

Dec. 5, 1967

HIDEIKU NAKAJIMA ET AL

3,356,517

HEAT COAGULATABLE PAPER COATING COMPOSITION

Filed Dec. 17, 1963

2 Sheets-Sheet 1

FIG. 1

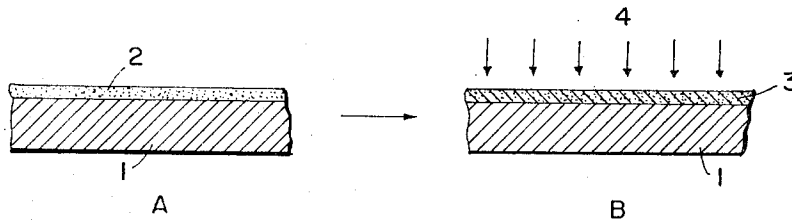


FIG. 2

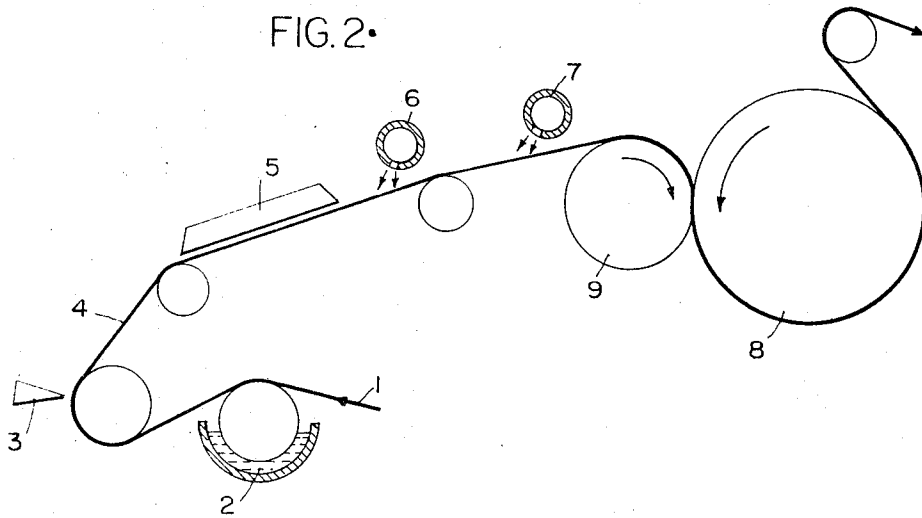
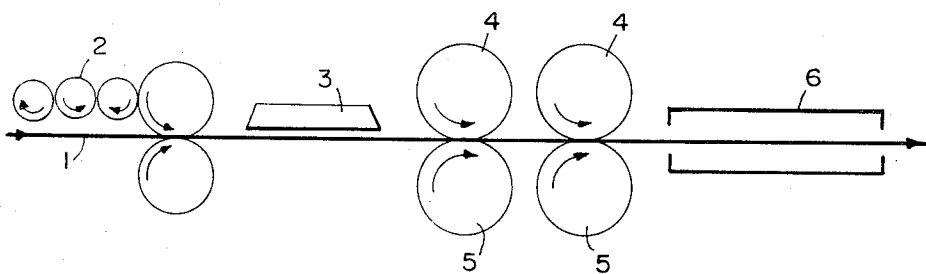


FIG. 3



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2 Sheets-Sheet 2

FIG. 4

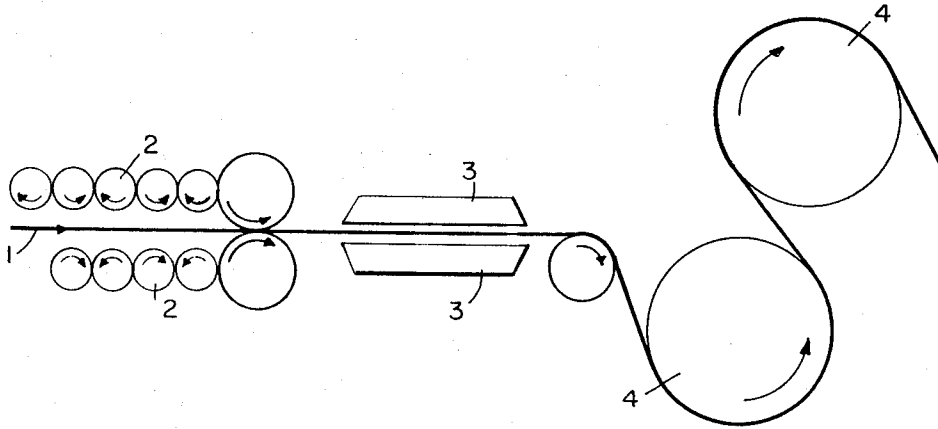
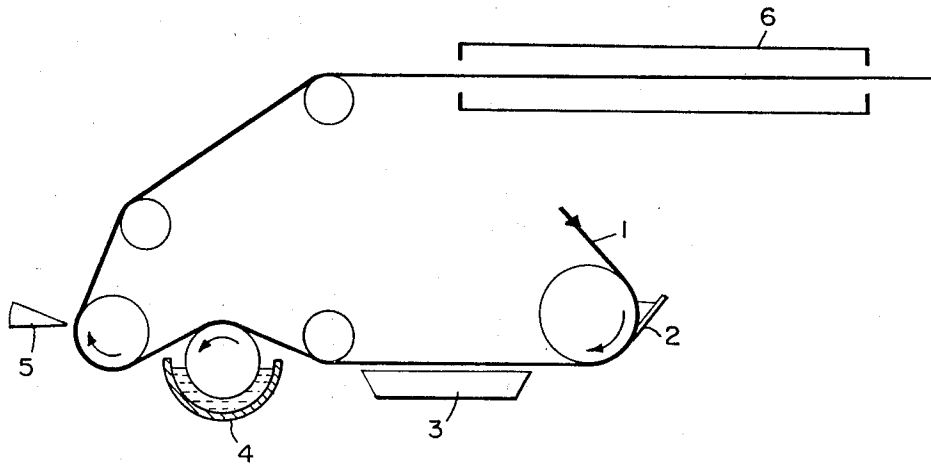


FIG. 5



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## HEAT COAGULABLE PAPER COATING COMPOSITION

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Filed Dec. 17, 1963, Ser. No. 331,220

7 Claims. (Cl. 106—148)

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

This application is a continuation-in-part of application Ser. No. 204,858, now abandoned, "Method of Making Coated Printing Paper," filed June 25, 1962, by the present inventors.

