esters; vinyl monomers such as vinyl chloride, vinylidene chloride, N-vinyl pyrolidone; and acrylonitrile or methacrylonitrile. Butyl acrylate, methyl methacrylate, and styrene are preferred.

[0018] The polymer used in this invention may also contain as polymerized units from 0 to 15 parts by weight, preferably 1 to 10 parts by weight, more preferably 1 to 5 parts by weight ethylenically unsaturated acid containing monomer or salts thereof. Suitable ethylenically unsaturated acid containing monomers include, but are not limited to acrylic acid, methacrylic acid, crotonic acid, phosphoethyl methacrylate, 2-acrylamido-2-methyl-1-propanesulfonic acid, sodium vinyl sulfonate, itaconic acid, fumaric acid, maleic acid, monomethyl itaconate, monomethyl fumarate, monobutyl fumarate, and maleic anhydride. Acrylic acid and methacrylic acid are preferred. Methacrylic acid is more preferred.

[0019] The polymer used in this invention may also contain as polymerized units from 0 to 25 parts by weight, preferably 0 to 15 parts by weight, more preferably 0 to 10 parts by weight of a fluorinated (meth)acrylate ethylenically unsaturated monomer, such as Zonyl™ products (Trademark of DuPont Chemical Company).

[0020] The polymer used in this invention may also contain as polymerized units from 0 to 25 parts by weight, preferably 0 to 15 parts by weight, more preferably 0 to 10 parts by weight of a silicone containing ethylenically unsaturated monomer, such as vinyl trimethoxy silane and methacryloxy propyl trimethoxy silane.

[0021] The polymer used in this invention may also contain as polymerized units from 0 to 80 parts by weight, preferably 0 to 50 parts by weight, more preferably 1 to 15 parts by weight of a monomer selected from C_6-C_{20} alkyl styrene and alkyl-alpha-methyl styrene, C_6-C_{20} alkyl dialkyl itaconate, C_{10}-C_{20} vinyl esters of carboxylic acids, C_8-C_{20} N-alkyl acrylamide and methacrylamide, C_{10}-C_{20} alkyl alpha-hydroxymethylacrylate, C_8-C_{20} dialkyl 2,2'-(oxydimethylene) diacrylate, C_8-C_{20} dialkyl 2,2'-(alkyliminodimethylene)diacrylate, C_8-C_{20} N-alkylacrylimide, and C_{10}-C_{20} alkyl vinylether.

[0022] The compositions of this invention may also contain as polymerized units from 0.1 to 10 parts by weight, preferably 0.1 to 5 parts by weight, more preferably 0.1 to 3 parts by weight, based on the polymer weight of a cross-linker selected from a cross-linking agent and a cross-linking monomer. By cross-linker is meant a compound which has at least 2 reactive groups which will react with acid groups found on the monomers of the compositions of this invention. Cross-linking agents useful in this invention include a polyaziridine, polyisocyanate, polycarbodiimide, polyamine, and a polyvalent metal. The cross-linking agent is optional, and may be added after polymerization has been completed.

[0023] Cross-linking monomers are cross-linkers which are incorporated with the monomers of the compositions of this invention during polymerization. Cross-linking monomers useful in this invention include acetoacetate-functional monomers such as acetoacetoxyethyl acrylate, acetoacetoxypropyl methacrylate, acetoacetoxyethyl methacrylate, allyl acetoacetate, acetoacetoxybutyl methacrylate, and 2,3-di(acetoacetoxy)propyl methacrylate; divinyl benzene, (meth)acryloyl polyesters of polyhydroxylated compounds, divinyl esters of polycarboxylic acids, diallyl esters of polycarboxylic acids, diallyl dimethyl ammonium chloride, triallyl terephthalate, methylene bis acrylamide, diallyl maleate, diallyl fumarate, hexamethylene bis maleamide, triallyl phosphate, trivinyl trimellitate, divinyl adipate, glyceryl trimethacrylate, diallyl succinate, divinyl ether, the divinyl ethers of ethylene glycol or diethylene glycol diacrylate, polyethylene glycol diacrylates or methacrylates, 1,6-hexanediol diacrylate, pentaerythritol triacrylate or tetraacrylate, neopentyl glycol diacrylate, cyclopentadiene diacrylate, the butylene glycol diacrylates or dimethacrylates, trimethylolpropane di-or tri-acrylates, (meth)acrylamide, n-methylol (meth)acrylamide, mixtures thereof, and the like. (Meth)acrylamide, n-methylol (meth)acrylamide, and mixtures thereof are preferred. The amount of cross-linker utilized is chosen such that the cross-linker does not interfere with film formation.

