

DESCRIPTION

TITLE OF INVENTION: POLYVINYL ACETAL RESIN

5 TECHNICAL FIELD

[0001]

The present invention relates to a polyvinyl acetal resin that has an excellent dispersing property and enables the production of a formed article having high mechanical
10 strength.

BACKGROUND ART

[0002]

Polyvinyl acetal resins are excellent in toughness, film formation, dispersing property for inorganic powder (e.g., pigment) and organic powder, and adhesiveness to surfaces to which the resins are applied. Polyvinyl acetal resins are thus used for applications such as ceramic green sheets and conductive pastes constituting multilayer
15 ceramic capacitors, inks, coating materials, enamels for baking, and wash primers, for example.

[0003]

In particular, a multilayer ceramic capacitor is typically produced through the following steps.

25 First, ceramic raw material powder is added to a binder resin such as polyvinyl butyral resin and uniformly mixed to prepare a slurry composition. The obtained slurry composition is applied to a release-treated surface of a support. The composition is subjected to heating or the
30 like to remove solvent and other volatile components, and then separated from the support to provide a ceramic green sheet. Next, the obtained ceramic green sheet is coated with a conductive paste by a method such as screen printing, where the conductive paste contains polyvinyl
35 butyral resin or the like as a binder resin. Sheets

obtained in this manner are stacked such that the ceramic green sheets and the conductive paste layers alternate with each other, and thermally pressure-bonded to provide a laminate. After debinding treatment, the laminate is fired, and external electrodes are sintered to the end surfaces of the obtained ceramic fired article. Through these steps, a multilayer ceramic capacitor can be obtained.

[0004]

Regarding the binder resin, Patent Literature 1 discloses a polyvinyl acetal resin obtained by generating acetic acid from residual sodium acetate in polyvinyl alcohol and acetalizing the polyvinyl alcohol using the obtained acetic acid as a catalyst. Patent Literature 1 discloses that using this polyvinyl acetal resin can prevent metal corrosion of surrounding equipment.

Patent Literature 2 discloses that using a polyvinyl acetal resin obtained by acetalizing a specific modified polyvinyl alcohol with acetaldehyde and butyraldehyde can increase the flexibility and the thermal fusing properties of a sheet obtained from the resin.

CITATION LIST

- Patent Literature

[0005]

Patent Literature 1: JP 3043106 B

Patent Literature 2: JP 3110146 B

SUMMARY OF INVENTION

- Technical problem

[0006]

However, for example, magnetic material powder such as ferrite powder is poorly dispersible. Using the polyvinyl acetal resin of Patent Literature 1 or 2 as a binder resin may cause magnetic material powder to

insufficiently disperse or to settle over time in the slurry composition. There is thus room for improvement in dispersing property and dispersion stability. Moreover, a sheet formed using such a slurry composition may have low mechanical strength and cause defects during processing of the formed sheet.

[0007]

The present invention aims to provide a polyvinyl acetal resin that has an excellent dispersing property and enables the production of a formed article having high mechanical strength.

- Solution to problem

[0008]

The present invention relates to a polyvinyl acetal resin having a water absorption per unit area of 2 mg/cm² or greater and 50 mg/cm² or less when formed into a film having a thickness of 10 μm.

The present invention is described in detail below.

[0009]

As a result of intensive studies, the present inventor has found out that adjusting the water absorption per unit area under predetermined conditions can improve the dispersing property for hard-to-disperse materials such as magnetic material powder and make it possible to produce a film having high mechanical strength. The inventor thus completed the present invention. The present invention can also achieve high adhesiveness to substrates.

[0010]

The polyvinyl acetal resin of the present invention has a water absorption per unit area of 2 mg/cm² or greater and 50 mg/cm² or less when formed into a film having a thickness of 10 μm. The water absorption per unit area within the above range allows an excellent ferrite dispersing property and improved strength of the resulting

sheet. The lower limit of the water absorption per unit area is preferably 3 mg/cm^2 , and the upper limit thereof is preferably 40 mg/cm^2 , more preferably 30 mg/cm^2 .

[0011]

5 The water absorption per unit area can be calculated by the following method.

Specifically, the polyvinyl acetal resin of the present invention is formed into a film having a thickness of $10 \text{ }\mu\text{m}$, dried at 70°C for three hours, and then left to
10 stand in an environment at a temperature of 20°C and a humidity of 55% for one hour or longer. A weight A of the film is then measured. Subsequently, a main surface of the dried formed film is exposed to warm water vapor having a temperature of 50°C . Exposure to water vapor is terminated
15 when waterdrops appear on the surface of the film. A weight B of the formed film is then measured. The water absorption can be calculated by subtracting the weight A from the weight B. The water absorption per unit area is calculated by dividing the water absorption by the exposed
20 area. Herein, the vapor density in the state in which waterdrops appear on a surface of the film is regarded as saturated vapor density.

[0012]

The polyvinyl acetal resin of the present invention
25 preferably has a water absorption rate of 0.2 mg/min or greater and 4.2 mg/min or less under the measurement conditions for the water absorption per unit area. When the water absorption rate is within the above range, high sheet strength can be obtained. The lower limit of the
30 water absorption rate is more preferably 0.3 mg/min , and the upper limit thereof is more preferably 4.0 mg/min .

The water absorption rate can be measured by the same method as for the water absorption per unit area. Specifically, the time from the start to the termination of
35 the exposure to water vapor is measured. The value of the

weight of the film per unit area divided by the exposure time is used as the water absorption rate.