Coated printing papers have been produced by several well known 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 treating the resultant dried and solidified coating layer with supercalender rolls 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 often break the web and cause an interruption of the papermaking process. In addition, the coated layer is often injured by undue friction with the roll, and by bruises on the roll caused by pieces picked up by the roll.

The so-called cast-coating method (See U.S. Patent No. 1,719,166 issued in 1929) is free from the above defects. A coated paper produced by this method has greater smoothness and a more mirror-like gloss than that from other methods.

An old cast-coating method comprises coating a paper with an aqueous coating composition containing pigments, bonding agent, oily material and 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.

In order to obtain a uniform cast-coated paper with no defects in the coating, the temperature of the metal surface must be lower than 100° C., and is usually 85° to 90° C. The moisture in the wet coated layer contacted with the metal surface is only gradually evaporated through the paper web. Consequently, this method has the disadvantage that the production rate of the coated paper may be extremely low.

Unless an oily material is added to the coating composition, separation of the coating from the heated metal surface is apt to result in injury and uneven gloss because of sticking of the layer to the metal. Therefore, it is another disadvantage of this method that in commercial practice the addition of the said oily material always depends on experience, and the control of amount of oily material is very difficult.

Various improvements attempting to overcome the said defects have not met with too much success.

One of the improvements comprises contacting the wet coating with an aqueous solution containing coagulant to cause setting of the coating, and then drying the paper

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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° to 150° C., may be employed to evaporate the water in the layer without injuring the coating. This method has an advantage of producing a cast-coated paper more rapidly than any of the previous methods.

The paper can be separated 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 waterproofness.

When an acid bath is used, the machinery must be carefully protected from corrosion by the acid. The fluctuation of the pH, or the acid concentration of the bath, generated by the continual immersion therein of the coated paper may result in a variation in the degree of coagulation. Troublesome pH adjustment of the bath is necessary to carry out satisfactory operation. When a coated paper is immersed into the acid bath at a high speed, there may occur accidents due to 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 is lowered in strength and becomes 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 coagulation of aqueous coating compositions comprising pigments and proteinaceous and latex adhesives, with or without surfactants, a coating composition has been discovered which may be very 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 the so-called 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 absorptive properties and one which is capable of being suspended by a suspending or dispersing agent can be made to undergo coagulation by modest heating, or heat flocculated by adjusting the stability of the 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 35° C., and as high as 90° to 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 mineral pigment, customarily used in coating papers.

This heat gelation or flocculation is usually reversible, i.e., cooling and mild stirring of the slurry returns it approximately to its original fluidity. In some cases it

may be irreversible and in others semi-reversible, i.e., it does not return to the same state of fluidity even with vigorous stirring.

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. 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.

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. The pigment must be dispersed in a slurry system that would not be fluid 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.

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. Latex adhesives usually are not efficient dispersants and generally speaking can be used in widely varying amounts without markedly affecting the stability of the 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 gellable slurry.

Heat gellable slurries have been made from just water, the pigment and the adhesive, and in some cases with just pigment, dispersant and water alone although these would not be paper-coating compositions because of the lack of adhesive. It is frequently desirable, however, to include efficient dispersing or suspending agents in the system. If their effect is such as to make the slurry so stable as to not be capable of undergoing heat gelation, it is possible to counter their effect by counteracting agents (or anti-suspending agents). These counteracting agents are usually electrolytes or ionizable materials such as mineral acids or salts. The dispersing agent used may be nonionic or ionic. The counteracting agents operate by reducing the repulsive forces between pigment particles, i.e., their tendency is to make a stable system less stable. As a general rule polyvalent ions are preferred because the higher the valence of the electrolyte, the more effective its action.

It has been observed that if the heat flocculation occurs at a lower temperature in the range of 35° to 60° C. 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 useful in this invention. 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.

Reference is now made to the accompanying drawings.

FIG. 1 shows a schematic view of the process of producing a coated paper according to the teachings of this invention. A in FIG. 1 shows the base paper 1 coated with the fluid coating composition of this invention and B shows the coated layer 3 coagulated on the surface of the paper 1 by heating 4.

FIG. 2 to FIG. 5 are diagrams of the embodiments of the equipments of the invention described in Examples 1 to 5.

Up to now, the application of heat to a wet coated layer on the surface of paper only hardened the coated layer by merely evaporating the moisture and lowering the moisture content of the wet layer.

In the cast-coating process wherein a portion of the moisture of the wet coated layer is evaporated to decrease the fluidity and the plasticity of the coating, and thereafter the semi-dried layer is cast, it is very difficult to give the layer a controlled and semi-dried state uniformly throughout its thickness and over all the width of the paper, particularly in industrial scale production.

According to the method of the present invention, when the coating of this invention is heated to a temperature from 35° to 90° C. preferably 40° to 60° C. or above, it rapidly and uniformly flocculates. Consequently, the present method is more advantageous in comparison with the conventional method in which the water or other volatile matters are evaporated from the wet coating, or coagulating liquid is contacted with the wet coating.

The present invention has several advantages:

The coated layer which is flocculated and fixed to the paper surface by heating is increased in its cohesion strength and it is easily separable from the heated metal surface on which the layer is pressed. It can be separated easily either in its completely dried state, or in its semi-dried condition. The gelled layer is neither easily injured by contact with other materials, nor easily dissolved by contact with water. The gelled coated layer may be successfully applied to the heated metal surface having a temperature as high as 150° C. without danger of marring the layer, and may be dried at a higher temperature than that previously used in any other conventional method. Furthermore, as the coated layer is preheated, greatly accelerated drying may result in a high production rate of the coated paper.

