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COATING COMPOSITION FOR ERASABLE PAPER COMPRISING POLYVINYL ACETATE EMULSION, HYDROXYETHYLATED STARCH DISPERSION AND COLLOIDAL SILICA AND ERASABLE PAPER COATED THEREWITH

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ABSTRACT OF THE DISCLOSURE

A coating for an erasable paper includes polyvinyl acetate, chemically modified starch and an anti-blocking agent mixed in approximately 14:5:1 proportions, respectively.

This invention pertains to coated paper, especially typewriter paper adapted to withstand erasure of indicia marked thereon, to efficient coating compositions therefor which are amenable to the various other treatments such papers may be required to undergo, and to processes for the application of such coatings.

INTRODUCTION

Erasability may be defined as the property which allows typewriter ink impressions to be removed by an ordinary pencil eraser without abrasive interference with retyping upon the erased area.

Typewriter impressions are generally made from a ribbon containing an oil base ink, such as carbon black in a toner or tint oil. Typing erasability should not, however, be acquired at the expense of compatability of the coated paper with signature inks, letterhead printing inks, and other indicia forming materials or processes.

In the past casein, starch, and synthetic resin systems have been employed for erasable paper. With each of these prior systems it is necessary to compromise one or more of the several optimum attributes. Casein coating compositions because of their viscosity require multiple passes through the coating size press for the deposit of a sufficiently thick surface film. Gum arabic may be deposited in one pass but it has little or no water resistance and cannot be lithographed. Starch coatings are brittle and the resultant paper flexure strength is poor. Synthetic resin systems are generally expensive and usually exhibit blocking, sticking together of sheets, and difficult to control writing quality variations.

OBJECTS

It is a general object of this invention to provide improved coated paper compatible with a wide range of writing, printing and other marking systems and especially adapted to allow rapid, clean erasure of typing corrections without deleterious effect upon subsequent retyping.

It is a further general object to provide improved erasable paper coating compositions which are economic, relatively easily controlled and which allow for deposit of an effective erasable coating during a single pass of a base paper web through a conventional size press.

It is a further general object to provide an efficient process for application of such coatings to conventional

base paper webs with conventional paper coating apparatus.

A specific object of this invention is to provide improved coated paper from which typing corrections may be rapidly and cleanly erased without deleterious effect upon subsequent retyping and which coated paper is water stable, unaffected by thermal indicia production processes, receptive to further sensitized coatings, and retentive of flexure strength and permanence of the base paper.

A further specific object is to provide an improved erasable paper coating composition employing readily available water dispersible ingredients in low viscosity, high solids, surface sizing formulations applicable to conventional base paper webs during a single pass through a conventional size press and yielding optimum typing erasability characteristics for the coated paper with conservation of the base paper attributes and improved handling characteristics especially including non-blocking of stacked sheets.

BRIEF STATEMENT OF INVENTION

In accordance with this invention, the improved erasable coating comprises polyvinyl latex emulsion, hydroxyethylated starch, and colloidal silica, according to the respective dry weight ratio of about 14:5:1, and water; the improved erasable paper comprises a base paper web coated with the improved coating composition; and the improved processes comprise single pass size press coating of the base paper web with the improved coating composition, followed by drying in air under specific conditions of temperature, viscosity, and acidity.

DETAILED DESCRIPTION OF INVENTION

While this invention is particularly pointed out and distinctly defined in the claims appended hereto, a better understanding together with additional objects and advantages will be had upon consideration of the following specification, including specific examples of optimum and preferred material and other parameter ranges.

While advantages may be realized in other environments, this invention contemplates application of the erasable coating composition to a base paper web by a conventional size press because of its recognized efficiency and economy. Viscosity of the coating composition is of primary concern and should be below the viscosity levels at which size press roll slippage is initiated with its attendant uneven coating, web weaving, and other costly and inefficient effects. On the other hand, viscosity usually varies directly with solids content of the coating composition and the latter factor should be great enough to yield a sufficient coating thickness during a single pass through the sizing apparatus. Operating cost is an obvious factor here, but coating non-homogeneities and other more subtle effects are also to be considered.

The paper to be coated according to this invention may be any typing paper grade but it is preferably a rag bond comprised of 75% chemical wood pulp and 25% cotton linter or rag fibers and treated with an internal size under alkaline conditions and an initial wet starch size during web formation.

