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POLYMER CONTAINING HYDROCARBON WAX AND ITS USE

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(56) Prior Art Documents
US 5434215
US 3696087
JP 57-108114

(57) Claim

1. A process for improving the properties of a substrate comprising organic materials of the group consisting essentially of paper, carton stock, board, wood, wood composites, plastic sheets and films comprising the steps of:

a. coating the substrate with a thermoplastic polymer obtained by emulsion or suspension polymerization of a mixture of ethylenically unsaturated monomers comprising:

i) 35-98 parts by weight (calculated on the total amount of monomers in the mixture) of C1-C18 alkyl(meth)acrylate;

ii) 0.05-5 parts of C3-C8 unsaturated carboxylic acid;

iii) 1-60 parts by weight of a vinyl aromatic monomer and which mixture is substantially free from C3-C8 conjugated diolefins,

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in the presence of 0.01 to 5 weight % calculated on the monomers of a hydrocarbon wax having a melting point of 40 to 80°C, which wax is incorporated in the polymer during polymerization; and

b. drying the coated substrate in the absence of any crosslinking reaction.

4. A process for preparing a polymer by an emulsion or suspension technique comprising polymerizing a mixture of monomers comprising:

(1) 35 to 98 parts by weight (calculated on the total amount of monomer in the mixture) of C1-C18 alkyl(meth)acrylate, preferably comprising butyl acrylate and/or 2-ethyl hexyl acrylate;

(2) 0.05 to 5 parts of a C3-C8 unsaturated carboxylic acid;

(3) 1 to 60 parts by weight of a vinyl aromatic monomer from the group comprising styrene and α-methylstyrene; and which mixture is substantially free from C3-C8 conjugated diolefins in the presence of a hydrocarbon wax having a melting point of 25 to 125°C.

AUSTRALIA

Patents Act 1990

COMPLETE SPECIFICATION

STANDARD PATENT

Applicant(s):

NATIONAL STARCH AND CHEMICAL INVESTMENT HOLDING CORPORATION and DUSSEK CAMPBELL LTD

Invention Title:

POLYMER CONTAINING HYDROCARBON WAX AND ITS USE

The following statement is a full description of this invention, including the best method of performing it known to me/us:

POLYMER CONTAINING HYDROCARBON WAX AND ITS USE

The invention relates to the use of certain polymeric materials containing an amount of hydrocarbon wax in the treatment of certain substrates to improve the properties of the latter. The invention also relates to certain improved substrates and certain polymeric materials containing a percentage of hydrocarbon wax.

German specification (DE-A-) 30 48 818 (BASF, Germany) discloses emulsions of polymers containing a conjugated diolefin, which emulsions are useful as an additive for concrete and mortar compositions, bridge and parking pavement compositions, etc. In particular, the citation discloses a polymer in the form of a latex which polymer comprises a conjugated C4-C6 diolefin monomer, preferably a polymer comprising a C4-C6 diolefin and a vinylaromatic compound and especially a polymer of a C4-C6 conjugated diolefin and a vinylaromatic monomer and one or more ethylenically unsaturated carboxylic acids or derivatives thereof. These known emulsions consequently always contain a substantial amount of conjugated diene such as butadiene or isoprene and at most small quantities of acrylics. Polymerizing mixtures of monomers comprising substantial amounts of lower diolefins has the drawback that pressure vessels (autoclaves) are required. Moreover polymeric materials containing substantial amounts of diolefin do not always have favorable properties.

US-A-3 696 067 (Trofimow) discloses vinylidene chloride based latexes obtained by polymerizing in an emulsion a mixture containing at least about 80 wt% vinylidene chloride, about 20 wt% of monoethylenic co-monomer and 1 to 4 wt% of paraffin wax. The effect of the paraffin wax is that it adds an anti-blocking effect or slipping effect to the previously known vinylidene chloride based latexes which were known to impart moisture vapour barrier properties to substrates .

