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METHOD OF COATING PAPER

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This invention relates to a process for coating paper or the like and, more particularly, to a process for applying a mineral coating to paper in such a manner that the coating is extremely smooth and presents a high quality printing surface.

In the manufacture of paper, mineral coatings are commonly applied to a base paper stock to impart opacity to the paper and to provide a smooth and receptive surface for a printing operation. For a high quality printing operation, it is necessary that the surface of the coated paper be very smooth and uniform. The necessary smooth and uniform coating is usually achieved by applying one or more coats of mineral coating to the paper. For a high quality sheet, the coating is usually applied in two coats. The coatings applied to the sheets usually comprise a mineral pigment and an adhesive which are united into a uniform aqueous dispersion which is then applied to the sheet. For the most satisfactory coating and where water resistance is necessary, it is desirable to insolubilize the adhesive so as to set the coating and to thereby impart water and rub resistance to the sheet. These properties are especially desirable in papers designed for printing by the offset process.

Typical adhesives which have been employed in coatings include starch and protein, the proteins usually employed being casein or soya bean protein. The protein adhesives are most readily insolubilized, the insolubilization usually being effected by a reaction with formaldehyde or a formaldehyde donor material.

Heretofore, the insolubilizing of a coating containing a protein such as casein as the adhesive has been carried out in several different ways. One way of insolubilizing the casein involves spraying, brushing or otherwise applying the formaldehyde or a suitable formaldehyde donor material in solution to the coated sheet. This method has not been altogether satisfactory since the application of the formaldehyde solution to the coating causes unevenness and the surface of the coating often "picks" as it is passed around rolls in subsequent operations. Also, it is necessary to dry the coated paper after the insolubilization step which requires additional drying capacity.

Another method of effecting insolubilization involves applying a formaldehyde solution to the back side of the sheet while the protein bearing top coating is still soft. Such a method can be employed only when one side of the sheet is to be coated. Further, this method is also not entirely satisfactory because the formaldehyde solution does not penetrate uniformly unless large amounts are used. A variation of this method involves first coating the sheet with the formaldehyde solution and while the sheet is still wet applying the mineral coating to the sheet. The immediate contact of the top coating with the formaldehyde solution in this method prevents proper migration of the adhesive into the sheet which is necessary to obtain a strong bond between the coating and the sheet.

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A third prior method involves adding formaldehyde or a formaldehyde donor material to the coating mixture before the coating is applied to the paper. The addition of the formaldehyde to the coating mixture increases the viscosity of the coating to the point where the coating will not flow evenly over the surface of the paper, resulting in coatings which are not level. This is especially troublesome where relatively heavy coats are to be applied because in order to reduce the viscosity of the coating suspension it is necessary to reduce the total solids content in the coating suspension. Even when diluted to lower viscosities the flow properties of the coating are affected and are not as good as desired. These problems limit this method either to lower coat weights or impose greater drying loads.

Accordingly, it is the object of this invention to provide a method of applying multiple-layer mineral coatings to paper, which method overcomes the disadvantages of the prior methods and is applicable to sheets coated on one or both sides. A further object of this invention is the provision of a coating method by which a relatively heavy coating which includes a casein binder may be insolubilized without affecting the uniformity of the coat. Other objects and advantages of the invention will become known from the following description of the invention.

The present invention utilizes a coating solution which has a high solids content but which has flow properties which will produce a smooth coat. This permits the application of a wide range of coating weights. The method of the invention also permits the use of higher coating speeds because of the better flow characteristics of the coating mixtures and shorter setting and drying times.

The method of the present invention involves the application of multiple coatings to the paper. The finish coating is comprised of a suitable mineral pigment and a protein binder. This finish coating is applied in the usual manner and is so constituted that it provides optimum flow properties to provide a smooth uniform coating. Prior to the application of the finish coating an undercoating is applied and dried. The undercoating includes, in addition to a mineral pigment and an adhesive, an insolubilizing agent for the finish coating. After the undercoating and finish coating are applied, the sheet is held until the insolubilizing agent in the undercoating insolubilizes the adhesive in the finish coating. The time for this reaction will vary widely depending upon several variables, including the insolubilizing agent used, pH of coating, drying temperatures, and the conditions under which the paper is stored.