[0024] Chain transfer agents may be used to control the molecular weight of the polymer composition. Suitable chain transfer agents include mercaptans, such as, for example, dodecylmercaptan. The chain transfer agent may be used at from 0.1% to 10% based on the total weight of the polymeric composition.

[0025] Fillers may be added to the polymers to be used in this invention. The fillers may improve the barrier coating properties such as water resistance, oil resistance, and blocking resistance of the polymer. By blocking is meant tackiness of the coated surface. Blocking is undesirable because the coated paper is frequently rolled, and blocking leads to difficulty in unrolling the coated paper. Suitable fillers include talc (magnesium silicate), calcium carbonate, titanium dioxide, clay (aluminum silicate), and plastic pigments such as polystyrene. The fillers may be admixed with the polymer to be used in this invention at levels ranging from 10% to 150% by weight based on the dry weight of the polymer.

[0026] The polymer used in this invention is typically used to modify paper substrates by applying the polymer to a paper substrate. The paper substrate may be selected from cardboard, paperboard, corrugated paperboard, Kraft paper, ream wrap and the like. The polymer may be applied to the paper substrate by a blade, knife, rod, or roll, or by spray applying, dipping, gravure, flexo, or kiss coating. Other coating methods known in the art may also be utilized. The polymer may be applied at from 1g/m^2 to 50g/m^2, preferably 5g/m^2 to 25g/m^2 to yield a dry thickness of from 1 micron to 50 microns, preferably 5 microns to 25 microns. The polymer is then dried. The polymer may be dried under ambient conditions. Forced air may be utilized to aid in the drying of the polymer. Heat may also be utilized in the drying of the polymer. The forced air may be heated, or the polymer coated substrate may be placed in a heated oven. The temperature of the heat may range from 35°C to 200°C. Other methods of drying known in the art such as the use of ultra violet or infra red, a steam heated cylinder, or an electrically heated bar may also be utilized.

[0027] The polymer may also be admixed with latexes in barrier coating applications to improve water repellency and recycle properties. Any latex may be used. Suitable latexes include, but are not limited to butyl acrylate/methyl methacrylate, butyl acrylate/styrene, styrene/butadiene, and vinyl acetate latexes. The amount of polymer admixed with the latex is typically from 1 to 50 parts by weight, preferably 5 to 45 parts by weight, more preferably 10 to 40 parts by weight. The admixture is typically applied to paper substrates as described above.

[0028] The following abbreviations are used throughout this patent application:
LMA = lauryl methacrylate SMA = stearyl methacrylate St = styrene MMA = methyl methacrylate BA = butyl acrylate MAA = methacrylic acid CD = methyl-β-cyclodextrin

[0029] The following Examples are intended to demonstrate the polymers that are useful in this invention and the benefits obtained when using the polymers in barrier coating applications. The Examples should not be construed as limiting the scope of the invention.

Example 1

[0030] For stage 1, 400 g deionized water, Triton® XN-45S (Trademark of Union Carbide Chemical Company) anionic surfactant, and 28.6 g CD were introduced into a 4-liter round bottom flask with four necks equipped with a mechanical stirrer, temperature control device, condenser, monomer and initiator feed lines, and a nitrogen inlet at room temperature. The contents were heated to 85°C while stirred under a nitrogen purge. A monomer emulsion was prepared separately. Solutions of 0.35% by weight sodium carbonate (based on the total monomer weight in stage 1 and stage 2) in 25 g deionized water and 0.35% by weight sodium persulfate (based on the total monomer weight in stage 1 and stage 2) in 30 g deionized water were introduced into the reaction kettle. The monomer emulsion was fed over a period of 20 minutes together with an initiator solution of 0.05% sodium persulfate (based on the total monomer weight in stage 1 and stage 2) in 210 g deionized water.

