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POLYVINYL ACETAL RESIN

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This invention relates to polyvinyl acetal resins and more particularly to polyvinyl acetal resins having characteristics which render them suitable for the preparation of transparent film or sheet, especially transparent film or sheet, such as is intended to be used as a support for light-sensitive photographic coatings.

Polyvinyl acetal resins have appeared to be adapted to the manufacture of transparent film or sheet such as is employed as a support for light-sensitive photographic coatings. However, of the large number of such resins prepared during the past few years, a very few have been discovered which come near meeting the exacting requirements of the art concerned with the manufacture of transparent film or sheet suitable for a support for photographic coatings. In fact, all of the polyvinyl acetal resins heretofore known have fallen short in some particular.

Now I have found a polyvinyl acetal resin which comes closer to meeting the above-mentioned exacting requirements than any known resin of this class. My new resin is a polyvinyl acetal resin in which a part of the acetal linkages are formed from acetaldehyde and a part from butyraldehyde. In addition to acetal groups, my new resin contains hydroxyl groups, and sometimes ester groups. My new resin is characterized by low water susceptibility, satisfactory solubilities in organic solvents, low organic solvent retention, high flexibility, high tensile strength and excellent wearing properties.

This new resin can be prepared—

(1) By treating a polyvinyl ester with acetaldehyde and butyraldehyde either simultaneously or successively, in the presence of a neutral de-esterifying agent, and acid de-esterifying catalyst and an acid acetal condensation catalyst;

(2) By treating a polyvinyl alcohol with acetaldehyde and butyraldehyde either simultaneously or successively, in the presence of an acetal condensation agent;

(3) By treating a polyvinyl acetal resin containing acetaldehyde acetal groups, butyraldehyde groups and ester groups with a de-esterifying agent; and

(4) By treating a polyvinyl acetal resin containing acetaldehyde acetal groups, butyraldehyde acetal groups and hydroxyl groups with an agent which converts a part of the hydroxyl groups to oxygen-containing organic residues e. g., ester groups.

The composition of my new resin can best be dealt with by viewing the resin as a mixture of a polyvinyl acetaldehyde acetal, a polyvinyl butyraldehyde acetal, a polyvinyl alcohol and a polyvinyl compound containing oxygen-bearing groups, such as a polyvinyl ester. However, it is to be understood that my new resin is not a mechanical mixture of the above-mentioned ingredients but is probably made up of polyvinyl chains to each of which is attached acetal groups, hydroxyl groups, and sometimes oxygen-bearing groups, as evidenced by the fact that my new resins cannot be separated into the above-mentioned ingredients. Viewed as a mixture, the composition of my new resin can be expressed as follows: a polyvinyl acetal resin containing a hydroxyl group content equivalent to not more than about 10 percent by weight of polyvinyl alcohol and an acetal group content equivalent to at least about 90 percent by weight of polyvinyl acetal except where the resin contains an ester group content equivalent to not more than about 10 percent by weight of polyvinyl ester when the acetal group content is equivalent to at least about 80 percent by weight of polyvinyl acetal, the polyvinyl acetal portion of the resin being made up in either case of from about 60 to about 80 percent by moles of polyvinyl acetaldehyde acetal and the remainder of polyvinyl butyraldehyde acetal.

In preparing my new resin by the first above-stated method, I have found that any polyvinyl ester, advantageously other than a polyvinyl formate can be used, for example, polyvinyl acetate, polyvinyl propionate, polyvinyl butyrate, polyvinyl acetate-propionate, polyvinyl acetate-oleate, or heteropolymers of vinyl esters and other polymerizable substances such as the heteropolymer of vinyl acetate and vinyl ethyl ether, or the like. Polyvinyl esters having molecular weights as expressed by the viscosities of their monomeric molar solutions (86.05 gm. per liter) in benzene at about 20°, ranging from 5 to 300 centipoises, have been found adaptable for the preparation of my new resins. In preparing the resin by the second of the above stated processes, I have found that polyvinyl alcohols generated by saponification of polyvinyl esters having molecular weights of the range just mentioned can be used. In either of these two processes the acetaldehyde and butyraldehyde employed can be either their monomeric or polymeric forms. These compounds can also be used in the form of derivatives which, under the conditions of the reaction, decompose, yielding the acetaldehyde or butyraldehyde. For example, instead of acetaldehyde, the diethyl acetal of acetaldehyde can be employed. In either of the Methods (1)

