

Use of partially acetalized polyvinyl alcohol as a surface material in writable or printable surfaces

The present invention relates to the use of polyvinyl alcohol which has been partially acetalized with aliphatic aldehydes as a surface material in writable or printable films, especially overhead films and films for laser printers and copiers, and for coatings on paper.

Overhead films are widely used in everyday office communication. Using special pens, the customary commercial overhead films can be written on either permanently or so as to be removable by washing. For this purpose the films are modified at least on one side, for example by coating with polyvinyl alcohol.

The published specification JP-A 4-216561 describes for this purpose the use of a commercially available polyvinyl alcohol which has been partially acetalized with an aromatic aldehyde and can be applied from a solvent mixture comprising water and isopropanol. According to JP-A 4-216561 the required performance properties such as writability and transparency are achieved. One disadvantage of the process described, however, is that a solvent mixture comprising water and an alcohol is required for the application of the polyvinyl alcohol.

The object of the present invention was to provide a surface material which can be applied from a purely aqueous system for a film on which a good, wipefast written image can be produced even with conventional "hydrophilic" pens.

It has surprisingly been found that polyvinyl alcohols having a degree of acetalization of less than 20 mol%, based on vinyl alcohol units, with an aliphatic C₁-C₈-aldehyde are suitable for use in overhead films.

The present invention therefore provides for the use of a water-soluble polyvinyl alcohol which has been partially acetalized with an aliphatic C₁-C₈-aldehyde and has a degree of acetalization of less than 20 mol%, based on vinyl alcohol units, as

a surface material in writable or printable films and also papers.

The partially acetalized polyvinyl alcohol to be employed in accordance with the invention preferably has a degree of acetalization from 1 to 15 mol%, in particular from 5 to 12 mol%, based on vinyl alcohol units.

An aliphatic C₁-C₆-aldehyde, especially C₄-aldehyde, is preferably incorporated as aldehyde component into the partially hydrolyzed polyvinyl acetals. Examples of suitable aldehydes are formaldehyde, acetaldehyde, n-propanal, isopropanal, isobutyraldehyde, t-butanal, n-pentanal, n-hexanal, n-heptanal, n-octanal, 2-ethylhexanal, and especially n-butyraldehyde.

The polyvinyl alcohol employed preferably has a degree of hydrolysis of from 70 to 100 mol%, in particular from 75 to 98 mol%. The viscosity of 4% strength by weight solutions of the polyvinyl alcohol employed, in water at 20°C (in accordance with Höppler, DIN 53015), is preferably from 1 to 100 mPas, in particular from 2 to 70 mPas.

In accordance with the invention the partially acetalized polyvinyl alcohol can be used in the form of supporting films or as a coating on support films or on papers. The thickness of such coats on support films is preferably from 0.1 to 100 µm, in particular from 1 to 10 µm.

The two required properties, good writability and good water resistance, are attained by means of two contrary material specifications. If the acetalization of the polyvinyl alcohol is too high, then the resulting water resistance (wipefastness) is good but ink drying is poor. If the degree of acetalization is too low, very good ink drying but a deficient water or moisture resistance is observed. The degree of acetalization must therefore be set such that both the water resistance and the ink drying are in a balanced proportion to one another.

Since the use of organic solvents is to be avoided, there is an upper limit on the level of the degree of acetalization. This limit is dependent on the hydrophilicity of

the aldehyde which is employed for acetalization, on the molecular weight of the polyvinyl alcohol employed and on its degree of hydrolysis, but is in any case below 20 mol%, based on the vinyl alcohol units. The level of the degree of acetalization at which the product is still soluble in water depends primarily, for a given aldehyde, on the molecular weight of the initial polyvinyl alcohol. The lower the molecular weight of the initial polyvinyl alcohol, the higher the possible degrees of acetalization. Correspondingly, the converse case also applies; of course: the higher the molecular weight of the initial polyvinyl alcohol, the lower the degrees of acetalization which can be achieved at which the product is still soluble in water.

At degrees of acetalization in the upper range between 15 and 20 mol%, based on vinyl alcohol units, the product is still just soluble in water at room temperature. Very rapid drying is obtained with materials having a degree of acetalization of up to 5 mol%, based on vinyl alcohol units. However, with a low degree of acetalization the wipefastness is generally low. At a degree of acetalization of at least 5 mol%, based on vinyl alcohol units, up to the maximum degree of acetalization determined by the solubility in water, the relationship between wipefastness and drying rate is particularly well balanced.

The partially acetalized polyvinyl alcohols which are to be used in accordance with the invention can be prepared both by means of free acid, present in the aqueous medium, and by using supported acids, as described for example in German Patent Application P 196 17 893.2. The latter has the advantage that the resulting product solution does not acquire an additional salt load due to the large quantities of alkali required to neutralize the amount of acid employed. This brings with it distinct advantages for the thermal strength and the transparency of the film. In certain circumstances salts may have a deleterious effect on the transparency and on other properties, for example the adhesion of the coating to the support films. The salt can usually be removed by using dialysis device. This technique, however, is laborious and costly.