[0031] For stage 2, a second monomer emulsion was prepared using 625 g deionized water, 7.8 g Triton® XN-45S anionic surfactant, and monomers. Immediately after the end of the stage 1 monomer emulsion feed, the stage 2 monomer emulsion was fed over a period of 3 hours together with the sodium persulfate initiator solution. The monomers of the first and second monomer emulsions were selected such that the polymers of Table 1 (based on weight percent monomer) were obtained.

Table 1

Polymer	SMA	LMA	BA	MMA	St	MAA	AN	Zonyl
1	40	0	10	0	49	1	0	0
2	0	40	10	0	49	1	0	0

Table 1 (continued)

Polymer	SMA	LMA	BA	MMA	St	MAA	AN	Zonyl
3[1]	40	0	10	0	47	1	0	0
4[1]	0	40	10	0	47	1	0	0
5[1]	40	0	0	0	57	1	0	0
6[1]	0	40	0	0	57	1	0	0
7*	0	0	50	0	49	1	0	0
Sample	SMA	LMA	BA	MMA	St	MAA	AN	Zonyl
8*[1]	0	0	50	0	47	1	0	0
9[2]	40	0	0	0	57	1	0	0
10	93	0	0	5	0	2	0	0
11	46	47	0	5	0	2	0	0
12[1]	40	0	5	42	0	1	10	0
13[1]	0	40	10	0	47	1	0	0
14[1]	40	0	5	42	0	1	0	10
15*[2]	0	0	50	0	47	1	0	0
16[1]	30	0	0	5	61	2	0	0
17[1]	0	30	0	5	61	2	0	0
18[4]	0	40	0	0	58	1	0	0
19[3]	0	40	0	0	58	1	0	0
20[1,5]	40	0	0	0	57	1	0	0
21[1,5]	0	40	0	0	57	1	0	0
22	10	0	40	0	49	1	0	0
23	20	0	30	0	49	1	0	0
24	35	0	15	0	49	1	0	0
25	50	0	0	0	49	1	0	0
26	65	0	0	0	34	1	0	0
27	80	0	0	0	19	1	0	0
28	0	35	15	0	49	1	0	0
29	0	50	0	0	49	1	0	0
30	0	65	0	0	34	1	0	0

* polymer that typically may be used as a barrier coating

[1] = contains 2% MOA (50% acrylamide / 50% n-methylol acrylamide)

[2] = contains 2% MAM (90% methacrylamide / 10% acrylamide)

[3] = contains 1% MOA (50% acrylamide / 50% n-methylol acrylamide)

[4] = contains 1% MAM (90% methacrylamide / 10% acrylamide)

[5] = contains 0.2% n-dodecyl mercaptan

[0032] Standard tests to establish the usefulness for polymer compositions in barrier coating applications include the Cobb test which measures water absorption on a polymer film over a given time, the Water Vapor Transmission Rate (WVTR) test which measures the amount of water vapor that permeates a polymer film over a given time, and a repulpability test which indicates whether or not the polymer film is readily removed from the paper substrate enabling the recycle of the paper. The polymers of Table 1 were tested by some of these tests to determine their usefulness in barrier coating applications.

Cobb Test

[0033] For most samples to be tested, a single, wet coat was applied to the uncoated side (back side) of a sheet of 224 g/m^2 basis weight, bleached paperboard using a wire-wound rod selected to give a dry coating weight of 10-15 g/m^2 when the coating was dried for 20 seconds at the drying temperature indicated in Table 2. For samples 22 through 30, a dry coating weight of 15-19 g/m^2 was applied to reduce the possibility of pinholes and the coating was dried at 150°C for 1 minute. The specimens were conditioned at 25°C and 50% relative humidity prior to testing. The coated samples were tested according to SCAN P 12:64, Water absorptiveness of sized (non-bibulous) paper and paperboard

(Cobb test), testing only the coated side of the paperboard and using an exposure period of 30 minutes instead of 120 seconds. For samples 1 through 21, four specimens per coating composition were tested. For samples 22 through 30, two specimens per coating composition were tested. For samples 1 through 22, non cross-linkable polymers were tested on films dried at 60°C, 90°C, 120°C, and 150°C and cross-linkable polymers were tested on films dried at 90°C, 120°C, 150°C, and 180°C. The results of the tests are shown in Table 2. For the results of this test, the lower the number, the better the performance.