or (2), the reaction is advantageously promoted by an acid acetal condensation agent, such as a strong acid, for example, H_2SO_4, alkylsulphuric acids or sulphonic acids, trichloracetic acid, or acid reacting salts, for example, ferric chloride, aluminium chloride or the like. Where deesterification is necessary the strong acid catalylsts are to be preferred since they serve also to promote deesterification. Sulphuric acids and sulphonic acids, particularly H_2SO_4, appear to have inherent properties other than their acid strength which make them particularly well suited for this reaction.

The deesterifying agent required in Method (1) can advantageously be a primary or secondary alcohol in the anhydrous or aqueous form. Such alcohols as lower aliphatic primary monohydric are especially suitable, for example, methyl, ethyl and propyl alcohols. Ethylene glycol can also be used. In preparing my new resin according to Method (1), it is advantageous to homogeneously disperse the polyvinyl ester in the dispersing agent and effect the reaction under such conditions that the reaction mixture is homogeneous throughout. Such a procedure ordinarily allows the acetal resin formation without stirring or agitation. However, it is quite possible though less advantageous to carry out the formation of my new resin by the method under (1), employing a suspension instead of a solution of the starting polyvinyl compound in a deesterifying medium. Ordinarily such a procedure requires agitation in order to assure a uniform reaction. Organic solvents which have no deesterifying action on the polyvinyl ester can be added to the reaction mixture if desired. Methyl acetate, ethyl acetate, benzene, heptone, nitroethane, ethylene, dichloride or the like can be added if desired. Ordinarily ketonic solvents such as acetone, should be avoided since they appear to induce color in the resin.

The following examples serve to illustrate the preparation of my new resin according to Method (1) which is probably the most advantageous method. These examples are merely illustrative and are not intended to limit my invention.

Example 1

20 parts of polyvinyl acetate (viscosity 45) were dissolved in a solvent mixture composed of 20 parts of ethyl alcohol and 36 parts of ethyl acetate. An aldehyde mixture containing 5.8 parts of paracetaldehyde and one part of butyraldehyde was added, taking care to obtain a uniform mixture. The catalyst mixture composed of two parts of concentrated sulfuric acid (specific gravity 1.84) and two parts of water, the mixture having previously been cooled to about 30° C. was then added. This reaction mixture was kept at 40° C. for about 170 hours, after which it was cooled to room temperatures, diluted with approximately two volumes of acetone and then poured slowly into a large volume of violently agitated water, causing the precipitation of the resin in a white fibrous form. After thoroughly washing with water, the resin was dried in an oven at about 140 to about 160° F. The washed and dried resin contained a hydroxyl group content equivalent to about 8.7 percent by weight of polyvinyl alcohol and an acetate group content equivalent to about 4.6 percent by weight of polyvinyl acetate. The polyvinyl acetal portion of the resin was made up of about 75 percent by moles of polyvinyl acetaldehyde acetal and 25 percent by moles of polyvinyl butyraldehyde acetal.

Example 2

A resin was prepared exactly as under Example 1 except that the composition of the aldehyde mixture which was added contained 5.1 parts of paracetaldehyde and 2.1 parts of butyraldehyde. The precipitated, washed and dried resin contained an acetaldehyde acetal group content equivalent to about 56.8 weight percent of polyvinyl acetaldehyde acetal, a butyraldehyde acetal group content equivalent to about 27.5 weight percent of polyvinyl butyraldehyde acetal, a hydroxyl group content equivalent to about 6.5 weight percent of polyvinyl alcohol and an acetate group content equivalent to about 5.2 weight percent of polyvinyl acetate. The polyvinyl acetal portion of the resin was made up of about 28 percent by moles of polyvinyl butyraldehyde acetal and about 72 percent by moles of polyvinyl acetaldehyde acetal.