JP-A-57 108 114 (Dainippon) and the WPI abstract thereof disclose the preparation and use of a wide range of polymers of the aqueous dispersion type based on a combination of numerous possible unsaturated monomers. These polymer dispersions are useful in the waterproofing of, e.g., umbrella cloth, rain coat, covering sheet for cars and waterproof sheet. The aqueous polymer is applied to such

a substrate together with a crosslinking agent like, e.g., aminoplast and then caused to react by a heating/curing treatment. For good results there often is a pre-treatment of the substrate with an water-repellant. Most of the mixtures of monomers polymerized in dispersion according to the citation do not comprise a vinylaromatic monomer, furthermore a conjugated diolefin (butadiene) is sometimes present. There is no disclosure or suggestion of polymerizing and using a mixture of monomers comprising a vinylaromatic monomer in the absence of a conjugated diolefin. Ipso facto there is no disclosure or suggestion of applying a coating of such a polymer dispersion to a substrate.

US-A-5 034 454 (Maska et al.) discloses water dispersible acrylic copolymers obtained by polymerization in a solution of the monomer in Cellosolve, especially butylcellosolve. The polymer solution is subsequently used as dip coatings for which purpose good flow properties are a requirement. To obtain these good flow properties a mixture of unsaturated polymers containing sulfonic acid/salt/ester and optionally a wax is used. The acrylic resin is subsequently crosslinked with an aminoplast curing agent.

For environmental reasons it is desirable to reduce the amount of plastic material used e.g. in packaging and to increase the use of recyclable materials. It has been proposed to use hydrocarbon waxes to upgrade, e.g., materials comprising fibers, metal or glass, in particular paper, wood, board and textiles usually by treatment with a molten hydrocarbon wax which has a low surface tension and penetrates easily, but this process is difficult to control. Moreover for recyclability and repulpability the large amount of wax often employed generally makes the fibers slip.

Consequently there has been a need for materials, especially materials comprising fibrous constituents such as paper, carton, board, wood and textiles which can be recycled and repulped without difficulties which materials possess improved properties such as hydrophobicity and/or moisture vapour resistance.

The present invention provides for the use of a polymer obtained by emulsion or suspension polymerization of an ethylenically unsaturated monomer or mixture of more than one such monomer in the presence of a hydrocarbon wax having a melting point of 25 to 125°C which is incorporated in the polymer during polymerization as a coating material for imparting to or improving hydrophobicity and/or

moisture vapour resistance of a substrate of the group comprising fibers, metal or glass, especially metal foil or glass fibers.

Thus, the invention provides a process for imparting to or improving hydrophobicity and/or moisture vapour resistance of a substrate especially a substrate of the group comprising organic fibers, or metal or glass, preferably comprising paper, wood, board and textile, by applying on the substrate a polymer obtainable by emulsion or suspension polymerization, preferably by emulsion polymerization, of an ethylenically unsaturated monomer or mixture of more than one such a monomer with a hydrocarbon wax having a melting point of 25 to 125°C incorporated in the polymer during polymerization.

The invention also provides a substrate of the group comprising fibers, metal or glass, preferably comprising paper, carton, board, wood and composite wood and textile coated with a polymer obtainable by emulsion or suspension polymerization, preferably by emulsion polymerization, of an ethylenically unsaturated monomer or mixture of more than one such a monomer in which polymer a hydrocarbon wax having a melting point of 25 to 125°C has been incorporated during polymerization.

Thus, the present invention provides for the use of a polymer obtained by emulsion or suspension polymerization, preferably by emulsion polymerization, of an ethylenically unsaturated monomer or mixture of more than one such monomer in the presence of a hydrocarbon wax having a melting point of 25 to 125°C which wax is incorporated in the polymer during polymerization as a coating material for imparting to or improving hydrophobicity and/or moisture vapour resistance of a substrate of the group comprising fibers, metal or glass, especially metal foil or glass fibers.

