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2,923,646

RELEASE-COATINGS, FILM- AND SHEET-CASTING BASES FOR SUBSTRATES

Arthur D. Jordan, Jr., Moorestown, N.J., assignor to Rohm & Haas Company, Philadelphia, Pa., a corporation of Delaware

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This invention relates to the preparation of coatings which are particularly adapted to be employed in the formation of what may be termed "release-coatings," which serve as casting bases on which a film-forming or sheet-forming composition may be cast and from which film or sheet can be readily removed by a simple stripping operation after the solidification thereof on such casting base. The invention is also concerned with methods of producing pellicular articles by casting film-forming compositions upon a base carrying a release-coating of the present invention.

This application is a continuation-in-part of my co-pending application Serial No. 633,840, filed January 14, 1957.

It is known to form films, sheets, and other pellicular articles by casting a solution containing a film-forming material, an aqueous dispersion containing a film-forming material, an organosol containing a film-forming material, or a molten film-forming material upon a substrate from which the pellicule can be removed by stripping. For this purpose, the substrate may be a polished metal surface such as a highly polished stainless steel or other metal surface which is resistant to corrosion by the material being case. It is also known to use such materials as cellophane (regenerated cellulose film), or polyethylene sheets or films as casting bases for certain materials which do not tend to adhere to such materials. There have also been various proposals to employ coated papers or coated paperboards for the purpose of providing a less expensive and more economical film and sheet-forming operation. However, the release-coatings heretofore employed on such bases generally result in imparting a rather dull surface on the face of the film or sheet which was formed in contact with the release-coatings.

It has now been discovered that release-coatings can be prepared from certain compositions as herein defined; and that either highly glossy, smooth surfaces or dull surfaces can be obtained on the face of the films and sheets formed in contact with such release-coatings. Thus, the present invention provides release coatings which may be applied to any type of substrate whether of a rigid material such as any metal which is either polished or unpolished, or of flexible materials such as those of plastic materials including cellophane and polyethylene, or on such porous substrates as leather, textiles, papers, and paperboards, and which are capable of producing films and sheets cast thereon whose surfaces formed in contact with the release-coatings are either dull or of highly glossy character.

The release-coatings of the present invention may be obtained from an aqueous coating composition in the form of an aqueous dispersion of (a) a water-insoluble linear addition polymer having a T_1 as defined hereinbelow of not above 30°C ., such as from about -50°C . to $+30^\circ\text{C}$., (b) certain salts of linear copolymers having low molecular weight, and (c) zinc oxide.

The T_1 value referred to is the transition temperature

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or inflection temperature which is found by plotting the modulus of rigidity against temperature. A convenient method for determining modulus of rigidity and transition temperature is described by I. Williamson, British Plastics, 23, 87-90, 102 (September 1950). The T_1 value here used is that determined at 300 kg./cm.^2 .

The proportions of the copolymer salt (component (b)) and the other polymer (component (a)) may generally be from 10 to 35 parts of the former to 90 to 65 parts of the latter, depending upon the particular components mixed. The amount of zinc oxide may be from about 5 to 40%, and is preferably about 10 to 20% on the weight of the total polymer solids of components (a) and (b) when a glossy surface is desired on the stripped film. The use of higher proportions, such as 30 to 40% produces a dull surface on the stripped film.

The first-mentioned polymer (component (a)) may contain a small proportion of hydrophilic groups up to about 2.5% by weight thereof in the polymer molecule, but it is preferred that the copolymer consist entirely of hydrophobic polymer units. The aqueous dispersion of this water-insoluble linear addition polymer may be formed by conventional emulsion polymerization or copolymerization procedures, such as are described in United States Patent 2,790,736, column 4, lines 8 to 74 (incorporated herein by reference), from a single monomer or from a mixture of monomers which form homopolymers or copolymers having a T_1 which is not above 30°C . Monomers which form sufficiently soft homopolymers include the acrylates of primary and secondary alcohols, such as those having from 1 to 18 carbon atoms. Other monomers which form sufficiently soft homopolymers include the methacrylates of alcohols having 5 to 18 carbon atoms. Homopolymers of any of these monomers or copolymers of a mixture of two or more of these monomers may be employed for the purpose of producing water-insoluble linear addition polymers for the aqueous coating compositions of the present invention. Preferably, however, the methyl, ethyl, propyl, or butyl acrylates are employed. Any of these monomers which form soft polymers may be copolymerized with such hardening comonomers as the lower alkyl methacrylates in which the alkyl group may have from 1 to 4 carbons, namely the methyl, ethyl, propyl, and butyl methacrylates, styrene, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl chloride, vinylidene chloride, and the like. The amount of hard comonomer that may be copolymerized with one of the soft monomers above depends upon the particular hard and soft comonomers to be copolymerized. The following list gives, for several typical copolymer systems, approximately the maximum amount of a particular hard comonomer that may be used with a particular soft comonomer to provide copolymers which have T_1 values of about 10°C . and lower. They are accordingly within the preferred range cited above and considerably more of the hard comonomer could be used to provide copolymers which are still within the maximum scope of the invention as defined by the upper T_1 limit of 30°C . For example, a copolymer of 64% by weight of ethyl acrylate and 36% of methyl methacrylate has a T_1 value of about 20°C ..