[0013]

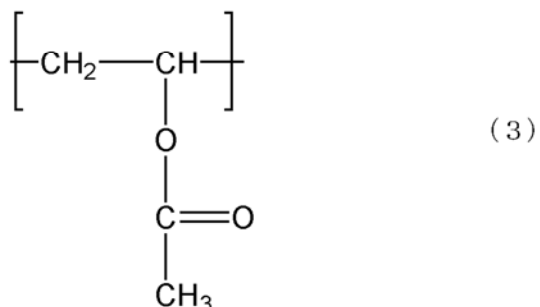
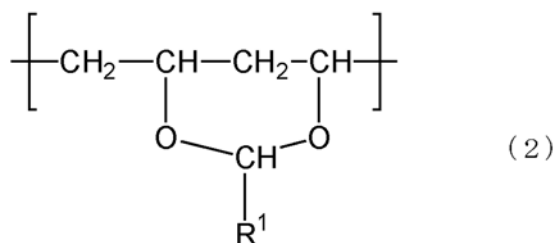
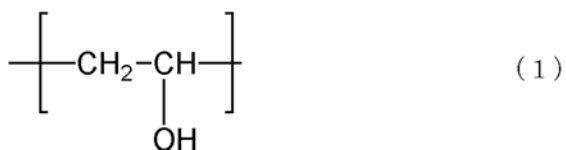
In the present invention, the polyvinyl acetal resin
5 that has a water absorption per unit area within the
predetermined range when formed into a film having a
thickness of 10 μm can be produced by adjusting factors
such as the degree of saponification, the average degree of
polymerization, and the hydroxy group half-width of the
10 polyvinyl alcohol as a raw material and acetalization
conditions. The polyvinyl acetal resin that has a water
absorption per unit area within the predetermined range
when formed into a film having a thickness of 10 μm can
also be produced by adjusting the hydroxy group content of
15 the polyvinyl acetal resin, the hydroxy group half-width of
the polyvinyl acetal resin quantified by IR measurement,
and the hydroxy group half-width of the polyvinyl acetal
resin in terms of mol% quantified by NMR measurement and IR
measurement.

20 [0014]

The polyvinyl acetal resin of the present invention
preferably contains at least a hydroxy group-containing
structural unit represented by the following formula (1),
an acetal group-containing structural unit represented by
25 the following formula (2), and an acetyl group-containing
structural unit represented by the following formula (3).

[0015]

[Chem. 1]



[0016]

In the formula (2), R^1 represents a hydrogen atom or a C1-C20 alkyl group.

5 [0017]

When R^1 in the formula (2) is a C1-C20 alkyl group, examples of the alkyl group include methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, pentyl, hexyl, heptyl, 2-ethylhexyl, octyl, nonyl, 10 decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, and octadecyl groups. Preferred among these are methyl and n-propyl groups.

[0018]

In the polyvinyl acetal resin of the present 15 invention, the lower limit of the amount of the hydroxy group-containing structural unit represented by the formula (1) (hereinafter also referred to as a "hydroxy group content") is preferably 35 mol%, and the upper limit thereof is preferably 85 mol%. The hydroxy group content

not lower than the lower limit makes it easy to adjust the water absorption per unit area to be within the predetermined range. As a result, a slurry composition obtained from the polyvinyl acetal resin of the present invention can have an excellent dispersing property and dispersion stability. Moreover, the resulting formed article can have improved mechanical strength and improved adhesiveness to substrates.

The hydroxy group content can be measured by ^{13}C -NMR, for example.

[0019]

In the polyvinyl acetal resin of the present invention, the lower limit of the hydroxy group half-width quantified by IR measurement is preferably 280 cm^{-1} , more preferably 290 cm^{-1} , and the upper limit thereof is preferably 420 cm^{-1} , more preferably 400 cm^{-1} . The hydroxy group half-width within the above range makes it easy to adjust the water absorption per unit area to be within the predetermined range. As a result, a slurry composition obtained from the polyvinyl acetal resin of the present invention can have an excellent dispersing property and dispersion stability. Moreover, the resulting formed article can have improved mechanical strength and improved adhesiveness to substrates.

[0020]

The polyvinyl acetal resin preferably has a hydroxy group half-width in terms of mol% of $0.01\text{ mol\%/cm}^{-1}$ or greater and $0.30\text{ mol\%/cm}^{-1}$ or less as determined by NMR measurement and IR measurement. When the hydroxy group half-width in terms of mol% is within the above range, the resulting ceramic green sheet can have high mechanical strength and can be less susceptible to appearance defects after cutting or dimensional changes after drying. The hydroxy group half-width in terms of mol% is more preferably $0.05\text{ mol\%/cm}^{-1}$ or greater and $0.290\text{ mol\%/cm}^{-1}$ or

less.

The IR measurement refers to measurement of an absorption spectrum by infrared absorption spectroscopy, and can be performed with an IR measurement device, for
5 example.

The hydroxy group half-width in terms of mol% can be calculated by measuring the hydroxy group half-width from the peak width at half the height of a peak appearing near 3,500 cm^{-1} in the IR measurement, then measuring the
10 hydroxy group content by NMR measurement, and dividing the hydroxy group content by the hydroxy group half-width.
[0021]

In the polyvinyl acetal resin of the present invention, the lower limit of the amount of the acetal
15 group-containing structural unit represented by the formula (2) (hereinafter also referred to as an "acetal group content") is preferably 1 mol%, and the upper limit thereof is preferably 50 mol%.