The ethylenically unsaturated monomer or mixture of more than one such monomer may comprise vinylaromatic compounds, such as styrene and α-methylstyrene, unsaturated carboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid and fumaric acid as well as derivatives there from as, e.g., acrylonitrile, acrylamide, methacrylonitrile, N-methylolacrylamide as well as their C1-C18 alkyl esters, particularly C1-C18 alkyl(meth)acrylate. As conjugated diolefin especially butadiene and isoprene are of practical importance.

Emulsion and suspension polymerization techniques are well-known in the art and are, e.g., disclosed in "Emulsion Polymerization", D.C. Blackley, Applied Science Publishers, 1974; in "Emulsion Polymerization and its Applications in Industry", Eliseeva, Ivanchev, Kuchanow and Lebedev, Khimia

1976 and in "Textbook of Polymer Science", F. W. Billmeyer, Wiley, 1975, Chapter 12, pgs. 341-342 and pgs. 343-347 which are incorporated herein by reference. In these polymerizations preferably a suitable free radical initiator can be used, for example ammonium and alkali persulphate, hydrogen peroxide or an organic peroxide, either alone or in conjunction with a reducing agent such as sodium metabisulphate, sodium formaldehyde sulphoxylate or ascorbic acid. To stabilize the latex, one or more surfactants of the nonionic or anionic type may be employed. Such surfactants are well-known in the art. For obtaining special effects minor amounts of other monomers - not being diolefins - for example acrylamide, N-methylolacrylamide can also be incorporated.

In a preferred embodiment of the invention the fibers are organic fibrous materials of the group consisting of paper, carton, board, wood and composite wood; woven and non-woven textiles; plastic sheet and film.

The invention provides a process for imparting to or improving hydrophobicity and/or moisture vapour resistance of a substrate especially a substrate of the group comprising organic fibers, or metal or glass, preferably comprising paper, wood, board and textile, by applying on the substrate a polymer obtainable by emulsion or suspension polymerization, preferably by emulsion polymerization, of an ethylenically unsaturated monomer or mixture of more than one such a monomer with a hydrocarbon wax having a melting point of 25 to 125°C, the wax having been incorporated in the polymer during polymerization. Within the term "applying on" is to be understood any method of applying a polymer film, i.e., coating with a brush or applicator, spraying, impregnating, etc. After applying the polymer containing the hydrocarbon resin on the substrate the coated substrate is dried, preferably at ambient temperature and the product obtained is ready for use. The addition of cross-linking agents, etc., is not recommended because it would lead to thermosetting resins and according to the present invention the coating consists of thermoplastic resin material. The degree of hydrophobicity and/or moisture vapour resistance is determined by the amount of polymer with incorporated hydrocarbon wax applied on the substrate. Dependent on the nature of the substrate and the degree of hydrophobicity and moisture vapour resistance desired the amount of polymer by weight applied on the substrate usually varies between 0.5 and 25%, preferably from 3 to 15% w/w.

The hydrocarbon waxes which are useful in the context of the present invention are hydrocarbon waxes obtainable from natural and synthetic sources, for example by petroleum refining and Fischer-Tropsch synthesis. Preferred are hydrocarbon waxes from petroleum refining. The term "hydrocarbon wax" as used herein covers inter alia paraffin waxes. Without wishing to be bound by theory the applicants have assumed on the basis of certain determined parameters that the hydrocarbon wax appears to have been grafted on the (co)polymer or encapsulated by the (co)polymer as a result of polymerizing the monomeric mixture by emulsion or suspension technique in the presence of a dissolved, emulsified or suspended hydrocarbon wax.

There is also provided a substrate of the group comprising fibers, metal or glass, preferably comprising paper, carton, board, wood and composite wood and textile coated with a polymer obtainable by emulsion or suspension polymerization, preferably by emulsion polymerization, of an ethylenically unsaturated monomer or mixture of more than one such a monomer in which polymer a hydrocarbon wax having a melting point of 25 to 125°C has been incorporated during polymerization.

