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[54] **BARRIER COATINGS**  
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**ABSTRACT:** This invention relates to the use of interpolymer latices of ethylene, vinyl chloride and acrylamide with or without small amounts of other monomers, as free films and coatings for fibrous substrates.

## BARRIER COATINGS

This invention relates to aqueous interpolymer latices which are useful in free film applications and for coating fibrous substrates. More particularly this invention is concerned with novel coated fibrous substrates in sheet and roll form in which the substrate may be paper, paperboard, preformed paper containers, fabric or other fibrous substrate like bases wherein the coating is an interpolymer latice of ethylene, vinyl chloride and acrylamide, with or without small quantities of other monomers.

Fibrous substrates such as paper, are widely used in packaging operations. Paper, however, has a very poor resistance to penetration by water vapor, gases, oil, solvents and greases. To improve the water vapor barrier resistance, paper has been coated with a variety of substances. The most common paper coating is wax. While wax coated paper has good water vapor barrier resistance in a smooth or uncreased condition, it has poor resistance after it is creased. Apparently the brittleness of the wax is so great that creasing causes it to fracture and break thereby providing many areas through which water vapor can pass with little or no resistance. Additionally, wax coated paper does not serve to form a hard and scuff resistant surface.

The coating of paper with asphalt has also been tried and although good water vapor barrier resistance is obtained, the coated paper has poor resistance after being creased. Additionally, asphalt is a black, toxic material which limits its application as a paper coating; particularly in the food packaging industry. Furthermore, asphalt coatings are subject to changes in flow properties with a variance in temperature.

Paper has also been coated with a film of polyethylene. The resulting polyethylene coated paper is found to have less resistance to water vapor penetration than wax coated paper when the coat is tested in a flat or smooth uncreased condition. The polyethylene coated paper is found to be a better barrier than the wax coated paper when creased.

To improve oil, solvent and grease resistance, paper has been treated with polyvinylidene chloride. The characteristic brittleness of polyvinylidene chloride causes failures of such coatings with creasing. Attempts to improve this limited flexibility by the use of plasticizers with the polyvinylidene chloride results in decreased efficiency of water and water vapor barrier properties. The poor impact resistance of the polyvinylidene chloride also results in the rupture of the film during high-speed scoring and creasing.

Plasticized polyvinyl chloride polymers are used in paper coating and free film barrier applications. Since the polyvinyl chloride is normally externally plasticized a loss in permanence of the resistance to water, oil, grease and solvents is experienced as a result of the extraction and bleeding of the plasticizer.

In view of the state of the art, it has become highly desirable to discover materials which are not only useful for coating fibrous substrates but are also useful as packaging materials per se as free films and will impart good oil, grease, solvent and water vapor barrier resistance.

It is accordingly an object of this invention to provide a material which will provide improved paper-coating compositions and which may also be used as a free film-packaging medium.

It is a further object of this invention to provide a material which will provide good oil, grease and solvent resistance in addition to improved water vapor barrier properties when used as paper-coating compositions and as a free film-packaging medium.

Other objects and advantages of the invention will be apparent to those skilled in the art from the following detailed description and claims.

In accordance with this invention it has been found that the above and still further objects are achieved by use of an ethylene/vinyl chloride/acrylamide interpolymer of the type hereinafter described.

The interpolymers which are prepared and used as coating compositions according to this invention in aqueous disper-