Methyl acrylate 75, ethyl acrylate 25,

Ethyl acrylate 76, methyl methacrylate 24,

Ethyl acrylate 78, styrene 22,

Ethyl acrylate 78, acrylonitrile 22,

Ethyl acrylate 20, butyl methacrylate 80,

n-Propyl acrylate 62, methyl methacrylate 38,

n-Propyl acrylate 72, acrylonitrile 28,

Butyl acrylate 58, methyl methacrylate 42,

Butyl acrylate 68, acrylonitrile 32,

Butyl acrylate 10, butyl methacrylate 90,

Butyl acrylate 57, styrene 43.

Copolymers of 35 to 65% by weight of butadiene with 65 to 35% respectively by weight of acrylonitrile or styrene are also useful copolymers having T_g values between -50°C . and $+30^\circ\text{C}$.

The emulsifiers or dispersing agents that may be used for preparing the monomeric emulsions before polymerization or dispersions of the polymer after polymerization may be anionic or non-ionic or a mixture of non-ionic type with an agent of anionic type. The amount of emulsifier or dispersing agent may depend upon the particular monomeric system, but in general is from $\frac{1}{2}$ to 3% by weight of the monomers employed.

Suitable anionic dispersing agents include the higher fatty alcohol sulfates, such as sodium lauryl sulfate, alkylaryl sulfonates, e.g. sodium or potassium isopropylbenzene sulfonates or isopropyl naphthalene sulfonates, alkali metal higher aryl sulfosuccinates, e.g. sodium octyl sulfosuccinate, sodium N-methyl-N-palmitoyltaurate, sodium oleyl isothionate, alkali metal salts of alkylaryl-polyethoxyethanol sulfates or sulfonates, e.g. sodium t-octylphenoxypolyethoxyethyl sulfate having 1 to 5 oxyethylene units.

Suitable non-ionic dispersing agents include the following: alkylphenoxypolyethoxyethanols having alkyl groups of about 7 to 18 carbon atoms and 6 to 60 or more oxyethylene units, such as heptylphenoxypolyethoxyethanols, octylphenoxypolyethoxyethanols, methyl-octylphenoxypolyethoxyethanols, nonylphenoxypolyethoxyethanols, dodecylphenoxypolyethoxyethanols, and the like; polyethoxyethanol derivatives of methylene-linked alkyl phenols; sulfur-containing agents such as those made by condensing 6 to 60 or more moles of ethylene oxide with nonyl, dodecyl, tetradecyl, t-dodecyl, and the like mercaptans or with alkylthiophenols having alkyl groups of 6 to 15 carbon atoms; ethylene oxide derivatives of long-chained carboxylic acids, such as lauric, myristic, palmitic, oleic, and the like or mixtures of acids such as found in tall oil containing 6 to 60 oxyethylene units per molecule; analogous ethylene oxide condensates of long-chained alcohols, such as octyl, decyl, lauryl, or cetyl alcohols, ethylene oxide derivatives of etherified or esterified polyhydroxy compounds having a hydrophobic hydrocarbon chain, such as sorbitan monostearate containing 6 to 60 oxyethylene units; etc.; also ethylene oxide condensates of long-chain or branched-chain amines, such as dodecylamine, hexadecylamine, and octadecylamine, containing 6 to 60 oxyethylene groups, block copolymers of ethylene oxide and propylene oxide comprising a hydrophobic propylene oxide section combined with one or more hydrophilic ethylene oxide sections.