The acetal group content within the above range can
20 enhance the toughness of the resin.

The lower limit of the acetal group content is more preferably 2 mol%, and the upper limit thereof is more preferably 45 mol%.

The acetal group content herein is calculated by
25 counting acetalized two hydroxy groups because an acetal group of a polyvinyl acetal resin is obtained by acetalizing two hydroxy groups.

The acetal group content can be measured by NMR, for
example.

30 [0022]

In the formula (2), R^1 is preferably a methyl group or a propyl group.

When R^1 in the formula (2) is a methyl group, the polyvinyl acetal resin of the present invention preferably
35 has an acetal group content (acetoacetal group content) of

1 mol% or greater and 50 mol% or less.

When R¹ in the formula (2) is a propyl group, the polyvinyl acetal resin of the present invention preferably has an acetal group content (butyral group content) of 1
5 mol% or greater and 10 mol% or less. The acetal group content within the above range allows high water absorption.

[0023]

In the polyvinyl acetal resin of the present
10 invention, the lower limit of the amount of the acetyl group-containing structural unit represented by the formula (3) (hereinafter also referred to as an "acetyl group content") is preferably 1 mol%, and the upper limit thereof is preferably 20 mol%.

15 The acetyl group content within the above range can enhance the toughness of the resin.

The lower limit of the acetyl group content is more preferably 2 mol%, and the upper limit thereof is more preferably 15 mol%.

20 The acetyl group content can be measured by NMR, for example.

[0024]

The polyvinyl acetal resin of the present invention may contain a structural unit containing an acid-modified
25 group.

Examples of the acid-modified group include carboxyl, sulfonic acid, maleic acid, sulfinic acid, sulfenic acid, phosphoric acid, phosphonic acid, and amino groups, and salts thereof. Preferred among these is a carboxyl group.

30 The modified polyvinyl acetal resin having the structural unit containing an acid-modified group has better compatibility with an epoxy resin to achieve high mechanical strength.

[0025]

35 The structural unit containing an acid-modified group

may have a structure in which an acid-modified group as a side chain is directly bonded to a carbon atom constituting the main chain or a structure in which an acid-modified group as a side chain is bonded to a carbon atom
5 constituting the main chain via an alkylene group.
[0026]

The structural unit containing an acid-modified group may have a steric structure in which two acid-modified groups are bonded to the same carbon atom constituting the
10 main chain or a steric structure in which one acid-modified group is bonded to a carbon atom constituting the main chain. Alternatively, the structural unit containing an acid-modified group may have a steric structure in which one acid-modified group is bonded to each of two adjacent
15 carbon atoms constituting the main chain or a steric structure in which an acid-modified group is bonded to only one of two adjacent carbon atoms constituting the main chain. A preferred structure is a steric structure in which two acid-modified groups are bonded to the same
20 carbon atom constituting the main chain or a steric structure in which one acid-modified group is bonded to each of two adjacent carbon atoms constituting the main chain. A more preferred structure is a steric structure in which two acid-modified groups are bonded to the same
25 carbon atom constituting the main chain, because such a structure increases the steric hindrance and thereby widens the network structure of a cured product obtainable by combining the polyvinyl acetal resin and an epoxy resin, and as a result can improve the flexibility of the cured
30 product to be obtained.
[0027]

The structural unit containing an acid-modified group may have a steric structure in which acid-modified groups are bonded to carbon atoms constituting the main chain on
35 one side (isotactic arrangement) or a steric structure in

which acid-modified groups are bonded to carbon atoms constituting the main chain at alternate positions along the chain (syndiotactic arrangement). The structural unit may have a steric structure in which the acid-modified groups are randomly bonded (atactic arrangement).

[0028]

In the case where the structural unit containing an acid-modified group has a structure in which an acid-modified group is bonded to a carbon atom constituting the main chain via an alkylene group, the alkylene group is preferably a C1-C10 alkylene group, more preferably a C1-C5 alkylene group, still more preferably a C1-C3 alkylene group.

[0029]

Examples of the C1-C10 alkylene group include linear alkylene groups, branched alkylene groups, and cyclic alkylene groups.

Examples of the linear alkylene groups include methylene, vinylene, n-propylene, tetramethylene, pentamethylene, hexamethylene, octamethylene, and decamethylene groups.

Examples of the branched alkylene groups include methyl methylene, methyl ethylene, 1-methyl pentylene, and 1,4-dimethyl butylene groups.

Examples of the cyclic alkylene groups include cyclopropylene, cyclobutylene, and cyclohexylene groups.

Preferred among these are linear alkylene groups, more preferred are methylene, vinylene, and n-propylene groups, and still more preferred are methylene and vinylene groups.

[0030]

The lower limit of the average degree of polymerization of the polyvinyl acetal resin of the present invention is preferably 200, and the upper limit thereof is preferably 5,000. The average degree of polymerization

within the above range allows the resulting coating film to have sufficiently high mechanical strength.

The lower limit of the average degree of polymerization is more preferably 300, and the upper limit thereof is more preferably 4,000.
[0031]

The polyvinyl acetal resin of the present invention may be produced by, for example, a method including polymerizing a monomer such as vinyl acetate to prepare a polyvinyl acetate resin, saponifying the polyvinyl acetate resin by adding an acid or alkali, and acetalizing the resulting polyvinyl alcohol resin.