sion or latex form generally contain from about 5 percent to about 70 percent ethylene, from about 30 percent to about 95 percent vinyl chloride, and from about 0.1 percent to about 10 percent of acrylamide. Part of the acrylamide in the interpolymer may be replaced by polar monomers such as acrylonitrile, acrylamide, N-(lower alkyl)acrylamide and N-(lower alkyl)methacrylamide containing from one to three carbon atoms in said lower alkyl groups, N-methylol acrylamide, N[2-(2-methyl-4-oxopentyl)]acrylamide, acrylic acid, methacrylic acid, and alkali metal and ammonium salts of acrylic and methacrylic acids, maleic acid, fumaric acid, half and complete alkali metal and ammonium salts of maleic and fumaric acid, aconitic acid, itaconic acid, citraconic acid, and alkali metal and ammonium salts thereof, half alkyl esters of maleic, fumaric, itaconic and citraconic acids having from one to six carbon atoms in each alkyl group, acrylyl and methacrylyl esters of hydroxyalkanoic acids having from two to about six carbon atoms in the alkanolic acid moieties, acrylamides and methacrylamides of aminoalkanoic acids having from two to about six carbons in the aminoalkanoic acid, hydroxyethyl and hydroxypropyl esters of acrylic, methacrylic, maleic, and fumaric acids, vinyl esters of alkanolic acids having from one to six carbon atoms such as vinyl acetate, vinyl propionate, and lower alkyl (one to six carbon atoms) sulfonic acid, phenylsulfonic acids, and alkylphenylsulfonic acids and acrylyl and methacrylyl esters of hydroxyalkylsulfonic acids having from one to six carbon atoms in said alkyl moieties, and hydroxyalkylsulfonamides having from one to six carbon atoms in said hydroxyalkyl moieties. The acrylamide generally should constitute at least 50 percent by weight of the third of polar monomer of said interpolymer, and preferably constitutes at least about 80 percent of said polar monomer. Thus the interpolymers as prepared in aqueous dispersed form are at least terpolymers containing ethylene, vinyl chloride, and acrylamide, and may be a quaternary or higher polymers containing one or more of the above exemplified additional polar monomers in small quantities but generally such additional monomers will not be present in the interpolymer in quantities greater than about 2 percent by weight.

It is preferred that the interpolymer contain from about 5 percent to about 70 percent ethylene, 30 percent to about 95 percent vinyl chloride, and from about 1 percent to about 5 percent acrylamide. A specific example of choice, as presently understood, is a terpolymer containing from about 19 to 23 percent ethylene, about 74 to about 78 percent vinyl chloride, and from about 2 to about 4 percent acrylamide.

Although the interpolymers used in the practice of this invention are generally unmodified, the modified interpolymers are included for use in this invention. The interpolymers are particularly amenable to hydrolytic modification by the use of small quantities of a strongly alkaline material such as an alkali metal hydroxide, or a quaternary ammonium hydroxide such as tetramethyl ammonium hydroxide, or by a strong acid such as the mineral acids, e.g., hydrochloric, sulfuric, phosphoric, nitric. The base of acid used preferably has an ionization constant higher than  $10^{-4}$  at 25° C.

The hydrolyzing treatment, performed with an acid or a base need not be performed to the same extent, especially if the interpolymer contains polar monomers in addition to the acrylamide. The aqueous dispersion or polymer latex of the ethylene, vinyl chloride, and acrylamide is generally treated with aqueous base or acid in an amount which is chemically equivalent to up to about 100 percent of the amide equivalent in the interpolymer.

Specific examples of polar monomers which may be used, as described above, to replace part of the acrylamide in the polymers of this invention include acrylonitrile, N-methacrylamide, N-ethylacrylamide, N-propylacrylamide, methacrylamide, acrylic, methacrylic, maleic, fumaric, itaconic, aconitic, and citraconic acids and alkali metal and ammonium salts of such acids, preferably the sodium, potassium or ammonium salts, alkyl esters of such acids, e.g., methyl

acrylate, ethylacrylate, butyl acrylate, methyl methacrylate, butyl methacrylate, ethyl methacrylate, monoethyl maleate, dipropyl fumarate, acrylyl 3-hydroxypropionate, methacrylyl 4-hydroxybutanoate, N-acrylyl acetamide, N-methacrylyl hexamide, 2-hydroxyethyl and 2-hydroxypropyl esters of acrylic, methacrylic, maleic, fumaric, itaconic, aconitic, and citraconic acids, vinyl formate, vinyl acetate, vinyl hexanoate, vinyl and alkyl esters of propanesulfonic acid, vinyl phenylsulfonate, acrylyl and methacrylyl esters of 2-hydroxypropylsulfonic acid, and N-acrylyl and N-methacrylyl 2-hydroxypropanamides.