To stimulate the coagulation or flocculation action, it is merely necessary to raise the temperature. Thus the method employing heat for the coagulation may be performed more simply and without accidents and without uneven promotion of the coagulation action, in comparison to that employing acid for the coagulation. Heat for the coagulation may be given either by radiation or by conduction, so the coagulation may be obtained more evenly and more easily than that obtained from the contact with coagulating liquid. Thus, the present invention has the advantage of freedom from worry about the control of coagulating liquid, the spattering of coagulating liquid, the flowing of excessive liquid over the paper surface, and the flowing of liquid to the reverse side of paper. The method of the present invention does not lower the strength of the paper which would promote breaking of the paper and the formation of wrinkles on the paper and can be advantageously and successfully applied to a thin paper. The mirror-like surface produced by the method has excellent resistance to water, good abrasion resistance in the humid state, and good printability for offset printing.

The opacity, bulk and brightness of the coating are much improved as compared to a calendered sheet where the coating is compacted by pressure. Also the cast coated paper of this invention has excellent fold properties.

In accordance with the method of invention, when a

layer of the present coating composition on a paper web is heated to an elevated temperature, it coagulates rapidly without the need to evaporate volatile matter such as water, and sets in the wet state to a layer that can be smoothed by casting. While cast-coating is a preferred embodiment of the paper-manufacturing process of this invention, other methods of imparting a smooth surface can be used.

A high-class printing paper with a high degree of smoothness and gloss has been manufactured by applying a conventional coating composition two times to the same surface of a paper, and finishing the twice-coated paper by treatment with a supercalender. The first coating layer fills the depressions in the paper surface and upon drying solidifies with a very smooth surface. The second coating layer is then applied over the first. The thus obtained paper has a high smoothness of surface. However, there may be some difficulties encountered in the second coating step: the second coating layer may be unevenly absorbed; coating stripes and mottling may form and drying of the first layer is required.

When the coating composition of the present invention is applied as the first or under-coating, however, the under-coating fills the depressions in the paper surface, and then is coagulated by the application of heat. The set layer in the undried state has good adaptability to the second or upper coating, and good receptivity of the coating composition. Therefore drying of the under-coating may be eliminated.

Inorganic pigments which can be used in the present invention include well-known pigments such as titanium white, barium sulfate, calcium carbonate, and the like, in addition to clay.

Adhesives used are proteinaceous adhesives such as milk casein and soybean protein. Along with the said adhesive, synthetic latex, synthetic resin emulsions, starch, and the like can be used as a bonding agent.

Any heating method by which a temperature of the coating layer is elevated above its coagulation temperature and below 100° C. can be employed in embodiments of the 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 heat gel satisfactorily unless some pigment was present. This indicates that the salts are not acting on the adhesive alone and that the pigment plays a part in the gelation. A pigment-free casein-polyvalent metal salt solution normally gels so easily that it will gel at room temperature. By taking proper precautions it is possible to avoid gelation of a casein-salt solution at room temperature but satisfactory heat gelation cannot be achieved in the absence of a pigment.

(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 gelable coatings containing salts were heated, the conductivity increased continuously and uniformly with the rise in temperature through and past the gel point. Thus, there was no significant change in the ionic activity of the salts present in the coating that could be the reason for the gelation.

(5) Heat gelable 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 the 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. An acid casein may contain a salt which may have some effect on gelation but the salt is usually a monovalent salt such as ammonium nitrate and its effect may be so small as to be almost negligible.

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.

Examples 1 through 12 give the results of the experiments concerned with the addition of electrolytes or counteracting agents to coating slurries that normally would be too stable to heat flocculate. The remaining examples illustrate other slurries that will heat flocculate but do not require the presence of a counteracting agent. Generally speaking, the use of electrolytes is preferred because the overall properties of the coatings are better when the amount of adhesive or binder used requires counteracting electrolytes to create borderline stability. The term "parts" means parts by weight.

#### EXAMPLE 1

To 20 parts of milk casein (precipitated by lactic or hydrochloric acid, same in the following examples), 0.34 part of caustic soda, 4 parts of dicyandiamide, and 76 parts of water were added, and the mixture was stirred at 70° C. until a homogeneous solution was made. The pH of the casein solution was 6.15. To 100 parts of coating clay, 80 parts of aqueous solution containing 0.3 part of sodium pyrophosphate was added, and a slurry thereof was made. The slurry was mixed with 10 parts of aqueous solution containing 2.2 parts of anhydrous barium chloride and stirred thoroughly. This resulted in a somewhat viscous paste which was then mixed with the above described casein solution under stirring. At first, the mixture was inclined to be somewhat coagulated, but by continued stirring, it was transformed to a liquid having a good fluidity. The adding, mixing and stirring operations were all conducted at room temperature, i.e. from 5° to 30° C. To the said liquid, 0.3 part of ammonium stearate dissolved in 3 parts of water, and then 0.5 parts of tributyl phosphate as a defoaming agent were added and the solids concentration of the coating composition was adjusted to 41% by addition of water. The pH of this coating composition was 5.75. When the temperature of the coating composition was elevated by heating, the coating composition rapidly coagulated at around 43° C.

As shown in FIG. 2, a quantity of this coating composition 2 equivalent to 20 g./m.<sup>2</sup> in dry weight was applied to paper 1 to 100 grams/m.<sup>2</sup>, by using an ordinary air

blade 3. Immediately after being coated the wet coated surface 4 was heated with an electric heater 5, and further was subjected to a spray of super-heated steam 6 and 7 directed opposite to the movement of the paper. Steam was blown mildly against the uncoagulated part of the wet coated layer 4 and strongly against the coagulated non-fluid part. The steam condensed into a water film on the coated surface 4 and gave up heat to the coating, rapidly coagulating it. The wet coating was heated to a temperature of from 50° to 80° C. The heated paper was pressed, by means of a rubber covered roll 9, against the surface 8 of a rotating chromium plated drum, having a temperature of 130° C., dried at a velocity of 70 m./minute, and separated therefrom. A paper having a high smoothness, a mirror-like gloss and very good resistance to water was obtained. For example, Wet Picking (IGT test method) of the paper of this example was found to be 120 cm./sec. in contrast to 95 cm./sec. of a conventional cast-coated paper.

