United States Patent Office 3,345,203 Patented Oct. 3, 1967

3,345,203

FINISHED TANNIN-CONTAINING SUBSTRATES

Benjamin B. Kine, Elkins Park, Michael Kalandiak, Ambler, and Peter R. Buechler, Langhorne, Pa., assignors to Rohm & Haas Company, Philadelphia, Pa., a corporation of Delaware

No Drawing. Filed Jan. 30, 1964, Ser. No. 341,401
9 Claims. (Cl. 117—76)

The invention is concerned with aqueous coating compositions especially useful for the finishing of substrates containing tannins, such as leathers and woods, and is particularly concerned with finished leathers and painted woods carrying a protective coat thereon which may be a multi-layer coat especially in the case of the finished leathers.

United States Patent 2,204,520 discloses a procedure for applying aqueous dispersions of emulsion-polymerized acrylic acid esters or the like to leathers. Such dispersions in practice are frequently provided with pigments and are generally covered with one or more final topcoats. The aqueous dispersion serves to fill imperfections and to level the surface of the leather and to improve the adhesion between any topcoats applied and the leather. The coating obtained from the aqueous dispersions disclosed in the patent provide good adhesion to many leathers and particularly to snuffed, buffed, and split leathers. However, on some types of full-grain leathers such coatings have poor adhesion. This poor adhesion is particularly noticeable on leathers which have been subjected to certain types of fat-liquoring, such as sperm oil, or which have acquired such a large amount of fatty deposits on the surface of the leather during fat-liquoring as to in effect provide a resist to aqueous coating compositions.

Difficulties are also sometimes encountered with the production of aqueous dispersions of the type disclosed in the above-mentioned patent which are capable of being applied by brushing. When such aqueous polymer dispersions are brushed upon the surfaces of leather or applied by other means involving a mechanical working or agitation of the dispersion, it frequently happens that specks or gummy clumps of polymer are deposited upon the surface of the leather. Another disadvantage of some finished leathers using the simple aqueous dispersions of acrylic esters is that they allow the migration to the topcoat of impurities or by-products left in the leather by the tanning process. With some types of topcoats and certain leathers and especially those that are obtained by vegetable tanning, this imgration results in a discoloration of the finish which is quite undesirable. In the application of water-base paints to wood surfaces, discoloration of the coating is also frequently caused by migration of leachable substances, such as tannins in the wood.

It has been discovered that these disadvantages can be overcome by the application to the leather or wood of one or more base coats or sub-coats of a copolymer of various lactams, such as N-vinyl-2-pyrrolidinone, with at least one ethylenically unsaturated comonomer in which the copolymer comprises about 5 to 15% by weight of the vinyl pyrrolidinone and at least 50% by weight of an acrylic acid ester in which the alcohol moiety has from 1 to 18 carbon atoms or a methacrylic acid ester in which the alcohol moiety has from 4 to 18 carbon atoms. Examples of these esters include cyclohexyl acrylate, benzyl acrylate, and the esters with (C_1–C_{18})alkanols, such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, and octadecyl acrylate.

The copolymer should have a T_1 value of 20° C. at the most, and in the case of application to leather or other flexible substrate, the T_1 value is preferably not over 5° C. in order that the finished leather will retain

flexibility and high impact resistance at low temperatures that may be encountered in use. Copolymers having a T_1 value from —40° C. to about 5° C. are especially valuable for application to flexible fibrous leather or wood substrates particularly when flexibility or resistance to impact at low temperatures is needed whereas copolymers having a T_1 value from —40° C. to 20° C. can be employed for finishing substantially rigid fibrous substrates of wood or leather.

The T_1 value referred to is the transition temperature 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 (September 1950). The T_1 value here used is that determined at 300 kg./cm.^{2}.