The first step of the process, therefore, is the application of an undercoating of a coating mixture which comprises formaldehyde or a formaldehyde donor as the insolubilizing agent and adhesive or binder and a mineral pigment in an aqueous suspension to the surface of paper. The paper may be of any suitable type for the purpose intended. The undercoating may be applied to an uncoated web or to a coated web, it will usually be applied to an uncoated web since two coatings will in almost every instance provide the desired printing surface. The coating preferably is applied by a transfer roll coating method instead of a water box or other method since the transfer roll coating method enables the application of a coating of relatively low moisture content which facilitates the application of a second coating and at the same time provides a smooth undercoating.

The mineral pigment in suspension in the undercoating mixture may be any suitable pigment which gives the desired properties to the paper. Typical mineral pigments which may be employed are clays, titanium dioxide, calcium carbonate, barium sulfate, diatomaceous silica, zinc sulfides, zinc oxide, etc. The mineral pigment is, of course, present in a finely dispersed form in suspension in the coating mixture.

The coating mixture for the undercoating also contains an adhesive or binder which does not react materially with the insolubilizing agent while the coating is being applied. Also, the adhesive should not be thickened materially in the presence of the insolubilizing material during the application of the coating and consequently makes it possible to apply an undercoating of optimum smoothness. Thus, adhesives such as dextrine type starches or oxidized starches are particularly suitable binders. Starch provides high fiber binding qualities, pick resistance and low cost. The adhesive or binder tends to seal the surface of the paper web, and the binder and mineral pigment in the first coating mixture form a smooth layer on the web over which the finish coating may be applied.

The formaldehyde donor comprises suitable material which releases formaldehyde or other aldehyde at room temperature or above. A solution of formaldehyde itself may be used as the donor. However, because of the offensive odor and toxicity of the fumes it should be used only in well ventilated plants and on paper for which the odor would not provide a problem. Wherever the term "formaldehyde donor" is used in the specification or claims it is understood to include formaldehyde itself, as well. Other formaldehyde donors which release formaldehyde rather slowly at the temperature at which the undercoating mixture is applied are preferred. Particularly preferred formaldehyde donors are hexamethylene tetramine; paraformaldehyde; monomethylol dimethyl hydantoin and similar compounds; formaldehyde resins such as melamine formaldehyde, urea formaldehyde; etc.

The amount of formaldehyde donor used in the first coating mixture is proportional to the amount of adhesive used in the second coating mixture. Enough of the formaldehyde donor is used to satisfactorily insolubilize or set the adhesive and usually a slight excess is used to insure complete insolubilization of the adhesive.

When the undercoating mixture contains a starch adhesive, a preferred donor material is a melamine formaldehyde resin since this resin reacts with the starch after it is coated on the paper to insolubilize the starch and to impart improved pick resistance and wet rub resistance to the sheet.

Generally, when using hexamethylene tetramine as the formaldehyde donor, the amount of hexamethylene tetramine used is within the range of from about 1 percent to about 10 percent by weight of the adhesive in the top coating mixture and preferably the amount is within the range of from about 2 percent to about 6 percent. When using formaldehyde resins as the formaldehyde donor, the amount of the resin used is from about 15 percent to about 25 percent by weight of the adhesive in the top coating mixture. When using formaldehyde itself, the amount needed is from about .1 percent to about 2 percent by weight of the adhesive in the top coating mixture. The use of formaldehyde, however, is not preferred as has been pointed out because of the odor problem.

The undercoating mixture, therefore, comprises an adhesive or binder, a formaldehyde donor and a mineral pigment in suspension in water. The amount of mineral pigment varies, depending upon the properties desired in the finished sheet, as does the amount of adhesive, in accordance with normal coating practice. The amount of solids in the coating as applied to the sheet also vary as in any other coating process and the pH and other conditions are maintained within normal limits. The normal pH of the coatings range about neutral to the alkaline side, i. e. from about 6.8–10.0, the preferred pH being between about 7.5 and 9.5. Of course, the exact pH in the range will depend upon the constituents employed so as to minimize any undesired side reactions.

The coating of the paper web with the first or undercoating mixture may be performed by any conventional coating process. However, the preferred method of application involves the use of a transfer roll coater. After the first or undercoating is applied, it may be dried by passing it over the usual heated rolls in the machine or in any other suitable manner after which the second or finish coating is applied.

The second or finish coating mixture comprises water, an adhesive which is insolubilized by the formaldehyde material, and a mineral pigment in suspension. The adhesive may be any suitable adhesive which is insolubilized by formaldehyde. The adhesive is preferably a proteinaceous adhesive such as casein or soya bean protein which is commonly used in paper coating mixtures and which is water dispersible.

