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PROCESS FOR COATING PAPER WITH A HEAT FLOCCULATABLE LATEX-BASED COMPOSITION AND THE RESULTANT PRODUCT

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ABSTRACT OF THE DISCLOSURE

A novel paper coating composition is disclosed that is fluid at conventional coating temperatures below 40° C. but gels to a firm state when heated to a temperature above 40° C. The aqueous coating composition comprises a conventional coating clay, an adhesive latex binder, and a dispersant for the clay. A minimal amount of the dispersant is used to secure the desired heat gelability. The coating composition does not require and is free from polyvalent, metal salt electrolytes that would counteract or reduce the dispersing action of the dispersing agent.

The process of using the novel coating composition is claimed, especially in conjunction with a cast coating step.

The present invention relates to an aqueous, latex-based paper-coating composition that turns to a non-flowable gel when moderately heated, and to a method for producing a coated paper therewith, especially a cast-coated paper having a high degree of flatness and smoothness and a gloss ranging from moderate to mirror-like.

This application is related to application Ser. No. 331,220 "Heat Coagulatable Paper Coating Composition," by Hideiku Nakajima and Hideo Shimizu filed simultaneously herewith.

Coated printing papers have been produced by several methods. One of them comprises coating a paper with an aqueous composition containing pigments and bonding or adhesive agents, drying until the coating layer is solidified, and supercalendering the dried coating to give smoothness and gloss to the coating. It is, however, undesirable to perform the finishing operation on a solidified and non-plastic coating. The high pressures applied reduce the bulk of the coated paper and deteriorate opacity and whiteness as well as the elasticity which is desirable in printing. In spite of the high pressure employed, satisfactory smoothness of the coating often cannot be obtained. The high pressures employed may break the web and cause an interruption of the paper-making process. In addition, the coated layer is often injured by undue friction with the roll, and by bruises on the roll caused by pieces of paper picked up by the roll.

Cast-coating of papers avoids the use of supercalenders. The cast-coating method comprises coating a paper with an aqueous coating composition containing pigments, bonding agent, and perhaps an oily material or the like, drying the paper while pressing the paper on a polished, heated, metal surface, and then, after a period required for drying, separating the paper from the metal. A coated paper is obtained that has a high smoothness and a mirror-like gloss without treatment by supercalender rolls.

Until recently the temperature of the metal surface had to be maintained below 100° C., usually in the range of 85 to 90° C., in order to obtain a uniform cast-coated paper with no defects in the coating. The moisture in the wet coated layer contacted with the metal surface was merely gradually evaporated through the paper web. Consequently, this method has the disadvantage that the production rate of the coated paper may be extremely low.

One improvement of the cast-coating process comprises

contacting the wet coating with an aqueous solution containing coagulant to cause setting of the coating, and then drying the paper by pressing it against a heated metal surface. This method comprises: coating paper with composition containing pigments, bonding agents such as casein and the like, and a chelate compound which is stable in alkaline solution; immersing the coated layer into an acid bath to lower the pH of the coating and to coagulate the layer chemically; drying the paper by pressing it against a heated metal surface; and then separating the paper from the metal surface. As the coating has already been coagulated, a metal surface temperature higher than 100° C., i.e. from 120° C. to 150° C., may be employed to evaporate the water without injuring the coating. This method has an advantage of producing a coated paper more rapidly than any of the previous methods. The paper can be separted more easily from the heated metal surface than in the conventional method and build-up of the coating composition in the casting nip does not occur because of the low fluidity of the layer. The coating also has good resistance to water.

The coagulation method has the following disadvantages because of the need to use an acid bath to coagulate the coating. When an acid bath is used, the machine must be carefully protected from corrosion by the acid. Troublesome pH adjustment of the bath is sometimes necessary. When a coated paper is immersed into the acid bath at a high speed, accidents may occur because of splashes of the acid around the bath, or the acid may flow to the other side of the paper. A striped pattern with uneven luster is sometimes formed on the surface of the cast-products because of mechanical contact with the fluid coated layer just before the acid section and because of the flow of excess acid on the coating. Another fundamentally important disadvantage is that it is difficult to use this technique with thin papers because when the paper with the wet coating is immersed in the acid bath, the paper may be lowered in strength and become breakable. The expected increase of the production rate may not be achieved because the additional water absorbed by the paper must be evaporated during the drying process.