Table 2

Cobb 30 Minutes Water Absorption (g/m^2)					
Polymer	60°C	90°C	120°C	150°C	180°C
None[1]	250	250	250	250	NT
1	4.4	3.7	3	3.5	NT
2	4.7	3.9	4.1	4.1	NT
3	NT	3.8	3.8	3.4	3.3
4	NT	6	4.1	4.1	3.7
5	NT	15.1	4.8	4.4	3.9
6	NT	43.7	11.5	5.3	3.4
7*	76.8	33	21	20	NT
8*	NT	7.1	7.5	7.2	7.7
9	NT	NT	NT	NT	NT
10	NT	NT	NT	NT	NT
11	4.6	4.9	5.3	5.4	NT
12	NT	74.8	47.0	13.2	9.7
13	NT	7.1	7.5	7.2	7.7
14	NT	12.3	12.3	10.9	11.4
15*	NT	6.5	6.2	6.4	6.1
16	NT	NT	NT	87.9	83.0
17	NT	NT	NT	84.0	83.8
18	NT	36.5	10.4	4.6	3.5
19	NT	45.7	26.2	7.9	3.1
20	NT	4.3	3.7	3.1	3.9
21	NT	6.0	3.9	3.3	3.7
22	NT	NT	NT	2.5	NT
23	NT	NT	NT	1.3	NT
24	NT	NT	NT	1.5	NT
25	NT	NT	NT	1.3	NT
26	NT	NT	NT	1.5	NT
27	NT	NT	NT	2.3	NT
28	NT	NT	NT	2.1	NT
29	NT	NT	NT	1.1	NT
30	NT	NT	NT	1.9	NT

* polymer that typically may be used as a barrier coating NT = not tested

[1] run for 5 minutes and extrapolated to 30 minutes

[0034] The results above show that the non cross-linkable polymers have very low water absorption at all drying temperatures tested. The cross-linkable polymers have lower water absorption as the drying temperature increases. It is understood that sometimes coatings have flaws that are termed pinholes. The presence of pinholes will allow water to penetrate the coating and therefore increase both the water absorption and the WVTR. The inventors inspected the coatings made from Polymers 16 and 17 by a staining technique where an excess amount of stain was contacted with the coated specimen for 5 minutes and the pinholes were counted. A large amount of pinholes were discovered.

WVTR Test

[0035] The WVTR test was run according to modified SCAN P 22:68. The test conditions were 25°C and 75% relative humidity. Non cross-linkable polymers were tested on films dried at 60°C, 90°C, 120°C, and 150°C. Cross-linkable polymers were tested on films dried at 90°C, 120°C, 150°C, and 180°C. For samples 22 through 30, a dry coating weight of 15-19 g/m^2 was applied to reduce the possibility of pinholes. For samples 1 through 21, six specimens per coating composition were tested. For samples 22 through 30, two specimens per coating composition were tested. The results are shown in Table 3. For the results of this test, the lower the number, the better the performance.