The ethylene, vinyl chloride, acrylamide interpolymers may be prepared by first mixing ethylene and vinyl chloride in an aqueous medium in the presence of any suitable anionic or nonionic emulsifier and any initiator capable of generating free radicals in the chemical mixture at the chosen reaction temperature and pressure. The acrylamide, preferably in aqueous solution either alone or mixed with the appropriate amounts of other polar monomers, is added to the polymerizing ethylene and vinyl chloride mixture gradually throughout the reaction. Since the acrylamide is very reactive, it cannot all be added at the start of the reaction. It is preferable to delay the addition of the acrylamide until about 40 to 50 percent of the desired conversion of the ethylene and vinyl chloride has been reached, since, in the final application of the latex, the surface of the polymer particles constitutes the locus of adhesion. This produces a shell-core latex in which the polar monomer is concentrated in the outer layers.

The foregoing ethylene/vinyl chloride/acrylamide interpolymers are readily prepared by various means known to the art. The ethylene/vinyl chloride/acrylamide interpolymers used in this invention are preferably prepared by a process which comprises mixing ethylene and vinyl chloride monomers in the presence of an alkaline buffered reduction-oxidation (redox) initiator-catalyst system, water and from about 1 percent to about 8 percent by weight based upon the monomer feed, or from about 4 percent to about 7 percent based upon the polymer product of an anionic or nonionic emulsifying agent having an hydrophilic-lipophilic balance (HLB) value of from about 10 to about 40, and reacting the mixture at a temperature and pressure and for a time sufficient to cause polymerization between the ethylene and vinyl chloride, and then to introduce acrylamide, either alone, or mixed with other monomers in minor amounts in an appropriate diluent such as water into the pressurized polymerizing reaction mixture of the ethylene and vinyl chloride.

The following detailed examples illustrate the preparation of the polymer latices used in this invention. In the polymer preparation examples, all of the polymerizations are carried out in a 3,820 ml. pressure vessel at 30° C. at a rotary stirrer speed of 600 r.p.m.

#### EXAMPLE 1

This example illustrates the preparation of a 21/76/3 ethylene/vinyl chloride/acrylamide terpolymer latex, and the post stabilization of such latex with an emulsifier.

##### REACTION VESSEL INITIAL CHARGE

11.0 g.	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (KPS)
15.0 g.	NaHCO <sub>3</sub>
0.8 g.	Fe(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O
1.5 g.	tetrasodium ethylenediaminetetraacetate (Na <sub>4</sub> EDTA)
1.2 g.	sodium lauryl sulfate (SLS)
H <sub>2</sub> O to make 1,700 ml.	
450 g.	vinyl chloride (VC1)
150 g.	ethylene (E)

The above ingredient mixture was heated to 30° C. with stirring to give a reaction pressure of 850 p.s.i.g. The polymerization was started by adding a 1 M sodium formaldehyde sulfox-

ylate NaHSO<sub>2</sub> · CH<sub>2</sub>O · 2H<sub>2</sub>(SFS)/1.5 M ammonium hydroxide (NH<sub>4</sub>OH) solution to the mixture at a rate of 5.2 ml./hr. at the same time 18 ml./hr. of a 25 percent SLS solution was added and the pressure was kept constant by the addition of pure vinyl chloride as required. After 3 hours had elapsed, a 50 percent solution of acrylamide in water solution was added at 40 ml./hr. The reaction stopped after 5.5 hours and the feed streams were turned off. A total of 1,330 g. of VC1, 95 ml. of the 50 percent acrylamide, 27 ml. of the 1 M SFS/1.5 M NH<sub>4</sub>OH solution, and 92 ml. of the 25 percent SLS solution had been added. The resulting polymer latex was vented out the bottom of the autoclave. A total of about 3,500 g. of the ethylene/vinyl chloride/acrylamide polymer latex was obtained containing 47 percent total solids, and 1.5 percent sodium lauryl sulfate (based on the weight of the polymer). It had a pH of 7.7. The composition of the terpolymer was about 21/76/3 ethylene/vinyl chloride/acrylamide. After addition of 1.5 percent of sodium dodecyl benzene sulfonate or 3 percent tridecyloxy(CH<sub>2</sub>CH<sub>2</sub>)<sub>13</sub>H, the latex was ready for use directly as a barrier coating.