By the detailed studies of the mechanism of the heat coagulation or so called heat-gelling of aqueous coating compositions comprising pigments and proteinaceous and latex adhesives, a latex-based coating composition has been discovered which can be rapidly coagulated or gelled by heat at and above a definite temperature, without the need to remove any volatile matter or use externally applied chemical treatments, and which may be employed in cast-coating and other paper coating methods.

In brief compass, the present invention is based on the discovery that a paper coating composition containing a mineral pigment with some adsorptive properties in combination with a latex adhesive and a proper amount of a suspending agent, which may be an adhesive of a different type, can be made to undergo coagulation by modest heating, or heat flocculated, by adjusting the stability of system with respect to flocculation of the pigment to be just beyond borderline stability at room temperature. Modest heating of such a slurry to an elevated temperature above about 40° C., and as high as 90°–100° C. for some particular slurries, causes the pigment to desorb the suspending agent and flocculate, with apparent gelation of the slurry to such a firm condition that the slurry will not flow, e.g. such that it cannot be poured from a beaker. This applies to the fairly high solids content slurries, over 30 weight percent and preferably over 40 weight percent total solids, customarily used in coating papers. This heat gelation or flocculation is usually reversible, i.e. cooling of the slurry with stirring returns it to its original viscosity.

Until the present invention, it was believed to be mandatory to incorporate polyvalent electrolytes or ionizable materials in a paper coating composition in order to create a heat gelable system. This was on the mistaken assumption that heat gelling or coagulation was solely the result of a change in the adhesive and that an electrolyte was needed to bring about this change in the adhesive to the extent and at the temperature desired.

It has now been found, however, that heat gelling does not depend uopn a change in the adhesive, but is primarily related to the state of suspension of the pigment. With this knowledge, it is possible to create heat gelable coating compositions for cast coating free from added electrolytes, especially polyvalent electrolytes such as salts of polyvalent metals, the presence of which may affect color besides having other deleterious effects.

In paper-coating slurries, the pigment is suspended because of the repulsive action of the like electrical charges on each of the pigment particles. The pigment particles carry a charge by virtue of having adsorbed some type of suspending or dispersing agent. Most of the mineral pigments customarily used in paper coating compositions are adsorptive to some extent and are useful in the practice of this invention. When designing a high solids system to have borderline stability, consideration must be given to all the ingredients in the slurry that effect the dispersing of the pigment particles. The customary proteinaceous and vegetable adhesives such as casein and soy protein have some pigment dispersing power, and this must also be taken into account. In one embodiment of this invention a proteinaceous adhesive is used to suspend the pigment without the use of added suspending agents. Latex adhesives usually are not efficient dispersants and generally speaking can be used in widely varying amounts without markedly affecting the stability of system. Latices as purchased, however, do contain chemical dispersants or surfactants and the effect of any such dispersants must be balanced out in compounding a heat gelable slurry.

Dispersing or suspending agents are usually present in a latex-based coating composition because frequently it is desirable to use them or because they are brought in with the latex or the pigment. In the practice of this invention their effect must not be such, however, as to make the slurry so stable as to not be capable of undergoing heat gelation. The pigment must be dispersed in a slurry system that would not be fluid with mild stirring or agitation without some type of a suspending or dispersing agent. Many of the commercial pigments available today contain a dispersant that was added to facilitate grinding and/or wettability. The amount and nature of this dispersant must be kept in mind in the practice of this invention.

It has also been observed that if the heat flocculation occurs at a lower temperaure in the range of 100° to 130° F. the point of flocculation is sharper and the gel is firmer. The closer the slurry is maintained to borderline stability, the lower will be the temperature required for flocculation because less suspending agent needs to be desorbed from the pigment. The heat flocculation also improves as the solids content of the slurry is increased. The coatings of the invention gel better when actually applied to a paper sheet as compared to the condition observed when gelation is carried out in a beaker because of the loss of some of the water of the coating to the paper web.

Prior art paper coating compositions contained far too much of materials that acted to disperse the pigment and thus were so stable as not to be capable of undergoing heat flocculation in the manner of this invention. The stability of some prior art formulations can be driven down to the desired point of borderline stability by the use of electrolytes, but most of them are much too stable under the conditions normally used in preparing them as to be gelable. In preparing a heat flocculable coating slurry in the manner of this invention, the total level of

all potential dispersants in the system must be such that the pigment is not suspended too efficiently. Usually some continuous stirring or agitation must be used to keep the slurry in a fluid condition at its temperature of preparation, but this is not always the case.