Table 3

WVTR (g/m^2/24hours)					
Polymer	60°C	90°C	120°C	150°C	180°C
None	600	600	600	600	NT
1	180.3	152.6	145.7	140.3	NT
2	157.6	138.3	133.5	142.4	NT
3	NT	133.8	130.9	123.4	123.8
4	NT	145.9	133.6	131.6	122.7
5	NT	374.4	130.1	101.2	93.7
6	NT	348.8	142.5	120.5	108
7*	505.8	393.7	353.7	346.8	NT
8*	NT	238.6	235.1	230.2	229.9
9	NT	NT	NT	NT	NT
10	568.3	550.2	543.3	502.5	NT
11	157.5	161.6	164.8	167.4	NT
12	NT	454.0	350.6	184.7	145.6
13	NT	238.6	235.1	230.2	229.9
14	NT	194.5	176.2	165.7	156.6
15*	NT	219.3	218.4	216.4	204.0
16	NT	NT	NT	536.8	545.7
17	NT	NT	NT	564.8	563.9
18	NT	434.3	284.1	135.6	104.3
19	NT	438.7	229.7	152.7	122.7
20	NT	98.5	95.7	93.1	106.1
21	NT	134.5	111.4	105.3	109.2
22	NT	NT	NT	114	NT
23	NT	NT	NT	101	NT
24	NT	NT	NT	78	NT
25	NT	NT	NT	64	NT
26	NT	NT	NT	74	NT
27	NT	NT	NT	88	NT
28	NT	NT	NT	90	NT
29	NT	NT	NT	64	NT
30	NT	NT	NT	73	NT

* polymer that typically may be used as a barrier coating

[0036] The results above show that the non cross-linkable polymers have very low WVTRs at all drying temperatures tested as compared with samples 7 and 8. The cross-linkable polymers have lower WVTRs as the drying temperature increases. As discussed in the Cobb test results, the presence of pinholes will allow water to penetrate the coating and therefore increase both the water absorption and the WVTR. The inventors inspected the coatings made from Polymers 16 and 17 by a staining technique where an excess amount of stain was contacted with the coated specimen for 5 minutes and the pinholes were counted. A large amount of pinholes were discovered.

The Effect Of Coat Weight On Water Absorption And WVTR

[0037] The effect of coat weight on water absorption and WVTR was tested by coating paperboard with different coat weights of Sample 5. Aliquots of Sample 5 were applied to paperboard to provide coat weights of 8 g/m^2, 10 g/m^2, and 15 g/m^2. A sample of each coated paperboard was dried at 90°C, 120°C, 150°C, and 180°C. Each sample was tested for Cobb 30 minutes and WVTR as described above. The results are shown in Table 4.

Table 4

Polymer	Cobb 30 Minutes (g/m^2)	WVTR (g/m^2/24hours)
5 8 g/m^2		
90°C	75.4	587.1
120°C	76.4	548.6
150°C	66	511.7
180°C	77.2	550.6
5 10 g/m^2		
90°C	15.1	374.4
120°C	4.8	130.1
150°C	4.4	101.2
180°C	3.9	93.7
5 15 g/m^2		
90°C	4.2	101.1
120°C	3.3	79.3
150°C	3.3	77.5
180°C	2.5	77.8
None	NT	599.6

[0038] The results above show that the polymers dramatically improve the WVTR when applied at a coat weight of 10 g/m^2 or greater. The polymers also dramatically improve the resistance to water absorption when applied at a coat weight of 10 g/m^2 or greater.

The Effect Of Fillers On Water Absorption And WVTR

[0039] The effect of fillers on water absorption and WVTR was tested by coating paperboard with admixtures of talc and the polymers used in this invention. The talc was added on a weight basis based on the dry weight of the polymer. Samples were applied to paperboard and dried at 150°C for 20 seconds. Each sample was tested for Cobb 30 minutes and WVTR as described above. The results are shown in Table 5.

Table 5

Polymer	Cobb 30 minutes (g/m^2)	WVTR (g/m^2/24hours)
5	4.4	101.2
5 + 20% talc	2.6	68.2
5 + 40% talc	3.3	46.6
6	5.3	120.5
6 + 20% talc	2.3	80.4
6 + 40% talc	2.7	53.5
12	13.2	184.7
12 + 20% talc	9.6	139.6
12 + 40% talc	7.0	97.7
14	11.8	165.7
14 + 20% talc	8.3	135.5
14 + 40% talc	7.4	103.9

[0040] The results above indicate that the addition of fillers to the polymers used in this invention improves both the water resistance and water permeability of the barrier coating. An increase in the amount of filler added also improved the water resistance and water permeability of the barrier coating.

