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PAPER COATING COMPOSITION AND METHOD OF MAKING

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This invention relates to paper coating compositions and to processes of making coated paper; and it has particular reference to the manufacture of coated paper of varnishing or gloss ink quality.

Coated paper as herein referred to consists of a paper base carrying on one or both sides thereof a smooth coating of mineral pigment (clay, calcium carbonate, etc.) and adhesive (usually casein) and commonly is used for fine printing. Coated paper of varnishing quality is required where a film of varnish is to be applied to the printed paper to enhance its over-all gloss. For best results the varnish must not penetrate into the paper too much as this results in diminished gloss. In gloss ink printing an ink is used which dries to a glossy, varnish-like finish, and generally for best results on coated paper the latter should be of a nature to prevent a high degree of penetration of the ink into the coating.

One general practice in making coated papers of varnishing and gloss ink quality consists in using relatively large amounts of casein in the coating composition in order to render the coating more resistant to penetration by varnish and ink.

Inasmuch as the paper may be printed on an offset press prior to varnishing, it is common practice to give the coating some degree of water resistance, and formaldehyde is frequently employed for this purpose. In using formaldehyde in casein paper-coating compositions, considerable care must be exercised since otherwise the coating composition may thicken greatly or even set up to a worthless solid mass. To avoid this difficulty it has been proposed to add the formaldehyde to the paper after the coating composition has been applied.

One object of the present invention is to provide an improved coating composition suitable for the production of high grade coated paper of varnishing or gloss ink quality. Another object is to provide a paper coating composition containing formaldehyde or similar aldehyde, which does not exhibit undesirable thickening properties. Another object is to provide a method of making coated paper having a high degree of resistance to varnish or ink penetration but without the use of the excessively large amounts of adhesive previously required to attain this property. Another object is to provide a method of producing coated paper, the coating having increased ink resistance, adhesiveness and other desirable properties. Another object is to provide a method of coating paper employing formaldehyde or similar aldehyde which is free from the objections previously associated with its use.

I have found that in coating compositions containing casein and formaldehyde, the effectiveness of the formaldehyde is greatly enhanced and its action considerably modified if the pH of the coating composition is raised to or maintained at 9.0 or above. Such coatings are generally more waterproof and adhesive and if the quantity of casein is kept above a certain minimum the coated paper made therefrom is extremely non-absorbent towards printing ink and varnish. This minimum casein content is, however, far below that required in coating compositions heretofore commonly required for coated paper of varnishing quality.

However, a coating composition such as has been described has no practical utility because it sets almost immediately after mixing to a thick unworkable mass. I have nevertheless experimentally prepared such a coating, and by exercising special precautions have applied the composition to paper within a few seconds after its preparation and found that the waterproofness, adhesiveness and especially the ink resistance were far in excess of papers previously made from coatings of similar composition having a lower pH.

I have discovered that the desirable properties of such a coating composition may be retained and the objectionable thickening prevented or at least delayed for many hours or even days by incorporating another aldehyde into the coating composition before the formaldehyde is added or before the coating has been made decidedly alkaline.

It is of course essential that the second aldehyde, e. g. acetaldehyde, be present in the coating composition before the formaldehyde has an opportunity to react with the casein in the alkaline medium. Thus the acetaldehyde may be added to the clay-casein-water composition followed by addition of the formaldehyde and finally of the alkali; or the acetaldehyde may be added to the clay-casein-water composition followed by the addition of the alkali and finally of the formaldehyde; in fact the ingredients may be added in any order provided the acetaldehyde is present before the final mixture of casein, formaldehyde and alkali is present. As will be pointed out more fully below, it is sometimes desirable to effect a combination of the formaldehyde and the other aldehyde in the presence of alkali, advan-

tageously by heat, before adding this to the coating composition.