In a preferred embodiment the present invention provides a substrate, process or use as set out above in which the amount of hydrocarbon wax is from 0.01 to 25, preferably from 0.05 to 5 wt% calculated on monomer.

In another preferred embodiment the present invention provides a substrate, process or use in which the hydrocarbon wax has a melting point between 40 and 80°C.

In still another embodiment the invention provides a substrate, process or use as set out above in which the hydrocarbon wax is substantially a saturated, aliphatic hydrocarbon.

In another embodiment the invention provides a process for preparing a polymer by emulsion or suspension technique, preferably by emulsion polymerization, comprising polymerizing an ethylenically unsaturated monomer or a mixture of such monomers in the presence of a wax in which the mixture of monomers is substantially free from (lower, here C3-C8) conjugated diolefins and contains an unsaturated carboxylic acid or derivative thereof and wherein the wax is a hydrocarbon wax having a melting point of 25 to 125°C.

In a preferred embodiment the invention provides a process as set out above in which the mixture of monomers is a composition of styrene, C1-C18 alkyl(meth)acrylate and unsaturated carboxylic

acid with a weight ratio of 0-70:30-100:0-10, preferably 1-60:35-98:0.05-5. A hydrocarbon wax incorporated in a styrene-acrylic latex according to the present invention was found very useful for the paper, wood and board industry and produced an excellent moisture vapour barrier coating on these substrates which was extremely hydrophobic.

In a preferred embodiment the invention provides a process as set out above in which the hydrocarbon wax is introduced in the polymerization mixture in the form of a solid wax dissolved in monomer or in the form of a wax emulsion/dispersion either in monomer or another extender. The extender can be, e.g., water or another suitable polar or non-polar liquid.

In still another preferred embodiment the invention provides a process in which the amount of hydrocarbon wax is from 0.01 to 25 wt%, preferably 0.05 to 5 wt.% calculated on monomer. Preferably the hydrocarbon wax has a melting point between 40 and 80°C.

It is further preferred that the hydrocarbon wax is substantially a saturated, aliphatic hydrocarbon.

In a preferred embodiment the invention provides a process as set out above in which the ethylenically unsaturated monomer or mixture thereof also comprises a vinylaromatic compound and/or alkyl(meth)acrylate in which the alkyl group contains 1 to 18 carbon atoms. More preferably the vinyl aromatic compound is styrene and/or *α*-methylstyrene.

In a preferred embodiment the invention provides a process as set out above in which the ethylenically unsaturated monomer or mixture of more than one such monomer comprises (meth)acrylic acid or C1-C18 alkylester thereof.

In another preferred embodiment the invention provides a process as set out above in which the ethylenically unsaturated monomer or mixture of more than one such a monomer comprises styrene, and/or methylmethacrylate, acrylic acid and butylacrylate and/or 2-ethylhexyl acrylate.

In another embodiment the invention provides a polymer obtained by polymerizing by an emulsion or suspension technique, preferably by emulsion polymerization, a monomer or mixture of monomers in the presence of a wax in which the mixture of monomers is substantially free from (lower) conjugated diolefin and contains an unsaturated carboxylic acid or derivative thereof and wherein the wax is a hydrocarbon wax having a melting point of 25 to 125°C. Preferably the polymer provided is obtained by polymerizing a mixture of monomers, which is a composition of styrene, C1-C18 alkyl(meth)acrylate

and C3-C8 unsaturated carboxylic acid with a weight ratio of 0-70:30-100:0-10, preferably 1-60:35-98:0.05-5.

In another embodiment the invention provides a polymeric composition with incorporated hydrocarbon wax as set out above in the form of a latex or dispersion.

One very useful method of investigating polymers with incorporated hydrocarbon wax is by differential Scanning Calorimetry (DSC). The DSC temperature peaks of wax or wax containing composition can be determined in the conventional way using a differential scanning calorimeter. A short survey of this method with some literature references is given in Ullmanns Encyklopädie der technischen Chemie, 4.Auflage, Band 5, pgs. 793-795.