Repulpability

[0041] The repulpability tests were done on uncoated Kraft paper and Kraft paper coated with sample 9. The average coating weight was 10 g/m^2 and the coating was applied to the smoother side of the paper. The coated paper was dried at 150°C for 20 seconds. Approximately 30 g of each paper was cut into 1.5 cm x 1.5 cm pieces. To each set of pieces was added 2 liters (1) of water to achieve a consistency of 15 g/l. The pH was adjusted to neutral by using hydrochloric acid and sodium hydroxide. The paper was repulped in a British Wet Disintegration device. The number of revolutions was 30,000. The pulp was diluted with water to a consistency of 3 g/l. The drainability of the diluted pulp was measured according to the Canadian Freeness method. Two parallel measurements were done and the results were expressed as milliliters.

[0042] The small pieces of the coatings in the pulp were observed under a stereo microscope, looking for the size of the pieces of coating and whether or not pulp fibers were attached to the pieces of coating.

[0043] The pulp was again diluted to a consistency of 1.63 g/l in order to make laboratory sheets of a grammage of approximately 60 g/m^2. The sheets were made with a special sheet mold and then dried in an oven for 2 hours in a way that they could not shrink. The tensile strength and elongation of the sheets were measured using 10 parallel samples. The results of the tests described above are shown in Table 6.

Table 6

Test	Uncoated	Coated
Energy Consumption (KWH)	1.7	1.7
Canadian Freeness (ml)	890	900
Grammage (g/m^2)	68.1	68.6
Elongation (%)	3.4	3.9
Tensile Strength (kN/m)	2.3	2.5

[0044] The data above demonstrates that the polymer coated paper performs as well as the uncoated paper in tests designed to show repulpability. The small pieces of the coatings observed under the stereo microscope showed tracks of fibers, but the fibers were not attached to the coating. These results indicate that the polymer coated paper is repulpable.

Claims

1. A method of modifying paper substrates comprising:
   applying a polymer to the paper substrate wherein the polymer comprises as polymerized units: a) from 1 to 100 parts by weight of at least one C_{12} to C_{40} alkyl ester of (meth)acrylic acid, b) from 0 to 99 parts by weight of at least one ethylenically unsaturated monomer, and c) from 0 to 15 parts by weight of at least one ethylenically unsaturated acid containing monomer or salts thereof.

2. The method according to Claim 1 wherein the polymer comprises as polymerized units: a) from 5 to 95 parts by weight of at least one C_{12} to C_{40} alkyl ester of (meth)acrylic acid, b) from 4 to 94 parts by weight of at least one ethylenically unsaturated monomer, and c) from 1 to 10 parts by weight of at least one ethylenically unsaturated acid containing monomer or salts thereof.

3. The method according to Claim 1 wherein the polymer comprises as polymerized units: a) from 10 to 90 parts by weight of at least one C_{12} to C_{40} alkyl ester of (meth)acrylic acid, b) from 9 to 89 parts by weight of at least one ethylenically unsaturated monomer, and c) from 1 to 5 parts by weight of at least one ethylenically unsaturated acid containing monomer or salts thereof.

4. The method according to Claim 1 wherein the polymer further comprises a cross-linker.

5. The method according to Claim 1 wherein the polymer further comprises a filler.

6. The method according to Claim 1 wherein the paper substrate is selected from cardboard, paperboard, corrugated paperboard, Kraft paper, and ream wrap.

7. The method according to Claim 1 wherein the polymer is admixed with from 50 to 99 parts by weight of a latex and the admixture is applied to a paper substrate.

8. The method according to Claim 7 wherein the polymer comprises as polymerized units: a) from 5 to 95 parts by weight of at least one C_{12} to C_{40} alkyl ester of (meth)acrylic acid, b) from 4 to 94 parts by weight of at least one ethylenically unsaturated monomer, and c) from 1 to 10 parts by weight of at least one ethylenically unsaturated acid containing monomer or salts thereof.

9. The method according to Claim 7 wherein the polymer comprises as polymerized units: a) from 10 to 90 parts by weight of at least one C_{12} to C_{40} alkyl ester of (meth)acrylic acid, b) from 9 to 89 parts by weight of at least one ethylenically unsaturated monomer, and c) from 1 to 5 parts by weight of at least one ethylenically unsaturated acid containing monomer or salts thereof.