In the present invention, the polyvinyl acetal resin that has a water absorption per unit area within the predetermined range when formed into a film having a thickness of 10 μm can be produced by acetalizing a polyvinyl alcohol having a degree of saponification, an average degree of polymerization, and a hydroxy group half-width within predetermined ranges. For example, the polyvinyl alcohol resin preferably has a hydroxy group half-width of 340 cm^{-1} or greater and 380 cm^{-1} or less.

The polyvinyl alcohol resin preferably has an average degree of polymerization of 200 or greater and 5,000 or less and preferably has a degree of saponification of 70 mol% or greater and 99.9 mol% or less.

The polyvinyl acetal resin of the present invention is particularly preferably an acetalized product of a polyvinyl alcohol resin having a degree of saponification of 75 mol% or greater.

Here, such a specific polyvinyl alcohol can be provided by, for example, choosing a polyvinyl alcohol based on measurement of the physical properties of multiple types of polyvinyl alcohols, choosing a polyvinyl alcohol from commercial polyvinyl alcohols by referring to provided information about their physical properties, or

synthesizing a polyvinyl alcohol with adjusted physical properties in predetermined processes.

[0032]

The acetalization may be carried out by a known
5 method and is preferably carried out in a water solvent, a solvent mixture containing water and an organic solvent compatible with water, or an organic solvent.

The organic solvent compatible with water may be, for example, an alcoholic organic solvent.

10 Examples of the organic solvent include alcoholic organic solvents, aromatic organic solvents, aliphatic ester solvents, ketone solvents, lower paraffin solvents, ether solvents, amide solvents, and amine solvents.

Examples of the alcoholic organic solvents include
15 methanol, ethanol, n-propanol, isopropanol, n-butanol, and tert-butanol.

Examples of the aromatic organic solvents include xylene, toluene, ethyl benzene, and methyl benzoate.

Examples of the aliphatic ester solvents include
20 methyl acetate, ethyl acetate, butyl acetate, methyl propionate, ethyl propionate, methyl butyrate, ethyl butyrate, methyl acetoacetate, and ethyl acetoacetate.

Examples of the ketone solvents include acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone,
25 methyl cyclohexanone, benzophenone, and acetophenone.

Examples of the lower paraffin solvents include hexane, pentane, octane, cyclohexane, and decane.

Examples of the ether solvents include diethyl ether, tetrahydrofuran, ethylene glycol dimethyl ether, ethylene
30 glycol diethyl ether, and propylene glycol diethyl ether.

Examples of the amide solvents include N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone, and acetanilide.

Examples of the amine solvents include ammonia,
35 trimethylamine, triethylamine, n-butylamine, di-n-

butylamine, tri-n-butylamine, aniline, N-methylaniline, N,N-dimethylaniline, and pyridine.

These may be used alone or in admixture of two or more thereof. From the standpoint of the ability to
5 dissolve resin and easy purification, particularly preferred among these are ethanol, n-propanol, isopropanol, and tetrahydrofuran.

[0033]

10 The acetalization is preferably carried out in the presence of an acid catalyst.

The acid catalyst is not limited, and examples thereof include mineral acids such as sulfuric acid, hydrochloric acid, nitric acid, and phosphoric acid, carboxylic acids such as formic acid, acetic acid, and
15 propionic acid, and sulfonic acids such as methanesulfonic acid, ethanesulfonic acid, benzenesulfonic acid, and p-toluenesulfonic acid. These acid catalysts may be used alone, or two or more types of compounds may be used in combination. Preferred among these are hydrochloric acid,
20 nitric acid, and sulfuric acid, and particularly preferred is hydrochloric acid.

[0034]

The aldehyde used for the acetalization may be an aldehyde having a C1-C10 chain aliphatic group, a C1-C10
25 cyclic aliphatic group, or a C1-C10 aromatic group. The aldehyde used may be a conventionally known aldehyde. The aldehyde used for the acetalization reaction is not limited, and examples thereof include aliphatic aldehydes and aromatic aldehydes.

30 Examples of the aliphatic aldehydes include formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, n-hexylaldehyde, 2-ethylbutyraldehyde, 2-ethylhexylaldehyde, n-heptylaldehyde, n-octylaldehyde, n-nonylaldehyde, n-
35 decylaldehyde, and amylaldehyde.

Examples of the aromatic aldehydes include aromatic aldehydes such as benzaldehyde, cinnamaldehyde, 2-methylbenzaldehyde, 3-methylbenzaldehyde, 4-methylbenzaldehyde, p-hydroxybenzaldehyde, m-hydroxybenzaldehyde, phenylacetaldehyde, and β -phenylpropionaldehyde.

Cyclic multimers such as paraldehyde and metaldehyde may also be used.

These aldehydes may be used alone, or two or more types thereof may be used in combination. Preferred among these aldehydes are formaldehyde, acetaldehyde, butyraldehyde, 2-ethylhexylaldehyde, n-nonylaldehyde, and paraldehyde because they have excellent acetalization reactivity and can give a sufficient internal plasticization effect and in turn favorable flexibility to the resulting resin. More preferred are formaldehyde, acetaldehyde, butyraldehyde, and paraldehyde because an adhesive composition particularly excellent in impact resistance and adhesiveness to metal can be obtained.

[0035]

The amount of the aldehyde to be added can be appropriately determined according to the acetal group content of the aimed polyvinyl acetal resin. In particular, the amount may be 60 to 95 mol%, preferably 65 to 90 mol% relative to 100 mol% of the polyvinyl alcohol. The amount in the range is preferred because the acetalization reaction can be efficiently carried out and unreacted aldehyde can be easily removed.