#### EXAMPLE 2

To 18 parts of milk casein, 0.35 part of caustic soda, 3.6 parts of dicyandiamide and 50 parts of water were added, and the mixture was stirred at 70° C. till a homogeneous solution was made. The pH of the casein solution was 6.3. To 100 parts of coating clay, 80 parts of aqueous solution containing 0.3 parts of sodium pyrophosphate was added and mixed to a slurry. This slurry was mixed with the casein solution and stirred. Then 1.3 parts of anhydrous calcium chloride dissolved in 25 parts of water was successively dropped into the mixture with continued stirring. During this addition the solution was inclined somewhat to be coagulated, but by continued stirring the solution was transformed to a liquid having good fluidity. To this paste was added 1.8 parts of gum arabic dissolved in 9 parts of water and then 10 parts of styrene butadiene latex (Dow Latex 512R, 50% solid), 0.6 parts of ammonium stearate and 0.5 parts of tributyl phosphate defoaming agent. The concentration of the coating composition was adjusted to 39% by weight. In this case, the addition and stirring operation were all conducted at room temperature, i.e. below 30° C. The pH of the thus obtained coating composition was 6.0. The coating composition had the property of being rapidly coagulated when heated to above about 45° C. The coating composition was applied to paper by using a method similar to that described in Example 1. A coated paper having mirror-like gloss and very good resistance to water was obtained.

#### EXAMPLE 3

A coating composition formulated as described in Example 2 was adjusted to a concentration of 46% by weight. Referring to FIG. 3, the coating composition was applied to paper 1 of 80 g./m.<sup>2</sup>, by using a roll coater 2. The amount applied was 20 g./m.<sup>2</sup> (dry weight). Thereafter the coated layer was immediately heated by the radiation from a source of infrared rays 3 to a temperature of from 50° to 90° C. and coagulated. The coagulated coating was pressed against the surface of a chromium plated roll 4 heated to a temperature of about 70° C., by means of a rubber covered roll 5, at the rate of 120 m./minute. The operation was repeated on successive set of rolls 4, 5 to give additional smoothness to the paper. The paper was dried through a conventional drier 6 to produce coated paper having a same degree of gloss as that of art paper.

#### EXAMPLE 4

The coating composition described in Example 3 was applied to both surfaces of paper 1 of 60 g./m.<sup>2</sup>, by using a roll coater 2, as shown in FIG. 4, so that a coating layer of 7 g./m.<sup>2</sup> dry weight was formed on each side. The coating was heated by a gas heater 3 to a temperature of from 50° to 90° C. The coagulated coated layer was dried by using a multidrum drier 4. The drums

were not stained and an on-machine coated paper having a high smoothness was obtained at the rate of 330 m./minute.

To 20 parts of milk casein 4 parts of dicyandiamide, 0.4 part of caustic soda and 76 parts of water were added, and the mixture was stirred at 70° C. until solution was made. The pH of the thus obtained casein solution was 6.4. To 100 parts of coating clay, 80 parts of aqueous solution containing 0.3 part of sodium pyrophosphate was added and a paste thereof was made, and the admixture of the said paste with the said casein solution was stirred. Then 30 parts of 2% formic acid solution was carefully dropped into the said mixed solution under vigorous stirring. When almost 27 parts of formic acid had been added, the coating composition was turned to a gel, but during the continuous stirring the gel was gradually dissolved. To this, the remaining formic acid was added drop by drop. Thereafter, 0.5 part by weight of tributyl phosphate was added and the coating composition was adjusted to 40% solids. The coating composition had the characteristic of being rapidly coagulated by heating at around 43° C. This coating composition was applied to paper 1 of 60 g./m.<sup>2</sup>, so as to be 6 g./m.<sup>2</sup> in dry weight, by using a trailing blade 2 as shown in FIG. 5. The paper was heated by using an electric heater 3 to a temperature of from 50° to 70° C. to coagulate the coating in situ. Over the coagulated coating layer, a common art-coating composition was applied by using color roll 4, and the top coating was adjusted so as to be 18 g./m.<sup>2</sup> in dry weight, by using an air blade 5, and the paper was dried at a speed of 230 m./minute by using a tunnel drier 6, and finished by a supercalender.

#### EXAMPLE 6

Twenty parts of milk casein, 4 parts of dicyandiamide, and 0.9 part of concentrated hydrochloric acid (35 weight percent), were dissolved in 120 parts of water at 70° C. The pH of the obtained milk casein solution was 2.65. To this casein solution cooked at 50° C., 5 parts of 10% aqueous solution of dodecyl sodium sulfate (anionic surface active agent) was added. To the solution thus obtained, and cooled at 20° C., an aqueous slurry containing 100 parts of coating clay, 0.3 part of sodium pyrophosphate, and 100 parts of water, was added. The thus obtained liquid admixture was very pasty, but by the continuation of strong agitation it was gradually converted to a stable coating composition with good fluidity.

To this composition, 5 parts of paraffin emulsion of 10% solid content, and 0.5 part of octanol were added. The resulting coating composition had a pH of 3.05 and a solid content of 35% by weight, and would coagulate strongly at from 82° to 87° C.

The coating composition was applied to a paper by the same process as shown in FIG. 2 and described in Example 1 except that the coating was heated to 90° to 95° C. A coated paper having a mirror-like gloss was produced.

#### EXAMPLE 7

Eighteen parts of soybean protein, 0.36 part of sodium hydroxide, and 3.6 parts of dicyandiamide were dissolved in 72 parts of water at 70° C. under stirring. The pH of the soybean protein solution was 6.90. An aqueous slurry was made by the addition of 100 parts of water containing 0.3 part of sodium pyrophosphate to 100 parts of coating clay. The soybean protein solution and the aqueous slurry were mixed together and stirred. To the resulting mixture from 6 to 7 parts of 10% aqueous solution of zinc chloride, 5 parts of 10% aqueous solution of ammonium stearate, and 0.5 part of octanol defoaming agent were added drop by drop.

The so obtained coating composition had a pH of 5.90 and a solid content of 38% by weight, and coagulated rapidly at about 47° C.

## EXAMPLE 8

Eighteen parts of milk casein, 0.81 part of concentrated hydrochloric acid (35% by weight), and 3.6 parts of dicyandiamide were dissolved in 108 parts of water at 70° C. with stirring. The milk casein solution was mixed with the aqueous slurry made by the addition of 100 parts of an aqueous solution containing 0.3 part of sodium pyrophosphate to 100 parts of coating clay, and the mixture was agitated. Then 4.5 parts of 10% aqueous solution of ethylenediamine followed by 5 parts of paraffin emulsion of 10% solid content and 0.5 part of octanol were added.

