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PAPER COATING

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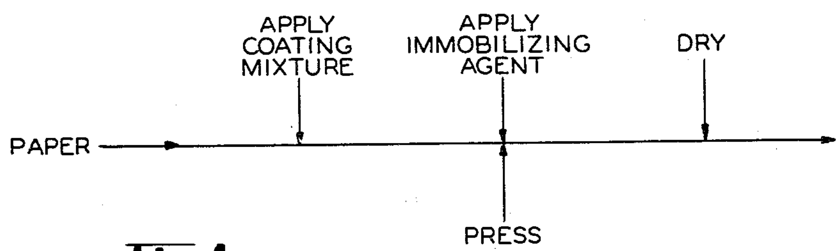

Fig. 1

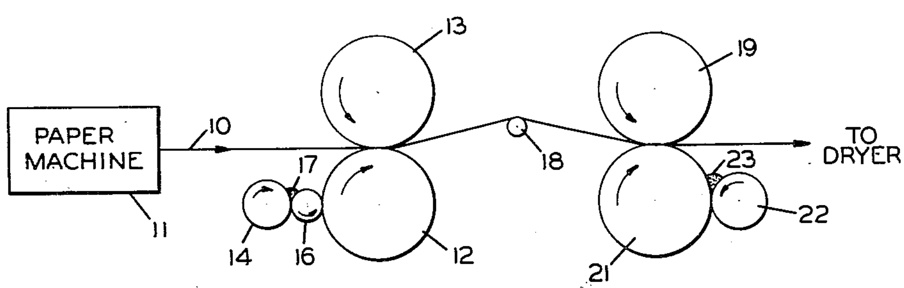

Fig. 2

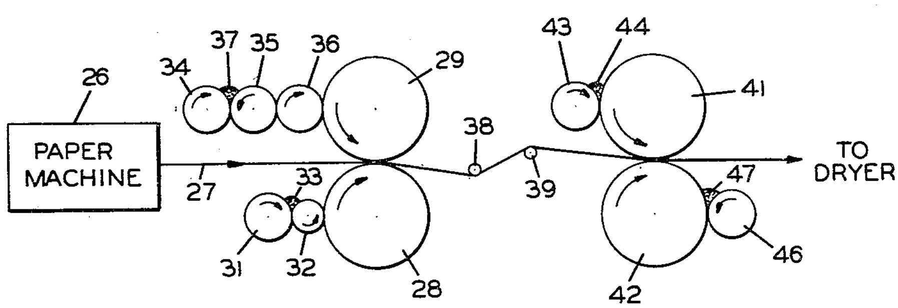

Fig. 3

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PAPER COATING

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11 Claims. (Cl. 117—64)

The present invention is directed to an improved process for coating paper, and is particularly directed to the coating of paper suitable for use in printing by the offset, letterpress, roto-gravure and other printing processes.

Papers used for printing purposes are of various types and have characteristics designed to suit the conditions of the printing process or processes employed. For certain purposes, it is desirable to use a paper which is coated with a pigment material such as clay or other mineral filler, the pigment being bonded to the surface of the base web by an adhesive binding material, common examples of which are starch and casein, and it is with this type of paper that the present invention is especially concerned.

In the past, several procedures have been followed in the manufacture of coated paper. In one of these procedures, a coating is applied to a suitable base web by means of a pressure roll mechanism. The pressure roll method of applying a coating makes possible quite high speed operation, but produces a coating which is not nearly as smooth and does not have nearly as good characteristics as might be desired. As a result, most of the paper produced in this manner has to be subjected to a very intense supercalendering operation subsequent to the application of the coating. Even then, the quality of the paper leaves much to be desired. Furthermore, the roll coating process is limited in its application to relatively thin coatings, e. g., less than about 12 lbs per side per ream of 3300 sq. ft per single application if excessive roughness is to be avoided.

Another process previously employed is the so-called cast coating procedure, in which a suitable coating layer is applied to a sheet by means of a roll or other applicator and the coated sheet is then pressed into contact with a smooth surfaced roll or casting drum. The coated sheet adheres very tightly to the roll or drum and normally cannot be removed from the roll until it has dried. This process produces very high grade coated paper, although it is very difficult to apply a coating to more than one side of the sheet by means of this process, and in no case can both sides be coated simultaneously.

Considerable care must be exercised in removing the dried sheet from the drying or casting surface in order to avoid cracking the coating on the paper and to facilitate this removal, it is common practice to apply a parting agent to the surface of the drying roll before the coated sheet is applied to the roll. To our knowledge, no single parting agent has proven satisfactory in all respects and much experimental work is still being carried out to develop suitable parting agents. In addition, the very nature of the process makes this procedure most suitable for the application of rather heavy coatings, on the order of 15 lbs. per side per ream.

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The major drawback, however, to the use of the cast coating process is the slow processing speed characteristic of this process. The relatively long time required for drying the coated sheet against the surface of the drying roll, of itself, makes the cast coating procedure a time-consuming and expensive process.

Attempts have been made to overcome this inherent difficulty of the cast-coating process. For example, in one proposed variation, the coating is applied to the sheet, and the coated sheet is then dried by passage through an air dryer or other mechanism. Subsequently, the dried coating is remoistened, and applied to the surface of a casting drum, whereon it is redried, similar to the conventional cast coating process. The supposed advantage of this variation is a reduction in the amount of moisture that must be evaporated from the sheet while it is in contact with the casting surface, with accompanying increase in the speed of operation of the equipment. The amount of moisture added during this remoistening operation is supposed to be just sufficient to render the coating semi-plastic, but not fluent, during the drying of the coating on the casting surface. In practice, the process gives rise to other difficulties, due primarily to the considerable lapse of time between application of the coating to the sheet and the forming and setting of that coating into the desired smooth surface.