The chemical reactions involved are apparently complicated and not well understood. In some cases, at least, there is reason to believe that the formaldehyde reacts with the other aldehyde to form aldol type condensation products, which do not immediately coagulate the coating. The effect of the second aldehyde is apparently to retard the combination of the formaldehyde with the casein in alkaline conditions, so that the pronounced thickening or coagulation of the coating which otherwise would occur within a few seconds or a few minutes is delayed for many hours. This fact makes such a coating composition a perfectly practical one for use in mill operations.

The pH of the final coating composition should be at least 8.5, and for best results it preferbaly should lie between about 9 and 11. For the purpose of obtaining this desired degree of alkalinity, sodium or potassium hydroxide may be used; but I prefer to use sodium carbonate or other alkaline sodium salt as the pH control is thereby somewhat simplified.

Due to its low cost, water solubility and general effectiveness in preventing pronounced thickening of the coating and in producing a very ink-resistant coated paper, acetaldehyde is a particularly desirable material to use in conjunction with the formaldehyde. However, the indications are that any aldehyde which is capable of combining with formaldehyde to form aldol type condensation products acts in the same way as acetaldehyde, differing somewhat in degree. Thus, propylaldehyde, butrylaldehyde, heptaldehyde, ethylpropyl acrolein, etc. may be employed. Due to the progressively increasing water-insolubility of the higher aldehydes, they are not as useful as the lower aldehydes. Some compounds not specifically called aldehydes but still having the characteristic aldehyde radical



may be used with more or less effectiveness. Thus aldol, ($CH_3CH(OH)CH_2COH$) and dextrose may be mentioned.

Although the invention is primarily concerned with the use of formaldehyde, compounds which produce formaldehyde readily upon decomposition, such as paraformaldehyde, may be used in its stead. In addition those aldehydes which react like formaldehyde in causing a pronounced thickening of coating compositions containing casein at high pH, may be used in place of formaldehyde and are capable of producing highly ink-resistant coatings. As examples may be mentioned acrolein and glyoxal.

In general those aldehydes are satisfactory substitutes for formaldehyde which when added to a coating composition at room temperature, consisting of 15 parts casein, 100 parts coating clay and 170 parts of water and having a pH of 9.5, cause it to set to a gel within 30 minutes, the quantity of aldehyde added being about 3% of the casein. On the other hand, aldehydes which do not cause any marked thickening of the coating under the above conditions, cannot be substituted for formaldehyde for the present purpose; in this class are acetaldehyde, propylaldehyde, etc.

The quantity of formaldehyde to be used is ordinarily about 1% to 3% of the casein and the amount of acetaldehyde or other aldehyde to be used is advantageously about equal to that of the formaldehyde.

As previously mentioned, the formaldehyde and other aldehyde may be first brought together under alkaline conditions (i. e. having a pH in excess of 9.0) before being incorporated into the pigment and casein of the coating composition. A condensation between the aldehydes ensues, preferably with the aid of heat. The degree of condensation thus effected depends upon the concentrations of the ingredients, the pH, the temperature and the duration of the treatment. Prolonged treatment at elevated temperatures may produce colored reaction products and finally resinous bodies are formed For my purpose the reaction should be terminated before the resins form, and ordinarily before the discoloration becomes too deep. The product resulting from the reaction is then added to a coating composition containing casein and mineral pigment. By selecting products of higher or lower degrees of condensation, coated papers having varying degrees of ink resistance and other properties may be produced. In the same way the useful life of the coating, i. e. the length of time during which it remains fluid enough to be applied and properly spread on paper, may be similarly varied.

My experiments indicate that the ink and varnish resisting qualities of the coated paper made according to this invention are sharply increased when the casein content of the coating composition is increased to about 13% or 14% of the weight of pigment—advantageously a good grade of coating clay. With this ratio of casein to clay, coated papers made by previous methods generally give papers which are far too absorbent to varnish to be acceptable. In previous practice it was necessary to increase the casein to 20 or more parts to provide a sufficiently non-absorptive coating for this purpose. However, using my method, papers containing in the coating 14 parts of casein per 100 parts clay may be obtained, which are comparable to or superior to prior art papers containing 20 or more parts of casein. Furthermore my papers do not suffer from many of the adverse properties of papers characterized by high casein contents, such as for example lowered opacity and increased curling tendencies.