The amount of solids in a wax or wax-containing composition at any given temperature as well as the melting point range may be determined by measuring the latent heat of fusion of each wax by using Differential Scanning Calorimetry (DSC) by a process described in Miller, W.J. et al. Journal of American Oil Chemists' Society, July, 1969, V. 46, No 7, pgs. 341-343, incorporated by reference. This procedure was modified as discussed below. DSC equipment used in the procedure is preferably the Perkin Elmer DSC-4.

Specifically the DSC is utilized to measure the total latent heat of fusion of multi-component systems which do not have a distinct melting point, but rather, melt over a temperature range. At an intermediate temperature within this range one is capable of determining the fraction of the latent heat required to reach that temperature. When acquired for a multi-component mixture of similar components such as commercial waxes, this fraction correlates directly to the liquid fraction of the mixture at that temperature. The solids fraction for the waxes of interest are, e.g., measured at 50°C and 60°C by running a DSC trace from 0 to 80°C and measuring the fraction of the total latent heat of fusion required to reach these temperatures.

The invention is illustrated by the following non-limiting example. All parts and percentages were taken by weight unless otherwise indicated.

Example 1

A solution of 0.30 parts of an anionic surfactant, (the sodium salt of sulphated lauryl alcohol), in 37.17 parts of deionized water was placed in a five-necked reaction flask equipped with a thermometer, agitator, condenser, nitrogen purge and suitable addition funnels. The flask was heated to 25°C and purged for 30 minutes with nitrogen.

A pre-emulsion was prepared by mixing a monomer phase "A" with a water phase "B". Monomer phase "A" was made as follows: 1.00 part of a paraffin wax having a melting point of 57 to 60°C, was dissolved in 40.50 parts of styrene, after which 54.50 parts of butyl acrylate, 4.00 parts of acrylic acid and 4.00 parts of a nonionic surfactant, (a nonylphenol ethoxylate containing 9 moles of ethylene oxide), were added. The water phase "B" was made as follows: 5.71 parts of a 70% solution of a nonionic surfactant, (a nonylphenol ethoxylate containing 30 moles of ethylene oxide), was dissolved in 40.70 parts of deionized water. Monomer phase "A" and water phase "B" were mixed together using a high speed mixer to make a pre-emulsion.

10% of the pre-emulsion was added to the reactor and stirred for 5 minutes. A solution of 0.25 parts ammonium persulphate in 0.88 parts of deionized water was added and stirred for 5 minutes, then a solution of 0.25 parts of sodium metabisulphite in 0.88 parts of deionized water and 0.18 parts of a 0.1% ferric ion solution was added. After 10 minutes, the continuous additions of the remainder of the pre-emulsion, a solution of 0.25 parts of ammonium persulphate in 7.96 parts of deionized water, and a solution of 0.25 parts of sodium metabisulphite in 7.96 parts of deionized water were commenced to last 3 hours. The temperature was increased over 20 minutes to 50°C, and maintained there for the duration of the slow additions.

At the end of the slow additions, the temperature was maintained at 50°C for 15 minutes, then 1.00 part of methyl methacrylate was added, followed by a solution of 1.13 parts of ammonia in 1.77 parts of deionized water. After 5 minutes a solution of 0.11 parts of ammonium persulphate in 0.88 parts of deionized water and a solution of 0.05 parts of sodium formaldehyde sulphoxylate in 0.88 parts of deionized water were added and stirred for 15 minutes. A solution of 0.11 parts of tertiary-butylhydroperoxide in 0.88 parts of deionized water was added, followed by a solution of 0.26 parts of ammonia in 0.26 parts of deionized water. The reactor was cooled to < 30°C, and the resultant latex filtered

through a 100 mesh nylon filter to remove any coagulum. The resultant latex had a solids content of 51.29%, pH of 4.8 and a viscosity of 1.15 Pa.s at 25°C.