As previously mentioned, the least desirable characteristic of the high speed, pressure roll coating process is the quality of the coated surface produced. We have observed that the roughness or lack of smoothness (usually called tracking or worminess) on the surface of the coating as it comes from the coating press is due to the fact that the surface portion of the coating layer adheres to the applicator roll. This causes the coating to split on the applicator roll with part of the coating remaining on the paper and a part remaining on the roll. A pattern of tracks is thereby formed on the outer surface of he coating and will be retained on the paper, the coarseness and character of the pattern being determined by the rheological behaviour of the coating mixture and various other factors. For example, an increase in coating weight will usually tend to produce a greater degree of worminess or tracking.

Furthermore, because of the inherent roughness and other irregulariites in the base sheet itself when using pressure roll coating methods, it has been difficult to produce a coating with a sufficiently level surface.

The difficulties outlined above are particularly troublesome in the pigment coating of paper intended for high grade printing stock. The applicabliity of this invention is not limited to that field, however, as it has applicability in other paper coating processes where level and smooth coatings must be achieved. For example, the process of the invention may be employed to provide a smooth barrier coating on greaseproof paper which coating will be readily strippable from drying rolls, or for the provision of initial coatings intended to be overcoated in a subsequent operation.

The overcoming of these difficulties and the provision of an improved method for coating paper which can be operated at very high speeds and which produces a level smooth coating on the paper, constitutes an important object of the present invention.

Another object of the present invention is to provide a method for coating paper which requires less severe supercalendering to produce a uniform, smooth printing surface, and which can be employed to apply coatings in a wide range of coating weights. In this connection, the printing industry has generally accepted the high gloss produced on papers coated by the pressure roll method as indicative of good printing qualities. Insofar as a glossy finish is characteristic of a severe supercalendering operation which smoothens and levels the coating, this standard is not inaccurate. However, gloss by itself is not an accurate measure of a paper's printabliity and is frequently detrimental because of the glare which it provides on the printed page.

There is a definite need commercially for a reasonably priced dull finish paper which has the printing properties of a glossy, heavily calendered sheet. The present invention provides a method for achieving that objective by eliminating the necessity for heavy calendering while retaining and in some respects improving the smoothness and levelness of the coating beyond that achieved in the glossy, heavily calendered papers now being used. Through the elimination of the heavy supercalendering pressures, the process of our invention makes it possible for the sheet to retain more of its natural resiliency, a factor which contributes to the excellent printing properties of the sheet.

While the present process is directed particularly to the use of relatively light calendering pressures, coated papers produced by our process can be given a high gloss finish, if gloss is desired for some purpose, through the use of calendering pressures of the magnitude now being employed in connection with pressure roll coating processes. Generally, the pressures applied to the calender stack in this type operation are on the order of 1000 to 2000 lbs. per lineal inch.

Still another object of the invention is to provide an improved method for coating paper characterized by the production of a paper which for any given degree of finish has better brightness retention, opacity, and bulk than can be produced by other methods.

As will hereinafter appear in some detail, we have discovered that a high quality coating for printing purposes can be obtained in a high speed process which involves coating a paper web, which is either uncoated or previously coated with other coatings, with a coating composition including a pigment filler and one or more reactable compounds by which the coating may be rapidly converted to a nonadherent, non-offsetting, hardened state by reaction of such reactable compound or compounds with a liquid immobilizing or setting agent. In most cases, the compound or compounds have adhesive properties and in that sense are "binders" for the filler.

In the usual practice of the invention, the base web is coated and then while the coating is still in a wet, mobile state, capable of offsetting upon a surface pressed against it, the coating is brought into contact with a pressure member to which a fluid immobilizing or setting agent capable of reacting rapidly with the aforementioned reactable compound or compounds is continuously applied. It is of great importance that the coating shall not be dried and shall remain mobile, at least on its surface, between the initial application of the coating to the sheet and the passage of the coated sheet into the reacting, pressure zone.

While a rotating pressure roll is the most common means for achieving the result sought, the term "pressure member" as used in this specification should be interpreted as including various types of mechanisms in which pressure can be applied on the coating jointly with the application of the immobilizing agent. The speed of the paper is such that the time of contact between the coated paper and the pressure member is of extremely short duration. The time is sufficient, however, to initiate the reaction between the setting agent and the settable compound in the paper coating so as to produce a condition of non-adherency or inability to offset at the surface of the coating.

Under some operating conditions, a well-defined, surface film or skin is formed on the coating. Substantially no water is lost in the coating due to the immobilization of the coating surface, the only moisture loss being that which occurs due to the natural absorbency of the base sheet. The simultaneous application of the immobilizing agent and the application of smoothing pressure to the undried coating provides a novel smoothing effect on the surface of the sheet, which can not be obtained if the two operations are used individually or in sequence.

The production of a condition of nonadherence or non-offsetting at the surface of the coating by simultaneous application of the immobilizing agent and pressure is, we believe, responsible for the improved results of the present process. Further, since the surface of the coating is almost instantaneously strengthened by the reaction, but still retains a large degree of flexibility, the coated paper can be stripped from the pressure member without difficulty and without splitting the coating after it passes through the pressure zone. Also, the immobilized, nontacky surface is sufficiently strong to permit the coated sheet to be brought into contact with the conventional driers without problems arising from coating sticking to the driers.

A further description of the present invention will be made in connection with the attached sheet of drawings in which:

Figure 1 is a simplified straight line flow diagram illustrating the various steps of the process in sequence;

Figure 2 is a schematic view of a coating assembly employing the principles of the present invention and arranged to apply a coating to a single side of a paper web; and

Figure 3 is another form of apparatus using the new process in which both sides of a paper web are coated.