The major constitutent of the coating composition is a polyvinyl latex in the form of a suitable dispersion of the type resulting from the aqueous emulsion polymerization of the vinyl acetate monomer. It should be realized, of course, that additives may be present in the emulsion

such as surface active agents and protective colloids. Further, in order to obtain certain characteristics, the latex, rather than being a vinyl acetate homopolymer, may be a copolymer resulting from inclusion of minor amounts of an acrylate monomer during emulsion polymerization. The film forming or heat seal temperature of the latex may be adjusted in this manner. Therefore, when polyvinyl acetate emulsion is specified hereinafter, the term should be understood as referring to an aqueous emulsion consisting essentially of polyvinyl acetate which may include minor copolymerized fractions of a vinyl acrylate derivative. Commercial equivalents of these polyvinyl latices are readily available.

The desirable characteristics of the polyvinyl latex include formation of a clear, continuous, water-resistant film. While this property has been employed for coating wall papers and the like, the concomitant brittleness of the film has presented an overriding disadvantage where adaptability to folding is necessary. Conversely, when such a latex has been modified to generate a flexible film, the concomitant softening has presented an overriding disadvantage of blocking, i.e. cohesion between adjacent coated surfaces. Applicant has discovered unique attributes of emulsion polymerized polyvinyl latex which, in the combinations of this invention, cooperate to produce a non-blocking coating retaining flexure strength and abrasion resistance.

Starch, of course, has been an historic surface coating material. Its primary advantage has been relatively low cost but this is offset by poor water resistance. As an additive, starches usually increase viscosity and hamper size press operations. Applicant has discovered, however, that starch reacted with ethylene oxide in an alkaline medium has special attributes in the coating composition of this invention. The colloidal properties of the hydroxyethylated starch appear to provide greater uniformity in the particulate mixture with the latex resins. In addition, the solids content of the mixture as plotted against viscosity, diverges from the normal solids viscosity function to yield a greatly improved solids content deposit per single size press pass. Applicant has found that hydroxyethylated potato starch is unique in its contributions to the coating composition of this invention. At respective ratios hereinafter further defined, maximum dry solids content of the resultant surface film with respect to application viscosity is achievable with positive increase in the erasability, flexure strength, water resistance and permanence of the coated paper.

The third major ingredient of the coating composition of this invention is colloidal silica such as is derived by dispersing a silica aerogel in water. Uniquely, this material when added according to specifically defined ratios, reduces the blocking tendencies of the latex films to a minimum without reduction in erasability of the coated paper. Further, effective amounts of colloidal silica have been found not to increase viscosity even though providing a significant increase in the solids content of the coating composition. It should be understood that the term colloidal silica as used in describing this invention refers to silica in the form of particles of colloidal dimensions, i.e. about .001 to .01 micron, in a stable aqueous dispersion.

As a minor ingredient whose use depends upon the type of emulsion polymerization system in which the polyvinyl latex was produced, a paraffin wax emulsion may be added to counteract the effect of surface active agents upon feathering of water base inks. This material adds some anti-blocking properties to the coated paper but it may also cause pen line skips. The latter may be corrected by use of an equal dry solids proportion of rosin size.

Other non-specific ingredients which may be employed include a defoaming agent and an alkali such as ammonium hydroxide for pH control.

In the following examples, the percentage quoted for each ingredient is in terms of the ratio of the dry solids weight of that material to the total dry solids weight. Stated values should be read as having a precision of ±½% and this meaning should be given to "about" as a qualifier.

The first example is of the most effective values and it is followed by examples chosen from the research data without regard to chronology for the purpose of illustrating the optimum and useful ranges of the several parameters. In each instance where heat seal temperature is specified, it is the temperature in degrees Fahrenheit at which a film formed from the specified latex can be fused to itself.

PRIMARY EXAMPLE

	Percent
(a) Polyvinyl latex consisting essentially of an aqueous emulsion of polyvinyl acetate, average particle size less than 0.2 micron, heat seal temperature to 165° F.	68
(b) Hydroxyethylated potato starch	25
(c) Colloidal silica	5
(d) Paraffin wax emulsion	<1
(e) Rosin size	<1
(f) Defoamer	<1
(g) Sufficient water to adjust total solids percentage composition of sample to 34½%.	
(h) Sufficient ammonium hydroxide to adjust sample to pH 8.4 to 8.5.	