Example 2

The procedure for Example 1 was followed, except that the paraffin wax used had a melting point of 51 to 54°C. The resultant latex had a solids content of 51.71%, pH of 5.0 and a viscosity of 2.52 Pa.s.

Example 3

The procedure for Example 1 was followed, except that the paraffin wax used had a melting point of 60 to 63°C. The resultant latex had a solids content of 52.37%, pH of 5.1 and a viscosity of 2.54 Pa.s.

Example 4

The procedure for Example 1 was followed, except that only 0.50 parts of paraffin wax was dissolved in monomer phase "A". The resultant latex had a solids content of 50.12%, pH of 5.0 and a viscosity of 1.17 Pa.s.

Example 5

The procedure for Example 1 was followed, except that only 0.25 parts of paraffin wax was dissolved in monomer phase "A". The resultant latex had a solids content of 50.43%, pH of 4.8 and a viscosity of 1.46 Pa.s.

Example 6

The procedure for Example 1 was followed, except that 2.00 parts of a 50% solids aqueous dispersion of a paraffin wax having a melting point of 60 to 63°C was added to the monomer phase "A", and water phase "B" consisted of 5.71 parts of a 70% solution of a nonionic surfactant, (a nonylphenol ethoxylate containing 30 moles of ethylene oxide), dissolved in 39.70 parts of deionized water. The resultant latex had 51.59% solids, pH of 4.3 and viscosity of 1.73 Pa.s.

Example 7

The procedure for Example 6 was followed, except that the 2.00 parts of a 50% solids aqueous dispersion of paraffin wax was added to the water phase "B", consisting of 5.71 parts of a 70% solution of a nonionic surfactant dissolved in 39.70 parts of deionized water. The resultant latex had 51.58% solids, pH of 4.6 and viscosity of 1.80 Pa.s.

Example 8

The procedure for Example 7 was followed, except that 4.00 parts of the 50% solids aqueous dispersion of paraffin wax was added to the water phase "B", (consisting of 5.71 parts of a 70% solution of a nonionic surfactant dissolved in 39.70 parts of deionized water). Additionally, the first stage initiator solutions contained 3.53 parts of deionized water instead of 0.88 parts. The resultant latex had 48.51% solids, pH of 4.3 and viscosity of 0.54 Pa.s.

Example 9

The procedure of Example 1 was followed except that monomer phase "A" was made as follows. 1.00 part of a paraffin wax having a melting point of 57 to 60°C was dissolved in 50.0 parts of styrene, after which 45.00 parts of 2-ethylhexyl acrylate, 4.00 parts of acrylic acid and 4.00 parts of a nonionic surfactant, (a nonylphenol ethoxylate containing 9 moles of ethylene oxide), were added. The resultant latex had 50.90% solids, pH of 3.6 and a viscosity of 2.10 Pa.s.

Example 10

The procedure of Example 1 was followed except that monomer phase "A" consisted of 50.0 parts of styrene, 45.00 parts of 2-ethylhexyl acrylate, 4.00 parts of acrylic acid and 4.00 parts of nonionic surfactant, (a nonylphenol ethoxylate containing 9 moles of ethylene oxide). 2.00 parts of a 50% solids aqueous dispersion of a paraffin wax having a melting point of 60 to 63°C were added to water phase "B", consisting of a solution of 5.71 parts of a 70 % solution of a nonionic surfactant, (a nonylphenol ethoxylate containing 30 moles of ethylene oxide) dissolved in 39.70 parts of deionized water. The resultant latex had 52.62% solids, pH of 4.2 and a viscosity of 1.60 Pa.s.

Example 11

The procedure of Example 10 was followed except that monomer phase "A" consisted of 30.50 parts of styrene, 54.50 parts of butyl acrylate, 10.00 parts of methyl methacrylate, 4.00 parts of acrylic acid and 4.00 parts of nonionic surfactant, (a nonylphenol ethoxylate containing 9 moles of ethylene oxide). The resultant latex had 51.25% solids, pH of 4.7 and a viscosity of 2.08 Pa.s.