As illustrated in Figure 1, in the process of the present invention a paper web is fed continuously into a coating zone where a coating mixture, which includes a pigment filler and a settable compound or compounds, is continuously applied to the moving paper web. Next, the resulting coated web is passed into a pressure zone where the wet, mobile coating is concurrently pressed by means of a pressure member and treated with a liquid immobilizing agent, the agent being one which will react rapidly with the aforementioned compound to produce a nonadherent strengthened material at the surface of the coating. In the next step of the process, the coated paper after its reaction with the immobilizing agent is passed into a drying zone where it is dried. In the particular coating apparatus illustrated in Figure 2, a paper web **10** is supplied from a paper machine **11**. It will be appreciated that while the process described is particularly adapted to provide an "on-the-machine" coating, it will be evident that the improved process is also applicable to "off-the-machine" coating where the paper is supplied from a reel or other storage means.

The paper web **10** passes into a coating nip between an applicator roll **12** and a backing roll **13**. In order to give an idea of the relative sizes of the various rolls involved, roll **12**, which should be resilient, may be a rubber covered roll twenty-five inches in diameter, having a plastometer reading of one hundred twenty-five. Roll **13** may be a twenty-five inch diameter roll, and it may be of metal or of a resilient material. If a resilient roll is used, it may constitute a rubber covered roll having a plastometer reading of ninety. All plastometer readings herein are P. & J. ⅛ inch ball values.

The coating is applied to the surface of the applicator roll **12** by means of a metering roll **14** and a nip metering roll **16** between which rolls a pond of coating material **17** is continuously maintained. The outer roll **14** should be resilient, and it may comprise a ten inch diameter rubber covered roll (plastometer reading of one hundred), while the nip metering roll **16** may be a six inch diameter chromium-plated, steel roll. The rolls **12** and **13** are driven to provide a linear web speed in the approximate range of 400–1200 feet per minute; these values, of course, are not limiting, but merely representative of the speeds which can be conveniently employed in the practice of our process.

In the illustrated structure, after the web **10** leaves the coating nip, it passes over a small diameter, reverse turning roll **18** which may be on the order of two or more inches in diameter, or a supported smoothing bar, which may be of the order of one-fourth inch in diameter. Next, the coated web passes into a reaction nip between a backing roll **19** and a reaction roll **21**, at least one of which should be a resilient roll. In one particularly satisfactory embodiment of the invention, the backing roll was a twenty-five inch, resilient, roll having a surface plastometer reading of forty-five, while the reaction roll **21** was a twenty-five inch chromium-plated, steel roll. A metering roll **22**, of resilient construction and having a plastometer reading of about thirty-five at its surface, was arranged to apply a pond **23** of the setting composition to the reaction roll **21** so as to form a film of the setting composition on the surface of the roll **21**.

As this film contacts the surface of the previously applied fluent coating, the reaction commences. The web speed is such that the application of the film to the coated web and the pressure exerted at the nip between the rolls **19** and **21** is of very short duration. As a result, the reaction proceeds to a point where the wet, plastic coating is rendered nontacky and hardened at least at the surface, the extent to which the hardening proceeds inwardly of the coating being dependent to a large extent on the thickness of the coating. When coating materials of the types to be hereinafter described are used, it appears that the reaction time involved in achieving a non-tacky, hardened surface does not exceed a fraction of a second, and preferably should not exceed 0.05 second. In other words, the coating should become sufficiently nonadherent within this short time interval to be readily releasable from the roll without drying. The coating may, of course, be held in contact with the roll surface for a longer period, if desired.

The nip pressures between the rolls **14**, **16** and **12**, may be approximately 60 pounds per linear inch; the nip pressures between the roll **12** and roll **13** may be approximately 50 pounds per linear inch and the nip pressure between rolls **19** and **21** may be approximately 80 pounds per linear inch.

The smoothing means, such as the roll **18** should be such as to make the coating on the paper as smooth as possible before the coated paper enters the reaction nip. At the nip, the pressure between the roll **19** and the roll **21** provides a very important additional smoothing at the time the reaction is taking place. In fact, without this additional smoothing effect, the coating, as applied by the usual pressure roll coating mechanism, may retain defects which will not be entirely erased during the reaction smoothing in most instances.

If, however, the coating is sufficiently smooth at the time of its initial application, which is the case with certain coating methods, the intermediate smoothing may be omitted. In this connection, it will be understood that the present invention has particularly important utility in effecting the immobilization, setting and further smoothing of coatings which are smoothed during or following the initial application thereof, for example, coatings which are smoothed or applied by the use of reverse roll coaters, smoothing bars, air knives, and the like.

Since the paper web is normally expanded somewhat during the coating process, it is usually desirable to rotate the rolls in the reaction train at a slightly higher velocity than the coating rolls. In the example given, where the coating rolls are operated to give a linear velocity of 465 feet per minute, the rolls in the reactor train should be operated to yield a linear speed of about 470 feet per minute. After the smooth, nonadherent coated web leaves the surface of the reaction roll **21**, it may be passed immediately to conventional driers where the moisture content of the coated web is reduced to the desired value without danger of having the coating adhere to guide rolls or drier rolls.

An apparatus for coating both sides of the paper web is illustrated in Figure 3. Similarly to the previously described apparatus, this mechanism may be used in conjunction with a paper machine schematically illustrated at **26** in an on-the-machine coater or with an unwind stand in an off-the-machine coater. A paper web **27** from either of these sources is passed into a coating nip between a pair of applicator rolls **28** and **29**. A metering train consisting of a metering roll **31** and a nip metering roll **32** applies a coating composition from a pond **33** located between the rolls **31** and **32** to the surface of the lower applicator roll **28**. Similarly, a train of rolls **34**, **35** and **36** applies a coating composition from a pond **37** to the surface of the upper applicator roll **29**.