Besides the N-vinylpyrrolidinone and acrylic acid esters, up to 30% by weight of the entire copolymer may be formed of units of vinyltoluene, styrene, methyl methacrylate, ethyl methacrylate, propyl methacrylate, acrylonitrile, or methacrylonitrile, or mixtures thereof provided the limit of 20° C. for the T_1 value is not exceeded. Small amounts up to 5% by weight of monomers containing reactive groups such as carboxylic acid (in acid or salt form), hydroxyl, amide, ureido, glycidyl, or amine groups may be employed. Examples of these monomers include acrylic acid, methacrylic acid, itaconic acid, fumaric acid, acrylamide, methacrylamide, methylol methacrylamide, methylol acrylamide, vinyl pyridine, hydroxyalkyl vinyl ethers or sulfides such as hydroxyethyl vinyl sulfide, ureidoalkyl vinyl ethers such as ureidoethyl vinyl ether, dialkylaminoalkyl methacrylates, acrylates, vinyl ethers or vinyl sulfides, as well as the N-dialkylaminoalkyl acrylamides such as dimethylaminoethyl methacrylate and diethylaminoethyl vinyl sulfide, glycidyl methacrylate, and so on.

It has been found that the copolymers of the vinylpyrrolidinone with acrylic esters which may or may not contain the other monomers mentioned hereinabove including those with reactive groups have outstanding mechanical stability so that they can be applied by vigorous brushing action without the development of specks or gummy clumps in the coating. The also prevent or greatly reduce the tendency of the finish to become discolored by migration of materials from the body of a wood or tanned leather substrate, and especially from vegetable tanned leather, into the topcoat thereof. In addition, these polymers having outstanding adhesion toward the wood and leather substrates and the preferred copolymers are characteized by a high degree of flexibility even under cold conditions down to —20° C.

Aqueous dispersions of the copolymer may be prepared by emulsion polymerization of the several components using conventional procedures. The molecular weight of the copolymer may be from 100,000 to as high as 10,000,000, the molecular weights below 500,000 being obtained by using a chain-terminator or regulator such as dodecylmercaptan. The preferred copolymers have molecular weights of at least 500,000 as they generally retain better flexibility at lower temperatures than those having lower molecular weights. The compositions may be applied to dense fibrous substrates, such as wood or leather, at concentrations of about 5 to 50% by weight of copolymer solids.

The composition may be applied without the addition of other materials to obtain a clear coating. However, it may be colored with dyes or pigments, the amount of dye being on the order of ¼% to 1% on the weight of copolymer, whereas the amount of pigment may be from 25 to 150% on the weight of the copolymer. On rigid substrates where flexibility is not a factor, even larger pigment/copolymer ratios may be employed depending

on the amount of migratory tannin material which may be anticipated. For example, in woods containing a large amount of migratory tannin such as cedar or redwood pigment concentrations in excess of 200% based on the copolymer should be avoided in order to permit sufficient concentration of polymer to serve as a barrier to tannin migration. However, for a wood such as a good grade of white pine where less migratory tannin is found, pigment concentrations up to 300% based on copolymer can be employed. The pigmented compositions are usually applied at 15 to 30% solids concentration.

Small amounts of other components such as wax, natural resins such as copal and shellac, or water-soluble salts of copolymers of 20 to 75% of acrylic or methacrylic acid with the balance of methyl methacrylate or ethyl acrylate or mixtures thereof, may be added. These various materials may either be dissolved in water or emulsified therein, the latter technique being particularly useful with wax. The proportion of wax or other related ingredients may amount to about 0.25% to 5% by weight of the total solids in the composition. These materials modify the coating and wax particularly is advantageous to improve the plateability and embossability.

The aqueous coating composition of the n-vinyl-pyrrolidinone copolymer may be applied by spraying, brushing, roll-transfer, or immersion, and application is followed by removal of excess and drying at temperatures from room temperature up to about 140° F.