I have found that soy bean protein can be substituted for casein in coating compositions of the present invention with good results.

In carrying out the invention the presence of calcium ions should be avoided where the mixed aldehydes are added directly to the coating composition. They materially diminish the ink resistant properties of the coated paper. Consequently compositions containing calcium sulfate and satin white, if used, should be treated to substantially eliminate calcium ions. One method of accomplishing this which I have found successful is by the addition of sodium carbonate followed shortly by the addition of casein. Nevertheless this fact does not preclude the use of calcium carbonate as a pigment, since in this case there are only a relatively few calcium ions present. Also by heating together casein and the mixed aldehydes before incorporation with the pigment this difficulty with calcium ions apparently does not occur.

In carrying out the process of the present invention the coating composition is first prepared as previously described. The viscosity of the

finished coating composition may be somewhat higher than that of the pigment-casein composition before adding the aldehydes. However this increase is not sufficient to give trouble in spreading or brushing onto the paper. With a standard Stormer viscosity apparatus using a 100 gram weight the time for 50 revolutions of the cylinder of the apparatus will seldom exceed 35 or 40 seconds for coatings made in accordance with the present invention. Furthermore, unlike the increase in viscosity due to formaldehyde alone, the slight thickening which may occur according to the present method may be controlled by good agitation of the composition. Either the coating composition should be heated to 160° F. or more before application to the paper, or the freshly coated paper should be heated to about 160° F. or more in order to fully develop the ink resisting qualities inherent in the coating composition. However if an aldol type condensation product is incorporated into the coating, then it is not necessary to heat either the coating or the freshly coated paper.

The following examples are given to further illustrate the invention: A coating composition was first prepared consisting of 100 parts coating clay, 14 parts casein, and water sufficient to give a total solids content of about 40%. The casein was dissolved by the use of soda ash to the extent of 7% of weight of the casein. The above coating composition was well mixed and to it was added an aldol type condensation product in amount equal to 5% of the weight of casein. The condensation product was prepared by mixing together 32.5 lbs. water, 12.5 lbs. of 40% formaldehyde, 5 lbs. of 99% acetaldehyde, and 5 lbs. of a 20% sodium carbonate solution. The temperature of this mixture rose to 130° F. by virtue of an exothermic reaction. Then the temperature was raised to 170–180° F. by heating on a water bath for two hours, after which the temperature was then allowed to fall to 105° F. The initial pH of this mixture was 10 and the final pH was about 8.5. This resulted in a combination of the formaldehyde and acetaldehyde to give an aldol type product, the exact composition of which was not determined. It was added to the above mentioned coating mixture, and additional sodium carbonate sufficient to give a total amount equal to 25% of the casein was then incorporated into the coating composition which now had a pH of 9.5. The resulting coating composition was a freely flowing mixture capable of being smoothed out into an even layer by means of a conventional brush coater. The coated paper resulting therefrom was very non-absorbent to printing ink regardless of whether the paper was dried at high or low temperatures. It had the ink resistance of a coated paper having about 50% more casein made by the older methods.

In another case 80 parts coating clay, 20 parts finely divided calcium carbonate and 15 parts casein were mixed together along with water to give a coating composition having about 42% solids. To this mixture was added successively 3% formaldehyde based on the casein and 3% butrylaldehyde based on the casein and 25% sodium carbonate based on the casein. The whole mixture was then heated to 170° F. for several hours. This coating when applied to paper gave a product having marked resistance to printing ink and to varnish in spite of the relatively small amount of casein used.