The paper web after leaving the coating nip has its coating smoothed by a pair of smoothing rolls or bars **38** and **39** located on opposite sides of the web. Next, the coated web is passed into the reaction nip between a pair of rolls **41** and **42**, which are driven at a slightly higher velocity than the applicator rolls **28** and **29** to allow for the slight expansion of the web which occurs during the coating operation. A metering roll **43** applies a solution of the immobilizing agent from a pond **44** to the surface of the roll **41** in the form of a thin film. Similarly, a second metering roll **46** applies an immobilizing composition from the pond **47** to the surface of the roll **42**. As in the previously described embodiment, the web velocity and the roll velocities are adjusted so that the coated surface is in contact with the immobilizing or reacting agent applied by the surface of the rolls **41** and **42** for a period of time sufficient to produce the desired hardened, surface condition, which in the case of the materials to be mentioned, is substantially less than one second, and preferably not in excess of about 0.05 second. The ability of the present invention to produce a condition of immobility and non-adherence in the coating in a very short interval of time is of especial importance in the simultaneous smoothing of both sides of the sheet.

After the reaction, the nonadherent, coated web is then conducted to suitable drying equipment. At least one of the rolls in each of the main roll combinations **28—29** and **41—42** should be resilient. Roll combinations structurally similar to the combinations **12—13** and **19—21** have been used with good results. In general, it will be understood that changes in the main roll combination **28—29** and **41—42** may require complementary changes in the cooperating roll combinations **31—32**, **34—35—36**, **43** and **46**. Desirable arrangements and combinations are disclosed in U. S. Patent No. 2,606,520 to Hoel.

After drying, the coatings produced by our process can be super-calendered by relatively light pressures of about 500 lbs. per linear inch (applied to the super-calendar stack) to produce coated papers having a dull finish and excellent printing properties. Because the coatings can be finished with such relatively light pressures, the present invention makes possible the inclusion of a super-calendar assembly as part of the same machine includes the coating mechanism, where previously, the super-calendar was necessarily a separate assembly.

The present invention is applicable to the coating of a wide variety of base sheets of varying composition and surface characteristics. For example, we have used successfully base sheets containing 50–55% groundwood with the balance chemical pulp, such as bleached kraft or bleached sulphite. A particularly satisfactory coated sheet has been made by use of a base sheet containing 40 percent bleached groundwood pulp and 60 percent chemical pulp consisting of one-half bleached kraft pulp and one-half bleached sulfite pulp. Very high quality coated paper has been made by the use of base sheets containing 100 percent chemical pulp, of which 70 percent has consisted of bleached, short-fiber kraft. Regardless of the type of base sheet used to achieve the best coating results, the base sheet should have as smooth a surface as possible before entering the coating equipment and when used with coating compositions as hereinafter described, should preferably have a moisture content of about 5–10 percent on a bone dry basis, although satisfactory results can be achieved with sheets of higher moisture contents.

The invention lends itself especially to multiple layer coating operations. To illustrate, a first or base coating or coatings of any desired weight can be applied by conventional procedures or by the process of the present invention, and this can be followed by an overlying or final coating according to this invention. Such combinations produce particularly high grade finished coatings. As an example of the procedure, a base coating of 5–15 pounds per side, per ream of 3300 square feet, has been applied to a suitable base sheet followed by an overlying, final coating of 5–15 pounds per side to produce a total coat weight of from about 10 to 30 pounds per side.

The various important advantages of the present invention can be realized in the application of various types of coatings, and the invention can be practiced by the use of various types of immobilizing agents. The primary requirement which dictates the selection of suitable coating compositions and suitable immobilizing agents is the requirement that the coating composition include a compound which can be rapidly immobilized into a non-adherent or at least a non-offsetting condition by an ingredient present in the material applied at the reaction nip.

As will be more evident from the following description, the word "immobilizing" as used in this specification should be interpreted to include various types of chemical and physical reactions. For example, one of the most suitable coating compositions useful for our process contains a proteinaceous adhesive such as casein or soya protein in the coating composition. These proteinaceous materials in alkaline solution react very readily with compounds such as papermaker's alum ($Al_2(SO_4)_3 \cdot 18H_2O$) or mixtures of papermaker's alum and formaldehyde, in solution, to form a hardened surface film which resists offsetting onto the surface of the reaction roll as the sheet is removed from contact with that roll. The term "immobilizing" when applied to the treatment of such materials and to cellulose derivatives would therefore relate primarily to a chemical reaction.

Still another type of material which is useful for our process either alone or in combination with the aforementioned proteinaceous adhesives is a latex of natural or synthetic rubber. "Latex," as the term is used herein, is a colloidal dispersion of an elastomer, usually in the form of negatively charged particles, and the "immobilization" of such dispersions usually involves the coagulation of the particles by the addition of an electrolyte, such as a solution containing divalent or trivalent metallic ions. A more comprehensive list of reactive materials suitable for practicing the present invention, either alone or in combination with others and immobilizing agents which are appropriate to each of the classes is given below:

Reactive Materials	Immobilizing Agents
I. Proteinaceous adhesives: A. Casein in alkaline solution. B. Soya protein in alkaline solution. C. Animal glues.	I. Bivalent and trivalent ions (particularly copper, zinc, aluminum), formaldehyde plus papermaker's alum.
II. Water soluble cellulose derivatives: A. Carboxy methyl cellulose. B. Carboxy methyl methyl cellulose.	II. Bivalent and trivalent ions (particularly aluminum and lead).
III. Alkali soluble cellulose derivatives: A. Hydroxy ethyl cellulose. B. Oxidized cellulose.	III. Acidic salts (particularly alum and ammonium sulfate).
IV. Latex of elastomers: A. Polychloroprene. B. Esters of polyacrylic acid. C. Polystyrene - butadiene copolymers. D. Isoprene - isobutylene copolymers. E. Polyacrylonitrile - butadiene copolymers. F. Natural rubber.	IV. Bivalent and trivalent ions (particularly aluminum and iron).
V. Emulsions of Polyvinyl compounds: A. Polyvinyl acetate emulsions. B. Polyvinyl chloride-acetate copolymers. C. Polyvinylidene chloride-vinyl chloride copolymers.	V. Electrolytes such as Na_2CO_3.
VI. Sodium alginate.	VI. Bivalent and trivalent ions (particularly calcium and aluminum).
VII. Sodium salt of styrene-maleic anhydride copolymers.	VII. Bivalent and trivalent ions (particularly aluminum and iron).