The base paper web is sized with this coating composition in a conventional top-roll-driven size press of a Barber drier coating machine. The viscosity of the coating composition is 65 to 70 seconds at 100° F. as measured with a Dudley Pipette (reference: 34 seconds for water). It is of utmost importance to note that the percentage dry solids of this example is much higher than the maximum percentage dry solids applicable from prior compositions for erasable paper coatings. Even at this high solids concentration, there is no slippage or weaving of the base paper web during the size press transit.

After air drying in the Barber drier at air temperatures initially exceeding the heat seal temperature of the latex, the paper is ready for immediate sheet preparation and handling. No measurable blocking is detectable between adjacent sheets pressed together under a pressure of 2 p.s.i. at 100° F. for 5 days.

The coated paper is found to allow clean erasure of typing with an ordinary pencil eraser within an elapsed time of at least 4 hours. Up to 24 hours after typing, erasures may still be made without interference with the legibility of retyping. No detectable abrasion of the base paper accompanies these erasures.

The coated paper is found to be compatible with all major printing processes for letterheads and the like ordinarily applicable to typewriter paper specifically including lithography and thermal processes. Particularly advantageous is the resistance of this paper to deleterious effects of toluene in certain further coating processes.

Permanence of the base paper is not detectably diminished. Accelerated oven aging tests indicate a 300 year retention of flexure strength for coated 25% rag bond paper.

Example A

The ingredients and proportions of the primary example are repeated except that particle size of the polyvinyl latex is increased. At average particle sizes significantly greater than 0.2 micron blocking is qualitatively increased and may occur near the bottom of basis weight stacks of cut sheets after prolonged storage at 100° F. Blocking becomes objectionable at average particle sizes greater than about 0.5 micron. These variations may be explained by the hypothesis that the smaller particles of the latex are effectively surrounded at all surfaces by the starch and silica particles and that this screening becomes markedly less effective when average latex particle size exceeds 0.5 micron.

Example B

The ingredients and proportions of the primary example are repeated except that the proportion of the polyvinyl latex is varied. Between about ±2 percentage points of the optimum proportions there is a qualitative change in the composite figure of merit for the coating composition and the divergence becomes significant at about 66% and 70%. Blocking increases with additional latex as does total cost; erasability and flexure strength decrease as the latex fraction is reduced. Above about 75% latex, the slope of the blocking versus latex content function is quite steep and cannot be improved by the use of higher heat seal temperature latices without embrittlement of the surface coating. Below about 60% erasability of typing without abrasion of the base paper does not leave a clear area for retyping, solution viscosity relative to total solids content presents size press difficulties, and flexure strength measured as a function of number of folds without rupture decline sharply.

Example C

The ingredients and proportions of the primary example are repeated except for the hydroxyethalated starch fraction. Substitution of different hydroxyethalated starches generally increases the composition viscosity for a given total solids content so that, if total solids content for one-pass coating is maintained, size press operation becomes erratic. With other starches the total solids content cannot be maintained with acceptable viscosities.

Similar difficulties become quantitative when the hydroxyethylated potato starch content is varied by more than about 2 percentage points, with viscosity increasing directly and blocking increasing in indirect proportion. At about 30% HE potato starch the necessary total solids content of the erasable coating cannot be maintained simultaneously with the viscosity necessary for reliable one pass size press operation, flexure strength falls off rapidly, and erasure erosion is evident. At about 20% the total cost of the coating composition becomes a very significant factor in the overall figure of merit and blocking accelerates beyond acceptable limits.

Example D

The ingredients and proportions of the primary example are repeated except that the proportion of the colloidal silica is varied. The presence of the effective proportion of this ingredient is easily recognized as critical. Increased blocking is immediately apparent as the colloidal silica fraction is reduced and blocking under the standard test cannot be avoided with a dry solids weight of less than 5% of the vinyl-starch solids. Erasability decreases as the colloidal silica fraction is increased and the decline is quantitative above 6%. The overall figure of merit function with respect to this variable slopes sharply above 7% due to poor erasability and precipitively below 4½% due to blocking. A unique advantage of this material is that its inclusion has no measurable effect upon coating composition viscosity within the effective and optimum ranges.

Example E

While the more restrictive percentage proportions of the primary example produce the optimum erasable coating composition, it is determined that a very advantageous working formulation may be stated for the main ingredients as 14:5:1 for the polyvinyl latex, the hydroxyethylated starch, and the colloidal silica, respectively, in terms of their dry solids content.