In accordance with the method of invention, when a layer of the present latex-based coating composition on a paper web is heated to an elevated temperature, it coagulates rapidly without the aid of the evaporation of volatile matter such as water, and sets while wet to a state that is amenable to casting. The method of the present invention has the advantage that pollution of the drum and injury of the paper surface does not occur upon contact of the paper with the coating drum. Also, the drying of the coagulated coated layer after the contact with heated drums is greatly promoted. While cast-coating is the preferred embodiment of the paper-manufacturing process of this invention, other methods of imparting a smooth surface can of course be used.

Inorganic pigments which can be used in the present invention include the well-known pigments such as zinc oxide, talc, zinc sulfide, titanium white, barium sulfate, hydrated alumina, ground limestone, blanc fixe, calcium carbonate, iron oxide, calcium silicate, carbon black and the like, in addition to clay.

Any heating method by which the temperature of the coating layer is elevated above its coagulation temperature and below 100° C. can be employed in this invention. Steam can be blown on the wet coating layer to heat it by condensation of the steam, or electric, gas, infrared ray, or high frequency heating can be used. Sufficient heating can be obtained by passing the paper through hot water, or conduction heating can be carried out by contacting the paper with a heated roll. It is only necessary for the coating to be heated fairly uniformly through all parts, and to be heated rapidly to a temperature higher than its coagulating temperature.

The beginnings of this invention had roots in experiments attempting to modify conventional coating compositions by the addition of electrolytes to cause them to, as it was initially called, heat gel. It was thought the electrolytes were acting on the adhesive. As might be expected, only some of the first experiments were successful but as the work progressed and the mechanism of pigment flocculation became clearer, possible explanations for several previously unexplainable experiments could be developed, as for example the following:

(1) A casein adhesive solution mixed with salts of polyvalent metals would not gel unless some pigment was present. This indicates that the salts were not acting on the adhesive alone and that the pigment played a part in the gelation.

(2) Coating slurries containing less dissolved casein required less of the polyvalent metal salts to heat gel them. Assuming equilibrium, less dissolved casein meant that there was less casein available as a colloid protecting the pigment slurry.

(3) A coating slurry containing 17 parts of casein and 7 parts of a butadiene-styrene adhesive required less salt for gelation than one containing 18 parts of the casein alone. A latex is a good adsorbent for the dissolved casein, and has little or no pigment dispersing properties; thus as the latex adsorbs casein less casein can remain on the pigment because it must be in equilibrium with that left in solution and the stability of the pigment slurry is lowered.

(4) When heat gellable coatings containing salts were heated, their conductivity increased continuously and uniformly with temperature through and past the gel point. Thus, there was no charge in the ionic activity of the salts present in the coating that could be the reason for the gellation.

(5) Heat gellable casein-type coatings with the lowest water retention gelled best or gelled easiest. Lower water

retention is an indication of less dissolved casein and thus of less protective colloid.

(6) A coating slurry based on an acid casein can be made to undergo heat gelation without the addition of polyvalent metal salts if the pH thereof is brought near enough to the isoelectric point of the casein. As the pH of the coating approaches the isoelectric point of the casein, less of the casein is dissolved and again there is less protective colloid.

These and other results lead to the conclusion that it was the stability of the pigment suspension that was the controlling factor. This permitted the development of coating compositions that did not depend on electrolytes to impart heat gelability, and also ones having lower temperature transition points and sharper transitions into the gel state.

The following table gives examples of this invention and comparative examples:

	This Invention		Comparative	
	A	B	C	D
Composition:				
Clay #1, grams			200	200
Clay #2, grams	200	200		
TSPP, grams			0.6	0.6
Latex #1, grams (dry basis)	16	26	16	26
Latex #2, grams (dry basis)	16		16	
Alkaline Casein, grams		4		4
NH_4OH (conc.), grams	3	0.5		0.5
Dicyandiamide, grams		0.8		0.8
TBP, ml	1	1	1	1
Properties:				
Brookfield viscosity	71	100	51	44
Electrical water retention	1.5-2	<½	1.5-2	1.5-2
pH	9.40	7.70	8.60	8.55
Percent solids	43	43	43	43
Heat gelation temp., ° F	160-180	160-180	None	None
Inspection of Coated Paper:				
Caliper mils	3.1	3.1	3.1	3.1
Gloss	77	75	81	75
Brightness	81.0	81.4	80.6	80.9
Opacity	92.3	92.4	92.5	91.9

Clay #1—An English coating clay predispersed with 0.4 gm. of TSPP per 100 gms. of clay.
Clay #2—The same clay but not predispersed; cf. U.S. Patent 2,500,972.
Latex #1—A butadiene-styrene latex (Dow 512R).
Latex #2—A butadiene-styrene latex modified by incorporation of a small amount of an acrylic monomer and α-β unsaturated di-basic acid, adjusted by addition of NH_4OH.
TSPP—Tetrasodium pyrophosphate.
TBP—Tributyl phosphate.

In compositions B and D the casein, dicyandiamide and ammonia were first mixed with 20 grams of water and then added to the remainder of the ingredients, see U.S. Patent 3,081,182. Suitable dilution water was used in all examples to achieve 43% solids.

Each composition was applied to a machine coated body stock at 10 pounds per ream with a laboratory air knife coater. Drying was by a radiant convection dryer (Arvin). The dried sheets were calendered 6 nips at 140–150° F. and 2000 pounds per linear inch. The sheets were preconditioned before calendering at 70° F. and 50% relative humidity.

Composition A can be applied to cast coating as follows: The composition is applied to a paper having a weight of 60 pounds per ream in an amount of 10 pounds per ream (500 sheets—24 x 30 inches). The wet coating is immediately heated to 200° F. by radiant heating and pressed against a rotating polished chrome plated drum by means of a rubber covered roll. The drum temperature is 250° F. and its velocity is 210 feet per minute. A paper having a high degree of smoothness and a mirror-like gloss is obtained.

In summary, this invention resides in an improved paper coating composition and the process and product based thereon. The composition consists of an aqueous slurry free from any significant amount of polyelectrolytes, especially those having polyvalent metal ions such as calcium, and containing a suspended or dispersed adsorptive paper-coating grade pigment, a dispersant therefor and an adhesive binder at least 30 percent of which consists of a synthetic latex adhesive. The stability of the suspension is adjusted so that it is slightly beyond border-line stability at about 25° C. and flocculates to a non-flowable

state at an elevated temperature above about 35° to 40° C. and as high as 90 to 100° C.

One preferred embodiment is based on a 100% latex system with a conventional dispersant, either ionic or non-ionic, being used for the pigment. This embodiment has the advantage of being particularly amenable to being smoothed by heated surfaces or rolls since the adhesive is thermoplastic.

In another embodiment, some and preferably substantially all of the requisite dispersing of the pigment is achieved by the means of a conventional proteinaceous adhesive with the balance of the adhesive required for bonding of the pigment being made up with a latex. This type of slurry has the advantage of giving a firm gel at a low temperature in the order of 40 to 50° C. For an acid casein, the adhesive binder should consist of preferably about 40 to 60 weight percent casein with the remainder being latex. With an alkaline casein only 10 to 30% of the total adhesive needs to consist of the casein because alkaline caseins are much more efficient dispersing agents for pigments.

Having described this invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

We claim:

1. A fluid paper coating composition comprising an aqueous slurry containing at least 30 weight percent solids, said solids being comprised of a suspended paper-coating grade pigment, a thermo-sensitive dispersant therefor and a synthetic latex adhesive binder, with the pigment dispersant being selected from the group consisting of casein, carboxylated synthetic latex or mixtures thereof and present in an amount sufficient to impart borderline stability to the pigment suspension at 25° C. with agitation and which allows the pigment suspension to flocculate to a non-flowable state at a temperature of 40° to 100° C. and said aqueous slurry being free from any significant amount of polyvalent metal salt electrolyte that counteracts the effect of said dispersant.

2. The composition of claim 1 wherein the pigment dispersant is alkaline casein with the mixture of alkaline casein and synthetic latex adhesive binder being comprised of from 10 to 30 weight percent alkaline casein.

3. The composition of claim 1 wherein the pigment dispersant is acid casein with the mixture of acid casein and synthetic latex adhesive binder being comprised of from 40 to 60 weight percent acid casein.

4. The composition of claim 1 wherein the synthetic latex adhesive binder is a carboxylated synthetic latex.

5. The paper coating process which comprises applying to a base sheet the coating composition claimed in claim 1 with the coating being applied at a temperature between 20° and 35° C., heating the applied coating to a temperature between 40° and 95° C. to gel said coating and thereafter drying the gelled coating.

6. The process of claim 5 wherein said base sheet is prime coated and wherein the drying is accomplished by casting the gelled coating against a smooth heated surface such that a cast-coated paper is produced.

7. The product produced by the process of claim 5.

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