The reactive materials listed above, as well as others which fall within the general classes set forth, vary in their effectiveness. Thus, carboxy methyl cellulose provides an excellent coating compound for the manufacture of printing papers. Hydroxy ethyl cellulose, in contrast, while satisfactory for use in some coating compounds, may not be satisfactory for other types, because of the relatively high concentration of alkali necessary to dissolve this material.

The alkali-soluble cellulose derivatives cannot be used with certain of the latices. Similarly, water soluble cellulose derivatives, such as carboxy-methyl cellulose, and water-soluble alginate, such as sodium alginate, may be degraded under the conditions necessary to maintain alkali-soluble cellulose derivatives in solution. Hence, these materials would not usually be used with the alkali-soluble cellulose derivatives. Starch is also degraded in alkaline solutions, and hence starch is not suitable as an extender for alkali-soluble cellulose derivatives.

In this connection, it will be understood that the various reactive binder materials listed above, while capable of being used alone, will most commonly be used in combination with each other or with an extender such as starch. Usually, because of cost consideration, it is desirable to use the smallest possible amount of reactive material or materials. The minimum amount that can be used successfully will vary somewhat, depending on the characteristics of that material and the operating conditions. The required flow, leveling and setting properties of the coating will also limit the maximum amount of reactive binder material that will be used.

The polyvinyls are brittle, unless plasticized, and when a flexible sheet is desired, those materials are desirably combined with another and more flexible type latex, such as styrene-butadiene. Latices are not always satisfactory when used alone, especially in roll coating operations, and preferably are combined with a protein or a starch in such coating formulations.

In general, when using the reactive materials specified above, it has been found that the coating composition should contain not less than about 5 parts of the reactive binder material per 100 parts of mineral. It will be understood, as previously pointed out, that more than one of the reactive materials may be used, and that in instances where cost is important, it will be found advantageous to include starch as an extender material in the coating composition. If more than one reactable binder is used in any given coating composition, the individual amounts of each binder can be reduced over that required if the binders are used alone. Carboxy methyl cellulose, as above noted, is particularly effective as a reactive material and can be used in smaller amounts than the proteinaceous binders or latices, and when used alone or in combination with other reactive materials, will reduce the total minimum amount of reactive binder required.

When using a proteinaceous adhesive, satisfactory coating compositions have been made by the combination of 100 parts mineral with from 12 to 16 parts by weight of the proteinaceous adhesive. If starch is added to the mixture, the amount of proteinaceous adhesive can be reduced to a value within the range of from about 8 to 10 parts, the total of the starch and the proteinaceous adhesive being in the range of from about 14 to 20 parts by weight to 100 parts by weight of mineral. When a latex is added, in addition to the starch, about 3 to 10 parts of latex solids may be employed and the amount of starch and protein may be correspondingly decreased so that the total content of proteinaceous adhesive, starch and latex is in the range of from 14 to 20 parts by weight per 100 parts of mineral. Satisfactory coating compositions can also be made by combination of proteinaceous adhesive and latex without starch. For roll coating operations with such combinations, a minimum of about 6 parts of the proteinaceous adhesive per 100 parts of mineral should be used with a minimum of from 8 to 14 parts of latex.

"Starch" as used herein is intended to refer to the modified starches commonly employed in paper coatings. Chemically modified or enzyme modified starches are typical.

When using a water-soluble cellulose derivative binding material, which is another of the particularly preferred reactive binder materials, satisfactory coating compositions will result from the use of mixtures containing 100 parts mineral and from about 14 to 18 parts of carboxy methyl cellulose. Because of costs and flow property considerations, it is generally preferred to use carboxy methyl cellulose in combination with starch or with starch and one or more of the other reactive binder materials, such as latex. When used with starch alone, it will generally be found satisfactory to provide from 2 to 6 parts by weight of carboxy methyl cellulose and from 10 to 14 parts by weight of starch to each 100 parts of mineral. Satisfactory coating compositions using carboxy methyl cellulose with starch and latex have been made by combining from 1 to 5 parts carboxy methyl cellulose with 4 to 14 parts of starch and from 3 to 10 parts latex per 100 parts of mineral, all on a weight basis. Carboxy methyl cellulose may also be used with latex alone. Such compositions will generally include from 4 to 6 parts carboxy methyl cellulose and from 10 to 14 parts latex per 100 parts of mineral.

In connection with the foregoing general examples, it should be kept in mind that the maximum economical binder content is usually from 15 to 20 percent by weight based on the mineral content of the composition.

The rather substantial number of available reactive materials makes possible a considerable variation in the coating compositions and large numbers of these, in addition to those specifically set forth above, will be apparent to those skilled in the art.

A choice of a particular immobilizing agent for a given compound will be based upon various considerations. For example, copper salts or iron salts would not be employed where it is desired to avoid any coloring in the set coating.

The best over-all immobilizing agent which we have found in our work is papermaker's alum

$$(Al_2(SO_4)_3 \cdot 18\ H_2O)$$

and the term "alum" as used in this specification and claims is intended to mean that compound. This compound not only has the ability to precipitate or coagulate binders of various types into a nonadherent form, but when used as an immobilizing agent where calcium carbonate is present in the filler, the alum provides a very definite brightening effect to the applied coating. This brightening effect has important commercial utility, and is one of the more unexpected advantages of the invention.

For most types of coating applied in weight of 2 to 20 pounds per side per ream of 3300 sq. ft., about 0.1 to 1 pound of alum per dried ream of paper will be sufficient to set the coating to the extent required. The same amount of immobilizing agent is appropriate for agents other than alum. The immobilizing solutions may also include such auxiliary materials as surface active agents or acids.

Our experience has indicated that a small excess of the immobilizing agent should be applied to the reaction roll in order to achieve the best results. That is, a sufficient amount of the agent should be applied to the roll to leave a film of the agent on the roll after the reacted coating is stripped from the roll. On the other hand, the excess should not be so large as to form a visible bead of the immobilizing agent in advance of the pressure nip, as premature reaction will occur in the coating and proper smoothing is not likely to be achieved.

In practicing this process, there should be a reasonable balancing and correlation of the coating film thickness with reference to the absorbency characteristics of the base sheet and to the flow properties of the coating suspension. The application of too thick a film by the coating apparatus may lead to surface rupture of the coating at the reaction nip and difficulty in releasing the coated paper from the reaction roll. If too thin a film is applied, the coating will be insufficient to fill in all the depressions in the web, with the result that the smoothness will not be as high as desirable.

The best coating mixtures have been found to contain about 35 to 60 percent by weight of solids, the major portion of the solids constituting coating clay, or a mixture of clay and calcium carbonate and the remainder of the solids constituting the binder material, which may include the reactable binder alone or in combination with a non-reactable binder such as starch. The minimum amount of binder is about 10 percent, based on the weight of the mineral pigment, and the usual amount is from about 14 to 20 percent. The ability to use such high solids content coatings is a distinct advantage for this process, as it decreases the drying load, and thereby permits faster coating speeds.

Control of the viscosity of the coating solution is also important to achieve best results. For pressure roll coating processes, we prefer to employ coating suspensions having a MacMichael viscosity of from about 40° to 80° (measured with a No. 26 wire at 40 R. P. M. and 70° F.). Coating suspensions with higher viscosities are more difficult to level, and those with lower viscosities are more liable to rupture in the nip. Generally higher values of viscosity can be handled satisfactorily when the coating applied is to be relatively heavy, and the lower viscosities are more appropriate for light weight coatings.

Illustrative coating mixtures suitable for use in the practice of the invention are given in the following specific examples:

Example I

The coating mixture had the following compositions:

100 parts by weight of coating clay, representing about 88.7 percent of the solids in the mixture;

6 parts by weight of carboxy methyl cellulose having a degree of substitution of 0.75 and a viscosity of 25 to 50 cps. (measured in a 2 percent concentration at 25° C.) representing 5.3 percent of the solids in the coating mixture;

12 parts by weight of a latex of a styrene-butadiene copolymer having a solids content of 48 per cent, representing 6 per cent of the solids in the coating mixture.

The clay was dispersed in a water solution with 0.3 percent solium hexametaphosphate and 0.1 percent of sodium hydroxide and the carboxy methyl cellulose and latex added to produce a coating mixture having a final solids content of 50 percent and a MacMichael viscosity of 70°.

For the above described coating mixture, the immobilizing agent employed consisted of a solution of papermaker's alum having a specific gravity of 1.18 at 25° C. About 0.5 lb. of alum per ream of paper was employed to immobilize the coating.

Example II

In each of the succeeding formulae, the pigment filler consisted of approximately 67 percent coating clay and 33 percent calcium carbonate. The pigments were dispersed in a water solution containing 0.3 percent of sodium hexametaphosphate and 0.2 percent sodium hydroxide. The composition of binders which were employed with this pigment filler are listed below, the parts by weight being based upon 100 parts of the mixture of clay and calcium carbonate.

(A)

15 parts soya protein

(B)

3 parts soya protein
12 parts latex of styrene-butadiene copolymer (50 percent solids)

(C)

3 parts soya protein
10 parts latex of styrene-butadiene copolymer
0.5 part medium viscosity carboxy methyl cellulose (viscosity of 300 to 800 cps. in 2 percent solution at 25° C.)

(D)

8 parts glue
1 part medium viscosity carboxy methyl cellulose
7 parts latex of styrene-butadiene copolymer

(E)

7 parts soya protein
7 parts starch
3 parts latex of styrene-butadiene copolymer

(F)

6 parts low viscosity carboxy methyl cellulose
12 parts starch

(G)

2 parts medium viscosity carboxy methyl cellulose
11 parts starch
4 parts latex of styrene-butadiene copolymer

(H)

10 parts latex of styrene-butadiene copolymer
6 parts starch

(I)

7 parts soya protein
7 parts starch
3 parts latex of polyacrylonitrile butadiene copolymer

(J)

10 parts soya protein or casein
3 parts polyvinylidene chloride-vinyl chloride copolymer
3 parts styrene-butadiene copolymer

(K)

6 parts sodium alginate
12 parts starch

(L)

1 part sodium alginate
12 parts starch
4 parts latex of styrene-butadiene copolymer

(M)

1 part sodium alginate
10 parts starch
6 parts plasticized polyvinylidene chloride-vinyl chloride copolymer

(N)

3 parts sodium salt of styrene-maleic anhydride copolymer
7 parts soya protein
8 parts starch

In each case, the coatings were effectively reacted into a hardened, non-offsetting, non-tacky surface film by the application of about 0.5 lb. of alum per ream of 3300 sq. ft.

Example III

In this formulation, the paper was coated with a pigment filler and a binder identical in composition to that shown in section E of the Example II. The coating was effectively immobilized by the application of 0.5 lb. of zinc chloride per ream in aqueous solution to the coating and after drying, the coating had an excellent smoothness and a level surface.

Example IV

The coating in this instance was identical with that described in section L of Example II. This coating was effectively immobolized by the application of 0.5 lb. of calcium chloride per ream of coated paper to produce an excellent printing surface after drying of the paper web and its coating.

Example V

100 parts clay dispersed in water containing 5 percent NaOH
8 parts hydroxyethyl cellulose (degree of substitution .35 to .4) dissolved in water containing 5 percent NaOH

This coating was effectively immobolized by the application of 0.5 lb. of alum per ream of coated paper.

Example VI

A good barrier coating for the manufacture of greaseproof paper was prepared by coating a base web with a composition containing 30 percent by weight ortho protein, 30 percent starch, and 40 percent of a latex of a styrene-butadiene copolymer. This coating was immobilized by the application of an aqueous solution of alum in amounts sufficient to provide 0.5 lb of alum per ream of paper. Upon drying, a smooth, level coating was produced on the paper.

The flow properties of coatings compounded as described in the foregoing can be readily adjusted to suit the type of coating mechanism employed. For example, if a pressure roll coater is used, a relatively high solids, high viscosity coating would be compounded. If an air knife or reverse roll coater is to be used, a lower solids, low viscosity type of coating would be made. The wide variety of reactable binders which this process can use therefore makes possible a wide range of coating flow properties.

Minor ingredients such as eveners, softening agents, wetting agents and dye stuffs can be added to any of the above coatings, as desired.

The present invention makes possible the production of high quality coatings of improved brightness, opacity, and bulk at low supercalendering pressures at speeds which could never previously be employed in the production of coated paper of comparable quality. The process of the present invention provides a coated paper of excellent printing quality, suitable for use in the offset, letterpress, and rotogravure processes.

This application is a continuation-in-part of our copending application, Serial No. 202,923, entitled "Paper Coating," filed on December 27, 1950, and now abandoned.

It will be evident that various modifications can be made to the processes described above without departing from the scope of the present invention.

We claim:

1. The process of coating paper which comprises continuously moving a web of paper, continuously applying to at least one surface of said web a coating composition containing from 35 to 60 percent by weight of solids and including a pigment and a hardenable binder, and relatively soon thereafter and without applying any intermediate drying step so that at least the outermost region of said coating remains in a wet, mobile, moldable state capable of offsetting upon a surface brought to bear upon the outer surface of said coating, contacting the outermost surface of the coating on said web with a pressure member, continuously applying a regulated amount of a liquid immobilizing agent to the surface of said pressure member before it is brought into contact with said coating, said liquid immobilizing agent being capable of almost instantaneously converting the outermost region of said binder to a non-tacky, hardened state, to almost instantaneously convert and render non-adherent and smooth a layer of said coating composition at the outermost surface thereof when said pressure member contacts said coating, said regulated amount of liquid immobilizing agent being insufficient to form a visible bead of the immobilizing agent at the point at which said pressure member first contacts said coating, withdrawing said coated web from pressure contact with said pressure member to produce a paper web which is provided with a smooth, continuous, level coating, the regulated amount of said liquid immobilizing agent being such that a film of such agent is left on said pressure member after said converted coating is withdrawn from said pressure member, and then drying the web and coating without further smoothing during the drying operation.

2. A method according to claim 1 wherein said reactive binder includes an alkaline solution of soya protein.

3. A method according to claim 1 wherein said reactive binder includes carboxy methyl cellulose.

4. A method according to claim 1 wherein said reactive binder includes a copolymer of polystyrene and butadiene.

5. A method according to claim 1 wherein said reactive binder includes sodium alginate.

6. A method according to claim 1 wherein said reactive binder includes a sodium salt of a styrene-maleic anhydride copolymer.

7. The process of coating paper which comprises continuously moving a web of paper, continuously applying to one surface of said web a coating composition containing from 35 to 60 percent by weight of solids and including a pigment and a hardenable binder, and relatively soon thereafter and without applying any intermediate drying step so that at least the outermost region of said coating remains in a wet, mobile, moldable state capable of offsetting upon a surface brought to bear upon the outer surface of said coating, contacting the outermost surface of the coating on said web with a rotating pressure member, continuously applying a regulated amount of a liquid immobilizing agent to the surface of said rotating pressure member before it is brought into contact with said coating, said liquid immobilizing agent being capable of almost instantaneously converting the outermost region of said binder to a non-tacky, hardened state to almost instantaneously convert and render non-adherent and smooth a layer of said coating

composition at the outermost surface thereof when said pressure member contacts said coating, said regulated amount of liquid immobilizing agent being insufficient to form a visible bead of the immobilizing agent at the point at which said pressure member first contacts said coating, maintaining said pressure member in engagement with said coating for a period of time at least equal to the period of time required to render said coating non-adherent to and non-offsetting on the surface of said pressure member, withdrawing said coated web from pressure contact with said pressure member to produce a paper web which is provided with a smooth, continuous, level coating, the regulated amount of said liquid immobilizing agent being such that a film of such agent is left on said pressure member after said converted coating is withdrawn from said pressure member, and then drying the web and coating without further smoothing during the drying operation.

8. The process of coating paper which comprises continuously moving a web of paper, continuously applying to one surface of said web a coating composition containing from 35 to 60 percent by weight of solids and including a pigment filler and a hardenable binder composition, and relatively soon thereafter and without applying any intermediate drying step so that at least the outermost region of said coating remains in a wet, mobile, moldable state capable of offsetting upon a surface brought to bear upon the outer surface of said coating, smoothing the coating on said web of paper and then contacting the outermost surface of the coating with a rotating pressure member, continuously applying a regulated amount of a liquid immobilizing agent to the surface of said rotating pressure member before it is brought into contact with said coating, said liquid immobilizing agent being capable of almost instantaneously converting the outermost region of said binder composition to a non-tacky, hardened state to almost instantaneously convert and render non-adherent and smooth a layer of said coating composition at the outermost surface thereof when said pressure member contacts said coating, said regulated amount of liquid immobilizing agent being insufficient to form a visible bead of the immobilizing agent at the point at which said pressure member first contacts said coating, maintaining said pressure member in engagement with said coating for a period of time at least equal to the period of time required to render said coating non-adherent to and non-offsetting on the outer surface of said pressure member, withdrawing said coated web from pressure contact with said pressure member to produce a paper web which is provided with a smooth, continuous, level coating, the regulated amount of said liquid immobilizing agent being such that a film of such agent is left on said pressure member after said converted coating is withdrawn from said pressure member, and then drying the web and coating without further smoothing during the drying operation.

9. The process of coating paper which comprises continuously moving a web of paper, continuously applying to at least one surface of said web a hardenable coating composition containing from 35 to 60 percent by weight of solids, and relatively soon thereafter and without applying any intermediate drying step so that at least the outermost region of said coating remains in a wet, mobile, moldable state capable of offsetting upon a surface brought to bear upon the outer surface of said coating, passing said web between a pair of press rolls, continuously applying a regulated amount of a liquid immobilizing agent to the roll surface which contacts the coated surface of said web of paper before said roll surface is brought into contact with said coating, said liquid immobilizing agent being capable of almost instantaneously converting the outermost region of said coating composition to a non-tacky, hardened state to almost instantaneously convert and render non-adherent a layer of said coating composition at the outermost surface thereof as said web passes

through said press rolls, said press rolls engaging said coated web with sufficient pressure to smooth the coated surface as said immobilizing agent contacts said mobile, moldable coating composition, said regulated amount of liquid immobilizing agent being insufficient to form a visible bead of the immobilizing agent in advance of the pressure nip of said press rolls, withdrawing said coated web from pressure contact with said press rolls to produce a paper web which is provided with a smooth, continuous, level coating, the regulated amount of said liquid immobilizing agent being such that a film of such agent is left on the press roll which contacts said coated surface after said converted coating is withdrawn from said roll, and then drying the web and coating without further smoothing during the drying operation.

10. The process of coating paper which comprises continuously moving a web of paper, continuously applying to at least one surface of said web, a layer of fluid coating material containing from 35 to 60 percent by weight of solids and including a pigment filler and a hardenable binder composition, and relatively soon thereafter and without applying any intermediate drying step so that at least the outermost region of said layer of fluid coating material remains in a wet, mobile, moldable state capable of offsetting upon a surface brought to bear upon the outer surface of said coating, passing said web into the nip between a pair of press rolls, continuously applying a regulated amount of a fluid reactive hardening material to the roll surface which contacts the coated surface of said web of paper before said roll surface is brought into contact with said coating, said fluid reactive hardening material being capable of almost instantaneously converting the outermost region of said coating material to a non-tacky, hardened state to almost instantaneously convert and produce a hardened, non-adherent surface condition at the outer surface of said coating during the passage of said web through said press rolls, said press rolls engaging said coated web with sufficient pressure to smooth the surface of said coating as said reactive material contacts said mobile, moldable coating material, said regulated amount of reactive material being insufficient to form a visible bead of the reactive material in advance of the pressure nip of said press rolls, withdrawing said coated web from pressure contact with said press rolls to produce a paper web which is provided with a smooth, continuous, level coating, the regulated amount of said reactive material being such that a film of such reactive material is left on the press roll which contacts said coated surface after the converted coating is withdrawn from said roll, and then drying the web and coating without further smoothing during the drying operation.

11. The process of coating paper which comprises continuously moving a web of paper, continuously applying to at least one surface of said web a coating composition containing from 35 to 60 per cent by weight of solids and including calcium carbonate and a hardenable binder composition, moving the coated paper without applying any intermediate drying step and while the outermost region of said coating remains in a wet, mobile, moldable state capable of offsetting upon a surface brought to bear upon the outer surface of said coating, into the nip between a pair of rotating press rolls, continuously applying a regulated amount of an aqueous solution of alum to the roll surface which contacts the coated surface of said web of paper before said roll surface is brought into contact with said coating, said aqueous solution of alum being capable of almost instantaneously converting the outermost region of said coating composition to a non-tacky, hardened state to almost instantaneously convert and render non-adherent a layer of said coating composition at the outermost surface thereof and to react with the calcium carbonate in said surface layer to effect an increase in the surface brightness of the coated web as said web passes through said press rolls, said press rolls engaging said coated web with sufficient pressure to smooth the coated surface and thereby produce during the time that said coated web is in the nip between the press rolls a smooth, hardened film resulting from the almost instantaneous reaction between said reactive material and said aqueous solution of alum, said hardened film preventing adherence and offsetting of the coating onto the pressure roll surface which contacts the coating during the pressure molding operation, said regulated amount of alum solution being insufficient to form a visible bead of the alum solution in advance of the pressure nip of said press rolls, withdrawing said coated web from pressure contact with said press rolls to produce a paper web which is provided with a smooth, continuous, level coating, the regulated amount of said alum solution being such that a film of said alum solution is left on the press roll which contacts said coated surface after the converted coating is withdrawn from said roll, and then drying the web and coating without further smoothing during the drying operation.

References Cited in the file of this patent

UNITED STATES PATENTS

1,060,366	Sadtler	Apr. 29, 1913
2,007,578	Madge et al.	July 9, 1935
2,183,858	Warren	Dec. 19, 1939
2,304,818	Grupe	Dec. 15, 1942
2,419,207	Fisher	Apr. 22, 1947
2,502,783	Erickson	Apr. 4, 1950
2,632,714	Loomer	Mar. 24, 1953
2,656,286	Fisher et al	Oct. 20, 1953
2,661,309	Azorlosa	Dec. 1, 1953
2,685,571	Stinchfield et al.	Aug. 3, 1954
2,698,259	Trosset et al.	Dec. 28, 1954