Instead of using one of the anionic or non-ionic emulsifiers mentioned, the copolymer salt (component (b)) may be employed as the emulsifier for the monomers in the emulsion copolymerization to form the aqueous dispersion of the water-insoluble copolymer (component (a)), or it may be used as a dispersing agent for dispersing a finely divided polymer or copolymer (component (a)) to form the aqueous dispersion thereof.

If the copolymer salt is used as the emulsifying or dispersing agent in the preparation of the aqueous dispersion of component (a), the amount used may be just sufficient to effect the emulsifying or dispersing actions required, in which event additional copolymer salt (component (b)) is added later to provide the proper relative proportions between components (a) and (b) as defined hereinabove. On the other hand, the full amount of the copolymer salt needed to form the proper proportion thereof in the final aqueous dispersion may be initially introduced to serve as the emulsifying or dispersing agent.

When the aqueous dispersion of the water-insoluble linear addition polymer (component (a)) is formed by means of one of the other emulsifying agents, it is merely necessary to add to the aqueous dispersion of component (a), thereby obtained, the proper proportion of the

copolymer salt. The product is an essentially stable dispersion which is relatively non-corrosive since it contains no strongly acid material, such as an acidic catalyst, commonly used in thermosetting aminoplast compositions. The concentration may be from 5 to 70% solids.

Component (b) is an ammonium salt of a low molecular weight copolymer selected from the group consisting of (1) copolymers of 20 to 30% by weight of methacrylic acid with 80 to 70% respectively of methyl methacrylate having molecular weights from about 500 up to about 35,000, (2) copolymers of maleic anhydride with styrene in approximately 1 to 1 molar ratio having molecular weights from about 500 to 100,000, and (3) copolymers of maleic anhydride with a branched-chain hydrocarbon selected from the group consisting of olefines and unsaturated terpenes having 4 to 10 carbon atoms such copolymers having an average molecular weight of about 500 to 5,000.

When component (b) is an ammonium salt of the methacrylic acid copolymers, it may be the simple ammonium salt or a complex zinc ammonium salt obtained in the manner hereinafter described. The methacrylic acid copolymers of low molecular weight within the range suitable for the present invention may be identified in terms of their viscosities in the form of their simple neutral ammonium salt at a concentration of 22% polymer solids in water. These viscosities should be from 2 to 30 poises. It is essential that the methacrylic acid copolymers do not contain an amount of methacrylic acid salt units in excess of 30% by weight since the release-coatings obtained from the mixed polymer compositions using such salts become noticeably and objectionally water-sensitive. On the other hand, the use of methacrylic acid copolymers containing less than 20% methacrylic acid salt units have the disadvantage of excessive viscosity and accompanying difficulties in the preparation of the release-coatings. These methacrylic acid copolymer salts may be obtained by naturalization with ammonium hydroxide to a pH of about 6.5 to 10 of an aqueous emulsion copolymer dispersion obtained by the emulsion copolymerization in the presence of about 3 to 5%, based on the weight of monomers, of a chain-transfer agent of a mixture of 20 to 30% by weight of methacrylic acid and 70 to 80% of methyl methacrylate.

Except for the inclusion of about 3 to 5% by weight, based on the weight of monomers, of a chain-transfer agent, the copolymer dispersion may be made by any of the conventional emulsion polymerization procedures. For example, the polymerization procedures disclosed in the passage of McLaughlin et al., United States Patent 2,790,736, column 4, lines 8 to 74, may be employed provided the proportion of a chain-transfer agent or chain regulator just specified above be included within the polymerization mixture in addition to the other ingredients. The passage of that patent just referred to is incorporated herein by reference. The chain-transfer agents which serve to reduce the molecular weight of the polymer obtained by the emulsion polymerization procedure in proportion to the amount of chain-transfer agents used may be any one of the following: long-chain alkyl mercaptans, e.g., t-dodecyl mercaptan, isopropanol, isobutanol, long-chain alcohols, e.g., lauryl alcohol, t-octyl alcohol, CCl_4 , C_2Cl_4 , and CBrCl_3 .

The styrene-maleic anhydride copolymers may be prepared by the process disclosed in Rowland United States Patent 2,606,891. The proportion of chain regulator may be from 1 to 5% or more as disclosed in the Rowland patent. Besides the use of the mercaptans listed in the Rowland patent, there may be employed instead any of the chain-transfer agents mentioned hereinabove for use in making the methacrylic acid copolymers.