NON-SPECIFIC INGREDIENTS

Maximum erasability with respect to protection of the base paper against abrasive erosion is a function of the total solids concentration in the aqueous dispersion of the coating composition at the size press. The limitation here is viscosity which increases directly with the total solids content. The optimum total solids composition value is found to be about 34%, the optimum range to be 32 to 40%, and the effective range to be 30 to 46½%.

As mentioned previously, defoaming colloids and paraffin emulsion may be added for their conventional operative purposes and the paraffin emulsion may contain rosin size, as also appreciated by the prior art.

It is important to note that the coating compositions of this invention may be adjusted to relatively high pH values with only small amounts of added alkali, less than 10 lbs. 26° Baumé ammonium hydroxide per 500 gal. of the coating composition. This is because of the relatively high pH values of the major ingredients. The unique result is that permanence of the coated paper is readily enhanced. The alkaline medium increases the mechanical stability of the latices and prevents any thickening action by the colloidal silica. Above pH 8.5 degradation of the latex is observable and below pH 8.4 the properties of the dispersion are adversely affected.

PROCESS EXAMPLES

Commercial polyvinyl latex and colloidal silica are employed as received and comprising approximately 50% dry solids and 35% dry solids, respectively, in water.

The commercial hydroxyethylated starch is prepared as a 20% dry solids solution by slurrying in water, heated to 185° F. for 25 min. and then cooled to 140° F. before mixing with the latex emulsion and silica colloid. These temperatures are most significant, the first for proper dispersion of the starch and the second for avoiding heat shock and precipitation of latex particles during mixing.

Minor amounts, less than 1%, of defoamer and paraffin-rosin size emulsion are included as desired.

The mixture pH is then adjusted to the final value of 8.4 to 8.5. Preferably the coating composition batch is employed immediately without any reheating. However, the mixture has good stability for at least 24 hours especially if insulated or if net heat loss is restricted by low temperature size tub heaters.

The coated web after a single pass through the size press is conveyed immediately to the air jet section of the Barber drier and contacted by heated air at a temperature between a maximum of 200° F. and a minimum determined by the heat seal temperature of the latex employed.

CONCLUSION

The coated paper made according to this invention and employing the coating compositions of the preferred examples exhibits the primary property of erasability of typing, cleanly and without erosion or other retyping disability. Further properties uniquely include compatibility with other indicia formation processes, thermography without blister or degradation, lithography without water smear or feather, and resistance to solvents such as tolulene. No less important attributes are the retention of flexure strength and permanence and the practical elimination of blocking. And there are the further economic advantages of low cost and amenability to efficient manufacturing procedures utilizing conventional apparatus.

While the invention has been set out and explained by way of specific examples and with respect to a preferred base paper and other definite parameters, it is to be understood that no restrictions are to be implied and that the apended claims are aimed to cover all modifications falling within the true spirit and scope of the invention.

What is claimed is:

1. A coating composition for erasable paper comprising polyvinyl acetate emulsion, hydroxyethylated starch dispersion, and colloidal silica according to the respective dry weight ratios of 14:5:1, and sufficient water to adjust the coating composition viscosity to between 65 and 70 seconds Dudley at 100° F.

2. A coating composition for erasable paper comprising polyvinyl latex, dry weight 60–75% of total solids; hydroxyethylated starch, dry weight 20–30% of total solids; colloidal silica, dry weight 4½–7% of total solids;

sufficient water to maintain total solids percentage composition by weight of 30–46½%; said polyvinyl latex consisting essentially of an aqueous emulsion of polyvinyl acetate having an average particle size less than 0.5 microns and heat seal temperature of 140°–185° F.

3. A coating composition for erasable paper comprising polyvinyl latex, dry weight 66–70% of total solids; hydroxyethylated starch, dry weight 23–27% of total solids; colloidal silica, dry weight, 5–6% of total solids; and sufficient water to maintain total solids percentage composition by weight of 32–40%; said polyvinyl latex consisting essentially of an aqueous emulsion of polyvinyl acetate having an average particle size less than 0.2 micron and a heat seal temperature of 140–185° F.

4. Erasable paper having a size coating formed thereon comprising polyvinyl acetate, hydroxyethylated starch, and colloidal silica according to the respective dry weight ratios of 14:5:1.

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