In another example the coating mixture was prepared in two steps. In the first step an aqueous mixture of 70 parts coating clay, 20 parts finely divided calcium carbonate and 10 parts satin white was thoroughly mixed together in the presence of 5 parts of casein A second preparation was made in which 10 parts of casein was used to which was added 0.45 parts of formaldehyde and the same amount of acetaldehyde and sodium carbonate in considerable excess of that required to dissolve the casein and sufficient to give this mixture a pH of about 9.5. This mixture at a solids content of about 9.4% was heated to 172–182° F. for 20 minutes. It was then cooled and added to the first composition. A coating composition containing clay, calcium carbonate, satin white and casein in the proportions above mentioned ordinarily gives coated papers that are extremely absorptive to printing ink. When modified as above described a sheet very non-absorbent to printing ink is obtained.

I have found that the method is eminently adapted to coating paper on the paper machine, especially for the production of coat-one-side label paper of varnishing quality. For this purpose the method described by Donald B. Bradner in application Serial No. 212,877 filed June 10, 1938, now Patent No. 2,229,621, was used, two layers of coating being applied to the wire side of the paper in the dryer section of the paper machine. The coating composition used on the base coat consisted of 100 parts coating clay, 15 parts casein dissolved in soda ash. This coating had a total solids content of about 40% and a pH of about 7.5. It contained no formaldehyde. A total weight of about 6 lbs. of coating (dry basis) per ream (25 x 38—500 sheets) was applied. After the application of this coating the paper passed around a few dryer cylinders and received another coating on top of the base coat. This coating composition was made up of 25 parts finely precipitated calcium carbonate, 75 parts coating clay, and 15 parts casein, and had a solids content of about 32%. To 300 gallons of this coating 250 ounces of 40% formaldehyde mixed in 5 gallons of water was added slowly. This is equivalent to about 5% HCHO on the casein. Then 5 gallons of 20% acetaldehyde mixed in 5 gallons of water was added. This is equivalent to about 6.3% CH_3CHO on the casein. After these two aldehydes had been thoroughly mixed in the coating, about 30 pounds of sodium carbonate dissolved in water was added, the mixture being continuously stirred all the time. This gave a pH of about 9.5. This coating composition was applied over the base coat to the extent of about 3 pounds (dry basis) per ream (25 x 38—500 sheets). The coated paper was then dried by heating on the remaining drying cylinders of the paper machine. The product was an extremely ink-resisting coated paper of outstanding value as a varnishing label paper.

I claim:

1. Process of preparing coating compositions which comprises mixing together protein adhesive selected from the class consisting of casein and soybean, mineral pigment, water, an aldehyde capable of causing an aqueous composition at room temperature having a pH of 9.5 and consisting of casein 15 parts, coating clay 100 parts and water 170 parts to set to a substantially solid gel within 30 minutes when added to the mixture in amount of 3% of the casein, another aldehyde being incapable of producing a marked thickening of the composition when similarly tested the

quantity of the first-named aldehyde being sufficient to cause a gelling of the coating in the absence of the second-named aldehyde, and the quantity of the second-named aldehyde being sufficient to retard the gelling action of the first-named aldehyde, and an alkaline compound sufficient to give the coating composition a pH of from 9.0 to about 11, the order of addition of the ingredients being such that the second named aldehyde is present before the composition contains the mixture of protein adhesive, the first named aldehyde and alkali, and thereafter heating the composition to at least 150° F. to improve the ink resisting properties thereof.

2. Process of preparing paper coating compositions which comprises mixing together casein, mineral pigment, water, formaldehyde, acetaldehyde, and an alkaline sodium compound to give a pH of from 9.0 to about 11 to the coating composition each aldehyde being of the order of from 1% to 3% of the casein content, the order of addition of the ingredients being such that the acetaldehyde is added before the composition contains the mixture of casein, formaldehyde and alkali, and thereafter heating the coating composition to at least 160° F. to improve the ink resisting properties thereof.