A third class of copolymer salts are those that may be obtained by copolymerization of maleic anhydride with

olefines or terpenes containing 4 to 10 carbon atoms including isobutylene, isoamylene, branched-chain hexenes, diisobutylene of the formula



tripropylenes including branched-chain types like $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}=\text{CH}_2$, and the terpenes may be dipentene, limonene, terpineol, and dicyclopentadiene. The copolymerization of maleic anhydride with these olefines and terpenes usually results in the production of low molecular weight polymers so that, in general, it is unnecessary to employ chain-transfer agents in order to produce copolymers having the molecular weight range desirable for the compositions of the present invention. These copolymers may be prepared by the procedure described in Hanford United States Patent 2,378,629 and the procedures disclosed therein are incorporated herein by reference. In general, their preparation may be summarized as being a bulk polymerization or solution polymerization in an organic solvent such as xylene or dioxane in the presence of a free radical initiator such as benzoyl peroxide, lauroyl peroxide, cumene hydroperoxide, t-butyl perbenzoate. The usual procedures for isolating the copolymer may be employed such as removal of the solvent and monomer by distillation or separation of the copolymer, when precipitated, by filtration.

As stated before, the simple ammonium or complex zinc ammonium salts of the various copolymers may be employed. In the case of maleic acid copolymers either with styrene, the olefines, or the terpenes, neutralization with ammonia at room temperature up to 50° to 70° C. produces both ammonium salt groups and amide groups in proportions corresponding substantially to the proportions in which such groups are present in the half-salt of the half-amide of the copolymer. Simple ammonium salts of the maleic anhydride copolymers may also be used, and these salts are obtained by neutralization with ammonium hydroxide at elevated temperatures above 70° C.

Both the simple ammonium salts and the maleamic acid salts such as those of the "half-salt of the half-amide" type can be converted into a complex zinc ammonium type of salt in a manner described hereinafter; and it is to be understood that when reference is made to an ammonium salt of any of the copolymers herein described; this is intended to embrace the simple ammonium salt, the maleamic acid salt, as well as the complex zinc ammonium salt whether or not it is formed from a simple ammonium salt or a maleamic acid salt.

The complex zinc ammonium salt may be obtained from the ammonium salts of the maleic acid copolymers or from the simple ammonium or maleamic acid salts of the maleic anhydride copolymers by adding ammonium hydroxide to a solution of zinc acetate or other water-soluble zinc salt, thereby initially precipitating zinc hydroxide, which is redissolved by the addition of more ammonium hydroxide, thereby producing a solution of the zinc ammonium acetate or other complex zinc ammonium salt which is then added to the aqueous dispersion of the ammonium salt of the copolymer. The complex zinc ammonium salt of the copolymer has the advantage that it produces a final coating having even greater resistance to water than coatings formed from the simple ammonium or amine salts thereof. The latter coatings, however, have good water-resistance which is adequate for most purposes. Generally, the simple ammonium copolymer salts are preferred because of their inexpensiveness.

Finely divided zinc oxide of 1 to 100 micron size, preferably of pigment grade, such as not over 40 to 50 micron size, may be suspended in the aqueous dispersions of the two polymers (Components (a) and (b)), especially when the simple ammonium salt of component (b) is used. It serves to cross-link the carboxyl-containing polymers on

drying, during which the ammonia is apparently replaced by the zinc ion.

The composition may be applied to the substrate to be coated in any suitable manner, such as by a knife coater or by dipping, roller-coating, spraying, brushing or the like. After application, it is merely necessary to pass the coated substrate, such as the paper, through the normal drying equipment. The dispersed polymeric materials coalesce during the drying to form a clear continuous film, which is highly glossy and resistant to water, to grease, and to blocking. The coating on the substrate obtained from the composition is essentially a mixture of the several components described hereinabove except that the copolymer salt groups are substantially converted into amide and/or imide form and zinc salt form as the result of the volatilization of ammonia and cross-linking with the zinc oxide with or without that of any complex zinc ammonium salt used.