The mineral pigment that is in suspension in the finish coating mixture may be any of the mineral pigments which were hereinbefore mentioned for use in the first coating mixture. The pigment suspended in the second coating mixture may be the same as that suspended in the first solution or it may be a different mineral pigment.

Other substances such as plasticizers and latex may be added to the coating mixture to obtain improved qualities of the finished sheet. Frequently a coating mixture which contains a protein such as casein has a tendency to foam and a suitable defoaming agent may be added to minimize foaming.

The finish coating mixture thus includes a proteinaceous adhesive or binder and a mineral pigment in aqueous suspension. This suspension may include a modifying substance such as latex or the like and it may contain one or more conditioning substances such as the defoaming agent. The proportions of the various constituents are varied in accordance with normal coating practice to produce an optimum coating on the sheet. The pH is preferably maintained in the range of from about 8.0 to 9.5. The finish coating is preferably applied by a transfer roll coater, but other methods may be employed.

After the finish coating has been applied, the paper web is dried and usually subjected to the action of calendering rolls. If these rolls are heated, the release of formaldehyde from the lower coating and the insolubilization of the second coating are accelerated.

Insolubilization may also be accelerated by heating the reel drum upon which the paper is rolled to accelerate the reaction on the reel. When holding under room temperature conditions the roll may have to be held for 1 to 3 weeks, but when the reel is heated the insolubilization will take place within a few days. The resultant coated paper has a very smooth coated surface and has excellent wet rub resistance which makes it especially suitable for all types of offset printing. Because the paper has high water resistance it is also useful in letterpress printing for labels or the like or in other types of printing where high water resistance is required.

The process is described here as it is usually carried out in a continuous operation on the paper machine. However, the process may also be discontinuous, with the base coat being applied on the paper machine, held at room temperature, and subsequently coated with the finishing coat on a separate coating machine. Or the entire operation may be carried out on a separate coating machine.

In the following paragraphs there is described a specific example of carrying out the invention:

In this example a 7 pound per ream undercoating is applied to each side of a 43 pound per ream basis weight paper web, followed by the application of a 6.5 pound per ream finish coating on each side. The undercoating mixture which is to be applied to both sides of the paper web is prepared by mixing 93 parts by weight of clay with 7 parts by weight of titanium dioxide, this mixture forming the mineral component of the undercoating. In a separate container water, 25 parts by weight of starch and 3 parts by weight of melamine formaldehyde resin are mixed together and the mixture is then heated to 90° C. The heated starch-resin solution is then added to the mineral mixture in the kneader. Ammonia or other alkali is added to adjust the pH to about 8.0. A dispersing agent, i. e. 0.5 part by weight of sodium hexametaphosphate, is also added and the entire coating mixture is kneaded to thoroughly mix all of the ingredients. The pH should be maintained within the range of from about 7.5 to about 8.5. The resultant coating mixture is diluted with water and worked until it contains 54 percent solids and has a Brookfield viscosity of 55° with a No. 6 spindle at 100 R. P. M. This mixture is applied to both sides of the paper by a transfer roll coater at a rate of 7.0 pounds per ream per side.

After applying the above said coating to both sides of the paper, the coated paper is dried in the drying section of the machine or coater and the finish coating is applied. The mineral component of the finish coating is prepared by first mixing together 81 parts by weight of clay, 9 parts by weight of titanium dioxide, 10 parts by weight of calcium carbonate, 0.5 part by weight of sodium hexametaphosphate, and enough, about 0.1–0.2 percent by weight, of a 50 percent sodium hydroxide or other alkaline solution to raise the pH to between 8.0 and 9.5. In a separate container 13 parts by weight of casein are solubilized by using 9 parts of concentrated ammonia solution, based on the weight of the casein. This casein adhesive is added to the mineral component above. To this mixture are added 2 parts by weight of latex solids (which includes 5 percent casein based on the dry weight of latex as a stabilizer), 1½ parts by weight of a sulfonated tallow as a plasticizer (a commercially available sulfonated tallow is sold under the name of Vegatol) and sufficient amount of foam inhibitor to minimize the foaming of the casein. This is then diluted with water and worked until the coating has a solids content of about 54 percent and a Brookfield viscosity of 45° under the above conditions. This coating is then applied to both sides of the paper on top of the dried undercoating described in the foregoing by a transfer roll coater at a rate of 6.5 pounds per ream per side.

The paper is then dried on the machine and wound onto reels, usually supercalendered, and aged one week at room temperature before use. The resultant paper which has a total coating weight of 27 pounds per ream is suitable for high quality printing operations.

Various features of the invention are set forth in the appended claims.

We claim:

1. A method of insolubilizing a protein adhesive in a coating on a paper web which comprises applying a first coating mixture to said web which includes an insolubilizing agent for a protein adhesive, a mineral pigment and a non-proteinaceous adhesive, drying said first coating, subsequently applying a second coating mixture to the coated paper web which includes a mineral pigment and a protein adhesive, and holding the coated web until said protein adhesive is insolubilized by said insolubilizing agent.

2. A method of insolubilizing a protein adhesive in a coating on a paper web which comprises applying a first coating mixture to said web which includes a formaldehyde donor material, a mineral pigment and a non-proteinaceous adhesive, drying said first coating, subsequently applying a second coating mixture to the coated paper web which includes a mineral pigment and a protein adhesive, said formaldehyde donor in said first coating mixture being in amount sufficient to react with and insolubilize said protein adhesive, and holding the coated web until said protein adhesive is insolubilized by said formaldehyde donor.

3. A method of insolubilizing a protein adhesive in a coating on a paper web which comprises applying a first coating mixture to said web which includes a formaldehyde donor material, a mineral pigment and a non-proteinaceous adhesive, drying said first coating, subsequently applying a second coating mixture to the coated paper web which includes a mineral pigment and a protein adhesive, said formaldehyde donor in said first coating mixture being in amount sufficient to react with and insolubilize said protein adhesive, holding the coated web until said protein adhesive is insolubilized by said formaldehyde donor, and heating said coated web during said holding to accelerate the insolubilization.

4. A method of insolubilizing a protein adhesive in a coating on a paper web which comprises applying a first coating mixture to said web which includes a formaldehyde donor material, a mineral pigment, and starch, drying said first coating, subsequently applying a second coating mixture to the coated paper web which includes a mineral pigment and casein, and holding the coated web until said casein is insolubilized by said formaldehyde donor.

5. A method of insolubilizing a protein adhesive in a coating on a paper web which comprises applying a first coating mixture to said web which includes a formaldehyde donor material, a mineral pigment, and starch, drying said first coating, subsequently applying a second coating mixture to the coated paper web which includes a mineral pigment and casein, holding the coated web until said casein is insolubilized by said formaldehyde donor, and heating said coated web during said holding to accelerate the insolubilization of said casein.

6. A method of insolubilizing a protein adhesive in a coating on a paper web which comprises applying a first coating mixture to said web which includes a melamine formaldehyde resin, a mineral pigment, and starch, drying said first coating, subsequently applying a second coating mixture to the coated paper web which includes a mineral pigment and casein, and holding the coated web until said casein is insolubilized by said melamine formaldehyde resin.

7. A method of insolubilizing a protein adhesive in a coating on a paper web which comprises applying a first coating mixture to said web which includes a melamine formaldehyde resin, a mineral pigment, and starch, drying said first coating, subsequently applying a second coating mixture to the coated paper web which includes a mineral pigment and casein, and holding the coated web until said casein is insolubilized by said melamine formaldehyde resin, the amount of melamine formaldehyde resin being from about 15 to 25 percent by weight of the amount of casein present in said second coating.

8. A method of insolubilizing a protein adhesive in a coating on a paper web which comprises applying a first coating mixture to said web which includes a melamine formaldehyde resin, a mineral pigment, and starch, drying said first coating, subsequently applying a second coating mixture to the coated paper web which includes a mineral pigment and casein, holding the coated web until said casein is insolubilized by said melamine formaldehyde resin, and heating said coated web during said holding to accelerate the insolubilization of said casein.

9. A method of insolubilizing a protein adhesive in a coating on a paper web which comprises applying a first coating mixture to said web which includes a melamine formaldehyde resin, a mineral pigment, and starch, drying said first coating, subsequently applying a second coating mixture to the coated paper web which includes a mineral pigment and casein and having a pH within the range of from about 8.0 to about 9.5, and holding the coated web until said casein is insolubilized by said melamine formaldehyde resin.

10. A method of insolubilizing a protein adhesive in a coating on a paper web which comprises applying a first coating mixture to said web which includes a formaldehyde donor material, a mineral pigment and starch and having a pH within the range of from about 7.5 to

about 9.5, drying said first coating, subsequently applying a second coating mixture to the coated web which includes a mineral pigment and casein and having a pH within the range of from about 8.0 to about 9.5, and holding the coated web until said casein is insolubilized by said formaldehyde donor.

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