One or more coats of the N-vinyl-pyrrolidinone copolymer dispersion may be applied. In the case of application to leather, the leather product thus obtained with one or more such coats may serve as a finished product particularly when it is desired only to impart a water-repellent surface to the leather and a particular copolymer is of highly hydrophobic character as a result of a long-chain hydrocarbon group in the acrylate or other component. In many cases, however, it is desirable to apply one or more additional coatings of a different type. For example, a finishing or topcoat may be applied using an aqueous latex or a lacquer containing a copolymer of vinylidene chloride (70 to 80%) with ethyl acrylate (20 to 30%) with or without pigment depending upon whether coloration is desired or not. Generally, lacquer compositions may be employed such as those which comprise as the film-forming material an addition polymer of vinyl, acrylic or related types, a cellulose derivative such as a nitrocellulose or cellulose organic acid esters such as cellulose acetate, cellulose acetate butyrate or the like. The lacquers may comprise a plasticizer if the film-forming agent itself is not adequately flexible. When a single lacquer or latex topcoating is applied over the coating obtained from the aqueous polymer dispersion, it may be clear, or it may be dulled by a filler or other suitable agent, such as a water-insoluble soap like aluminum stearate, or silica, or it may be colored with a white or suitably colored pigment. Preferably, on leather at least two lacquer or latex topcoatings are applied in succession over the coating obtained from the aqueous dispersion. When two such lacquer coatings are applied, the first is preferably pigmented to augment the color and covering obtained by the pigment, if any, applied by the coating from the aqueous dispersion and the second lacquer coating is preferably clear or merely dulled to provide the glossiness or flatness desired in the final surface.

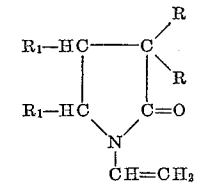
Each of the subsequently applied coatings should be dried before any later coating is to be applied and drying may be effected as before either at normal room temperature in the ambient atmosphere or at somewhat elevated temperatures up to 50° C.

If desired, in the case of finishing leather, the leather may be embossed after the coating applied by the aqueous dispersion has been dried on the leather and before subsequent lacquer or aqueous latex coatings are applied, or embossing may be applied at any time after subsequent coatings are applied but preferably before the last or final coat. Such embossing should, in all cases, be applied to the coated leather in a dry condition.

All sorts of leathers may be finished by the compositions described hereinabove including upholstery leather, case leather, and garment leathers. It may be applied to leathers obtained by any tanning procedure and as pointed out hereinabove, the N-vinylpyrrolidinone coating serves to prevent migration of materials from the body of the leather into the topcoating where such materials could effect discoloration. This prevention of discoloration is particularly valuable in connection with vegetable tanned leathers. The finished leathers are characterized by a high degree of adhesion of the coatings to the leather as well as excellent flexibility even at low temperatures. Because the aqueous compositions used in making the base or sub-coats are quite resistant to mechanical action, the coatings obtained even by procedures employing severe brushing are quite uniform in character.

In the application to wood substrates, and especially to redwood and cedars, the copolymer compositions of the present invention may be applied as a primer or sealing coat over bare wood or over wood which carries an old paint layer, derived from either an oil-base or water-base paint. The wood surface in any event may be sanded and/or wire-brushed to remove any loosely adhered material. For some purposes, the wood may be provided simply with a plurality of coats of the composition of the present invention so that it supplies not only the primer but also the finish coats thereof. However, any finishing composition may be applied in one or more coats over one or more priming coats of a copolymer of the present invention and the priming coat serves to prevent migration of such materials as tannins or lignins which would normally tend to discolor the top or finish coat. The topcoating materials used may be of oil-base or water-base paints including any of the finishing compositions mentioned in connection with the finishing of leather above. Thus, the finishing compositions may include drying-oil paint systems, alkyd resin systems, and water-base paints of vinyl acetate, acrylic ester, or butadiene-styrene or -acrylonitrile polymers.

Instead of N-vinyl-2-pyrrolidinone per se any N-vinyl lactam of the following general formula may be used:



wherein R is selected from the group consisting of hydrogen and methyl and R_1 is selected from the group consisting of hydrogen, methyl, and ethyl.

As other illustrative examples of such N-vinyl-pyrrolidinones the following may be mentioned:

5-methyl-N-vinyl-2-pyrrolidinone
5-ethyl-N-vinyl-2-pyrrolidinone
3,3-dimethyl-N-vinyl-2-pyrrolidinone
3-methyl-N-vinyl-2-pyrrolidinone
3-ethyl-N-vinyl-2-pyrrolidinone
4-methyl-N-vinyl-2-pyrrolidinone
4-ethyl-N-vinyl-2-pyrrolidinone

In the following examples which are illustrative of the present invention, the parts and percentages are by weight unless otherwise indicated.

Example 1

An aqueous dispersion containing about 45% of a copolymer of 85% ethyl acrylate (EA) and 15% N-vinyl-2-pyrrolidinone (NVP) was prepared by a conventional emulsion polymerization procedure using 1% of sodium lauryl sulfate (on monomer weight). A similar dispersion

of poly(ethyl acrylate) was prepared in the same manner. The two dispersions were compared in respect to their ability to withstand "pilling" on application to a skin surface. By "pilling" is meant the tendency to form into a series of small pill-like agglomerations upon being brushed or rubbed onto the skin surface because of the failure of the polymer to adhere to the surface rather than cohere to itself.

The two polymers were tested for this ability to rub without pilling by three independent trained observers, each familiar with this type of problem. Each observer placed several drops of the emulsion to be tested on the palm of his hand after thorough washing to remove dirt or other debris which could form a coagulating nucleus. Each then rubbed the emulsion onto the surface by a circular motion with a finger of the other hand. The unmodified polyethyl acrylate dispersion quickly pilled. The test polymer prepared in this example was rubbed to dryness on the palm without pilling by each of the three observers.

For application to leather the following three formulations were prepared:

A. A swab base coating composition was prepared by mixing 20 parts of a rutile titanium dioxide dispersion in water (containing 35% TiO_2 and about 0.13% of sodium polyacrylate), 6 parts of an aqueous dispersion containing 16% of a sulfonated hydrocarbon wax, 25 parts of the 85EA/15NVP copolymer dispersion diluted to 25% solids concentration, and 49 parts of water.

B. A spray color coating composition was prepared by mixing 32 parts of the aforesaid TiO_2 dispersion, 6 parts of the aforesaid sulfonated wax dispersion, 42 parts of the copolymer dispersion (diluted to 25%), 8 parts of a 12% casein solution in ammoniated water, and 12 parts of water

C. A spray topcoating composition was prepared by mixing 30 parts of the aforesaid TiO_2 dispersion, 9 parts of the aforesaid sulfonated wax dispersion, 23 parts of the copolymer dispersion (diluted to 25%), 14 parts of the aforesaid casein solution, 12 parts of a suspension of 1 part of silica gel in 11 parts of an aqueous solution containing about 13% of an ammonium salt of a copolymer of about 85% ethyl acrylate and about 15% methacrylic acid, 3% of an ammonium salt of a maleic anhydride/diisobutylene copolymer, and 3% of tert-octylphenoxyethanol, and 14 parts of water.

Three additional formulations designated A', B', and C' were made in the same fashion except the 85EA/15NVP copolymer dispersion was replaced by a poly(ethyl acrylate) (100 EA) dispersion diluted to 25% solids.

Two pieces of vegetable-tanned leather were finished, one by application in succession of the formulations A, B, and C in that order, and the other by application of formulations A', B', and C' in that order.

The "Swab Base Coat" was applied by taking a standard felt swab used for leather swab coat formulations, wetting it with the formulation and then brushing it across the surface of a leather strip 8 inches wide cut from backbone to belly from a commercial unfinished side of leather. After application, the excess fluid was wiped from the swab on the side of the metal tray containing the formulation. The semi-dry swab was then used to level the material on the surface of the leather and wipe off the excess. During this latter stage of the operation it was noted that pilling occurred with the formulation A' using the polyethylacrylate dispersion so that small agglomerates were left scattered over the leather surface. No such pilling or agglomerates were found with the formulation A containing the N-vinyl pyrrolidinone copolymer.

The leathers were dried in a heated closet at 50° C. for one hour. Then the Spray Color Coat was sprayed on using a De Vilbiss hand spray gun at 65 lbs. air pressure and a number 306 nozzle. Both the formulations Bond B' sprayed satisfactorily without difficulties. However the agglomerates on the polyethyl acrylate (A'+B') coated leather became more noticeable because of the accretion of extra material.

The leathers were dried overnight at room temperature. Next morning they were plated in a hydraulic press under a smooth polished metal plate at 150° F. using a pressure of 1050 lbs./sq. inch. The agglomerates on the polyethyl acrylate coated leather, although flattened, were still very apparent.

The topcoats were then sprayed on similarly to the color coats. The agglomerates on the polyethyl acrylate (A', B', and C',) coated leather again became still more apparent due to accretions. The leathers were dried and then evaluated by a panel of trained observers for break and appearance. The break was found to be comparable. It was very good for both leathers. The appearance of the polyethyl acrylate coated leather was inferior, however, because of the agglomerates on the surface.

Comparative standard tests were run on the coated leathers.

In the following table, certain tests referred to are described in the following publications:

(1) "Upholstery Leather: Industry Specifications and Standards," published by Upholstery Leather Group, Inc., 141 E. 44th St., New York 17, N.Y.

(2) Journal of Research of National Bureau of Standards, volume 42, pages 481–497.

(3) Ford Motor Company Manufacturing Standards, April 1955, Test MIFI–2–3 Specification 3.11.

The test is followed by the designation (1), (2), or (3) to indicate where the description is to be found. The results were as follows:

Test	Results	
	Polyethylacrylate	EA/NVP Copolymer
Taber (CS–10 Wheel, 500 g., 1,000 cycles) (3).	G–	G
Wyzenbeek (30,000 rubs) (1)	VG	VG
Scheiffer (15 lbs., 2,500 cycles) (2)	VG, VG–, VG–	E, E, E
Blocking Test (3)	Moderate cling, no damage.	Slight cling, damage.
Newark Flex (50,000 flexes) (1)	E–, E–, VG	E–, E–, E–

G=Good; VG=Very Good; E=Excellent.

From this it can be seen that the NVP-copolymer was comparable in all respects to the polyethyl acrylate polymer but possessed greater stability when swabbed on the leather because of a better adhesion to the leather surface during the rubbing process. This prevented the formation of unsightly agglomerates which spoiled the appearance of the leather coated with polyethyl acrylate dispersions and which in seasoning machine applications in tanneries has been shown to build up on brushes and prevent adequate application.

Example 2

A leather was finished in the same way as in Example 1 using a copolymer of 95% EA/5% NVP. No pilling was evident in actual leather applications. The same appearance advantages were obtained as with the NVP-copolymer used in Example 1. Break was even better than that obtained in Example 1.

Example 3

Aqueous dispersions of the following two copolymers were prepared as in Example 1.

EA/2–EHA/NVP=80/10/10
EA/2–EHA/NVP=87.5/2.5/10

where:
EA=ethylacrylate
2–EHA=2-ethylhexylacrylate
NVP=N-vinyl-2-pyrrolidinone.

These two plus the copolymer described in Example 2 were formulated with a titanium dioxide pigment to form a water-base paint having a pigment to binder ratio of 3:2 and a pigment volume concentration of approximately 30%. The three paints were then used to coat a respective one of three cedar shingles.

A fourth water-base paint was prepared in the same way from a commercially available acrylic latex polymer and a fourth cedar shingle was painted with it.

The dried painted sections were each cut in half. One-half of each section was wrapped and stored in a dark dry chamber to avoid discoloration. The other half-sections were placed in a disiccator jar over water and stored in a heated closet (55° C.) for three weeks. At this time half of the fourth shingle stored in the high temperature, high humidity chamber showed extensive discoloration of the paint, whereas the others showed much less.

Example 4

The copolymers described in Examples 1, 2 and 3 and two commercial ethyl acrylate-methyl methacrylate copolymer dispersions were formulated with a white pigment as in Example 3, adjusted with water, and sprayed on separate pieces of vegetable-tanned handbuff leather.

The leather pieces were dried in a heated closet at 50° C. for two hours. Then they were plated in a hydraulic press under a full grain plate at 180° F. using a pressure of 1050 lbs./sq. inch.

A white color coat (a commercial type) was sprayed over the first coats and dried for two hours in the hot closet. A conventional clear topcoat was sprayed and dried in the hot closet for 16 hours.

Three groups of samples were obtained for comparison of effectiveness of basecoats in preventing discoloration. One group was stored in the dark in a refrigerator as controls. Another group was stored at 25° C. in an atmosphere saturated with moisture. A third group was stored at 50° C. in an atmosphere saturated with moisture.

After one day's storage at 50° C., and after 7 days' storage at 25° C., the respective samples were removed for observation. It was noted that the N-vinyl-2-pyrrolidinone copolymers were outstandingly superior to the commercial copolymers in preventing discoloration.

Example 5

An aqueous dispersion was prepared as in Example 1 of a copolymer of 55% butyl methacrylate, 5% styrene, 5% dimethylaminoethyl methacrylate, 20% butyl acrylate, and 15% NVP. The resulting copolymer dispersion was formulated with titanium dioxide pigment to form a water-base paint having a pigment to binder ratio of 3:2 and a pigment volume concentration of about 35%. The paint was applied to exterior surfaces of masonry and wood including redwood sidings. The paint was resistant to discoloration resulting from migration of tannins.

Example 6

(a) The procedure of Example 5 was repeated with similar results with an aqueous disperson of a copolymer of 64% ethyl acrylate, 10% vinyltoluene, 10% NVP, 2.5% N-methylol-acrylamide, 1.5% acrylamide, and 1% of acrylic acid.

(b) The paint prepared in part (a) hereof was applied to panels of siding prepared from cedar, redwood, and aluminum, dried in the ambient atmosphere and then baked for 3 minutes at 150° C. The coatings adhered well and were durable and weather-resistant.

Example 7

The procedure of Example 5 was repeated with similar results with an aqueous dispersion of a copolymer of 60% ethyl acrylate, 14% acrylonitrile, 10% methyl methacrylate, 5% NVP, and 11% glycidyl methacrylate.

Example 8

The procedure of Example 5 was repeated with similar results with an aqueous dispersion of a copolymer of 40% methyl acrylate, 25% butyl acrylate, 20% vinyltoluene, 10% NVP, and 5% N-methoxymethyl methacrylamide.

We claim:

1. As an article of manufacture, a solid substrate containing a tannin and having a coating thereon comprising a water-insoluble linear copolymer, having an apparent second order transition temperature in the range of —40° C. to +20° C., of 5 to 15% by weight of N-vinyl-2-pyrrolidinone and 85 to 95% by weight of at least one compound selected from the group consisting of (C_1–C_{18})-alcohol esters of acrylic acid and (C_4–C_{18})alcohol esters of methacrylic acid.

2. As an article of manufacture, a leather having a coating thereon comprising a water-insoluble linear copolymer, having an apparent second order transition temperature in the range of —40° C. to +5° C., of 5 to 15% by weight of N-vinyl-2-pyrrolidinone and 95 to 85% by weight respectively of at least one (C_1–C_{18})-alcohol ester of acrylic acid.

3. As an article of manufacture, a leather having a coating thereon comprising a water-insoluble linear copolymer, having an apparent second order transition temperature in the range of —40° C. to +5° C., of 5 to 15% by weight of N-vinyl-2-pyrrolidinone, at least 50% by weight of a compound selected from the group consisting of (C_1–C_{18})-alcohol esters of acrylic acid and (C_4–C_{18})-alcohol esters of methacrylic acid, and up to 5% by weight of another copolymerizable monoethylenically unsaturated monomer containing a reactive group selected from the group consisting of carboxylic acid, amino, amide, hydroxyl, glycidyl, and ureido groups.

4. As an article of manufacture, a leather having a coating thereon comprising a water-insoluble linear copolymer, having an apparent second order transition temperature in the range of —40° C. to +5° C., of 5 to 15% by weight of N-vinyl-2-pyrrolidinone, at least 50% by weight of a compound selected from the group consisting of (C_1–C_{18})-alcohol esters of acrylic acid and (C_4–C_{18})-alcohol esters of methacrylic acid, up to 5% by weight of another copolymerizable monoethylenically unsaturated monomer containing a reactive group selected from the group consisting of carboxylic acid, amino, amide, hydroxyl, glycidyl, and ureido groups, and up to 30% by weight of at least one monomer selected from the group consisting of styrene, vinyltoluene, methyl methacrylate, ethyl methacrylate, propyl methacrylate, acrylonitrile and methacrylonitrile.

5. As an article of manufacture, a leather having a coating thereon comprising a water-insoluble linear copolymer, having an apparent second order transition temperature in the range of —40° C. to +5° C., of 5 to 15% by weight of N-vinyl-2-pyrrolidinone and 85 to 95% by weight of at least one compound selected from the group consisting of (C_1–C_{18})-alcohol esters of acrylic acid and (C_4–C_{18})-alcohol esters of methacrylic acid and, superimposed of said layer, at least one coating of another film-forming component selected from the group consisting of cellulose esters and vinyl resins.

6. As an article of manufacture, a solid substrate of wood containing a tannin and having a coating thereon comprising water-insoluble linear copolymer, having an apparent second order transition temperature in the range of —40° C. to +20° C., of 5 to 15% by weight of N-vinyl-2-pyrrolidinone and 95 to 85% by weight respectively of at least one compound selected from the group consisting of (C_1–C_{18})-alcohol esters of acrylic acid and (C_4–C_{18})-alcohol esters of methacrylic acid.

7. As an article of manufacture, a solid substrate of wood containing a tannin and having a coating thereon comprising a water-insoluble linear copolymer, having an apparent second order transition temperature in the range

of —40° C. to +5° C., of 5 to 15% by weight of N-vinyl-2-pyrrolidinone, at least 50% by weight of a compound selected from the group consisting of (C_1–C_{18})-alcohol esters of acrylic acid and (C_4–C_{18})-alcohol esters of methacrylic acid, and up to 5% by weight of another copolymerizable monoethylenically unsaturated monomer containing a reactive group selected from the group consisting of carboxylic acid, amino, amide, hydroxyl, glycidyl, and ureido groups.

8. As an article of manufacture, a solid substrate of wood containing a tannin and having a coating thereon comprising a water-insoluble linear copolymer, having an apparent second order transition temperature in the range of —40° C. to +5° C., of 5 to 15% by weight of N-vinyl-2-pyrrolidinone, at least 50% by weight of a compound selected from the group consisting of (C_1–C_{18})-alcohol esters of acrylic acid and (C_4–C_{18})-alcohol esters of methacrylic acid, up to 5% by weight of another copolymerizable monoethylenically unsaturated monomer containing a reactive group selected from the group consisting of carboxylic acid, amino, amide, hydroxyl, glycidyl, and ureido groups, and up to 30% by weight of at least one monomer selected from the group consisting of styrene, vinyltoluene, methyl methacrylate, ethyl methacrylate, propyl methacrylate, acrylonitrile, and methracrylonitrile.

9. As an article of manufacture, a solid substrate containing a tannin and having a coating thereon comprising a water-insoluble linear copolymer, having an apparent second order transition temperature in the range of —40° C. to +20° C. and a molecular weight in the range of 100,000 to 10,000,000, of 5 to 15% by weight of N-vinyl-2-pyrrolidinone and 85 to 95% by weight of at least one compound selected from the group consisting of (C_1–C_{18})-alcohol esters of acrylic acid and (C_4–C_{18})-alcohol esters of methacrylic acid.

References Cited

UNITED STATES PATENTS

2,204,520	6/1940	Walker et al.	117—142
2,828,223	3/1958	McWherter et al.	117—76
2,901,457	8/1959	Stoner et al.	117—142 X
3,048,496	8/1962	Buechler et al.	117—142 X
3,061,569	10/1962	Stoner et al.	117—142 X
3,142,664	7/1964	Bauer	260—86.1 X

WILLIAM D. MARTIN, *Primary Examiner.*

T. G. DAVIS, *Assistant Examiner.*