This coating composition had a pH of 5.05, and a solid content of 35%, and coagulated rapidly at about 45° C. When the amount of aqueous ethylenediamine solution was about 6.5 parts or higher, the coating composition could not be coagulated by heating.

## EXAMPLE 9

Twenty parts of milk casein, 4 parts of dicyandiamide, and 0.6 part of sodium hydroxide, were dissolved in 60 parts of water at 70° C. The pH of the casein solution was 7.50. When the casein solution, cooled to about 30° C., was subjected to the dropwise addition of 10 parts of Golfix as cationic surface active agent (a commercial name of the product sold by Soryu Co., Japan, which is a dicyandiamide-formaldehyde condensate polymer), the solution changed to slightly emulsified low viscosity liquid.

The aqueous slurry was made by mixing 80 parts of coating clay and 20 parts of titanium white with 100 parts of an aqueous solution containing 0.3 part of sodium pyrophosphate. When the modified casein solution and the aqueous slurry were mixed together and stirred, the mixture became at first viscous, but by continuation of stirring it became fluid. Five parts of 10% aqueous solution of ammonium stearate and 0.5 part of octanol was added. The thus obtained coating composition had the pH of 7.30, and a solid content of 38%. It rapidly coagulated at about 42° C.

## EXAMPLE 10

Into a vessel containing 40 parts of water at 40° C. the following materials were added under vigorous agitation:

	Parts
Casein .....	9
Gelatin .....	0.5
Dicyandiamide .....	1.8
Sodium hydroxide .....	0.165
Potassium oleate .....	0.5

Stirring was continued for 15 minutes to ensure complete solution of the casein. Then 0.25 part of tributyl phosphate, an anti-foam agent was added. The solution was cooled to 24° C.

In a heavy duty stirrer the following materials were mixed:

	Parts
Cold water (at about 13° C.) .....	37.5
Fine coating clay .....	52.5
Sodium pyrophosphate .....	0.1

Stirring was continued for 30 minutes. Then there was added a solution of 1.3 parts of calcium chloride in 5 parts of cold water. This caused immediate thickening of the clay slurry to a crumbly mass. The casein solution at 24° C. was immediately stirred into the crumbly mass, which rapidly converted it into a thin liquid. After it had been well stirred, 5.2 parts of a latex containing 48% of styrene-butadiene copolymer were added. The pH value of this mixture was 5.9. A sample of the resulting coating composition was gradually heated. At 54° C. the mixture set to a semi-solid gel. When the gel was cooled again and stirred it once more became liquid.

The coating composition was applied by means of an

air-knife coater, in amount equivalent to about 22 grams per square meter, to one side of a paper body-stock weighing 67 grams per square meter. The coated web was immediately heated to 75° C. which gelled the layer of coating so that it was firm to touch. The coated surface was then at once passed through a pool of boiling water and into very firm contact with a polished chromium-plated roll having a temperature of 127° C. No wash-off of coating occurred in the pool of boiling water. The sheet was removed from the chromium surface after 3 seconds contact, and was then found to have a very glossy, mirror-finish, cast surface.

## EXAMPLE 11

Into a vessel containing 40 parts of water at 40° C. the following materials were added under vigorous agitation:

	Parts
Casein .....	9
Dicyandiamine .....	1.8
Sodium hydroxide .....	0.165
Sodium stearate .....	0.5

Stirring was continued for 15 minutes, then 0.25 part of tributylphosphate defoamer was added. The solution was cooled to about 28° C.

In a vessel provided with heavy duty agitation the following materials were mixed:

	Parts
Water .....	37.5
Coating clay .....	52.5
Sodium pyrophosphate .....	0.1

Stirring was continued for 30 minutes. There was then added 1.1 parts of MgSO<sub>4</sub>·7H<sub>2</sub>O (hydrated magnesium sulfate or Epsom salt) dissolved in 5 parts of cold water. This caused the clay to set to a thick mass. The casein solution was added and the mixture became fluid with continued agitation. Finally 5.2 parts of a latex containing 48% of styrene butadiene copolymer were added. The pH of this mixture was 6.3. A sample of this coating mixture was observed to gel to a semi-solid mass when heated to approximately 50° C. When the gel was cooled again and stirred it once more became liquid.

The coating composition was applied by means of an air-knife coater, in amount equivalent to about 18 grams per square meter, to one side of a paper body-stock weighing 67 grams per square meter. The coated web was immediately heated to 75° C. which gelled the layer of coating so that it was firm to touch. The coated surface was then passed through a pool of heated water and into very firm contact with a polished chromium-plated roll having a temperature of 127° C. No wash-off of coating occurred in the pool of boiling water. The sheet was removed from chromium surface after 3 seconds contact, and was then found to have a very glossy, cast surface.

Electrolytes effective in the present invention for modifying coating slurries that normally are unduly stable include water-soluble acids, salts, or bases, the solutions of which have a cation such as Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Pb<sup>++</sup>, Zn<sup>++</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Sr<sup>++</sup>, Ba<sup>++</sup>, Al<sup>+++</sup>, H<sup>+</sup>, and NH<sub>4</sub><sup>+</sup>, and an anion such as SO<sub>4</sub><sup>---</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CNS<sup>-</sup>, PO<sub>4</sub><sup>---</sup>, OH<sup>-</sup>, etc. Organic electrolytes such as an organic acid, i.e. formic acid, acetic acid, tartaric acid, citric acid, lactic acid, phthalic acid, etc. and organic amines, i.e. ethylenediamine, monoethanolamine, triphenylamine, diethylamine, etc., can be used. Surface active agents ionizable in aqueous solution are also useful, such as, for example, cationic, anionic, and amphoteric surface active agents. Examples of cationic surface active agents are Golfix (a trade name of a dicyandiamine-formaldehyde condensate polymer from Soryu Dyes & Chemicals Co.), and Hyamine 10X (a commercial name of a product from Rohm & Haas Co., which mainly contains di-isobutylcresoxy-ethoxy-ethyl-dimethylbenzyl ammonium chloride). Anionic surface active

agents, such as dodecyl sodium sulfate, turkey red oil and alkaline salts of higher fatty acids, such as potassium stearate, can be used; a useful amphoteric surface active agent is Nissan Anon. BT (a commercial name of the product from Nihon-Yushi Co., which mainly contains cetyl betaine.  $Al^{+++}$  and  $Ca^{++}$  contained in satin-white, which is generally used as a coating pigment may all be used as effective ions in the coating composition of the invention.