[0036]

By mixing the polyvinyl acetal resin of the present invention with magnetic material powder, a solvent, and the like, a slurry composition can be produced. The present invention encompasses a slurry composition containing the polyvinyl acetal resin of the present invention, magnetic material powder, and a solvent.

The lower limit of the amount of the polyvinyl acetal resin of the present invention in the slurry composition of the present invention is 20% by weight, more preferably 25% by weight, and the upper limit thereof is preferably 65% by weight, more preferably 60% by weight.

[0037]

The slurry composition of the present invention contains magnetic material powder.

Examples of the magnetic material powder include metal particles, metal oxide particles, and metal nitride particles.

[0038]

Examples of metal particles used as the magnetic material powder include particles containing iron, particles containing cobalt, particles containing nickel, and particles containing alloys containing these metals.

Examples of the alloys include Fe-Ni, Fe-Co, Fe-Cr, Fe-Si, Fe-Al, Fe-Cr-Si, Fe-Cr-Al, Fe-Al-Si, and Fe-Pt.

[0039]

The metal oxide is preferably ferrite. Specific examples thereof include MnFe_2O_4 , CoFe_2O_4 , NiFe_2O_4 , CuFe_2O_4 , ZnFe_2O_4 , MgFe_2O_4 , Fe_3O_4 , MnFe_2O_4 , Cu-Zn ferrite, Ni-Zn ferrite, Mn-Zn-ferrite, Ba ferrite, and Ni-Cu-Zn ferrite.

[0040]

Examples of the metal nitride include Fe_2N , Fe_3N , Fe_4N , Fe_{16}N_2 , and $\text{Sm}_2\text{Fe}_{17}\text{N}_3$.

[0041]

The magnetic material powder may be, for example, spherical, elliptic, disc-shaped, needle-shaped, bar-shaped, flat, tetrapod-shaped, perforated, or porous. In particular, the magnetic material powder is preferably spherical from the standpoint of dispersion and the like.

[0042]

The magnetic material powder may be surface-treated with a silane coupling agent. Surface treatment of the

magnetic material powder with a silane coupling agent can prevent or reduce aggregation of the magnetic material powder when a large amount of the magnetic material powder is compounded.

5 [0043]

Examples of the silane coupling agent include aminosilanes such as N-phenyl-3-aminopropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-(2-aminoethyl)aminopropyltrimethoxysilane, 3-(2-aminoethyl)aminopropylmethyldimethoxysilane, and 3-(2-aminoethyl)aminopropyltriethoxysilane, vinylsilanes such as vinyltrimethoxysilane, vinyltriethoxysilane, and vinyltriacetoxysilane, methacrylic silanes such as 3-methacryloxypropyltrimethoxysilane and 3-methacryloxypropylmethyldimethoxysilane, mercaptosilanes such as 3-mercaptopropyltrimethoxysilane, 3-mercaptopropylmethyldimethoxysilane, and 3-mercaptopropylethoxysilane, epoxysilanes such as 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 3-glycidoxypropyltriethoxysilane, and 3-glycidoxypropylmethyldiethoxysilane, ureidosilanes such as 3-ureidopropyltriethoxysilane, isocyanate silanes such as 3-isocyanatepropyltrimethoxysilane and 3-isocyanatepropyltriethoxysilane, alkylsilanes such as methyltrimethoxysilane, dimethyldimethoxysilane, trimethylmethoxysilane, ethyltrimethoxysilane, n-propyltrimethoxysilane, isopropyldimethoxysilane, isobutyltrimethoxysilane, and cyclohexylmethyldimethoxysilane, and phenyltrimethoxysilane.

[0044]

Examples of the method for surface-treating the magnetic material powder with a silane coupling agent

include a wet method in which the magnetic material powder is treated in a solution in which the magnetic material powder is dispersed, a dry method in which the magnetic material powder is directly treated as powder, and an
5 integral blend method in which the magnetic material powder is treated in a resin composition in which the magnetic material powder is dispersed in a resin. In particular, a wet method is preferred to prevent or reduce aggregation of the magnetic material powder.

10 [0045]

The lower limit of the average particle size of the magnetic material powder is preferably 0.1 μm , and the upper limit thereof is preferably 100 μm .

15 The magnetic material powder having an average particle size within the above range can further improve the adhesiveness to substrates.

The lower limit of the average particle size of the magnetic material powder is more preferably 0.5 μm , and the upper limit thereof is more preferably 70 μm .

20 The average particle size can be measured by a laser diffraction-type particle size distribution analyzer, for example.

[0046]

25 The lower limit of the amount of the magnetic material powder in the slurry composition of the present invention is preferably 5% by weight, more preferably 10% by weight, and the upper limit thereof is preferably 40% by weight, more preferably 35% by weight.

[0047]

30 The solvent may be water or an organic solvent compatible with water as described above.

Examples of the organic solvent compatible with water include alcohols.

[0048]

35 The slurry composition of the present invention may

contain a resin other than the polyvinyl acetal resin, such as acrylic resin or ethylcellulose as far as it does not impair the effects of the present invention.

The slurry composition of the present invention may
5 further contain a plasticizer, a lubricant, an antistatic agent, and/or the like as far as it does not impair the effects of the present invention.