After the product solution has been prepared and neutralized, the solution can be applied direct. In the case of prolonged standing periods, preservation may be

advantageous. The solution of the partially acetalized polyvinyl alcohol can be cast to form self-supporting films or can be applied to support films. Suitable support film materials which can be coated with the partially acetalized polyvinyl alcohol are the customary film materials, examples being polyethylene terephthalate (PET), polypropylene (PP), polyvinyl chloride (PVC), polymethyl methacrylate (PMMA) and polycarbonate (PC).

The coating of these support films with the material according to the invention can take place by known methods. Suitable examples are the so-called wiper method or the use of a doctor blade.

Features of the resulting surface materials are that they are readily writable and printable with conventional "hydrophilic" commercial pens and, respectively, with laser printers, especially inkjet printers, and copiers and that the applied inscription is wipefast.

Example 1

Preparing a partially acetalized polyvinyl alcohol

98.6 grams of butyraldehyde (99%) were added to a 15% strength by weight solution of a polyvinyl alcohol of the type ®Mowiol 4-98 (Hoechst AG, degree of hydrolysis 98 mol%) and the mixture was stirred at room temperature. Subsequently, 253 ml of 20% strength by weight hydrochloric acid were metered in over a period of 60 minutes. The mixture was subsequently heated to 30°C over the course of 120 minutes and adjusted to a pH of 7 to 8 with 10% strength by weight sodium hydroxide solution. Dissolved salts were removed from the product solution by means of a dialysis device. The viscosities, measured in accordance with DIN 53015 (Höppler falling ball viscometer), at 20°C were 4.68 mPa·s for a 4% strength by weight aqueous solution and 28.36 mPa·s for an 8% strength by weight aqueous solution. The degree of acetalization was 12 mol%, based on vinyl alcohol units.

Example 2**Preparing a partially acetalized polyvinyl alcohol**

68.9 g of butyraldehyde (98.8%) were added to a 15% strength by weight solution of polyvinyl alcohol Mowiol 10-98, and this mixture was reacted in accordance with German Patent Application P 196 17 893.2 at 7°C with supported acids, which catalyze the acetalization reaction but are not dissolved in the aqueous medium. Subsequently, the reaction solution was adjusted to a pH of 7 to 8 using aqueous sodium hydroxide solution. The viscosities, measured in accordance with DIN 53015 (Höppler falling ball viscometer), at 20°C were 9.98 mPa·s for a 4% strength by weight aqueous solution and 71.5 mPa·s for an 8% strength by weight aqueous solution. The degree of acetalization was 8 mol%, based on vinyl alcohol units.

Investigation of the isolated products by differential scanning calorimetry (DSC) (in accordance with DIN 53765) shows clearly how the glass transition temperature (T_g) rises as the degree of acetalization increases in comparison with the initial polyvinyl alcohol. The relationship found is depicted in Figure 1.

Coating utility:

The polyvinyl alcohol from Example 1 with a degree of acetalization of 12 mol% and a solids content of 15% by weight was applied using a doctor blade to a 100 μm thick polyethylene terephthalate film. The film was subsequently dried at 100°C for 2 minutes. The film which results after drying on the polyethylene terephthalate film has a thickness in the range from 2 to 5 μm . The resulting composite was written on using a customary commercial ballpoint pen, for example a pen of the brand Uni-ball micro (Faber-Castell GmbH). The ink dried within a very short time on the film and could not be wiped away merely by hand. On projection with a customary overhead projector, the text on the screen was distinct and clearly legible.

Patent claims

1. The use of a water-soluble polyvinyl alcohol which has been partially acetalized with an aliphatic C₁-C₈-aldehyde and has a degree of acetalization of less than 20 mol%, based on vinyl alcohol units, as a surface material in writable or printable films or papers.
2. The use as claimed in claim 1, wherein the degree of acetalization of the partially acetalized polyvinyl alcohol is from 1 to 15 mol%, based on vinyl alcohol units.
3. The use as claimed in claim 1, wherein an aliphatic C₁-C₆-aldehyde is incorporated in the partially acetalized polyvinyl alcohol.
4. The use as claimed in claim 1, wherein n-butyraldehyde is incorporated in the partially acetalized polyvinyl alcohol.
5. The use as claimed in claim 1, wherein a polyvinyl alcohol having a degree of hydrolysis of from 70 to 100 mol% has been employed for the partial acetalization.
6. The use as claimed in claim 1, wherein a polyvinyl alcohol having a Höppler viscosity of its 4% strength by weight solution in water at 20°C of from 1 to 100 mPa·s has been employed.
7. The use as claimed in claim 1, wherein the partially acetalized polyvinyl alcohol is employed in the form of self-supporting films.
8. The use as claimed in claim 1, wherein the partially acetalized polyvinyl alcohol is employed as a coating with a thickness of from 0.1 to 100 µm.



9. The use as claimed in claim 1, wherein the film material is selected from the group consisting of polyethylene terephthalate (PET), polypropylene (PP), polyvinyl chloride (PVC), polymethyl methacrylate (PMMA) and polycarbonate (PC).
10. The use as claimed in claim 1, wherein the films are employed as overhead films.



Abstract**Use of partially acetalized polyvinyl alcohol as a surface material in writable or printable surfaces**

The use of a water-soluble polyvinyl alcohol which has been partially acetalized with an aliphatic C₁-C₈-aldehyde and has a degree of acetalization of less than 20 mol%, based on vinyl alcohol units, as a surface material in writable or printable films and also papers.

No suitable figure

Fig. 1