A proteinaceous adhesive generally has an isoelectric point. When its solution has a higher pH than the isoelectric point, salts of divalent metals such as alkaline-earth metals, organic acids, inorganic acids, and cationic or amphoteric surface active agents can be used. When its solution has a lower pH than the isoelectric point, ordinary salts, and bases, organic amines, and anionic or amphoteric surface active agents can be used.

When the pH of the solution of proteinaceous adhesives such as milk casein and soybean protein, is far from its isoelectric point, namely, the solution is strongly acidic or alkaline, a large quantity of effective electrolyte must be added in practicing the invention. Otherwise, when the pH of the solution is near to the isoelectric point, namely in ranges from 2.5 to 8.5, only a relatively small quantity of electrolyte is necessary.

From a practical standpoint, the preferred operation is at a pH value slightly above the isoelectric point of the protein. In this range the most effective electrolytes appears to be (1) soluble salts other than salts of alkali metals and ammonium, and (2) soluble organic and inorganic acids and acid salts. The preferred electrolytes are soluble salts of the alkaline-earth metals and of magnesium, zinc, aluminum, zirconium and tin.

The heat-setting property and the stability of the obtained coating composition are better in the latter case than in the former. It should be noted that when an excessive quantity of electrolyte is added, the coating composition may coagulate at room temperature, and when insufficient is added, it may not coagulate upon being heated. The coating composition is preferably prepared at a temperature in the range from 10° C. to 30° C.

Such a coating composition, when sufficient attention is paid to the preparation, may be stable for keeping at room temperature. A very stable coating composition which will not invite coagulation, sedimentation, nor separation, can be obtained by addition of a small quantity of water-soluble bonding agent such as gelatine, gum arabic, starch, carboxymethyl cellulose, polyvinyl alcohol, and the like as a protective agent. In the preparation of the coating composition of the invention from a normally heat stable coating slurry, the addition of the electrolyte is not restricted by the admixing order, and any mixing order of the components of the coating composition can be employed.

#### EXAMPLE 12

Salt peptized casein as described in U.S. Patent No. 3,081,182 was prepared by adding 12 parts casein, 2.4 parts dicyandiamide, 2.4 parts of ammonium nitrate, 0.5 part tributyl phosphate, 1.0 part potassium oleate, 1.0 part Defoamer Ahco 124 (Arnold Hoffman) to 35 parts of water with stirring. This mixture was heated on the steam bath to 75° C. with continued agitation until a smooth dispersion was obtained. A slurry of English coating clay was prepared by mixing 100 parts of the clay (oven dry basis) and 0.3 part tetrasodium pyrophosphate with 62 parts of water. The clay slurry with 42 additional parts of water was added to the casein dispersion under agitation. A thickening or coagulation took place which with continued mixing thinned and became a smooth, fluid mixture. To the mixture of clay and casein 12.5 parts of a 48% solids styrene-butadiene latex (Dow 512R) were added. The total solids were adjusted to 38%. This coating, identified as Coating A, did not gel upon heating and was used as the control.

Sheets coated with Coating A with an air blade at a coating weight of 12 pounds per ream were immediately placed between two forced hot air electric heaters and dried for 20 seconds at a temperature of about 100° C. After conditioning at 50 percent R.H. the sheets were calendered 6 nips at 2140 pounds per lineal inch. This coating is the control or blank for tests of the effects of various amounts of salts. The following coatings were coated, conditioned, calendered and tested in the same manner.

Coating B was prepared as for Coating A with the addition of 4 parts calcium formate dissolved in 36 parts water added before dilution to 38% total solids. This coating gelled at a temperature of 44–48° C. The coated sheets showed improved brightness and opacity.

Coating C, prepared as for Coating A before dilution, was modified by the addition of 2 parts of barium acetate dissolved in 18 parts water. Dilution water was then added to bring the total solids to 38%. This coating gelled at a temperature of 55–60° C. The coated sheets showed improved brightness, opacity, gloss and bulk.

In another modification of the formula, Coating D was made by the addition of 3 parts of strontium acetate dissolved in 27 parts water to Coating A before dilution. After the addition of the strontium acetate solids were adjusted to 38%. This coating gelled at 49–55° C. Improvements in brightness, gloss, opacity and bulk as compared to Coating A were seen with this formula.

Coating E prepared as for Coating A but before the dilution water was modified by the use of 0.5 zinc sulfate dissolved in 24.5 parts of water after which solids were adjusted to 38%. This coating gelled at 55–60° C. when heated. The coated sheets exhibited better brightness, gloss, opacity and bulk than Coating A.

#### EXAMPLE 13

An English coating clay (not predispersed, cf. U.S. Patent 2,500,972) was used to prepare the following slurries, both of which were heat gelable. This particular clay was used because it is not predispersed but can be easily dispersed by simple mixing. An acid casein adhesive alone was used as the suspending agent. The slurries were formed by making 50% solids slurry from the undispersed clay and water with the subsequent addition of the casein and sufficient water to form a 40% solids slurry.

	Parts
Slurry A:	
Clay -----	100
Casein -----	12
Dicyandiamide -----	2.4
Ammonium nitrate -----	2.4
Tributyl phosphate -----	1.0
Water (in casein dispersion) -----	36.0
55 Slurry B:	
Clay -----	100
Casein -----	2.35
Strong ammonia water -----	0.30
Tributyl phosphate -----	1
60 Water (in casein dispersion) -----	9.40

Gelation was checked by heating a small beaker of the slurry in a steam bath. The slurry was considered gelled when it would no longer pour from the beaker. Reversibility was checked by subsequently cooling the gelled slurry in a cold water bath and stirring. Both slurries formed a firm, reversible gel at 43° to 49° C.