- Advantageous Effects of Invention

10 [0049]

The present invention can provide a polyvinyl acetal resin that has an excellent dispersing property and enables the production of a formed article having high mechanical strength.

15

DESCRIPTION OF EMBODIMENTS

[0050]

The present invention is more specifically described in the following with reference to, but not limited to,
20 examples.

[0051]

(Example 1)

(Production of polyvinyl acetal resin)

An amount of 500 g of a polyvinyl alcohol resin
25 (degree of saponification 88 mol%, average degree of polymerization 600, hydroxy group half-width 350 cm^{-1}) was added to 2,500 g of pure water and stirred at a temperature of 90°C for about two hours for dissolution. This solution was cooled to 40°C . To the solution was added 10 g of
30 hydrochloric acid having a concentration of 35% by weight. The solution temperature was cooled to 5°C , and 75 g of acetaldehyde was added. This temperature was maintained to perform acetalization reaction. The solution was then maintained at a solution temperature of 65°C for five hours
35 to complete the reaction, and 40 g of an aqueous sodium

hydroxide solution was added for neutralization reaction, whereby a polyvinyl acetal resin was obtained.

The obtained polyvinyl acetal resin was subjected to ^{13}C -NMR (nuclear magnetic resonance spectroscopy) to
5 measure the acetal group content (acetoacetal group content, butyral group content), the hydroxy group content, and the acetyl group content.

The obtained polyvinyl acetal resin was also subjected to IR measurement using HORIBA FT-720 (produced
10 by Horiba, Ltd.) to measure the hydroxy group half-width. Table 1 shows the results.

After the measurement of the hydroxy group half-width, the hydroxy group content measured by ^{13}C -NMR was divided by the hydroxy group half-width to calculate the
15 hydroxy group half-width in terms of mol%.

[0052]

(Example 2)

A polyvinyl acetal resin was obtained as in Example 1 except that a polyvinyl alcohol resin (degree of
20 saponification 88 mol%, average degree of polymerization 600, hydroxy group half-width 345 cm^{-1}) was used. The measurements performed as in Example 1 showed that the acetal group content (acetoacetal group content, butyral group content), the hydroxy group content, the acetyl group
25 content, the hydroxy group half-width, and the hydroxy group half-width in terms of mol% were as shown in Table 1.

[0053]

(Example 3)

A polyvinyl acetal resin was obtained as in Example 1 except that a polyvinyl alcohol resin (degree of
30 saponification 88 mol%, average degree of polymerization 600, hydroxy group half-width 345 cm^{-1}) was used, and that the amount of acetaldehyde added was changed to 7.0 g. The measurements performed as in Example 1 showed that the
35 acetal group content (acetoacetal group content, butyral

group content), the hydroxy group content, the acetyl group content, the hydroxy group half-width, and the hydroxy group half-width in terms of mol% were as shown in Table 1. [0054]

5 (Example 4)

A polyvinyl acetal resin was obtained as in Example 1 except that a polyvinyl alcohol resin (degree of saponification 88 mol%, average degree of polymerization 600, hydroxy group half-width 380 cm^{-1}) was used, and that
10 15.0 g of butyraldehyde was added instead of acetaldehyde. The measurements performed as in Example 1 showed that the acetal group content (acetoacetal group content, butyral group content), the hydroxy group content, the acetyl group content, the hydroxy group half-width, and the hydroxy
15 group half-width in terms of mol% were as shown in Table 1. [0055]

(Example 5)

A polyvinyl acetal resin was obtained as in Example 1 except that a polyvinyl alcohol resin (degree of
20 saponification 88 mol%, average degree of polymerization 600, hydroxy group half-width 370 cm^{-1}) was used, and that the amount of acetaldehyde added was changed to 110 g. The measurements performed as in Example 1 showed that the acetal group content (acetoacetal group content, butyral
25 group content), the hydroxy group content, the acetyl group content, the hydroxy group half-width, and the hydroxy group half-width in terms of mol% were as shown in Table 1. [0056]

(Example 6)

30 A polyvinyl acetal resin was obtained as in Example 1 except that a polyvinyl alcohol resin (degree of saponification 90 mol%, average degree of polymerization 600, hydroxy group half-width 335 cm^{-1}) was used, and that the amount of acetaldehyde added was changed to 7.0 g. The
35 measurements performed as in Example 1 showed that the

acetal group content (acetoacetal group content, butyral group content), the hydroxy group content, the acetyl group content, the hydroxy group half-width, and the hydroxy group half-width in terms of mol% were as shown in Table 1.

5 [0057]

(Example 7)

A polyvinyl acetal resin was obtained as in Example 1 except that a polyvinyl alcohol resin (degree of saponification 90 mol%, average degree of polymerization
10 4,500, hydroxy group half-width 345 cm^{-1}) was used, and that the amount of acetaldehyde added was changed to 75 g. The measurements performed as in Example 1 showed that the acetal group content (acetoacetal group content, butyral group content), the hydroxy group content, the acetyl group
15 content, the hydroxy group half-width, and the hydroxy group half-width in terms of mol% were as shown in Table 1.
[0058]

(Example 8)

A polyvinyl acetal resin was obtained as in Example 1 except that a polyvinyl alcohol resin (degree of
20 saponification 88 mol%, average degree of polymerization 600, hydroxy group half-width 345 cm^{-1}) was used, and that the amount of acetaldehyde added was changed to 115 g. The measurements performed as in Example 1 showed that the
25 acetal group content (acetoacetal group content, butyral group content), the hydroxy group content, the acetyl group content, the hydroxy group half-width, and the hydroxy group half-width in terms of mol% were as shown in Table 1.
[0059]

30 (Example 9)

A polyvinyl acetal resin was obtained as in Example 1 except that a polyvinyl alcohol resin (degree of
saponification 95 mol%, average degree of polymerization 600, hydroxy group half-width 345 cm^{-1}) was used, and that
35 the amount of acetaldehyde added was changed to 110 g. The

measurements performed as in Example 1 showed that the acetal group content (acetoacetal group content, butyral group content), the hydroxy group content, the acetyl group content, the hydroxy group half-width, and the hydroxy group half-width in terms of mol% were as shown in Table 1.

[0060]
(Example 10)

A polyvinyl acetal resin was obtained as in Example 1 except that a polyvinyl alcohol resin (degree of saponification 82 mol%, average degree of polymerization 600, hydroxy group half-width 345 cm^{-1}) was used, and that the amount of acetaldehyde added was changed to 60 g. The measurements performed as in Example 1 showed that the acetal group content (acetoacetal group content, butyral group content), the hydroxy group content, the acetyl group content, the hydroxy group half-width, and the hydroxy group half-width in terms of mol% were as shown in Table 1.

[0061]
(Comparative Example 1)

A polyvinyl acetal resin was obtained as in Example 1 except that a polyvinyl alcohol resin (degree of saponification 88 mol%, average degree of polymerization 600, hydroxy group half-width 335 cm^{-1}) was used. The measurements performed as in Example 1 showed that the acetal group content (acetoacetal group content, butyral group content), the hydroxy group content, the acetyl group content, the hydroxy group half-width, and the hydroxy group half-width in terms of mol% were as shown in Table 1.

[0062]
(Comparative Example 2)

A polyvinyl acetal resin was obtained as in Example 1 except that a polyvinyl alcohol resin (degree of saponification 88 mol%, average degree of polymerization 600, hydroxy group half-width 335 cm^{-1}) was used, and that the amount of acetaldehyde added was changed to 140 g. The

measurements performed as in Example 1 showed that the acetal group content (acetoacetal group content, butyral group content), the hydroxy group content, the acetyl group content, the hydroxy group half-width, and the hydroxy group half-width in terms of mol% were as shown in Table 1. [0063]

(Comparative Example 3)

A polyvinyl acetal resin was obtained as in Example 1 except that a polyvinyl alcohol resin (degree of saponification 88 mol%, average degree of polymerization 600, hydroxy group half-width 335 cm^{-1}) was used, and that the amount of acetaldehyde added was changed to 5 g. The measurements performed as in Example 1 showed that the acetal group content (acetoacetal group content, butyral group content), the hydroxy group content, the acetyl group content, the hydroxy group half-width, and the hydroxy group half-width in terms of mol% were as shown in Table 1. [0064]

(Comparative Example 4)

A polyvinyl acetal resin was obtained as in Example 1 except that a polyvinyl alcohol resin (degree of saponification 92 mol%, average degree of polymerization 600, hydroxy group half-width 345 cm^{-1}) was used, and that the amount of acetaldehyde added was changed to 6 g. The measurements performed as in Example 1 showed that the acetal group content (acetoacetal group content, butyral group content), the hydroxy group content, the acetyl group content, the hydroxy group half-width, and the hydroxy group half-width in terms of mol% were as shown in Table 1. [0065]

(Comparative Example 5)

A polyvinyl acetal resin was obtained as in Example 1 except that a polyvinyl alcohol resin (degree of saponification 90 mol%, average degree of polymerization 600, hydroxy group half-width 470 cm^{-1}) was used, and that

the amount of acetaldehyde added was changed to 75 g. The measurements performed as in Example 1 showed that the acetal group content (acetoacetal group content, butyral group content), the hydroxy group content, the acetyl group content, the hydroxy group half-width, and the hydroxy group half-width in terms of mol% were as shown in Table 1. [0066]

<Evaluation>

The polyvinyl acetal resins obtained in the examples and the comparative examples were evaluated as follows. Table 1 shows the results.

[0067]

(1) Measurement of water absorption per unit area and water absorption rate

Each of the polyvinyl acetal resins obtained in the examples and the comparative examples was formed into a film having a thickness of 10 μm by a doctor blade method, dried at 70°C for three hours, and then left to stand in an environment at a temperature of 20°C and a humidity of 55% for one hour or longer. The weight A of the film was then measured.

Subsequently, a main surface of the film was exposed to warm water vapor having a temperature of 50°C. Exposure to water vapor was terminated when waterdrops appeared on the surface of the film. The weight B of the film was then measured. The water absorption was calculated by subtracting the weight A from the weight B. The water absorption per unit area was calculated by dividing the water absorption by the exposed area.

The exposed area in the examples and the comparative examples herein was 40 cm^2 .

Further, the time from the start to the termination of the exposure to water vapor (exposure time) was measured. The value of the weight of the film per unit area divided by the exposure time was calculated as the

water absorption rate.

[0068]

(2) Dispersing property test (ferrite dispersing property)
(Production of slurry composition)

5 To 50 g of the obtained polyvinyl acetal resin were
added 21.4 g of ion-exchanged water, 28 g of ferrite as
magnetic material powder, and 0.6 g of glycerol as a
plasticizer. After stirring at 1,200 rpm for 1.5 hours
using a disperser produced by PRIMIX Corporation,
10 deaeration was performed at 1,000 rpm for 30 minutes using
Thinky Mixer produced by Thinky Corporation. Thus, a
slurry composition was produced. The ferrite used was Ni-
Cu-Zn ferrite.