The use of zinc oxide has the remarkable characteristic of increasing the temperature at which blocking occurs to a point above the charring temperature of paper which occurs at about 180° C. The coating becomes completely integral in the sense that the usual solvents that remove the emulsifiers used in making the emulsion copolymers (component (a)) from coatings obtained therefrom in normal fashion and even from the other systems of the present invention show little or no removal of such emulsifiers from the "integral" coatings made with the systems of the present invention using zinc oxide in the proportions above. The coatings obtained with zinc oxide are especially valuable because of their high block-resistance and resistance to solvents and plasticizers. They are, accordingly, useful as film-and sheet-casting bases. Thus paper or other substrate carrying such a coating can be formed in a continuous band and a film-forming solution or dispersion in organic solvents or plasticizers of a vinyl or acrylic polymer may be applied to the coated face of the base, dried, and fused at elevated temperatures, such as up to 180° C. or more. The cooled casting can then be stripped and a glossy face is obtained on the side of the cast film or sheet which had previously been in contact with the casting support when zinc oxide content is about 5 to 20% as stated hereinbefore. Previously used organosol-release coatings for paper and like bases have generally produced dull surfaces on the face of the cast film which had been in contact with the release-coatings or they have had the disadvantage of being water-sensitive or water-soluble. The coatings of the present invention are insensitive to moisture and grease-resistant.

As indicated above, the coating composition formed of the aqueous dispersion of components (a), (b), and (c) in the proportions defined hereinabove may be applied to any substrate either of flexible or rigid character, such as of metal, wood, glass, cement, concrete, or stone whether smooth and polished or unpolished. It may be applied to fibrous and non-fibrous substrates including those of textiles and various plastic materials such as films and sheets of cellophane, polyethylene, nylon, especially that of the polyamide type, polyethyleneglycolterephthalate, and so on.

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 so forth, 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 plaster-board. It may be used as a release-coating on a paper

to be used as a liner in a concrete molding form or adapted to be used for covering freshly-laid concrete roads.

The release-coatings of the present invention may be employed on the surface of the backing strip, made either of paper or Holland cloth, for supporting the adhesive-coated face of a pressure-sensitive tape that is to be stripped therefrom. Thus, this release-coating may be employed as a protective interlayer between the strippable backing or facing and the adhesive surface of various types of pressure-sensitive adhesive tapes including electrical tapes and so on. This release-coating may also be used in strippable films and papers of the photographic arts.

For many of these purposes, the non-blocking and mar-resistant characteristics of the coated products are quite important. An important advantage is also the fact that no high temperatures are required, nor is any acid catalyst required to convert the coated films into water-insoluble or non-blocking coatings. The use of the aqueous dispersions also avoids the danger of fire and the toxic effects on operators. It requires no equipment for solvent recovery.

In the following examples, which are illustrative of the present invention, the parts given are by weight unless otherwise indicated. The heat-seal temperature referred to is the temperature at which two coated sheets first begin to show traces of sticking together sufficiently to mar the coating upon separation of the sheets.

Example 1

(a) An aqueous dispersion is prepared containing 100 parts of the ammonium salt of a copolymer of about 87% ethyl acrylate, 10.5% methyl methacrylate, and 2.5% itaconic acid in 116 parts of water; 28 parts of zinc oxide (passing a 325 mesh screen) are dispersed in 28 parts of water with 0.06 part of *t*-octylphenoxypolyethoxyethanol containing about 12 oxyethylene units, and 0.2 part of the ammonium salt of the approximately 1:1 mole ratio copolymer of maleamic acid/diisobutylene copolymer. The zinc oxide dispersion is mixed into the copolymer dispersion with agitation. Then a solution in 142 parts of water of 40 parts of the ammonium salt of the approximately 1:1 mole ratio copolymer of maleamic acid/diisobutylene copolymer is mixed with agitation into the zinc oxide/copolymer dispersion. A chipboard coated with the composition and dried showed no blocking at 180° F. and 100% relative humidity when a plurality of the coated boards were stacked upon one another under a weight of 2½ lbs./sq. in. The coated board showed a heat-seal temperature of above 400° F.

(b) An organosol composed of:

100 parts of polyvinyl chloride,
30 parts of dioctyl phthalate,
30 parts of epoxidized soybean oil,
20 parts xylene, and
10 parts of methyl ethyl ketone

is cast on the coated face of the coated paper of part (a). It is dried by heating at 140° F. about ten minutes, and then heating at 350° F. about ten minutes to dry and fuse the vinyl resin. It is cooled and stripped. The stripped film is tough, coherent, and glossy on both faces.

(c) A 15% solution of a copolymer of 85% vinyl chloride and 15% vinyl acetate is spread over the coated surface of the paper prepared in part (a) hereof. The cast film is dried ten minutes at 140° F., ten minutes at 220° F. and cooled. On stripping, the self-supporting film obtained is glossy on both faces.