Example 12

The procedure of Example 10 was followed except that monomer phase "A" consisted of 54.50 parts of butyl acrylate, 40.50 parts of methyl methacrylate, 4.00 parts of acrylic acid and 4.00 parts of nonionic surfactant, (a nonylphenol ethoxylate containing 9 moles of ethylene oxide). The resultant latex had 51.72% solids, pH of 5.5 and a viscosity of 1.25 Pa.s.

Comparative Example 1

The procedure of Example 1 was followed, except that no paraffin wax was added to monomer phase "A". The resultant latex had 50.61% solids, pH of 5.1 and viscosity of 0.89 Pa.s.

Comparative Example 2

1.00 part of a 50% solids aqueous dispersion of a paraffin wax having a melting point of 60-63°C was added to 100 parts of the latex of comparative Example 1.

Films of the latices of Example 1, Comparative Example 1 and Comparative Example 2, and the paraffin wax emulsion were examined by Differential Scanning Calorimetry on a Perkin Elmer DSC 4 scanning at 10°C per minute over a range of 0 to 80°C. The enthalpy curve of the latex of Comparative Example 1 showed no characteristics except for a softening point at approximately 10°C. The paraffin wax emulsion showed a typical paraffin wax enthalpy curve with a peak at 65.9°C. The DSC trace of a film of the latex of Comparative Example 2 showed a peak at 66.7°C with an enthalpy figure typical of 1% of wax mixed with a polymer. The DSC curve of the latex of Example 1 showed a wax melt peak, but the enthalpy was reduced to less than 25% of that of the theoretical wax/polymer mix, and the peak temperature was reduced 49.5°C.

The latices of Example 1 and Comparative Example 2 were extracted with cyclohexane, and the extracts analyzed by Gas Liquid Chromatography on a Perkin Elmer 8320 GLC using a high temperature capillary column with non-polar stationary phase. Comparison of the GLC results for the extract of Example 1 with that of Comparative Example 2 showed that 80 to 90% of the wax in the latex of Example 1 is not available for extraction. It would appear from these two pieces of evidence that the polymer latex of Example 1 might have formed a grafted copolymer with the wax.

The hydrophobic character of the latices of the invention was shown by measurement of the contact angle of water droplets on a polymer film, water vapour transmission rates through coated kraft paper and water absorption of coated kraft paper, and these measurements are tabulated in the table.

Polymer films of 10 thou (0.25 mm) wet thickness were cast on microscope slides and allowed to dry at 15 ± 5°C for 7 days. Droplets of deionized water of approximately 0.006 g in weight were dropped from a micrometer syringe at a height of 9 mm above the film, and the image of the droplet projected on a screen. The dimensions of the image were measured, and the contact angle determined from tables of 2 r/h, (where r = radius and h = height of the drop). Contact angles quoted are the average of five measurements.

Polymer latices were applied at a dry coating weight of 10 to 12 gm^{-2} to 150 gm^{-2} virgin kraft paper using a wire wound "Mayer bar" on an automated laboratory R.K. Coater, Model KCC 202. Coated papers were dried at 15 ± 5°C for 3 days. The Water Vapour Transmission Rate (WVTR) was measured at a temperature of 25 ± 0.5°C and 75 ± 2 % relative humidity according to BS 3177:1959, (Method for determining the Permeability to water vapour of flexible sheet materials used for packaging), and is expressed as grams per square meter per day. The "Mayer bar" is described in "Coatings Technology Handbook", Ed. D. Satas, Marcel Dekker 1991, Chapter 10.

The Cobb value was measured according to BS 2644:1980, (Method for Determination of Water Absorption of paper and board), and is the mass of water absorbed by 1 m^2 of the substrate at 15 ± 5°C over 30 minutes, expressed as grams per square meter.