Example 3

A resin was prepared according to the procedure outlined in Example 2, except that the polyvinyl acetate employed possessed a molecular weight indicated by a viscosity of 15 centipoises. The precipitated, washed and dried resin contained a hydroxyl group content equivalent to about 7.9 weight percent of polyvinyl alcohol and an acetate group content equivalent to about 3.3 weight percent of polyvinyl acetate. The polyvinyl acetal portion of the resin was made up of about 25 percent by moles of polyvinyl butyraldehyde acetal and about 75 percent by moles of polyvinyl acetaldehyde acetal.

In precipitating the resins prepared as indicated in the above examples, the strong acid catalyst can first be neutralized with suitable neutralizing agents, such as aqueous ammonia, if desired. This results in the formation of ammonium salts which ordinarily must be removed from the finished resin by washing. Reprecipitation and/or extensive washing are ordinarily necessary to remove the last traces of catalyst acid or its salt in case a neutralizing agent has been added. Instead of precipitating the resin as described in the above examples, the volatile solvents of the reaction mixture can be removed by steam distillation.

The catalyst concentrations can be varied from those given by way of illustration in the above examples. However, it has been found that high concentrations of catalyst in general tend to produce resins possessing unsatisfactory color and containing side-reaction products. Higher temperatures likewise tend to produce resins having color and containing side-reaction products. The amount of strong acid catalyst can advantageously be equal to from about 1 to about 5 percent by weight of the total reaction mixture, in no case equaling more than about 20 percent by weight of the starting polyvinyl compound. The temperature employed is advantageously not more than about 50° C., 35° to 45° C. being suitable.

The aldehyde can be added simultaneously or successively. In the presence of alcohols the aldehydes appear not to react at comparable rates, the butyraldehyde reacting somewhat more rapidly at least when the acetaldehyde is used in its polymeric form as in the above examples. Accordingly it is ordinarily advantageous to use about the proportion of butyraldehyde desired to be combined in the resin or a slight excess thereof together with an excess of acetaldehyde. The rates at which the aldehydes react vary depending upon the state of molecular aggregation of

aldehyde, the nature and amount of alcohol used in the deesterifying medium, the temperature and the concentration of catalyst so that it is ordinarily most satisfactory to determine by actual test what proportions of aldehydes in the reaction mixture give the desired molecular ratio of aldehydes combined in the resin.

The process illustrated in the above examples is probably the most advantageous one for producing my new resin. Produced according to this process my new resin ordinarily contains a small ester group content, i. e. one equivalent to not more than about 10 percent. by weight of polyvinyl ester. This ester group content can be further reduced by removing the ester groups, advantageously by alkaline saponification. This can be accomplished by dispersing the resin in pyridine, adding sodium hydroxide and warming.

When preparing my new resin according to Method (2) above, no ester group content obtains unless the starting polyvinyl alcohol (which is ordinarily prepared by a saponification of a polyvinyl ester) should contain a small ester group content to begin with. In preparing my new resin by Method (2), it is advantageous to suspend the polyvinyl alcohol in a reaction medium which will dissolve the acetal resin as it forms. Lower aliphatic alcohols, particularly isopropyl alcohol, are suitable for this purpose. The catalyst can be any of those mentioned above, the amount being as low as possible to avoid side-reactions. The temperatures employed are advantageously not more than about 70° C. The aldehydes need not be added simultaneously, but, when added simultaneously the precautions as to determination of relative rates of reaction of the aldehydes stated above should be observed. After completion of the reaction the reaction mixture is ordinarily a solution from which the resin can be obtained by precipitation in water or by steam distilling away the volatile solvent. The resin should be thoroughly washed to rid it of catalyst acid, aldehydes and solvent. The catalyst acid can be neutralized if desired during precipitation of the resin. Aqueous ammonia is suitable as a neutralizing agent. The resin prepared from a polyvinyl alcohol containing a small hydroxyl group content (up to 10 percent. by weight of polyvinyl alcohol) can be treated with esterifying agents if desired in order to introduce a small ester group content. This can be accomplished by dispersing the resin in pyridine and treating with organic acid chlorides or anhydrides. Other oxygen-bearing groups can also be introduced into my new resin by treating with agents which react with hydroxyl groups, e. g. alkylating agents.

In preparing my new resins, either from a polyvinyl ester or a polyvinyl alcohol, the only satisfactory method of determining the completion of the reaction is by isolating and purifying a test portion of the resin, followed by analysis thereof. A satisfactory resin has been formed when the resin contains not more than about 10 percent by weight of polyvinyl alcohol and not more than about 10 percent by weight of polyvinyl ester. While there are several methods of determining hydroxyl group content, a method which appears to give concordant results is to suspend a sample of the resin in pyridine and add a known amount of acetic anhydride in excess. After warming, to assure reaction (until the resin is all in solution and about one hour thereafter) water is added to decompose the excess of acetic anhydride and the mixture titrated with a base to determine the acetic acid present. From the acetic acid, the amount of acetic anhydride used and the hydroxyl group content can be calculated. The ester group content can be determined by suspending the resin in pyridine and adding a known amount of sodium hydroxide in excess. After warming, to assure reaction, the excess sodium hydroxide can be determined with an acid. From the amount of sodium hydroxide used up, the ester group content can be calculated. While I have found that the hydroxyl group content should ordinarily be not more than about 12 percent, calculated as weight of polyvinyl alcohol, and that the ester group content should ordinarily be not more than about 10 percent, calculated as weight of polyvinyl ester, it is to be particularly noted that the determination of these hydroxyl and ester groups is a more or less uncertain matter even under the most rigorous control now possible, and that I accordingly regard as equivalents resins having the properties of solubility, particularly in acetone, low water absorption, etc. which properties characterize the resins described in the above examples. In other words, the limits of hydroxyl and ester group content have been set as a guide to the art and cannot be regarded as too definite. The same is true for the butyraldehyde and acetaldehyde analyses.

The herein described resins can be made into transparent film or sheet by dissolving the resin in suitable organic solvents, such as acetone, methyl alcohol or ethylene dichloride, or mixtures of organic solvents, and spreading the thus prepared flowable composition onto a film-forming surface, such as a glass or metal plate, or a revolving drum. Upon evaporation of the volatile portion of the composition, which evaporation may be accelerated by heating, for example, with warm air, the film or sheet can be stripped from the film-forming surface. The detached film or sheet can then be subjected to curing by treating with warm air at suitable temperatures, the details of which are well known to those skilled in the art of manufacturing supports for light-sensitive coatings. The resulting film or sheet is permanently transparent, substantially water-proof, and of comparatively low inflammability. The moisture absorption of such transparent film or sheet is very low, in fact lower than any film or sheet made from polyvinyl acetal resins heretofore known, the resin at the same time possessing suitable solubility in organic solvents. Low moisture absorption in transparent film or sheet used for light-sensitive photographic coatings is a necessity since otherwise the finished photographic film would undergo distortion and acquire waviness when in contact with moisture or aqueous solutions such as are encountered during the processing of the exposed photographic film. Transparent film or sheet made from these resins has a suitably low organic solvent retention. This is especially important when manufacturing transparent sheet or film from flowable compositions as described above, because the film or sheet can be readily cured (removal of all but a very small amount of the solvent) by practical methods for example heating with warm air. Film or sheet insufficiently cured will undergo shrinkage with age, the shrinking resulting in curling and crinkling of the film or sheet.

Transparent sheet or film made from such resins has a particularly high resistance to wear. This is an important advantage when the transparent film is used as a support for photographic film which is intended for motion pictures, owing

to the fact that the film is subjected to considerable wear and rough usage in the motion picture projection machines. Films made from these resins show a much greater resistance to wear than any heretofore known films made from resinous materials. The herein-described resins are further characterized by suitable flexibilities, the transparent film or sheet made from the resins showing excellent resistance to accelerating aging tests in that brittleness does not develop. At the same time, transparent film or sheet made from these resins possesses suitable tensile strengths and suitably high softening points. Transparent sheet or film which is likely to be subjected to higher temperatures, such as are encountered in motion picture projection machines, must possess sufficiently high softening points that it does not soften and twist or distort during handling.

Transparent film or sheet made from my new resins has proven on long-time tests to have no deleterious effect on photographic coatings applied thereto.

My new resin can be pressed into blocks and skived to thin sheets or layers which can be used as a laminating material between sheets of glass, particularly if suitably plasticized. My new resin is compatible with a number of plasticizers, such as tributyl phosphate, triphenyl phosphate, tricresyl phosphate, diamyl phthalate, dibutyl phthalate, di- and triglyceryl esters, such as acetates, propionates, butyrates and the like, glycerol acetal esters, such as butyraldehyde acetal of glycerol monoacetate, monobutyrate, monovalerate or the like, glycerol acetal ethers, such as the acetaldehyde of glycerol monoethyl ether or dodecylether, monochloronaphthalene and the like.

My new resin can be successfully molded or extruded when suitably plasticized.

What I claim as my invention and desire to secure by Letters Patent of the United States of America is:

1. A polyvinyl acetal resin containing a hydroxyl group content equivalent to not more than about 10 per cent by weight of polyvinyl alcohol and an acetal group content equivalent to at least about 90 percent by weight of polyvinyl acetal, the polyvinyl acetal portion of the molecule being made up of from about 60 to about 80 percent by moles of polyvinyl acetaldehyde acetal and the remainder from polyvinyl butyraldehyde acetal.

2. A polyvinyl acetal resin containing a hydroxyl group content equivalent to not more than about 10 percent by weight of polyvinyl alcohol, an ester group content other than a formate group content equivalent to not more than about 10 percent by weight of polyvinyl ester and an acetal group content equivalent to not more than about 80 percent by weight of polyvinyl acetal, the polyvinyl acetal portion of the molecule being made up of from about 60 to about 80 percent by moles of polyvinyl acetaldehyde acetal and the remainder of polyvinyl butyraldehyde acetal.

3. A polyvinyl acetal resin containing a hydroxyl group content equivalent to not more than about 10 percent by weight of polyvinyl alcohol, an acetate group content equivalent to not more than about 10 percent by weight of polyvinyl acetate and an acetal group content equivalent to not more than about 80 percent by weight of polyvinyl acetal, the polyvinyl acetal portion of the molecule being made up of from about 60 to about 80 percent by moles of polyvinyl acetaldehyde acetal and the remainder of polyvinyl butyraldehyde acetal.

4. A polyvinyl acetal resin containing a hydroxyl group content equivalent to a small percent by weight of polyvinyl alcohol, an ester group content other than a formate group content equivalent to a small percent by weight of polyvinyl ester, at least about 85 percent of the weight of the resin being polyvinyl acetal and the polyvinyl acetal portion of the resin being made up of from about 60 to about 80 percent by moles of polyvinyl acetaldehyde acetal and the remainder of polyvinyl butyraldehyde acetal.

5. A polyvinyl acetal resin containing a hydroxyl group content equivalent to a small percent by weight of polyvinyl alcohol, an acetate group content equivalent to a small percent by weight of polyvinyl acetate, at least about 85 percent of the weight of the resin being polyvinyl acetal and the polyvinyl acetal portion of the resin being made up of from about 60 to about 80 percent by moles of polyvinyl acetaldehyde acetal and the remainder of polyvinyl butyraldehyde acetal.

6. A polyvinyl acetal resin, the polyvinyl acetal portion of the resin being made up of from about 60 to about 80 percent by moles of polyvinyl acetaldehyde acetal and the remainder of polyvinyl butyaldehyde acetal.

7. A polyvinyl acetal resin containing a hydroxyl group content equivalent to a small percent by weight of polyvinyl alcohol, an ester group content other than a formate group content equivalent to a small percent by weight of polyvinyl ester, at least about 85 percent of the weight of the resin being polyvinyl acetal and the polyvinyl acetal portion of the resin being made up of about 70 percent by moles of polyvinyl acetaldehyde acetal and about 30 percent by moles of polyvinyl butyraldehyde acetal.

8. A polyvinyl acetal resin containing a hydroxyl group content equivalent to a small percent by weight of polyvinyl alcohol, an acetate group content equivalent to a small percent by weight of polyvinyl acetate, at least about 85 percent of the weight of the resin being polyvinyl acetal and the polyvinyl acetal portion of the resin being made up of about 70 percent by moles of polyvinyl acetaldehyde acetal and about 30 percent by moles of polyvinyl butyraldehyde acetal.

9. A transparent film or sheet, suitable as a support for light-sensitive photographic coatings, when made from the resin defined by claim 1.

10. A transparent sheet or film, suitable as a support for light-sensitive photographic coatings, when made from the resin defined by claim 2.

11. A transparent sheet or film, suitable as a support for light-sensitive photographic coatings, when made from the resin defined by claim 3.

12. A transparent sheet or film, suitable as a support for light-sensitive photographic coatings, when made from the resin defined by claim 5.

13. A transparent sheet or film, suitable as a support for light-sensitive photographic coatings, when made from the resin defined by claim 6.

14. A transparent sheet or film, suitable as a support for light-sensitive photographic coatings, when made from the resin defined by claim 8.

15. A process for preparing a polyvinyl acetal resin comprising reacting a polyvinyl ester other than polyvinyl formate with a mixture of acetaldehyde and butyraldehyde, in the presence of a strong acid catalyst and a neutral deesterifying agent, the proportions of the acetaldehyde and butyraldehyde in the reaction mixture being such

that the polyvinyl acetal portion of the resin contains from about 60 to about 80 percent by moles of polyvinyl acetaldehyde acetal, the remainder being polyvinyl butyraldehyde acetal.

16. A process for preparing a polyvinyl acetal resin comprising reacting a polyvinyl acetate with a mixture of acetaldehyde and butyraldehyde, in the presence of a strong acid catalyst and a neutral deesterifying agent, the proportions of the acetaldehyde and butyraldehyde in the reaction mixture being such that the polyvinyl acetal portion of the resin contains from about 60 to about 80 percent by moles of polyvinyl acetaldehyde acetal, the remainder being polyvinyl butyraldehyde acetal.

17. A process for preparing a polyvinyl acetal resin containing a hydroxyl group content equivalent to not more than about 10 percent by weight of polyvinyl alcohol and an ester group content other than a formate group content equivalent to not more than about 10 percent by weight of polyvinyl ester, comprising reacting of polyvinyl ester other than polyvinyl formate, in the presence of a neutral deesterifying agent, an acid deesterifying catalyst and an acid acetal condensation catalyst, with a mixture of acetaldehyde and butyraldehyde, the proportions of the acetaldehyde and butyraldehyde in the reaction mixture being such that the polyvinyl acetal portion of the resin contains from about 60 to about 80 percent by moles of polyvinyl acetaldehyde acetal and the remainder being polyvinyl butyraldehyde acetal.

18. A process for preparing a polyvinyl acetal resin containing a hydroxyl group content equivalent to not more than about 10 percent by weight of polyvinyl alcohol and an acetate group content equivalent to not more than about 10 percent by weight of polyvinyl acetate, comprising reacting a polyvinyl acetate, in the presence of a neutral deacetylating agent, an acid deacetylating catalyst, and an acid acetal condensation catalyst, with a mixture of acetaldehyde and butyraldehyde, the proportions of the acetaldehyde and butyraldehyde in the reaction mixture being such that the polyvinyl acetal portion of the resin contains from about 60 to about 80 percent by moles of polyvinyl acetaldehyde acetal and the remainder being polyvinyl butyraldehyde acetal.

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