10. The method according to Claim 7 wherein the polymer further comprises a cross-linker.

11. The method according to Claim 7 wherein the polymer further comprises a filler.

12. The method according to Claim 7 wherein the latex is selected from the group consisting of butyl acrylate/methyl methacrylate, butyl acrylate/styrene, styrene/butadiene, and vinyl acetate latexes.

13. The method according to Claim 7 wherein the paper substrate is selected from cardboard, paperboard, corrugated paperboard, Kraft paper, and ream wrap.

14. An article comprising:
a paper substrate coated with the polymer of Claim 1.

15. An article comprising:
a paper substrate coated with the admixture of Claim 7.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 30 8765

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	DATABASE WPI Section Ch, Week 199647 Derwent Publications Ltd., London, GB; Class A13, AN 1996-472258 XP002131917 & JP 08 239407 A (KINDAI KAGAKU KOGYO KK), 17 September 1996 (1996-09-17) * abstract * ---	1-15	D21H23/22 D21H27/10 //D21H19/56
X,D	US 5 521 266 A (LAU WILLIE) 28 May 1996 (1996-05-28) * column 4, line 9 - line 29 * * column 8, line 12 - line 19 * ---	1-15	
A,D	WO 94 26513 A (INT PAPER CO) 24 November 1994 (1994-11-24) * claims * ---	1-15	
X	DATABASE WPI Section Ch, Week 199404 Derwent Publications Ltd., London, GB; Class A97, AN 1994-031678 XP002131920 & JP 05 339101 A (KANZAKI SEISHI KK), 21 December 1993 (1993-12-21) * abstract * ---	1-15	**TECHNICAL FIELDS SEARCHED (Int.Cl.7)** D21H
X	DATABASE WPI Section Ch, Week 199805 Derwent Publications Ltd., London, GB; Class A14, AN 1998-047310 XP002131919 & JP 09 296390 A (OJI PAPER CO), 18 November 1997 (1997-11-18) * abstract * --- -/--	1-15	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	1 March 2000	Naeslund, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
&: member of the same patent family, corresponding document

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 30 8765

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	DATABASE WPI Section Ch, Week 199536 Derwent Publications Ltd., London, GB; Class A82, AN 1995-273334 XP002131918 & JP 07 173799 A (MITSUI TOATSU CHEM INC), 11 July 1995 (1995-07-11) * abstract * ---	1-15	
A,D	US 5 539 021 A (PATE JAMES E ET AL) 23 July 1996 (1996-07-23) * the whole document * -----	1-15	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	1 March 2000	Naeslund, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 99 30 8765

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

01-03-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 8239407 A	17-09-1996	NONE	
US 5521266 A	28-05-1996	AU 705906 B	03-06-1999
		AU 3442395 A	09-05-1996
		BR 9504598 A	27-05-1997
		CA 2161620 A	29-04-1996
		CN 1133849 A	23-10-1996
		EP 0710675 A	08-05-1996
		FI 954863 A	29-04-1996
		JP 8208727 A	13-08-1996
		SG 54088 A	16-11-1998
		US 5710226 A	20-01-1998
		US 5760129 A	02-06-1998
		ZA 9508846 A	25-07-1996
WO 9426513 A	24-11-1994	US 5763100 A	09-06-1998
		AU 6786494 A	12-12-1994
		EP 0697961 A	28-02-1996
		US 5837383 A	17-11-1998
		US 5989724 A	23-11-1999
		US 5654039 A	05-08-1997
JP 5339101 A	21-12-1993	NONE	
JP 9296390 A	18-11-1997	NONE	
JP 7173799 A	11-07-1995	NONE	
US 5539021 A	23-07-1996	AU 700877 B	14-01-1999
		AU 5726396 A	24-12-1996
		BR 9609133 A	17-02-1999
		CA 2220866 A	12-12-1996
		EP 0830414 A	25-03-1998
		JP 11506797 T	15-06-1999
		NO 975642 A	04-12-1997
		WO 9639461 A	12-12-1996
		US 5688842 A	18-11-1997

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82