#### EXAMPLE 14

The following slurries were prepared to investigate the effect that different types of pigment had on the heat gelability of the slurries. An acid casein was used as the adhesive and was prepared by cooking the following ingredients at 75° C. for ¼ hour.

	Parts
Casein -----	100
Dicyandiamide -----	20
NH <sub>4</sub> NO <sub>3</sub> -----	20
Water -----	300

The slurries were prepared by mixing to a uniform paste at 50% solids, and diluting to 40% solids. The weights of the pigments are moist weights. TBP in the formulas is tributyl phosphate and TSPP is tetrasodium pyrophosphate.

Slurries 1 through 16 heat gelled at 38-49° C. Slurry 17 gelled at 66-77° C.

(1) *Slurry No. 1*

English Coating Clay (not predispersed) -----	gm	100
Acid casein cook -----	gm	53
T.B.P. -----	gm	1
Dilution water for 40% S.		

(2) *Slurry No. 2*

#1 Georgia Coating Clay, predispersed with polyphosphate (Lustraclay, Southern Clays, Inc.) -----	gm	105
Water -----	gm	95
10% calcium formate -----	ml	10
Acid casein cook -----	gm	58

(3) *Slurry No. 3*

Premium grade Georgia Coating Clay, predispersed with polyphosphate (Nuclay, Southern Clays, Inc.) -----	gm	105
Water -----	gm	95
10% calcium formate -----	ml	20
Acid casein cook -----	gm	45

(4) *Slurry No. 4*

High Grade English Coating Clay -----	gm	105
Water -----	gm	95
T.S.P.P. -----	gm	0.5
10% calcium formate -----	ml	20
Acid casein cook -----	gm	30

(5) *Slurry No. 5*

Hydroscopic Clay (ASP 403) -----	gm	105
Water -----	gm	95
T.S.P.P. -----	gm	0.25
Acid casein cook -----	gm	14
10% calcium formate -----	ml	5

(6) *Slurry No. 6*

Predispersed #2 Georgia Coating Clay -----	gm	105
Water -----	gm	95
10% calcium formate -----	ml	40
Acid casein cook -----	gm	40

(7) *Slurry No. 7*

Hydrated Alumina (Paperad) -----	gm	285
Water -----	gm	190
T.B.P. -----	ml	2
10% calcium formate -----	ml	20
Acid casein cook -----	gm	55½

(8) *Slurry No. 8*

Ground limestone (Camelwite) -----	gm	685
Water -----	gm	190
T.B.P. -----	ml	2
10% calcium formate -----	ml	100
Conc. acetic acid -----	ml	3
Acid casein cook -----	gm	85½

(9) *Slurry No. 9*

Blanc fixe -----	gm	210
Water -----	gm	190
T.B.P. -----	ml	2
10% calcium formate -----	ml	10
Acid casein cook -----	gm	29

(10) *Slurry No. 10*

ZnO (Photox) -----	gm	210
Water -----	gm	190
T.B.P. -----	ml	2
Acid casein cook -----	gm	145½

(11) *Slurry No. 11*

Talc -----	gm	52½
Water -----	gm	87½
T.S.P.P. -----	gm	0.25
10% calcium formate -----	ml	10
Acid casein cook -----	gm	18

(12) *Slurry No. 12*

SiO <sub>2</sub> (Cabosil) -----	gm	17
Water -----	gm	150
10% calcium formate -----	ml	10
Acid casein cook -----	gm	113½

(13) *Slurry No. 13*

Precipitated CaCO <sub>3</sub> -----	gm	210
Water -----	gm	190
T.B.P. -----	ml	2
Acid casein cook -----	gm	30

(14) *Slurry No. 14*

TiO <sub>2</sub> (Anatase—water dispersible slurry) -----	gm	210
Water -----	gm	190
T.B.P. -----	ml	2
10% calcium formate -----	ml	10
Acid casein cook -----	gm	56

(15) *Slurry No. 15*

ZnS -----	gm	210
Water -----	gm	190
Acid casein cook -----	gm	143

(16) *Slurry No. 16*

Calcium silicate (Microcel) -----	gm	43
Water -----	gm	200
T.S.P.P. -----	gm	0.25
Acid casein cook -----	gm	55

(17) *Slurry No. 17*

Iron oxide in 238 gm. water -----	gm	200
Acid casein cook -----	gm	44
Butadiene - styrene latex (Dow 512R) (dry basis) -----	gm	20
T.B.P. -----	ml	1
10% calcium formate solution -----	ml	60

## EXAMPLE 15

The following slurries were prepared to investigate the effect of different types of dispersants on heat gelation. English coating clay, undispersed, was used in all of these examples. The suspending agents possessed different efficiencies for suspending the clay and few of the slurries are formulated exactly alike. The slurries were made up with what appeared to be borderline stabilities and were tested for gelability in a beaker. All indicated weights in the formulas are dry weights unless otherwise stated.

(1) *TSPP slurry*

Clay -----	gm	100
TSPP -----	gm	0.13
Water -----	gm	95
Soft gel at 49°-54° C.		

(2) *SAPP slurry*

Clay -----	gm	124
Sodium acid pyrophosphate (Na <sub>2</sub> H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ·6H <sub>2</sub> O) -----	gm	0.25
Water -----	gm	95
Soft gel at 60°-70° C.		

## 15

## (3) Detergent slurry

Clay	gm	124
Specially fused sodium-zinc phosphate glass (Calgon T)	gm	0.30
Water	gm	95
T.B.P.	ml	1

Mild gel 82°-93° C.

## (4) Victamide slurry

Clay	gm	119
Ammonium salt of an amido-polyphosphate (Victamide, Victor Chemical Co.)	gm	0.40
Water	gm	95
T.B.P.	ml	1

Mild gel at 70°-80° C.

## (5) Quaternary ammonium chloride slurry

Clay	gm	100
Quaternary ammonium chloride (Katapone VV-328) solution	drops	30
Water	gm	95
T.B.P.	ml	1

Mild gel at 82°-93° C.

## (6) Tamol 850 slurry

Clay	gm	124
Tamol 850	drops	13
Water	gm	95
T.B.P.	ml	1

Mild gel at 82°-93° C.