Example 2

A coating composition is prepared containing 100 parts of a copolymer of 87% by weight of ethyl acrylate, 10.5% by weight of methyl methacrylate, and 2.5% of itaconic acid, 40 parts by weight of the ammonium salt of a 1:1 mole ratio styrene-maleamic acid copolymer

obtained by a copolymerization procedure using about 3% of a chain-transfer agent on the weight of the comonomers, and 28 parts of zinc oxide. The viscosity of a 22% solids solution obtained by heating at 105° C. for two hours the aqueous dispersion of the ammonium salt of the 1:1 mole ratio styrene/maleamic acid copolymer is 7000 centipoises indicative of a molecular weight of about 50,000 to 100,000. The solids concentration of the coating composition was about 22%, and it was applied to a chipboard and dried. An organosol of the composition described in part (b) of Example 1 was applied in the manner described therein. The film was easily stripped after fusion and had glossy surfaces on both sides.

Example 3

A release-coating was applied to chipboard as in Example 1 except that the composition employed was a 22% solids composition in an aqueous medium, the solids being formed of 100 parts of a copolymer of 80% of ethyl acrylate and 20% of methyl methacrylate, 40 parts of the ammonium salt of a copolymer of 27.5% by weight of methacrylic acid with 72.5% by weight of methyl methacrylate formed by copolymerization at about 85° C. in the presence of about 3% by weight of bromotrichloromethane as a chain-transfer agent, and 28 parts of zinc oxide. The organosol described in part (b) of Example 1 was applied to the coated chipboard in the manner described in Example 1 (b). The film stripped therefrom was extremely glossy on both faces.

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

I claim:

1. As an article of manufacture, a solid substrate carrying on at least one surface thereof, a coating comprising a mixture of (a) a water-insoluble linear addition polymer having a T_g value not over 30° C., (b) an ammonium salt of a copolymer having a molecular weight from about 500 to 100,000 selected from the group consisting of (1) copolymers of 20 to 30% by weight of methacrylic acid and 70 to 80% by weight of methyl methacrylate which form ammonium salts having, at a concentration of 22% in water at room temperature, a viscosity between 2 and 30 poises, (2) copolymers of styrene and maleic anhydride in approximately 1:1 mole ratio, and (3) copolymers in approximately 1:1 mole ratio of maleic anhydride with a compound selected from the group consisting of branched-chain olefines having 4 to 10 carbon atoms and unsaturated terpenes having 4 to 10 carbon atoms; and (c) zinc oxide, the proportions between (a) and (b) being 65 to 90 parts by weight of (a) to 10 to 35 parts of (b) and the amount of (c) being from 5 to 40% based on the total weight of (a) and (b).

2. An article as defined in claim 1 in which the substrate is formed of paper.

3. An article as defined in claim 1 in which the substrate is a paperboard.

4. As an article of manufacture, a fibrous substrate having on at least one surface thereof a coating comprising a mixture of (a) a water-insoluble linear addition polymer having a T_g value not over 30° C., (b) an ammonium salt of an approximately 1:1 mole ratio copolymer of maleamic acid and diisobutylene, said salt having an average molecular weight of about 500 to 5,000, the proportions between (a) and (b) being 65 to 90 parts of (a) with 10 to 35 parts of (b) and (c) 5 to 40% by weight of zinc oxide based on the total weight of (a) and (b).

5. As an article of manufacture, a fibrous substrate having on at least one surface thereof a coating comprising a mixture of (a) a water-insoluble linear addition polymer having a T_g value not over 30° C., (b) an ammonium salt of an approximately 1:1 mole ratio co-

polymer of maleamic acid and styrene having an average molecular weight between about 500 and about 100,000, the proportions between (a) and (b) being 65 to 90 parts of (a) with 10 to 35 parts of (b), and (c) 5 to 40% by weight of zinc oxide based on the total weight of (a) and (b). 5

6. As an article of manufacture, a fibrous substrate having on at least one surface thereof a coating comprising a mixture of (a) a water-insoluble linear addition polymer having a T_1 value not over 30° C., (b) an ammonium salt of a copolymer of 20 to 30% by weight of methacrylic acid with 70 to 80% by weight of methyl methacrylate, said ammonium salt having, at a concentration of 22% in water at room temperature, a viscosity be-

tween 2 and 30 poises, the proportions between (a) and (b) being 65 to 90 parts of (a) with 10 to 35 parts of (b), and (c) 5 to 40% by weight of zinc oxide based on the total weight of (a) and (b).

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