#### EXAMPLE 2

This example illustrates the preparation of the base-modified ethylene/vinyl chloride/acrylamide terpolymer.

Using the same reaction vessel and ingredients as are described in example 1, except that only 10.0 g. of KPS, and only 0.5 g. of SLS was used in the initial ingredient charge. The SFS/NH<sub>4</sub>OH solution was added at the rate of 4 ml./hr. and the SLS solution was added at 8 ml./hr. The polymerization reaction stopped after 5.75 hours with a total of about 1,340 g. of vinyl chloride, 100 ml. of acrylamide solution, 23 ml. of SFS/NH<sub>4</sub>OH solution, and 43 ml. of 25 percent SLS being added. The resulting terpolymer latex was poststabilized by mixing therewith an additional 17 ml. of 25 percent sodium lauryl sulfate (SLS). The stabilized latex was then vented from the bottom of the reaction vessel. There was obtained 3,460 g. of material containing 49 percent total solids, 1 percent of the SLS and essentially the same terpolymer as described in example 1. The particle size of this polymer latex was somewhat larger than that of example 1.

This stabilized ethylene/vinyl chloride/acrylamide terpolymer latex was warmed at 50° C. for 4 to 16 hours after adding 0.4–2.0 g. of sodium hydroxide (added thereto as a 10 percent NaOH in water solution) per kilogram of latex.

#### EXAMPLE 3,

A four monomer component polymer latex was prepared as follows:

A pressure reaction vessel was initially charged with  
 9.0 g. KPS  
 12.0 g. NaHCO<sub>3</sub>  
 0.8 g. Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O  
 1.5 g. Na<sub>4</sub>EDTA  
 0.5 g. SLS  
 H<sub>2</sub>O to make 1,700 ml.  
 575 g. Ethylene  
 470 g. Vinyl Chloride

This mixture was sealed and warmed to 1,550 p.s.i.g. Polymerization was started by pumping into the vessel contents a 1 M SFS/1.5 M NH<sub>4</sub>OH solution at the rate of 4 ml./hr. At the same time 10 ml./hr. of a 25 percent SLS was added. Vinyl chloride sufficient to keep the pressure constant was added throughout the reaction. At the end of 3 hours of polymerization an aqueous solution containing 40 percent acrylamide and 10 percent sodium acrylate was added to the reactor at the rate of 24 ml./hr. After 6 hours, the reaction stopped and a total of 591 g. of vinyl chloride, 52 ml. of 25 percent SLS, 27 ml. of SFS/NH<sub>4</sub>OH and 72 ml. of the acrylamide/solution acrylate solution had been added. Unreacted ethylene and vinyl chloride were vented from the top of the reactor to lower the pressure to about 250 p.s.i.g., and then the latex was taken out through the bottom of the reactor.

There was thus obtained about 3,060 g. of latex containing 43 percent solids, and 1.1 percent sodium lauryl sulfate. The polymer composition was a 21/76/2.3/0.7 ethylene/vinyl chloride/acrylamide/sodium acrylate polymer. It was suitable for use directly as a coating composition for paper and paperboard. The procedure is repeated substituting for the sodium acrylate an equivalent amount of sodium methacrylate. An ethylene/vinyl chloride/acrylamide/sodium methacrylate of substantially the same monomer proportions is obtained.

Interpolymers prepared in a manner analogous to the procedure described in example 1 are shown in table I.

TABLE I

Example No.	VC1 %	Ethylene %	Acrylamide	Latex % Polymer Solids	% SLS
4	74.9	25	0.50	47.3	0.9
5	70.5	27	2.36	45.7	1.79
6	74.0	25	1.48	48.1	1.40
7	72.2	27	0.65	47.7	2.06

## SLS—Sodium lauryl sulfate

The interpolymers prepared in examples 4 through 7 are modified with sodium hydroxide to obtain hydrolyzed polymer latices having the following solids content:

Example No.	Example No. of Table I	Latex % Polymer Solids
8	4	46.1
9	5	44.2
10	6	46.9

## EXAMPLES 11-16

Following the procedure of example 3 an equivalent amount of the component tabulated below is substituted for the sodium acrylate to obtain a latex polymer described below composed of substantially the same proportions as the product of example 3.

11. Component =	Hydroxyethyl acrylate
Polymer =	Ethylene/vinyl chloride/acrylamide/hydroxyethylacrylate
12. Component =	N-isopropylacrylamide
Polymer =	Ethylene/vinyl chloride/acrylamide/N-isopropylacrylamide
13. Component =	N-ethylmethacrylamide
Polymer =	Ethylene/vinyl chloride/acrylamide N-ethylmethacrylamide
14. Component =	A diammonium salt of itaconic acid
Polymer =	Ethylene/vinyl chloride/acrylamide/diammonium itaconate
15. Component =	Monobutyl acid maleate
Polymer =	Ethylene/vinyl chloride/acrylamide/monobutyl acid maleate
16. Component =	N-methacrylylpropionamide
Polymer =	Ethylene/vinyl chloride/acrylamide/N-methacrylylpropionamide

The fibrous substrates such as paper which may be coated according to this invention with an ethylene/vinyl chloride/acrylamide interpolymer latex to produce a product of enhanced barrier characteristics may contain from about

0.5 to 90 pounds of ethylene/vinyl chloride/acrylamide interpolymer on one side per ream. (A ream is 3,000 sq. ft. and equals 500 sheets, 24 inches by 36 inches.) Generally, however, about 1 to 20 pounds of ethylene/vinyl chloride/acrylamide interpolymer is adequate while 1 to 4 pounds is all that is needed for many purposes.

The fibrous substrates to which the compositions are applied in carrying out the present invention include papers of all types, such as bond-writing paper, fibrous paperboards such as cardboard, chipboard, carton stock, and the like, wrapping papers or boards, or liners for containers intended for the packaging of foods, greases, chewing gum, soap, soap powders, cosmetics, calking compounds, etc. The coated papers may also be used as wallpapers, papers for lining drawers and shelves, especially in linen closets, kitchen cabinets and the like, and the coated paper or paperboards may be used as book covers or book pages.

The coatings may be applied to building construction papers and boards, such as the facing paper on plasterboard. It may be used as a release coating on a paper to be used as a liner in a concrete molding form of adapted to be used for covering freshly laid concrete roads.

The processes for applying the interpolymer coating to the fibrous substrate are well known in the art. Such techniques include spraying, roller coating, air knife coating, trailing blade coating, curtain coater and use of a Mayer rod (machine).

The following examples illustrate the advantageous and unexpected properties which are achieved by the use of the ethylene/vinyl chloride/acrylamide latexes of the present invention in coating fibrous substrates and as free films, but it is not intended that this invention be limited by or to the examples.

The ethylene/vinyl chloride/acrylamide interpolymer latexes are utilized as barrier coatings for fibrous substrates according to the following procedure.

The ethylene/vinyl chloride/acrylamide latex is applied to the felt side of the fibrous substrate by means of a wire wound rod. Coating rod numbers 6, 18 and 28 may be utilized in applying the film. A No. 6 rod has a smaller wire diameter and more winds for a given rod length which deposits a light continuous wet film whereas the No. 28 rod has a larger wire diameter and fewer winds per inch which deposits a much heavier film.

The fibrous substrate is mounted on a flat glass surface, the wire wound rod is placed in the draw-down bar which is positioned at the top of the substrate, latex is then poured across the substrate just in front of the draw-down bar, the draw-down bar is pulled at a uniform speed across the fibrous substrate leaving behind a uniformly even wet latex film. All coated samples are exposed to 120° C. for 2 minutes, then calendered.

The coatings are then tested for oil resistance. The test procedure is hereinafter described and the results are listed in table II. Samples are conditioned according to TAPPI T402m-49 before testing. The paper base stock used in the testing hereinafter described is 50 lb. bleached kraft.

**Oil Resistance—Creased box test**—A 6 inches by 6 inches coated one side specimen blank is folded diagonally from corner to corner, each fold is subjected to a 5 lb. pressure. The blank is further folded 1 inch from each edge and then made up into a 4 inch by 4 inch box having 1 inch sidewalls with the coated surface inside. All creases, except those made by the sidewall folds converge as an apex in the center of the box bottom. Fifty cubic centimeters No. 10 SAE oil is poured into the box and the time required to penetrate the creased areas is noted.

TABLE II.—OIL BARRIER PROPERTIES OF ETHYLENE/VINYL CHLORIDE INTERPOLYMERS

Coating	Percent solids	Coating weights lbs./1000 ft. <sup>2</sup>	Test sample	Time, min.	Type of failure
Polyvinylidene chloride <sup>1</sup> .....	60	4.35	.....	13	11 penetrations along creases, 20 penetrations in uncreased areas
Latex of Example 4.....	47.3	3.97	.....	14	1 penetration in crease, 25 penetrations in uncreased areas.

TABLE II.—OIL BARRIER PROPERTIES OF ETHYLENE/VINYL CHLORIDE INTERPOLYMERS

Coating	Percent solids	Coating weights lbs./1000 ft. <sup>2</sup>	Test sample	Time, min.	Type of failure
Latex of Example 5.....	47.5	3.44	-----	180	1 penetration occurred in corner after 70 minutes. Remainder of sample clear after 3 hours.
Latex of Example 6.....	48.1	3.64	-----	180	1 penetration occurred in corner after 74 minutes. Remainder of sample clear after 3 hours.
Latex of Example 7.....	47.7	3.52	-----	180	1 penetration occurred in side crease after 72 minutes. Remainder of sample clear after 3 hours.
Polyvinylidene chloride <sup>1</sup> .....	60	5.8	{	1	15 9 penetrations in crease. 25 penetrations in increased areas.
				2	17 13 penetrations in crease. 20 penetrations in increased areas.
Latex of Example 8.....	46.1	4.3	{	1	16 1 penetration in crease, 4 penetrations in body.
				2	16 2 penetrations in crease, 6 penetrations in body.
Latex of Example 9.....	44.2	3.5	{	1	11 2 penetrations in crease, 6 penetrations in body.
				2	12 1 penetration in crease, 6 penetrations in body.
Latex of Example 10.....	49.9	4.2	{	1	38 No crease failure, 3 penetrations in body.
				2	39 No crease failure, 3 penetrations in body.

<sup>1</sup> Daran 220—Dewey and Almy.

NOTE.—All coatings—double coat, one side No. 6 rod.

Replacement of the latex of example 5 with latices of examples 11 through 16 produces substantially the same result. Fibrous paperboards such as chipboard, cardboard and carton stock exhibit the excellent properties as obtained in table II when coated with the latices of examples 5 through 10. Coated papers provided by the present invention have utility for many purposes which will be obvious to those skilled in the art. In particular, the coated papers may be used to wrap food products where it is desired to prevent the transmission of moisture from the atmosphere to the packaged product. The coated papers are easily heat sealed and hold liquids well. As a result, such coated papers can be used in the manufacture of paper drinking cups and the like. Continuous films are easily formed at a lower application weight than required with the use of prior art materials.

The films exhibit better oil draining and are not wet by oil as is found with the use of polyvinylidene chloride.

Although the interpolymers of this invention are particularly useful as coatings for fibrous substrates, they are also useful as packaging materials per se as free films. The free films may be prepared by casting a layer of the latex on a glass surface, drying and then removing the film. Free film may also be prepared by coagulating the polymer from the latex, washing and then extruding the film by methods known to the art.