3. Process of preparing coating composition which comprises mixing together protein adhesive taken from the class consisting of casein and soybean, mineral pigment, water, an aldehyde capable of causing an aqueous composition at room temperature having a pH of 9.5 and consisting of casein 15 parts, coating clay 100 parts, and water 170 parts, to set to a substantially solid gel in 30 minutes when added to the mixture in amount of 3% of the casein, and a second aldehyde incapable of producing a marked thickening of the composition when similarly tested, then adding an alkaline compound of a fixed alkali metal to give a pH of from 9.0 to about 11 to the coating composition and heating the composition to at least 160° F. to enhance the ink resistance properties thereof, the quantity of the first-named aldehyde being sufficient to cause a gelling of the coating in the absence of the second-named aldehyde and the quantity of the second-named aldehyde being sufficient to retard the gelling action of the first-named aldehyde.

4. Paper coating composition which comprises a fluent aqueous mixture comprising protein adhesive taken from the class consisting of casein and soybean, mineral pigment, an aldehyde chosen from the group consisting of formaldehyde, acrolein, and glyoxal in amount sufficient to cause a gelling of the coating, and a compound chosen from the group consisting of acetaldehyde, propylaldehyde, butryaldehyde, heptaldehyde, ethyl propyl acrolein, aldol, and dextrose in amount sufficient to retard the gelling action of the members of the first-named group, said coating composition having a pH of from 9.0 to about 11.

5. Fluid aqueous paper coating composition comprising, as the adhesive a protein selected from the class consisting of casein and soybean, mineral pigment, an alkaline aqueous solution, an aldehyde capable of causing an aqueous composition at room temperature having a pH of 9.5 and consisting of casein 15 parts, coating clay 100 parts, water 170 parts, the parts being by weight, to set to a substantially solid gel within 30 minutes when added to the mixture in amount of 3% of the casein, and a second aldehyde incapable of producing a marked thickening of the composition when similarly tested, the quantity of the first-named aldehyde being sufficient to cause a gelling of the coating in the absence of the second-named aldehyde, and the quantity of the second-named aldehyde being sufficient to retard the gelling action of the first-named aldehyde, said coating composition having a pH of from 8.5 to about 11.

6. A paper coating composition comprising an aqueous mixture of casein, mineral pigment, and a product resulting from the combination of two aldehydes in an alkaline medium, one of said aldehydes being capable of causing an aqueous composition at room temperature, having a pH of 9.5 and consisting of casein 15 parts, coating clay 100 parts, water 170 parts, the parts being by weight, to set to a substantially solid gel within 30 minutes when added to the mixture in amount of 3% of the casein, and a second aldehyde incapable of producing a marked thickening of the composition when similarly tested, the quantity of the first-named aldehyde being sufficient if added alone to the coating composition to cause a gelling of the coating, and the quantity of the second-named aldehyde being sufficient to retard the gelling action of the first-named aldehyde, said coating composition having a pH of from 9.0 to about 11.

7. Paper coating composition which comprises an aqueous mixture of casein, mineral pigment, and a product resulting from the combination of formaldehyde and an aldehyde incapable of producing a marked thickening of an aqueous coating composition at room temperature, having a pH of 9.5 and consisting of casein 15 parts, coating clay 100 parts, water 170 parts, the parts being by weight, within 30 minutes when added to the mixture in amount of 3% of the casein, said coating composition having a pH of from 9.0 to about 11 and a viscosity not exceeding 55 seconds as determined with a Stormer viscosity apparatus for 50 revolutions using a 100 gram weight, and the quantity of formaldehyde being sufficient to cause a gelling of the coating in the absence of the second aldehyde, and the quantity of second aldehyde being sufficient to retard the gelling action of the formaldehyde.

8. Paper coating composition which comprises a fluent aqueous mixture of casein and mineral pigment to which has been added formaldehyde and another aldehyde capable of forming an aldol condensation product with formaldehyde, said coating composition having a pH of from 9.0 to about 11, and the quantity of formaldehyde being sufficient if added alone to the coating composition to cause a gelling of the coating and the quantity of the other aldehyde being sufficient to retard the gelling action of the formaldehyde

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