## (7) Polyelectrolyte slurry

Clay	gm	124
Na salt of carboxylated polyelectrolyte (Tamol 731, Rohm & Haas)	drops	24
Water	gm	95
T.B.P.	ml	1

Medium gel at 60°-70° C.

## (8) Quadrifos slurry

Clay	gm	124
Sodium tetraphosphate (Na <sub>6</sub> P <sub>4</sub> O <sub>13</sub> )	gm	0.11
Water	gm	95

Medium gel at 54°-66° C.

## (9) Polyethyleneimine slurry

Clay	gm	100
50% of P.E.I.	drops	9
Water	gm	95

Medium gel at 70°-80° C.

## (10) Organic amino acid slurry

Clay	gm	100
N-lauryl beta amino propionic acid (Deriphat 170 C.)	drops	25
Water	gm	95

Soft gel at 60°-70° C.

## (11) Gum arabic slurry

Clay	gm	100
28% gum arabic solution	drops	15
Water	gm	95

Soft gel 70°-80° C.

## (12) Styrene-maleic anhydride slurry

Clay	gm	100
50% S.M.A. (1430H-Texas Butadiene)	drops	9
Water	gm	95

Soft gel at 50°-60° C.

## (13) Styrene-maleic anhydride slurry

Clay	gm	100
50% S.M.A. (4000H-Texas Butadiene)	drops	8
Water	gm	95

Soft gel at 50°-60° C.

## 16

## (14) Acid casein slurry

Clay	gm	100
Casein peptized by NH <sub>4</sub> NO <sub>3</sub> dicyandiamide	gm	12
T.B.P.	gm	1

Dilution water for 40% solids.  
Firm gel at 38°-50° C.

## (15) Alkaline casein slurry

Clay	gm	100
Ammonium casein	gm	2.35
T.B.P.	gm	1

Dilution water for 40% solids.  
Firm gel at 38°-50° C.

## (16) Polyvinyl alcohol slurry

Clay	gm	100
10% polyvinyl alcohol (Elvanol 51-05) solution	ml	22
Water	gm	95

Medium gel at 60°-77° C.

## (17) Polyvinyl alcohol slurry

Clay	gm	100
10% polyvinyl alcohol (Elvanol 71-30) solution	ml	20
Water	gm	95

Medium gel at 60°-77° C.

## (18) Latex slurry

Clay	gm	100
25% solids NH <sub>4</sub> OH adjusted modified styrenebutadiene latex <sup>1</sup>	gm	29
Water	gm	95

Firm gel at 38°-50° C.

<sup>1</sup> See U.S. Ser. No. 263,118 filed Mar. 6, 1963.

## (19) Carboxymethyl cellulose slurry

Clay	gm	124
10% solids, CMC (70-LL, Hercules Powder)	gm	5
Water	gm	95

Very soft gel at 60°-70° C.

## (20) Alkylene soy protein slurry

Clay	gm	100
Delta soy protein dissolved by ammonia	gm	2
Water	gm	95
T.B.P.	ml	1

Medium gel at 60°-70° C.

## (21) Animal glue slurry

Clay	gm	100
10% solids animal glue	gm	47
Water	gm	95
T.B.P.	ml	1

Good gel at 55°-65° C.

## (22) Styrene-acrylate latex slurry

Clay	gm	119
10% styrene-acrylate latex (Modicol VE, Nopco)	gm	13
Water	gm	95
T.B.P.	ml	1

Medium gel at 55°-65° C.

## (23) Starch slurry

Clay	gm	124
25% cationic starch solution (Keotac 490, Hubinger)	gm	61
Water	gm	95

Medium gel at 70°-80° C.

The conclusions reached from these experiments were:

(1) Any material that will serve as a reasonably good dispersant for the adsorptive mineral pigment in a paper

coating slurry can be used to make a heat flocculating system.

(2) Different suspending agents may be used to make slurries having different temperatures of heat gelation.

(3) The pigment can be anionically, cationically or nonionically dispersed and still have a heat gelable slurry.

(4) The dispersant used must make a fluid suspension of the pigment in a system that would not be fluid without this dispersant. The total level of all potential dispersants in the slurry must not be so high as to suspend the pigment too efficiently.

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

What is claimed is:

1. In a process for producing a coated printing paper wherein an aqueous coating slurry is applied to a paper web and dried thereon, said aqueous coating slurry having a total solids content of at least 30 weight percent and comprising a paper coating-grade adsorptive mineral pigment and an adhesive binder selected from the group consisting of proteinaceous and synthetic latex adhesives, said slurry containing a dispersing agent that has a dispersing action on said mineral pigment; the improvement comprising controlling, during the preparation of said aqueous coating slurry, the amount of said dispersing agent acting on said mineral pigment such that the aqueous coating slurry is stable at 25° C. and sets a non-flowable state at an elevated temperature in the range of 35° to 100° C. because of flocculation of said mineral pigment, said aqueous coating slurry being applied to said paper web at a temperature at which it is in a flowable state and thereafter the resulting coating being heated to said elevated temperature prior to drying.

2. The process of claim 1 wherein after said coating is heated to said elevated temperature it is pressed against

a heated smooth surface before drying to cast the same and to at least partially dry it.

3. The process of claim 1 wherein said aqueous coating slurry has added to it during its preparation a dispersing agent distinct from said adhesive binder which dispersing agent is at least in part absorbed by said mineral pigment at 25° C. and at least in part desorbed by said mineral pigment at said elevated temperature.

4. The process of claim 3 wherein the amount of said dispersing agent is in excess of that required to maintain said aqueous coating slurry at border-line stability at 25° C. and an electrolyte is added to said aqueous coating slurry during its preparation in an amount sufficient to render said aqueous coating slurry unstable at said elevated temperature.

5. The process of claim 4 wherein said electrolyte is a poly-valent metal salt electrolyte and said dispersing agent is an ionic dispersing agent.

6. The process of claim 1 wherein after said coating is heated to said elevated temperature but prior to drying a second coating is applied thereover.

7. The process of claim 1 wherein said adhesive binder is at least in part casein and said casein serves at least in part as said dispersing agent.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,356,517

December 5, 1967

Hideiku Nakajima et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 17, line 28, "sets a" should read -- sets to a --.

Signed and sealed this 29th day of July 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents