Nov. 17, 1964 J. J. CLANCY ETAL 3,157,533

STARCH STABILIZED CASEIN COATING EMULSIONS

Filed July 17, 1963 3 Sheets-Sheet 1

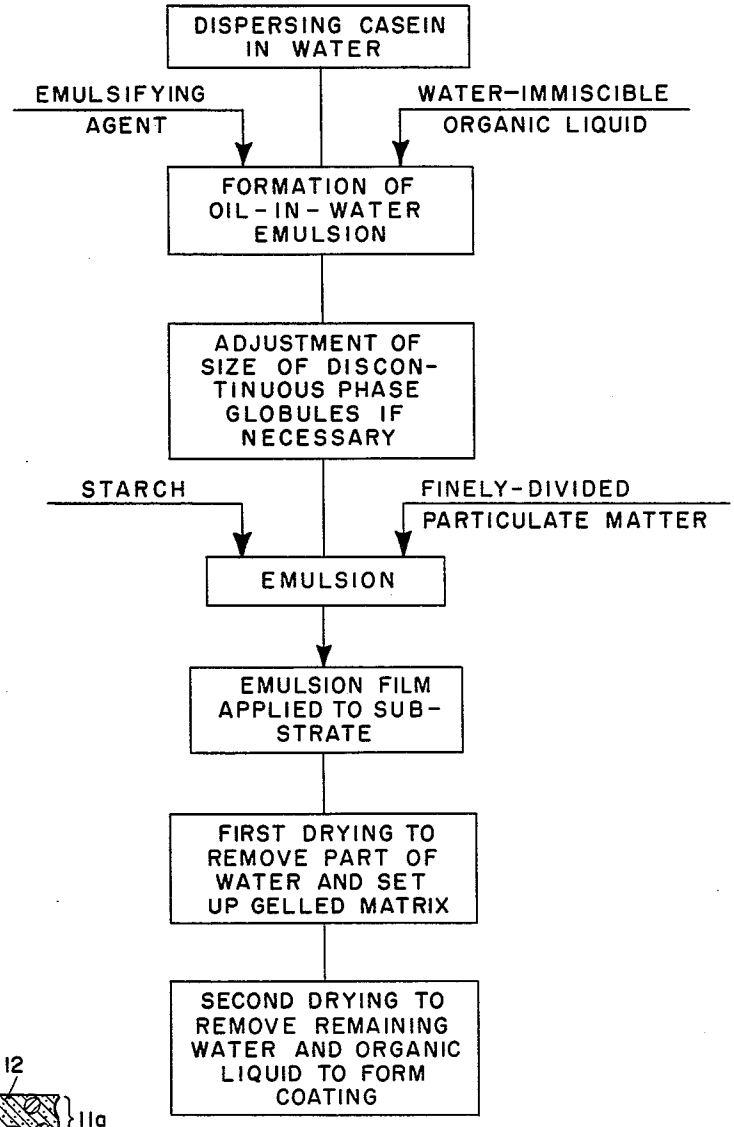


Fig. 1

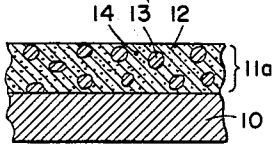


Fig. 2

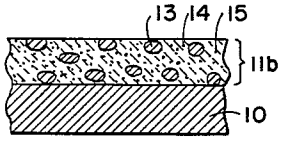


Fig. 3

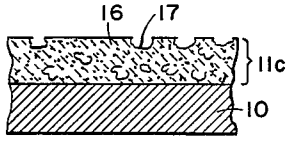


Fig. 4

John J. Clancy
David W. Lovering
Richard S. Brenneman
Robert C. Wells
INVENTORS

BY

Attorney

STARCH STABILIZED CASEIN COATING EMULSIONS

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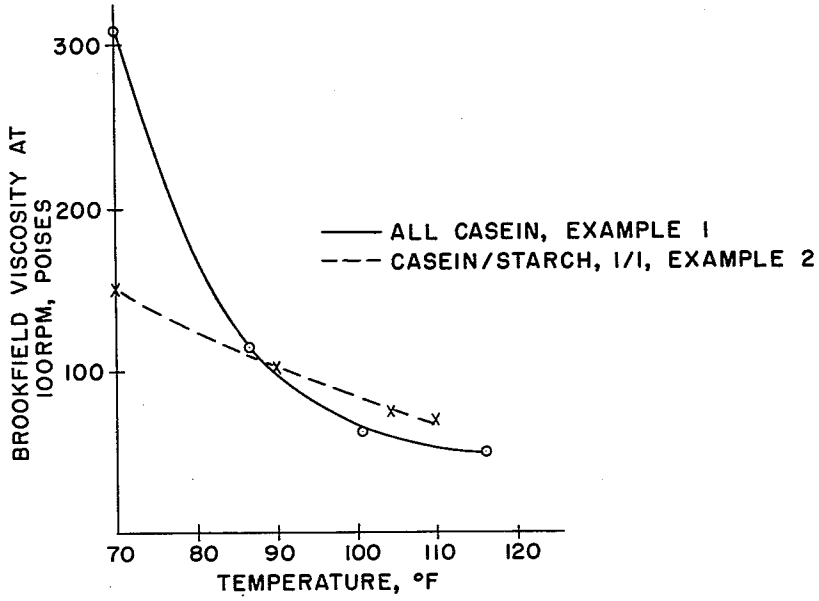


Fig. 5

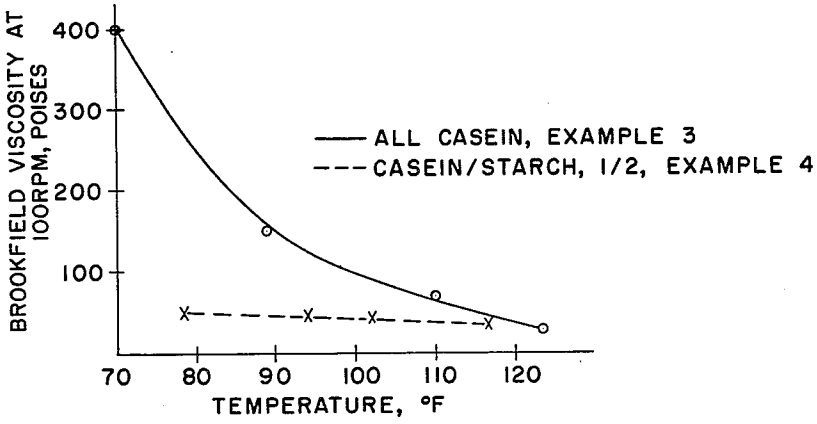


Fig. 7

John J. Clancy
David W. Lovering
Richard S. Brenneman
Robert C. Wells
INVENTORS

BY

Attorney

Nov. 17, 1964 J. J. CLANCY ETAL 3,157,533

STARCH STABILIZED CASEIN COATING EMULSIONS

Filed July 17, 1963 3 Sheets-Sheet 3

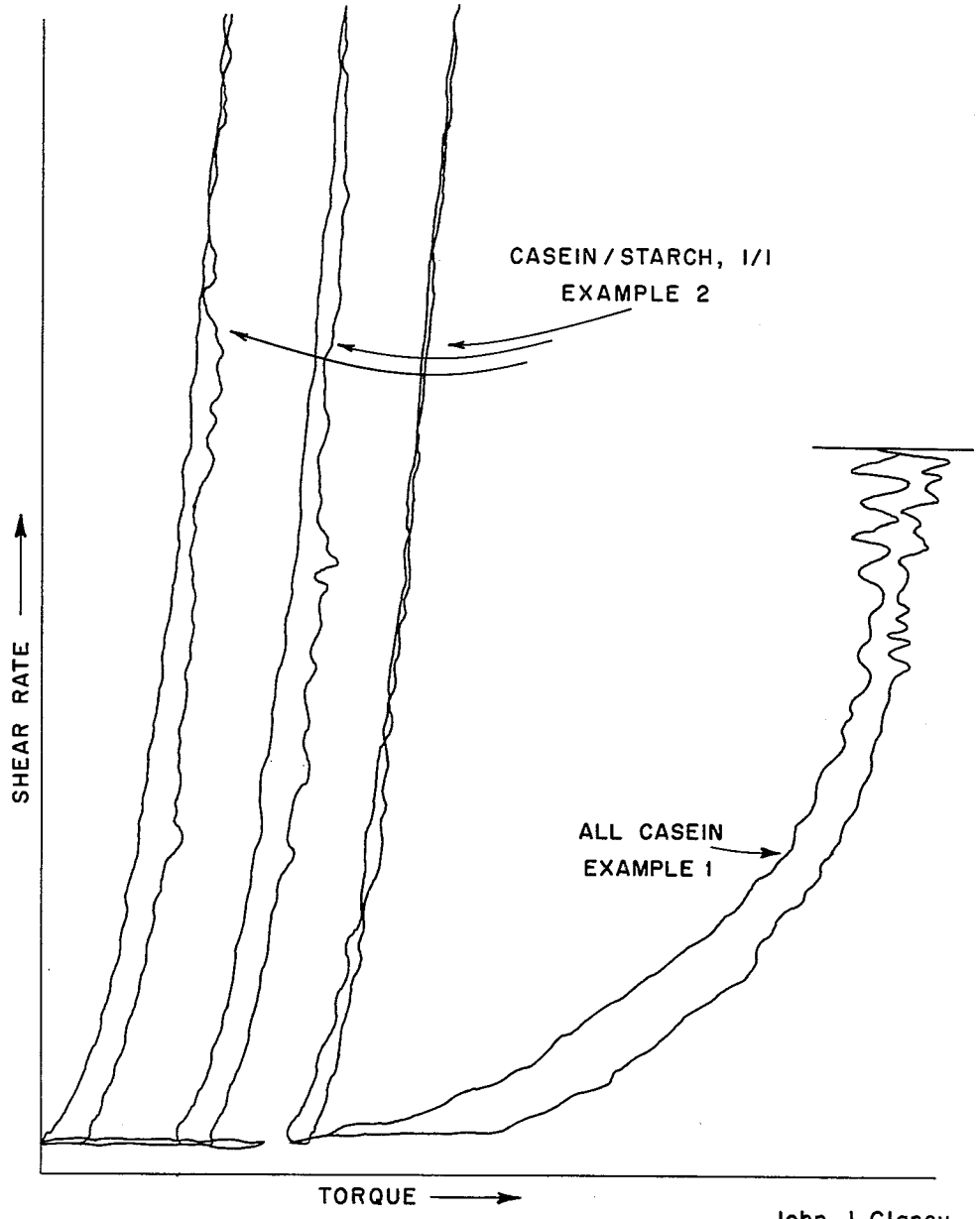


Fig. 6

John J. Clancy
David W. Lovering
Richard S. Brenneman
Robert C. Wells
INVENTORS

BY Bruce A. Lyon
Attorney

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3,157,533
STARCH STABILIZED CASEIN COATING EMULSIONS

John J. Clancy, Westwood, David W. Lovering, Needham, Richard S. Brenneman, Natick, and Robert C. Wells, Arlington, Mass., assignors to Arthur D. Little, Inc., Cambridge, Mass., a corporation of Massachusetts

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24 Claims. (Cl. 117—156)

This invention relates to paper coating and paper products, and more particularly to the coating of publication and other printing papers.

Papers of all weights and grades are coated for one reason or another—to give them good printing qualities as well as brightness and opaqueness, or to change their physical properties and/or their appearance. This invention is concerned with a novel coating composition and a method of applying it in a manner to impart brightness and opacity to paper, while at the same time enhancing its printing quality. The coating composition of this invention is moreover designed to be used with the high-speed coating equipment commonly employed for coating publication papers. It achieves these advantages with coating weights which are materially less than conventional coatings now used on publication papers.

Although the composition and method of this invention for applying coatings to paper is applicable to many different types of paper (from thin tissue papers to heavy paperboard) it will be described herein as applied to publication-type papers for convenience and clarity of presentation. Moreover, it is particularly well suited to publication papers inasmuch as it achieves good brightness and opacity with light coating weights at an economic cost and with outstanding coating application characteristics.

In a copending application, Serial No. 60,358, filed on October 4, 1960, in the names of John J. Clancy, David W. Lovering, and Robert C. Wells, now Patent No. 3,108,009, and assigned to the same assignee as this application, there is described a novel type of coating and method of applying it which achieves extremely high brightness and opacity through the formation, from an emulsion coating composition, of a porous type coating structure which is described as a binder matrix containing uniformly distributed throughout multitudinous air-binder interfaces of a specified size. These air-binder interfaces contribute intense brightness and opacity to the coating by virtue of their light scattering characteristics, and at the same time reduce the overall weight of the coating not only through their superior optical properties which allow a lighter coating to be used but by virtue of the fact that they substitute air for the high density pigments normally used in a paper coating.

In this copending application, Serial No. 60,358, the binder matrix is formed of all proteinaceous material, or a mixture of proteinaceous material and some elastomeric materials. These coatings are particularly well adapted to the coating of boxboard and other grades of paper and board and to use with coating equipment commonly employed in their manufacture. This composition was tailored to meet boxboard requirements and is in commercial use today, demonstrating technical and economical advantages over conventional clay binder formulations previously used.

Publication papers are customarily coated with water slurries containing starch and clay, or casein and clay. A typical raw coating stock has a basis weight which ranges from 27 to 29 pounds per ream (3,300 sq. ft.) and has applied to it about 12 pounds of dry coating (total on both sides). Thus, the final weight of the publication paper may range from about 39 to about 41 pounds per ream. A publication paper which has six pounds of dry coating

weight on each side per ream, will typically have on each side a dry coating volume of 70 cubic inches and a dry coating thickness of about 3.8 microns.

Publication paper finds wide use in periodicals and with the frequent increases in bulk mailing rates, the weight of such paper becomes of paramount importance to publishers. It follows therefore that if it were possible to materially reduce the weight of coating on publication sheets, it would be possible to realize material savings in mailing and shipping charges. However, this cannot be done by merely reducing the weight of the coating raw stock, by reducing the coating weight, or by reducing both, for such weight reductions cause the paper to experience one or more deficiencies. Reducing the basis weight of the coating raw stock lowers the strength of the paper and decreases the opacity and bulk of the coated sheet. Moreover, it detracts from the runnability of the paper in the press room. Runnability in a paper is a characteristic which permits its use in a commercial printing press in essentially trouble-free conditions, or in a manner so that down-time of the press is kept to a minimum and long runs can be made without interruption. Since the majority of periodicals are printed by web-fed high-speed letter-press operations, these properties cannot be sacrificed.

Any substantial reduction in the weight of conventional clay-starch or clay-casein coating applied to the raw stock will result in a loss of printability, particularly in regard to printing smoothness and control of ink holdout. Neither does the solution to the problem lie in the use of materials which have higher brightness or opacity and thus require less coating volume and thickness. In this case it will be found that difficulties in printing will be encountered, inasmuch as the presently used high-speed letter-press requires a minimum coating thickness to obtain necessary coating resiliency in order to print evenly over the surface of the paper. Thus, a minimum thickness is required to cancel out any unevenness of the paper itself and also to achieve uniformity in printing smoothness and ink holdout.

Because of the special requirements of publication paper coatings which are not common to boxboard coatings, the novel type of coating composition and method of applying it described in the above-identified Serial No. 60,358, while offering high brightness and opacity, is not ideally suited to the high-speed coating techniques required in the coating of publication paper. The manufacture of publication paper is highly completitive and in its manufacture it is necessary to operate at high rates of speed in order to attain economic operation. Usually the method of coating application is different from that used in the manufacture of boxboard and the rheological properties and solids content of the coating must be adapted to be compatible with a high-speed method of application. Publication paper is normally coated with a trailing blade coater at rates approaching 2,500 feet per minute. These high-speed coating operations place severe demands on a coating, both in application and drying.

In the application of the coating under these conditions, extremely high shear rates are encountered and the coating must flow instantaneously and uniformly to keep the final paper free from streaks and "coating patterns" which adversely affect printing characteristics. Any tendency for the coating to become dilatant, or to resist uniform flow will show up as defects in the printed product. The attainment of pattern-free coating at very high speed is achieved through good coating viscosity control over the temperature range at which the coating is accomplished and under the conditions of high shear stresses which prevail in the coating composition as it is handled by high-speed coaters.

Further, it is desirable to be able to work with coating compositions which do not contain an excessive amount of water, that is, with coatings that have a relatively high

solids content, based upon the amount of coating which is applied. For publication coating, the coating composition of U.S. Serial No. 60,358, although usable, does not provide the optimum in high solids content from an economic point of view. However, the use of an emulsion coating which contains a highly volatile organic solvent such as kersosene as one of the liquids possesses inherent advantages over the typical water slurry coating of clay and casein or of clay and starch, inasmuch as the volatile organic has a lower heat of vaporization than water. The drying load and the rate at which drying can be accomplished is a direct factor in the cost of the coating operation and of the resultant coated paper. Moreover, the drying rate should be compatible with the coating rate so that it is not a contributing factor in reducing the speed of the operation.

In coating a publication paper it is necessary also to be able to control ink holdout. This is a property which controls the rate at which the ink is absorbed into the coating surface and into the paper. Ink holdout is directly related to the gloss and uniformity of the printed surface. Low or uneven ink holdout will result in a dull or uneven print and conversely high ink holdout will result in a brighter glossy print. On the other hand, excessive ink holdout may promote chalking or lack of adhesion between dried ink and paper coating. Thus, it is desirable that the ink is not absorbed too rapidly, but that a portion of it remain on the surface and contribute gloss to the print.

Finally, as pointed out above it is necessary to reduce the weight of the coating on the coated paper in order to reduce shipping and mailing charges. However, as also pointed out this is not a matter of merely reducing the coating thickness or volume since it is necessary to maintain the thickness of the coating, which in turn maintains the bulk resiliency required in printing. This is a necessary characterstic of letter-press printing and it is required to take up the lack of uniformity in the sheet of paper and give good printing smoothness while filling in the unevenness of the paper sheet itself. Finally, it is also required that the coated paper have at least as good pick resistance as the coatings now used on publication paper.

It is therefore a primary object of this invention to provide a coating composition of the emulsion type which exhibits application and drying properties required of a coating to be used on high-speed coating apparatus. It is another object of this invention to provide a coating composition of the character described which possesses rheological properties insuring a stable viscosity and temperature index under the conditions of shear which prevail in high speed coaters. It is another object of this invention to provide a bright opaque coating which is materially lighter in weight than now used, but which at the same time retains essentially the same bulk and resiliency of the present coatings in order to make it readily adaptable to presently used high-speed printing techniques. It is yet another object of this invention to provide a coating composition which has a relatively high solids content considered in terms of the amount used and in terms of the amount of liquid which must be removed. It is yet another object of this invention to provide such a coating composition which reduces drying load and rates. Another object of this invention is to provide a coating composition and a resultant coated paper which permits accurate control of ink holdout.

It is another primary object of this invention to provide improved publication papers coated on both sides with a light-weight coating which permits material savings in the cost of mailing and shipping. It is another object of this invention to provide such publication papers which exhibit controlled ink holdout and good pick resistance. Other objects of the invention will in part be obvious and will in part be apparent hereinafter.

The invention accordingly comprises the several steps

and the relation of one or more of such steps with respect to each of the others, and the article possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated by the claims.

The coating composition of this invention attains the objects set forth by incorporating into an emulsion-type coating, comprising an oil-in-water emulsion, a quantity of starch used as a viscosity stabilizer. Many attempts have previously been made to blend casein and starch in a coating composition but the experiments have failed because it has always been considered that protein and starch adhesives were incompatible. By the addition of an excess of alkali a more compatible mixture could be made, but then it was found that the casein contributed little or nothing to increasing the water resistance or the bonding strength of the starch unless the adhesive coating was essentially all casein. If the proportions were reversed and a small amount of casein was added to a starch coating, then the bonding strength was reduced. (See for example Casey, "Pulp and Paper," vol. III, p. 1595 (1961).) Moreover, it has always been difficult to maintain a uniform mixture of casein and starch, and if the conditions were not right the two would spontaneously precipitate. Thus, it is totally unexpected that the combination of these two materials in an emulsion type coating would not only be workable, but would also be capable of imparting to the coating outstanding rheological properties making it particularly suitable in high-speed coating operations. In the prior art, when casein and starch were combined it was found that the strength of the mixture was not equal to the sum of the strength of the two components, for under these conditions it was sometimes found that the starch did not add anything to the strength of the casein and acted only as an inert material. (See for example Sutermeister and Browne, "Casein and Its Industrial Applications," p. 294 (1939).) However, in the coating composition of this invention there is attained a synergistic effect in that the starch contributes viscosity control, is completely compatible with the casein blending with it in the binder film; and moreover does not in any way detract from the pick strength, opaqueness and brightness of the original oil-in-water emulsion coating.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings in which:

FIG. 1 is a flow diagram showing the making of the coating compositions and the manner in which it is applied to a paper substrate;

FIGS. 2 through 4 illustrate in a diagrammatic fashion the formation of the coating of this invention;

FIG. 5 is a plot of viscosity vs. coating temperature for coating compositions made with and without starch;

FIG. 6 is a plot of torque vs. shear rate for the coating compositions of FIG. 5; and

FIG. 7 is a plot of viscosity vs. coating temperature for another coating composition with and without starch.

Briefly, the coating composition of this invention may be characterized as an oil-in-water emulsion in which a water dispersion of a proteinaceous binder and a starch form the continuous phase, and a water-immiscible organic liquid having a boiling point above water is present as a discontinuous phase. The globules forming the discontinuous phase should range in size from about 0.5 to 1.5 microns, and the continuous phase should contain a finely-divided particulate material suspended therein and designed to impart desired physical characteristics to the surface of the coating.

In forming the coating composition a water suspension or solution of the proteinaceous binder is made and then a water-immiscible organic liquid added under conditions to provide the desired emulsion. To this then is added starch cooked in water and the finely-divided particulate

material. Suitable emulsifying agents may also be used to obtain the desired physical characteristics of the emulsion. The coating composition, which preferably has a solids content of at least 20%, is then applied to the paper surface as a continuous film while retaining the original emulsion structure.

Drying of the film to remove the liquids is carried out in such a manner that a portion of the water is first removed from the continuous phase thereby setting up a gelled matrix in which the droplets of the discontinuous phase are retained in essentially their original size and spatial distribution which they occupied in the emulsion coating. Finally, the remaining portion of the water and the organic liquid are removed through heating so that the final coating may be described as one consisting of a binder matrix containing the starch and finely-divided particulate matter and having uniformly distributed throughout multitudinous air-binder interfaces which are essentially equivalent in size to the liquid droplets forming the discontinuous phase of the emulsion coating. This means that substantially all of the air-binder matrix interfaces which impart brightness and opacity to the coatings are, in their maximum dimension, from about 0.5 to 1.5 microns in size, with no appreciable number exceeding 5 microns.

The addition of substantial quantities of starch to the coating composition achieves viscosity stability at temperatures ranging from 90° to 120° F. and permits the coating composition to be applied to paper at very high speeds. Moreover, the physical characteristics of this improved coating composition are such that once it is deposited on the paper it is smooth and free of any undesirable patterns related to coating techniques. Thus, the coating composition and the resulting coated paper contain a combination of casein and starch, heretofore believed to be undesirable in conventional coatings.

FIG. 1 illustrates diagrammatically the process of forming the coating composition and its application to a substrate such as publication paper. With reference to this flow diagram, it will be helpful to discuss the general formulation of the coating, the components and their weight ratios, and finally the actual formation of the coating in the desired configuration on the substrate.

The liquid coating composition comprises an oil-in-water emulsion. The continuous phase is an aqueous dispersion of a mixture of a binder-matrix material and of starch (serving as a viscosity control agent) and containing finely-divided particulate material suspended therein. The discontinuous phase is a water-immiscible organic liquid present in globules within a specific size range.

The binder-matrix material is a film forming material capable of setting up first in a gel-like matrix with the removal of a portion of the water in which it is dispersed and then in an essentially continuous film having air-binder interfaces formed through its volume. Suitable binder-matrix materials are selected from the group consisting of casein, alpha protein, water-dispersible elastomers (natural and synthetic rubbers) and mixtures thereof. In the case of elastomeric materials it is desirable to use an appreciable percentage by weight of casein or alpha protein in the binder.

Inasmuch as casein is the preferred binder-matrix material, the following description will be given using casein as the binder. However, it is not meant to limit the binder material to casein.

In formulating the liquid coating composition it is first necessary to form the proteinaceous material such as casein or alpha protein, which forms the binder, into a suitable water dispersion or solution. This can be done most conveniently with the aid of a solubilizing agent which is alkaline in nature. Such solubilizing agents include, but are not limited to, ammonium hydroxide, sodium hydroxide, sodium tetraborate, sodium carbonate, and trisodium phosphate. Any of the known solubilizing agents for casein can be used in the process of formulating the coating of this invention.

Inasmuch as casein or other protein-containing components in an unmodified state are known to be somewhat sensitive to water or to moderate pressure and since this is undesirable in a publication coating paper, it is necessary to add to the coating composition a modifying agent which will convert the casein portion to an essentially water-insoluble condition in the final coating. This may be conveniently done by adding to the binder solution an inorganic metal salt which is appreciably soluble in the binder solvent and which forms an insoluble derivative with the binder. Thus, in the case of casein it has been found satisfactory to add zinc sulfate. The resulting coating then apparently comprises a substantially water-insoluble zinc salt of casein making the final coating also containing the starch less sensitive to water than an unmodified casein-starch mixture. Other metallic ions such as copper, aluminum and chromium may also be used to convert these binders to an essentially insoluble form. The manner in which a material such as zinc sulfate is added to form the zinc caseinate is well known in the art and need not be described further. Typical formulations using zinc sulfate in this role will be illustrated in the examples given below.

The liquid forming the discontinuous phase of the emulsion must be a water-immiscible organic liquid having a boiling point above that of water at the drying temperature required, but for practical considerations in its removal during drying, this boiling point should not exceed about 500° F. Moreover, at the initial drying temperature, the discontinuous phase liquid must have a vapor pressure below that of water in order to permit the first portion of the water to be removed to set up the matrix in a gel form without any substantial removal of the organic liquid. Suitable water-immiscible organic liquids include, but are not limited to, xylene, kerosene, mineral spirits, high flash naphthas, ketones such as butyl methyl ketone and amyl ethyl ketone, paraffin hydrocarbons such as octane, and the higher-boiling acetates such as butyl acetate or amyl acetate.

The final choice of the liquid forming the discontinuous phase may also require the consideration of such factors as that which will give the brightest coating for a given weight per unit area of surface for a specific film forming material; that which will prove to be the most compatible with other components such as a binder, the dispersing agent and any particulate additive, dye or dyes added; and that which will meet certain other requirements such as toxicity, inflammability, adaptability to production procedures, cost and the like.

Inasmuch as the mixing of the coating composition of this invention requires a thorough dispersing of one liquid in another, each of which is immiscible in the other, it is desirable to add a dispersing agent such as those commonly used to prepare emulsions. Such a dispersing agent may be one of the appropriate soaps such as ammonium, sodium or potassium oleate or stearate or other suitable emulsifying agents. The dispersing agent may be formed in situ by a reaction between a weak organic acid and an alkali metal ion furnished, for example, from an excess of solubilizing agent. Thus, if stearic acid is added to a coating mixture containing an excess of ammonium ions, ammonium stearate is formed and serves as a dispersing agent.

Generally, the weight ratio of binder-matrix material plus the starch to the liquid of the discontinuous phase will range from about 1:1 to about 1:10. The actual ratio will depend upon the characteristic of the final coating desired. As a rule, the smaller amount of matrix material, the higher the brightness of the final coating, and a preferred ratio is about 1:5.

In preparing the binder solution, or dispersion, it has been found desirable to formulate solutions having from about 5% to about 40% solids content by weight while

the amount of dispersing agent will generally vary from about 2 to about 5 parts by weight to 100 parts by weight of the liquid of the discontinuous phase. The higher solids content solutions are to be preferred since they decrease the ultimate drying load and rate.

The starch which is added as a viscosity controlling agent to the binder-matrix material may be any type of starch which is normally used in paper coatings. Thus, it may be oxidized starch, enzyme-converted starch, the so-called aldehyde starches, or a starch which has been hydrolyzed to a lower molecular weight. Many treatments are available to convert starch to the necessary molecular weight and properties suitable for use in paper coating compositions. The various starches suitable for use in our coating composition are described in detail in TAPPI Monograph Series—No. 17, "Starch and Starch Products in Paper Coating" (1957). The starch which is introduced is prepared by cooking first in water for about 10–15 minutes at about 190° F. and is added as a relatively thin water dispersion containing from 20% to 35% by weight of starch. The starch is preferably added to the emulsion at a temperature of about 160° to 170° F. The ratio of binder-matrix material such as casein to starch may vary over a range from about 1:1 to 1:5. In general, if less starch is used, some difficulty in viscosity control at high temperatures will be encountered; while if an excessive amount of starch is used, some difficulty in forming the desired film structure is experienced.

Finally, there is added to the coating composition a finely-divided particulate matter designed to contribute to the surface of the coating film additional desired physical properties, particularly good printing quality and high pick resistance.

The particulate additives suitable for incorporation in the coating of this invention may be defined as finely-divided particulate matter generally of inorganic origin which are inert to the binder material, to the starch, and to the discontinuous phase liquid under the condition which the film coating is applied to the substrate. The particulate matter is preferably sized finer than 12 microns; however, particle sizes up to those which can be substantially permanently bonded by the film forming binder-matrix material may be used. The final surface characteristics of the modified film coating will control the size of the particulate matter; thus, if a coarse surface is undesirable, then the particulate matter will be sized within the finer size range.

It is important to note that the particulate additive used in the coating of this invention is not present in the role of a pigment insofar as the term pigment is used generally to denote a material which contributes opacity to a system. On the contrary, it can be shown that although many of the particulate additives can in some coatings and sizes be considered pigments, they contribute no brightness or opactities to the coating of this invention; rather they contribute desirable properties to the surface of the coating. In some instances, the particulate matter actually somewhat reduces opacity and brightness for a given coating weight. The particulate additive may be further characterized as a material which is substantially wetted by either the water solution of the matrix material or by the discontinuous phase liquid and which can be permanently bonded within the final matrix film. The particulate additive may also possess other more specific characteristics such as being highly absorbent to the liquid medium of the ink used in printing, or the capability of imparting modification in the appearance of the surface such as a metallic appearance which would be created by the use of finely-divided aluminum powder or flakes as a particulate additive.

Typical particulate additives include, but are not limited to, chalk, clay, titania, hydrated calcium silicate, metallic powder such as aluminum and bronze, carbon black and colored pigments such as an ultramarine blue and the like.

The amount of particulate additive which may be added may be as high as about three to four times the weight of the binder-matrix material, e.g., casein, plus the starch present. Generally, for making film coating suitable for printing, it will be preferable to the use weight ratios of binder-matrix material plus starch to particulate additive of from about 1:0.5 to 1:4.

In mixing the coating composition of this invention, it is desirable to make up the binder solution (containing the insolubilizing agent) separately, and then while stirring very rapidly add the discontinuous phase liquid containing the dispersing agent. If the dispersing agent is to be formed in situ the acid reactant is added to the liquid used to form the discontinuous phase, and the basic reactant to the binder solution. Subsequent to the formation of the emulsion, it may be necessary to further process the emulsion to adjust the size range of the discontinuous phase globule, that is, of the globules of the water-immiscible organic liquid making up this discontinuous phase. This may be done by any known technique such as passing the emulsion through a homogenizer. Inasmuch as the size range of the globules making up the discontinuous phase of the emulsion is later to determine the size range of the interfaces in the finished dry coating, it is necessary to make this adjustment so that the discontinuous phase globules range in size from about 0.5 to 1.5 microns with no appreciable number exceeding 5 microns.

While the emulsion is maintained at a temperature of about 120–130° F., the hot water solution of the starch is added with further stirring to completely incorporate the starch into the continuous phase of the emulsion, that is, into the casein or other proteinaceous binder material solution. After the incorporation of the starch the particulate material is added to complete the formulation of the coating composition. It is only necessary to insure that these particles are uniformly dispersed in the continuous phase of the emulsion coating. Although the particulate additive can be put into the discontinuous phase, it is preferable to introduce it into the continuous phase. This preference is based on the fact that the continuous phase liquid is generally more viscous than the discontinuous phase liquid and thus is more suitable to effectively suspend the particulate additive. Moreover, better binding of the particulate additive is achieved by adding it to the continuous phase.

Once the coating has been thoroughly mixed it is applied to the substrate by any well known coating technique, and in the case of publication paper by high-speed coating apparatus, e.g., a trailing blade coater. It is not necessary to completely dry the substrate, i.e., the publication paper prior to the application of the coating. Thus, the coating may be an on-machine operation during the actual manufacturing of the paper. Generally, the emulsion coating is applied at a temperature of between about 90° and 100° F. in keeping with high-speed coating techniques. However, it may be applied over a wide temperature range (e.g., 75° to 150° F.) so long as the temperature is maintained relatively constant.

It is to be noted that the emulsion is applied as a continuous film with the emulsion structure being retained as it existed in the original emulsion coating. This may be clearly seen with reference to FIGS. 2 and 4 wherein the actual formation of the coating from the emulsion is illustrated in a much enlarged, diagrammatic fashion. In FIG. 2, the coating **11***a*, which is the emulsion coating, is applied to a suitable substrate **10** such as publication paper. The coating will be seen to be made up of the continuous phase **12** containing the casein and the starch. The starch is not identifiable but is an essential part of the continuous phase and is therefore not present as a particulate material. Dispersed within the continuous phase is the finely-divided particulate material **14**. Globules **13** of the water-immiscible organic liquid forming the discontinuous phase are also dispersed in the con-

tinuous phase 12. After the coating has been applied to the substrate, heat is applied to first remove a portion of the water from the continuous phase causing the binder-matrix material containing the starch to set up in the form of a continuous gel-like film 15 illustrated in FIG. 3 which shows the intermediate coating stage as gel-like coating 11*b*. Subsequently additional heat is applied to remove the remaining water and discontinuous phase liquid to give the coating 11*c* of FIG. 4. In the beginning of the drying, it is necessary that there exist a differential in the rates at which the water and the discontinuous phase liquid are removed to form the very small air-binder interfaces which distinguish the coating of the invention. As will be seen in FIG. 3, during the initial phase of the drying step required to create the gel matrix 15 and retain the emulsion structure, the continuous phase material probably shrinks to some extent; but the globules 13 of the water-immiscible organic liquid making up the discontinuous phase remain in essentially the same position and retain the same size as they did in the original emulsion structure of the coating before it was applied. Finally, in FIG. 4 with the removal of the remaining portion of the water and of the discontinuous phase liquid, some of the globules rupture and there are defined within the coating 11*c* the air-binder matrix interfaces 17, in the binder matrix/starch film 16, which contribute the opacity to the coating. Again as in the case of FIG. 3, these binder interfaces retain essentially the same location, size and structure as the discontinuous phase globules had in the emulsion and range in size from about 0.5 to 1.5 microns, giving rise to air-matrix interfaces in the coating of FIG. 4 in the same size range.

It will also be seen from these figures that the coating in FIG. 4 represented by 11*c* is an essentially continuous film coating containing these air-binder interfaces uniformly distributed throughout.

The following examples which are means to be illustrative, and not limiting, are given to further describe the formulation of coating compositions, their application to a typical substrate and their rheological properties as contrasted to a coating which does not contain starch.

EXAMPLE 1

A control coating composition without starch was made as follows. 200 pounds of casein was stirred into 800 pounds of water and the mixture was heated to 150° F. At this temperature 35 pounds of ammonium hydroxide (28% concentration) was added and the casein dispersion maintained at 150° F. for about 10 minutes until a casein solution had been formed. In a separate vessel 17.5 pounds of zinc sulfate heptahydrate was dissolved in 150 pounds of water. This zinc sulfate solution was then added to the casein solution at 150° F. While the mixture of casein and zinc sulfate was maintained at this elevated temperature, 35 pounds of additional ammonium hydroxide and 22.5 pounds of oleic acid were added. Finally, 348 pounds of a kerosene cut which was No. 9 refined oil (boiling range of 335° F.) was added to the hot casein solution with sufficient agitation to control kerosene particle size between 0.5 and 1.5 microns. After the emulsion had been formed a slurry made up of 525 pounds of No. 1 coating-grade clay in 375 pounds of water and 1.5 pounds of sodium hexametaphosphate (a clay dispersant) was stirred into the emulsion and uniformly distributed throughout the casein solution forming the continuous phase. This coating composition had a solids content of 30%.

EXAMPLE 2

For comparison, a 30% solids content coating was prepared in accordance with this invention. It was made by mixing 100 pounds of casein in 450 pounds of water and adding to this mixture 17.5 pounds of ammonium hydroxide (28% concentration) when the casein water mixture had been brought to 150° F. The mixture was maintained at this temperature for ten minutes; and then to it was added a solution containing 10 pounds of zinc sulfate heptahydrate in 100 pounds of water. To the zinc sulfate containing casein solution was then added 35 pounds of additional ammonium hydroxide, 22.5 pounds of oleic acid and 348 pounds of the kerosene. The ammonia and oleic acid were added first and then the kerosene added with agitation sufficient to emulsify the liquid mixture and to form kerosene particles as discontinuous phase globules, ranging in size from 0.5 to 1.5 microns. In a separate container, 100 pounds of an oxidized starch was heated in 400 pounds of water to between 190° and 195° F. for 15 minutes. This thin starch-water mixture was then added to the emulsion. Finally, 525 pounds of No. 1 coating-grade clay mixed in water to form a slurry containing 375 pounds of water and 1.5 pounds of sodium hexametaphosphate was added to the emulsion. The final coating composition was mixed thoroughly at slow speed to blend in the clay.

The binder matrix material in this coating was a mixture of casein and starch in a 1:1 ratio. The starch was found to be present in a continuous film with the casein and was not identifiable as particulate matter as were, of course, the clay particles.

The fact that the starch serves as a viscosity stabilizer in high-speed coating may be shown by a comparison of the rheological properties of the coating compositions of Examples 1 and 2.

The Brookfield viscosities were obtained at four temperatures, using two different r.p.m.'s for the two compositions with the following results, the data in Tables 1 and 2 corresponding to the compositions of Examples 1 and 2, respectively.

Table 1

COATING WITHOUT STARCH

Temp., ° F.	Viscosity, Centipoises		Viscosity Index [1]
	10 r.p.m.	100 r.p.m.	
70	54,800	30,800	1.78
87	17,200	11,600	1.48
105	9,600	6,200	1.55
116	8,000	5,250	1.52

[1] Ratio of viscosity at 10 r.p.m. to viscosity at 100 r.p.m.

Table 2

COATING WITH STARCH

Temp., ° F.	Viscosity, Centipoises		Viscosity Index [1]
	10 r.p.m.	100 r.p.m.	
70	44,000	15,200	2.91
90	26,400	10,100	2.62
104	19,200	7,400	2.60
110	18,400	7,200	2.54

The data for the viscosities at 100 r.p.m. are plotted in FIG. 5. These data and the plot of FIG. 5 clearly illustrate the stabilizing effect which starch has over the temperature range considered. The coating composition of Example 1 without starch exhibited a drop from 30,800 to 5,250 centipoises for an increase in temperature of 40° F. (70° to 110°) amounting to a factor of near 6; while the starch containing coating showed a drop from 15,200 to 7,200 centipoises over the same temperature range, or a factor of a little more than 2. Thus, these data show that variations in coating temperature will have little influence upon the coating composition of this invention but marked influence on a comparable coating without starch. This in turn has important ramifications in high-speed coating where viscosity stability over a temperature range is necessary.

Of equal importance is the effect upon viscosity at any one temperature with increase in shear. This effect is illustrated by the viscosity index given in Tables 1 and 2. By increasing the rotational speed of the blade of the Brookfield viscosimeter from 10 to 100 the shear forces acting upon the liquid coating compositions were increased. The average viscosity index for the all-casein composition was 1.56 while for the casein-starch composition it was 2.67. This means that high shear forces decrease the viscosity of the coating composition to a much greater degree than in the case of the all-casein coating. In high-speed coating this shear thinning is required to give the liquid coating desired flow properties to achieve rapid covering with no coating patterns. With the release of the shear forces in the coating operation the viscosity should again increase to cause the coating to set up rapidly in the smooth pattern-free deposition it attained while under shear forces. Thus, the greater differential in viscosity under different shear conditions shown by the coating of Example 2 coupled with the higher viscosities at coating temperatures (90° F. to 120° F.) impart to the coating of this invention the rheological properties required in high-speed coating and not possessed by the boxboard type coating designed for low coating rates and air-knife application.

In order to illustrate the difference in rheological properties between the coating compositions of Examples 1 and 2 a rheogram was made and it is reproduced in FIG. 6. This is a plot of torque versus shear rate as determined on a Hercules high-gear viscosimeter. The purpose of the rheogram is to determine the effect on the torque contributed by an increase in shear. It is obvious that the greater this effect is, the greater the resistance to flow will be which is exhibited by the composition. With increased resistance to flow comes difficulties in obtaining a smooth, level, pattern-free coating. An examination of FIG. 6 shows that there is very little increase in torque (or flow resistance) with increasing shear on the coating composition of Example 2.

In contrast, the coating without starch (Example 1) shows a marked increase in flow resistance and a definite indication of "chattering" at high shears, the latter being a sign of instability in the system.

The coating compositions of Examples 1 and 2 were applied by means of an RDS laboratory coating rod to sheets of a publication coating raw stock, 27 pounds per ream (3,300 square feet basis). A standard clay-starch coating was likewise used to coat sheets of the same stock to achieve essentially the same characteristics. The coating weights, volumes and thicknesses are summarized in Table 3.

Table 3

Coating	Dry Coating Weight, lbs./ream/side	Dry Coating Volume, Cubic inches	Dry Coating Thickness, microns
Clay-starch	5.0	59.0	3.2
Example 2	2.0	61.2	3.3

A comparison of the Example 2 coating composition with the clay-starch coating shows that the former results in a dry coating having a volume and thickness equal to the clay-starch coating but a weight which is less than one-half of this standard coating, thus the coating of this invention represents an important reduction in weight without sacrificing any volume required for bulk resiliency in printing.

EXAMPLE 3

A second control coating was made up containing 23% solids by dispersing 100 pounds of casein in 450 pounds

of water and heating it to 150° F., at which point 17 pounds of ammonium hydroxide (28% concentration) was added. After this mixture had been maintained for about 10 minutes at 150° F. a solution of 10 pounds of zinc sulfate heptahydrate in 50 pounds of water was added and then 9 pounds of additional ammonium hydroxide and 6 pounds of oleic acid added to the hot casein solution containing the zinc sulfate. Finally, 133 pounds of mineral spirits (boiling range of 340° to 405° F.) was stirred in with sufficient mixing to obtain an emulsion in which the particle size of the casein ranged from 0.5 to 1.5 microns. Into this emulsion was then added a clay slurry made up of 100 pounds of No. 1 coating clay in 50 pounds of water containing 0.5 pound of sodium hexametaphosphate. The clay was blended into the emulsion with sufficient stirring to achieve uniform distribution of the particulate matter in the continuous phase of the emulsion.

EXAMPLE 4

A coating comparable to that of Example 3 containing 23% solids was made up to include starch in the ratio of 2 parts of starch to 1 part of casein. This was done by mixing 440 pounds of casein in 2,017 pounds of water and 88 pounds of ammonium hydroxide (28% concentration) and then adding 27.5 pounds of zinc sulfate heptahydrate dissolved in 267 pounds of water. Finally, to this was added 39.6 pounds of ammonium hydroxide in 26.4 pounds of oleic acid. The oil-in-water emulsion was formed by adding 1,760 pounds of the mineral spirits of Example 3 with sufficient stirring to give an emulsion having particle sizes ranging from 0.5 to 1.5 microns. To the continuous phase of the emulsion was then added 880 pounds of enzyme-converted starch dissolved and heated for 15 minutes between 190° and 195° F. in 3,520 pounds of water. Finally, a clay slurry containing 70% solids and 1,890 pounds of clay with a clay dispersant, was added to the emulsion and blended to be uniformly distributed throughout the continuous phase. Temperatures used throughout this formulation were essentially the same as those used in Example 2.

Viscosities at different temperatures and under different conditions of shear were obtained as for the coating compositions of Examples 1 and 2. The data tabulated in Tables 4 and 5 correspond to Examples 3 and 4, respectively. The viscosities at 100 r.p.m. are plotted in FIG. 7.

Table 4

COATING WITHOUT STARCH

Temperature, ° F.	Viscosity, Centipoises		Viscosity Index
	10 r.p.m.	100 r.p.m.	
70	71,200	>40,000	
89	21,200	14,600	1.45
110	12,000	6,400	1.88
123	6,000	3,000	2.00

Table 5

COATING WITH STARCH

Temperature, ° F.	Viscosity, Centipoises		Viscosity Index
	10 r.p.m.	100 r.p.m.	
79	28,000	5,200	5.4
94	27,200	4,520	6.0
102	21,200	4,000	5.2
117	20,000	3,480	5.7

The stability of the Example 4 composition containing two parts of starch to one part of casein is even more

marked than that of Example 2 where equal amounts of stach and casein were used. Moreover, the viscosity index (average of 5.57) is greater showing a greater tendency for the Example 4 composition to flow freely under high shear stresses, thus making it particularly well suited to high-speed coating application.

The application properties of the above coatings were evaluated on a pilot Massey coater. The Massey coater is a print roll coater which transfers a thin film of coating from one roll to another and finally prints the coating from a rubber-covered roller onto the paper. The coating in this type of application must spread uniformly over the rolls without "long necking out in the nips" and forming a pattern on the rolls. The all-casein coating of Examples 1 and 3 had very poor transfer properties and formed a heavy ridge and "crow's-feet" patterns on the rolls which resulted in uneven coverage of the base paper. The starch-casein coatings of Examples 2 and 4, however, spread uniformly on the transfer rolls and the coated paper was essentially free from coating pattern, being covered uniformly. Print tests on the two coatings confirmed these observations. The starch-casein coatings had acceptable printing smoothness and uniform ink holdout while the casein coatings without starch had poor printing smoothness and a mottled appearance due to uneven ink holdout. No difference in pick strength was noted between the two coatings.

EXAMPLE 5

A coating composition was prepared in accordance with this invention in which the ratio of casein to starch was 1:4. One hundred pounds of a 12% casein dispersion in water was mixed with 100 pounds of water, 2 pounds of ammonium hydroxide (28%) and 4 pounds of oleic acid. This was heated to 120° F. and 120 pounds of xylene was added with stirring to form an emulsion. Forty-eight pounds of an oxidized starch was heated in 144 pounds of water at 195° F. for 15 minutes. After cooling the starch solution to 150° F. it was added to the 120° F. emulsion and then 260 pounds of a 70% clay water slurry was blended in until smooth. The starch-casein coating at 31% total solids had a high shear torque, 4 dynes/cm.^{2}, considerably below that of a comparable casein coating, 12 dynes/cm.^{2} at 30% total solids, thus indicating that even higher solids could be achieved. Both coatings applied to one side of a publication coating raw stock increased its brightness by 2–3%, and the opacity by 4–5% at a coating weight of 2–3 pounds per side. The pick resistance of both coatings was sufficient to give no coating pick on the IGT Print Testing apparatus using a #3 Tack Rated Ink at speeds up to 250 ft./min. Proofpress prints of the two coatings indicated no essential difference in printing smoothness. Other proofpress prints, however, showed that the starch-casein coatings had ink holdout comparable to conventional publication paper coatings and less ink holdout than the casein-based coatings.

As in other paper coating processes, the coated paper may be calendered as a final step in the process of this invention. Calendering tends to impart additional smoothness and uniformity to the coated surface and in some cases it contributes additional gloss. Calendering may also partially collapse some of the coating structure and detract from the optical properties, but this is not marked unless calendering pressures are too severe.

The data presented illustrate the marked changes in rheological properties contributed by the addition of starch to a proteinaceous porous film coating and the importance of these changes to the achievement of a coating composition suitable for high-speed application. Thus there is provided a coating suitable for publication papers which are customarily coated and dried at very high speeds. This coating, moreover, represents a material decrease in coating weight which is directly translatable into cost savings in shipping and mailing. Commercial trials have demonstrated the feasibility of reducing the basis weight of publication paper from 40 pounds to 31 or 32 pounds per ream—a reduction of approximately 20%. Since the final dry coating does not represent any decrease in volume, it is amenable to letter-press printing which relies on the bulk and resiliency of a coating for overall uniformity of printing. Moreover, since no reduction has been made in the raw coating stock runability characteristics of the final coated paper will not be impaired.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above method and in the composition set forth without departing from the scope of the invention, it is intended that all matter contained in the above description as shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

We claim:

1. A coating composition suitable for high-speed application to a substrate to form on said substrate a bright, opaque film exhibiting good printing characteristics and controlled ink holdout, comprising an oil-in-water emulsion having

(*a*) a continuous phase comprising

(1) an aqueous dispersion of a film-forming binder-matrix material selected from the group consisting of casein, alpha protein, water-dispersible elastomers and mixtures thereof,

(2) starch, and

(3) a particulate additive; and

(*b*) a discontinuous phase comprising globules of a volatile water-immiscible organic liquid having a boiling point above water and present in a globule size range between about 0.5 and about 1.5 microns with no appreciable number exceeding 5 microns; said starch being present in a quantity sufficient to significantly reduce the viscosity of said coating composition under high shear and to stabilize the viscosity of said coating composition over a temperature range from 70° F. to 120° F.

2. Coating composition in accordance with claim 1 wherein said binder-matrix material is casein and the weight ratio of said casein to said starch ranges between 1:1 and 1:5.

3. Coating composition in accordance with claim 1 wherein said particulate additive is clay, and the weight ratio of binder-matrix material plus starch to clay ranges between 1:0.5 and 1:4.

4. Coating composition in accordance with claim 1 wherein said water-immiscible organic liquid is mineral spirits.

5. Coating composition in accordance with claim 1 wherein the solids content of said composition is at least 20%.

6. Coating composition in accordance with claim 1 wherein the weight ratio of binder-matrix material plus starch to water-immiscible organic liquid ranges between 1:1 and 1:10.

7. Method of coating a substrate with a bright, opaque, substantially continuous film suitable for receiving printing under conditions of controlled ink holdout, comprising the steps of

(*a*) forming an oil-in-water emulsion, said emulsion consisting essentially of a continuous phase characterized as an aqueous dispersion of a film-forming binder matrix material selected from the group consisting of casein, alpha protein, water-dispersible elastomers and mixtures thereof, starch and particulate material, and a discontinuous phase of a vola-

tile water-immiscible organic liquid having a boiling point above water and present as globules in a size range between 0.5 and 1.5 microns with no appreciable number exceeding 5 microns; said starch being present in a quantity sufficient to significantly reduce the viscosity of said coating composition under high shear and to stabilize the viscosity of said coating composition over a temperature range from 70° F. to 120° F;

(*b*) applying a film of said emulsion to the surface of said substrate;

(*c*) stabilizing the structure of the applied emulsion film by evaporating first a portion of the water of said emulsion and forming thereby a matrix of said said film-forming matrix binder material and starch having uniformly distributed throughout said particulate material and said globules of said water-immiscible organic liquid, the dimensions of said globules remaining substantially equivalent to those of the said discontinuous phase in said applied emulsion film; and

(*d*) then evaporating any remaining water from said matrix and evaporating said water-immiscible organic liquid from said globules to provide multitudinous air-binder interfaces, the sizes of which correspond substantially to the size of said globules and range in dimension from about 0.5 to 1.5 microns with no appreciable number exceeding 5 microns.

8. Method in accordance with claim 7 wherein said substrate is publication coating raw stock and said coating is accomplished on both sides of said stock.

9. Method in accordance with claim 7 wherein said continuous phase of said emulsion comprises an aqueous solution of casein and starch having clay uniformly distributed throughout, the weight ratio of casein to starch ranging between 1:1 and 1:5 and of casein plus starch to clay ranging between 1:0.5 and 1:4.

10. Method in accordance with claim 7 wherein said discontinuous phase is mineral spirits present in a weight ratio of binder matrix material plus starch to said mineral spirits of between 1:1 and 1:10.

11. Method in accordance with claim 7 further characterized by the step of calendering the resulting coated substrate.

12. Method of coating a substrate with a bright, opaque subtantially continuous film exhibiting good printing characteristics and controlled ink holdout, comprising the steps of

(*a*) making an emulsion coating by the following steps

(1) forming a water solution of casein,

(2) adding to the casein solution an insolubilizing agent for said casein to form a continuous phase liquid,

(3) dispersing in said continuous phase liquid a volatile water-immiscible organic liquid thereby to form an oil-in-water emulsion in which said organic liquid is present as the discontinuous phase in globules ranging between 0.5 and 1.5 microns in size with no appreciable number exceeding 5 microns,

(4) adding to said emulsion a cooked starch-water mixture the quantity of starch contained therein being sufficient to significantly reduce the viscosity of said coating composition under high shear and to stabilize the viscosity of said coating composition over a temperature range from 70° F. to 120° F., and

(5) incorporating into said emulsion a particulate additive;

(*b*) applying a film of said emulsion thus formed to the surface of said substrate;

(*c*) stabilizing the structure of the applied emulsion film by evaporating first a portion of the water of said emulsion and forming thereby a matrix of said film-forming matrix-binder material and starch having uniformly distributed throughout said particulate material and said globules of said water-immiscible organic liquid, the dimensions of said globules remaining substantially equivalent to those of the said discontinuous phase in said applied emulsion film; and

(*d*) then evaporating any remaining water from said matrix and evaporating said water-immiscible organic liquid from said globules to provide multitiudinous air-binder interfaces, the sizes of which correspond substantially to the size of said globules and range in dimension from about 0.5 to 1.5 microns with no appreciable number exceeding 5 microns.

13. Method in accordance with claim 12 wherein said casein solution has a solids content of from 5% to 40%, said starch-water mixture has a solids content of from 20% to 35% and said emulsion coating at the time it is applied to said substrate has a solids content of at least 20%.

14. Method in accordance with claim 12 wherein said emulsion is formed and applied at an elevated temperature.

15. Method in accordance with claim 12 wherein said substrate is publication coating raw stock and said coating is accomplished on both sides of said stock.

16. Method in accordance with claim 12 further characterized by the step of calendering the coated substrate.

17. A coated product comprising a flexible substrate carrying permanently adhered thereto an opaque, substantially continuous film exhibiting good printing characteristics and controlled ink holdout, said film being characterized as a dried, essentially uncollapsed residue of an emulsion wherein the continuous phase of said emulsion becomes said film which consists essentially of a blend of film-forming binder material and starch in which the quantity of said starch is at least 50% by weight of said blend, said film having a particulate material embedded therein and having distributed throughout its entire volume multitudinous air-binder interfaces, the sizes of which are substantially equivalent to the globules making up the discontinuous phase of the original emulsion and vary in maximum dimension from about 0.5 to 1.5 microns with no appreciable number exceeding 5 microns, thereby providing a uniformly cavernulous substantially continuous structure capable of scattering light to impart opaqueness to said film, said film-forming binder material being selected from the group consisting of casein, alpha protein, water-dispersible elastomers, and mixtures thereof.

18. A coated product in accordance with claim 17 wherein said substrate is publication coating raw stock coated on both sides and said coated product is publication paper.

19. A coated product in accordance with claim 17 wherein said binder material is casein and said particulate material is clay.

20. A coated product in accordance with claim 19 wherein the weight ratio of casein to starch ranges between 1:1 and 1:5, and of casein plus starch to clay between 1:0.5 and 1:4.

21. A coated product comprising a flexible substrate carrying permanently adhered thereto an opaque, substantially continuous film exhibiting good printing characteristics and controlled ink holdout, said film consisting essentially of a blend of film-forming binder material and starch in which the quantity of said starch is at least 50% by weight of said blend, said film having a particulate material embedded therein and having distributed throughout its entire volume multitudinous air-binder interfaces, the sizes of which vary in maximum dimension from about 0.5 to 1.5 microns with no appreciable number exceeding 5 microns, thereby providing a uniformly cavernulous substantially continuous structure capable of scattering light to impart opaqueness to said film, said

film-forming binder material being selected from the group consisting of casein, alpha protein, water-dispersible elastomers, and mixtures thereof.

22. A coated product in accordance with claim 21 wherein said substrate is publication coating raw stock coated on both sides and said coated product is publication paper.

23. A coated product in accordance with claim 21 wherein said binder material is casein and said particulate material is clay.

24. A coated product in accordance with claim 23 wherein the weight ratio of casein to starch ranges between 1:1 and 1:5, and of casein plus starch to clay between 1:0.5 and 1:4.

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RICHARD D. NEVIUS, *Primary Examiner.*