[0069]

15 (Measurement of particle size distribution)

 To the obtained slurry composition were added 5 g of
ethanol and 5 g of toluene. They were stirred to produce
an evaluation solution.

 The evaluation solution was then subjected to
20 particle size distribution measurement using a laser
diffraction-type particle size distribution analyzer
(produced by HORIBA, Ltd., "LA-910") to determine the D50
particle size of the magnetic material powder. The D50
particle size after the solution was left to stand at 23°C
25 for one week was also measured in the same manner. The
rate of change in D50 particle size was calculated and
evaluated in accordance with the following criteria.

A: A rate of change of less than 30%

B: A rate of change of 30% or greater and less than 60%

30 C: A rate of change of 60% or greater and less than 100%

D: A rate of change of 100% or greater

[0070]

(3) Adhesiveness to substrates

(Production of resin sheet)

35 The obtained polyvinyl acetal resin was applied using

a coater to a release-treated PET film to give a dried thickness of 15 μm and dried at 70°C for 120 minutes to produce a resin sheet.

[0071]

- 5 The obtained resin sheet was applied to various substrates (SPCC, PET, and PC) to give a dried thickness of 20 μm and then dried to provide adhesiveness measurement samples.

10 The adhesiveness of the obtained measurement samples was evaluated using a cross-cut test specified in JIS K 5400.

[0072]

(4) Stress at upper yield point, strain at break, and stress at break

- 15 (Sheet strength)

 The stress at the upper yield point (MPa), the strain at break (%), and the stress at break (MPa) of the obtained resin sheet were measured in conformity with JIS K 7113 using a tensile tester (AUTOGRAPH AGS-J produced by Shimadzu Corporation) at a tensile speed of 20 mm/min.

[0073]

[Table 1]

	Slurry composition										Evaluation					
	Polyvinyl acetal resin										Ferrite dispersing property	Adhesiveness to substrates			Resin sheet evaluation	
	Average degree of polymerization	Acetoacetal group content (mol%)	Butyral group content (mol%)	Hydroxy group content (mol%)	Hydroxy group half-width (cm ⁻¹)	Hydroxy group half-width in terms of mol% (mol%/cm ⁻¹)	Acetyl group content (mol%)	Water absorption (mg/cm ²)	Water absorption rate (mg/cm ² ·min)	Particle size distribution		SPCC	PET	PC	Stress at upper yield point (MPa)	Stress at break (MPa)
Example 1	600	30.0	0	58.0	315	0.184	12	3.5	0.4	A	10	6	4	80	100	260
Example 2	600	30.0	0	58.0	310	0.187	12	5.0	0.5	A	10	6	4	70	95	290
Example 3	600	3.0	0	85.0	300	0.283	12	10.0	1.1	B	10	4	4	60	80	310
Example 4	600	0.0	3.5	84.5	330	0.256	12	5.0	0.6	C	10	4	4	100	90	220
Example 5	600	43.0	0	45.0	320	0.141	12	2.5	0.3	A	10	8	6	85	105	300
Example 6	600	3.0	0	87.0	290	0.293	10	48.0	3.5	B	10	4	4	60	75	230
Example 7	4500	30.0	0	60.0	310	0.194	10	5.2	0.4	C	10	4	4	125	135	350
Example 8	600	45.0	0	43.0	300	0.143	12	3.2	0.3	B	10	8	6	80	100	305
Example 9	600	30.0	0	65.0	300	0.217	5	12.0	1.3	B	10	6	4	100	90	230
Example 10	600	24.0	0	58.0	300	0.193	18	9.5	0.8	C	10	6	4	65	100	300
Comparative Example 1	600	30.0	0	58.0	275	0.211	12	1.9	0.2	D	10	4	4	50	70	200
Comparative Example 2	600	55.0	0	33.0	280	0.118	12	1.8	0.1	D	10	6	6	45	55	170
Comparative Example 3	600	0.5	0	87.5	270	0.324	12	1.5	0.1	D	10	4	4	105	110	30
Comparative Example 4	600	0.8	0	91.2	310	0.294	8	52.0	4.5	D	8	2	2	115	125	10
Comparative Example 5	600	30.0	0	60.0	425	0.141	10	1.8	0.2	D	10	4	4	130	135	105

INDUSTRIAL APPLICABILITY

[0074]

5 The present invention can provide a polyvinyl acetal resin that has an excellent dispersing property and enables the production of a formed article having high mechanical strength.

CLAIMS

Claim 1. A polyvinyl acetal resin having a water
absorption per unit area of 2 mg/cm² or greater and 50
5 mg/cm² or less when formed into a film having a thickness
of 10 μm.

Claim 2. The polyvinyl acetal resin according to
claim 1, having an average degree of polymerization of 200
10 to 5,000.

Claim 3. The polyvinyl acetal resin according to
claim 1 or 2, having an acetal group content of 1 to 50
mol%.
15

Claim 4. The polyvinyl acetal resin according to any
one of claims 1 to 3, which is an acetalized product of a
polyvinyl alcohol resin having a degree of saponification
of 75 mol% or greater.
20

Claim 5. A slurry composition comprising:
the polyvinyl acetal resin according to any one of
claims 1 to 4;
magnetic material powder; and
25 a solvent.