EXAMPLE	CONTACT ANGLE °	WVTR $gm^{-2}day^{-1}$	COBB VALUE gm^{-2}
1	100	45	12.3
2	104	80	2.8
3	103	90	2.0
4	79	69	4.8
5	76	59	10.1
6	104	52	2.4
7	107	56	1.7
8	104	52	25.7
9	109	41	6.6
10	108	62	7.6
11	103	53	13.1
12	104	100	0.2
Comparative 1	67	176	33.8
Comparative 2	100	100	3.6

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for improving the properties of a substrate comprising organic materials of the group consisting essentially of paper, carton stock, board, wood, wood composites, plastic sheets and films comprising the steps of:

a. coating the substrate with a thermoplastic polymer obtained by emulsion or suspension polymerization of a mixture of ethylenically unsaturated monomers comprising:

i) 35-98 parts by weight (calculated on the total amount of monomers in the mixture) of C1-C18 alkyl(meth)acrylate;

ii) 0.05-5 parts of C3-C8 unsaturated carboxylic acid;

iii) 1-60 parts by weight of a vinyl aromatic monomer and which mixture is substantially free from C3-C8 conjugated diolefins,

in the presence of 0.01 to 5 weight % calculated on the monomers of a hydrocarbon wax having a melting point of 40 to 80°C, which wax is incorporated in the polymer during polymerization; and

b. drying the coated substrate in the absence of any crosslinking reaction.

2. The process of Claim 1 in which the amount of hydrocarbon wax is from 0.05 to 5 wt.%, calculated on the total amount of monomers added.

3. The process of Claim 1 in which the hydrocarbon wax is substantially a saturated, aliphatic hydrocarbon.

4. A process for preparing a polymer by an emulsion or suspension technique comprising polymerizing a mixture of monomers comprising:

(1) 35 to 98 parts by weight (calculated on the total amount of monomer in the mixture) of C1-C18 alkyl(meth)acrylate, preferably comprising butyl acrylate and/or 2-ethyl hexyl acrylate;

(2) 0.05 to 5 parts of a C3-C8 unsaturated carboxylic acid;

(3) 1 to 60 parts by weight of a vinyl aromatic monomer from the group comprising styrene and α-methylstyrene; and which mixture is substantially free from C3-C8 conjugated diolefins in the presence of a hydrocarbon wax having a melting point of 25 to 125°C.

5. A process of Claim 4 in which the hydrocarbon wax is introduced in the polymerization mixture in the form of a solid wax dissolved in monomer or in the form of a wax emulsion/dispersion either in monomer or another extender.

6. The process of Claim 4 in which the amount of hydrocarbon wax is from 0.01 to 25%, preferably 0.05 to 5 wt% calculated on monomer.

7. The process of Claim 4 in which the hydrocarbon wax has a melting point between 40 and 80°C.

8. The process of Claim 4 in which the hydrocarbon wax is substantially a saturated, aliphatic hydrocarbon.

9. A process of Claim 4 in which the mixture of monomers comprises (meth)acrylic acid and C1-C18 alkylester thereof.

10. A polymer obtained by the process of Claim 4.

11. A coated substrate produced by the process of claim 1.

Dated this 28th day of July 1997
NATIONAL STARCH AND CHEMICAL INVESTMENT HOLDING CORPORATION and DUSSEK CAMPBELL LTD
By their Patent Attorneys
GRIFFITH HACK
Fellows Institute of Patent
Attorneys of Australia

ABSTRACT OF THE DISCLOSURE

The invention relates to the use of a polymer obtained by emulsion or suspension polymerization of an ethylenically unsaturated monomer or mixture of more than one such a monomer in the presence of a hydrocarbon waxy having a melting point of 25 to 125°C which is incorporated in the polymer during polymerization as a coating material for imparting or improving hydrophobicity and/or moisture vapor resistance of a substrate of the group comprising organic materials and metal. Also the invention provides a process for imparting or improving hydrophobicity and/or moisture vapour resistance of an organic substrate by coating the substrate with a polymer obtained by emulsion or suspension polymerization. Also the invention provides certain polymeric materials which are useful for the above identified purposes.