The following examples in table III illustrate the advantageous and unexpected properties which are achieved by the use of the ethylene/vinyl chloride/acrylamide latexes as free films. The interpolymers as free films show excellent low rates of moisture vapor transmission calculated on a film thickness of 1 mil.

The test methods used to determine the physical properties of the free film of ethylene/vinyl chloride/acrylamide are listed below with explanatory notes.

Moisture-Vapor Transmission Rate—A.S.T.M. 3-988 (tropical atmosphere) Reported as grams H<sub>2</sub>O/100 sq. inches/24 hrs. at 100° F. and 90 percent relative humidity.

Low-temperature Flexibility—Low-temperature flexibility is one of the most important properties of elastomeric vinyl compositions. While many plasticizers will produce flexible compositions at room temperature, the flexibility of these compositions at low temperature may vary considerably; i.e., plasticized polyvinyl chloride compositions that are flexible at room temperature often become very brittle and useless at lower temperatures. Low-temperature flexibility tests employed herein are according to the Clash-Berg method. This method determines the torsional flexibility of a plastic at various temperatures. The temperatures at which the vinyl composition exhibits an arbitrarily established minimum flexibility is defined as the low-temperature flexibility of the composition. This value may also be defined as the lower temperature limit of the plasticized composition's usefulness as an elastomer.

The results set forth in table III show that the internally plasticized latices exhibit superior MVTR values than corresponding externally plasticized polyvinyl chloride system at the same modulus (low temperature flexibility).

TABLE III.—PROPERTIES OF FREE FILMS OF ETHYLENE/VINYL CHLORIDE INTERPOLYMERS

Film composition	Low temperature flexibility (T) <sup>1</sup> ° C.	MVTR <sup>1</sup>
25 Latex of Example 1.....	-19	2.7
Polyvinyl chloride plasticized with 44 phr. di-2-ethylhexyl phthalate.....	-19	11.0
Latex prepared in accordance with the procedure of Example 1 wherein the latex is 26% ethylene/71% vinyl chloride and 3% acrylamide.....	-30	4.6
30 Polyvinyl chloride plasticized with 55 phr. di-2-ethylhexyl phthalate.....	-30	14.0

<sup>1</sup> Moisture Vapor Transmission Rate—g. H<sub>2</sub>O/100 sq. in./24 hrs. (1 mil basis) 100° F. plus 90% RH.

35 The interpolymers of this invention may also be used as one component of a series of barrier coatings applied in tandem. For example, the interpolymer is applied by a trailing blade. An additional coating of polyvinyl acetate or polyvinyl alcohol and the like is then applied by an air knife coating technique. The order in which the coatings are applied may also be reversed. This multiple coating technique provides additional protection in respect to barrier properties.

40 The coating compositions may be modified by addition of polyvinyl resins such as polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polyvinyl alcohol and the like. The type and amount of polyvinyl resins used to modify the ethylene/vinyl chloride/acrylamide latex coating compositions will be determined by the properties desired in each specific application. These modified coating compositions must necessarily still provide the essential protective properties such as good oil, water and gas resistance.

45 While this invention has been described with respect to certain embodiments, it is not so limited and it is to be understood that variations and modifications thereof may be made without departing from the spirit or scope of this invention.

50 The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Coated substrate having improved oil, grease, water and water vapor resistance, comprising a fibrous substrate having at least one surface thereof coated with a barrier film deposited from a latex wherein said barrier film consists essentially of an interpolymer selected from the group consisting of (a) an interpolymer containing from about 5 to about 70 percent ethylene, from about 30 to about 95 percent vinyl chloride, and from about 0.1 to about 10 percent of at least one other polar monomer including at least about 0.1 percent to about 10 percent of acrylamide, any remainder of said polar monomer content being selected from the group consisting of acrylonitrile; methacrylamide; N-(alkyl) acrylamide and N-(alkyl) methacrylamide having from one to three carbon atoms in each alkyl group; N-methylol acrylamide; N-[2-(2-methyl-4-oxopentyl)] acrylamide; acrylic and methacrylic acid and the alkali metal and ammonium salts thereof; maleic and fumaric acids; half and complete alkali metal and ammonium salts of maleic and fumaric acids; itaconic, citraconic

and aconitic acids and the alkali metal and ammonium salts thereof; half alkyl esters of maleic, fumaric, itaconic and citraconic acids having from one to six carbon atoms in each alkyl group; acrylyl and methacrylyl esters of hydroxy alkanolic acids having from two to six carbon atoms in said alkanolic acid moieties; acrylamide and methacrylamides of aminoalkanoic acids having from two to six carbon atoms in each aminoalkanoic acid moiety; hydroxyethyl and hydroxypropyl esters of acrylic, methacrylic, maleic and fumaric acids; vinyl esters of alkanolic acids having from one to six carbon atoms; alkyl sulfonic acids having from one to six carbon atoms; phenyl sulfonic acids; alkyl phenyl sulfonic acids having from one to six carbon atoms in each alkyl; acrylyl and methacrylyl esters of hydroxy alkyl sulfonic acids having from one to six carbon atoms in each alkyl, and hydroxy alkyl sulfonamides having from one to six carbon atoms in each hydroxy alkyl, and (b) interpolymers of the type described in (a) treated with an acid or a base having an ionization constant higher than about  $10^{-4}$  in amounts equivalent to up to about 100 percent of the amide content of said interpolymer.

2. Substrate of claim 1 wherein the polar monomer content is a combination of acrylamide and N-methylol acrylamide.

3. Coated substrate of claim 1 wherein the interpolymer is a terpolymer containing about 19 to 23 percent ethylene, about 74 to 78 percent vinyl chloride and about 2 to 4 percent acrylamide.

4. Coated substrate of claim 1 wherein the fibrous substrate is paper and the interpolymer is a terpolymer containing about 19 to 23 percent ethylene, about 74 to 78 percent vinyl chloride and about 2 to 4 percent acrylamide.

5. Coated substrate of claim 1 wherein the fibrous substrate is paper, the interpolymer is a terpolymer containing about 19

to 23 percent ethylene, 74 to 78 percent vinyl chloride and about 2 to 4 percent acrylamide and the fibrous substrate is coated on at least one side with from about 1 to 4 pounds of interpolymer per each side coated per each 3,000 square feet of paper.

6. Coated substrate of claim 1 wherein the other polar monomer content of the interpolymer is acrylamide in combination with methacrylamide.

7. A fibrous substrate in accordance with claim 1 wherein the interpolymer is a terpolymer containing from about 5 to 70 percent ethylene, from about 30 to 95 percent vinyl chloride and from about 0.1 to 10 percent acrylamide.

8. A fibrous substrate in accordance with claim 1 wherein the substrate is coated with about 1 to about 20 pounds of interpolymer on one side per each 3,000 square feet of substrate.

9. A fibrous substrate in accordance with claim 1 wherein the substrate is coated with about 1 to about 4 pounds of interpolymer on one side per each 3,000 square feet of paper.

10. A fibrous substrate as described in claim 1 wherein the interpolymer is a terpolymer containing about 19 to 23 percent ethylene, about 74 to 78 percent vinyl chloride, and from about 2 to 4 percent acrylamide in aqueous dispersion treated with sodium hydroxide in an amount stoichiometrically equivalent to about 10 to 100 percent of the amide group content of said terpolymer.

11. A coated fibrous substrate in accordance with claim 1 wherein the substrate is paper.

12. A coated fibrous substrate in accordance with claim 1 wherein the substrate is paperboard.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,632,424 Dated January 4, 1972

Inventor(s) Paul R. Graham and August F. Ottinger

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In column 3, in Example I, line 65 should read  
"0.8g.  $\text{Fe}(\text{No}_3)_3 \cdot 9\text{H}_2\text{O}$ ".

In column 4, line 19, the formula should read  
" $(\text{CH}_2\text{CH}_2\text{O})_{15}\text{H}$ ".

In column 7, in Table II, the Percent Solids for the  
Latex of Example 10 should be "46.9" instead of 49.9.

Signed and sealed this 1st day of August 1972.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents