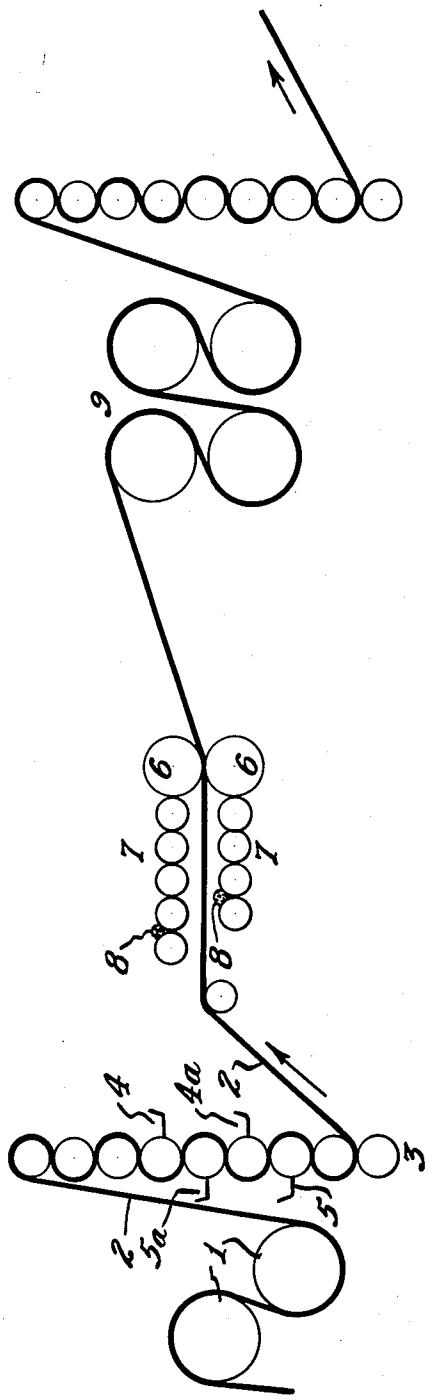
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PROCESS OF PRODUCING MOISTURE RESISTANT COATED PAPER WEBS

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PROCESS OF PRODUCING MOISTURE RESISTANT COATED PAPER WEBS

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My invention relates generally to that mode of producing coated paper and board wherein the surface of the felted web is first treated to plasticize it, after which a coating substance is applied by imprinting. As described in my Patent No. 2,419,207, dated April 22, 1947, in the practice of such a process I pass the felted web from the paper machine driers through a stack of calender rolls on which I apply to the surface of the web a plasticizing solution containing starch, polyvinyl alcohol, or other substances or mixtures of them, the effect in combination with the working incident to the passage of the web through the steel calender rolls being to smooth, soften and plasticize the surface of the web, laying down protruding fibers thereon and fitting the web for the reception of a mineral coating, the application of which is the next step in the process. The coatings, normally a suspension of mineral pigment in water with a binder such as starch, have a high solids content. They may be applied by an imprinting process as distinguished from ones in which the coating is flowed onto the web and smoothed thereon with brushes, rolls or the like. The coating is imposed upon the web surface or surfaces while they are still in the plasticized condition; and by reason of the pretreatment which the surfaces have received, excellent results are obtained with exceedingly thin coatings which, in practice, are seldom more than about one-thousandth of an inch in thickness and usually are much thinner.

In a copending case in the names of myself and B. E. Sooy, which is now U. S. Patent No. 2,515,340 there is taught a procedure for rendering such coatings highly moisture resistant. It was known that when certain resinous substances were incorporated in the coating material and treated with suitable catalysts, the result was an insolubilizing of the coating including the starch binder therein. The resinous substances taught in the said copending case comprise urea-formaldehyde resin and melamine aldehyde resin, both of which require an acidic substance as a catalyst. By reason of progressive catalyzation and reaction, difficulties were encountered in continuously applying coating substances containing both the resin and the catalyst, in consequence of which an important part of the teachings of the said patent resides in the concept of applying the resin and the catalyst to the web in separate increments whereby, in essence, they are not permitted to interact until after their application to the web. Thus it becomes possible to apply the resin along with the initial plasticizing solution, while causing the coating substance to carry the catalyst. Conversely, the resinous substance may be dissolved or dispersed in the mineral coating mixture, the catalyst being applied to the surface of the web on the breaker stack of calenders, either separately from the plasticizing solution or in admixture with it. The initial application of the catalyst to the web followed by an over printing of coating mixture containing the resin has certain advantages in confining the resin largely to the coating as distinguished from bringing it into direct contact with the fibrous surface of the web which, under these circumstances, can absorb some of it. But the acidic catalysts are corrosive and tend to impair the hot metal calender rolls.

The present invention has as one of its principal objects a solution of the problem just pointed out.

It is an object of my invention to provide a process of making moisture resistant coated papers continuously without the disadvantages which flow from attack of the steel calender rolls by the acidic catalyst.

It is an object of my invention to provide a coating process in which the catalyst can be buffered or rendered non-corrosive at the time of its application but in which the acidic nature of the catalyst which is required for its proper catalytic activity can be rapidly developed without delaying or impeding the coating process.

In my Patent No. 2,370,344, dated February 27, 1945, there is described a process of making colored coated paperboard wherein coloring substances may be applied along with the plasticizing solution, later permeating the mineral coating and producing the desired coloration in the finished stock. Also in Patent No. 2,515,340, above identified, processes are described of making a colored product resistant to moisture and to loss of color in the presence of moisture or moisture and abrasion. It has been found that with certain coloring matters inclusive of organic dyestuffs, pigments, both organic and inorganic, lakes, toners and the like, which are either water soluble or water dispersible, a moisture resistant coated web may be produced which is singularly resistant to color loss by methods involving a proper insolubilizing of the starchy binder of the coating mixture. The teachings of the present invention are applicable to the procedures of these patents.

The various objects of my invention and others which will be set forth hereinafter or will be apparent to one skilled in the art upon reading this specification, are accomplished by that procedure of which I shall now describe an exemplary embodiment. Reference is made to the accompanying drawing wherein I have diagrammatically indicated apparatus with which my process may be carried on.

My new process provides for the reduction or elimination of the corrosion of polished steel calender rolls in the breaker stack of calenders which immediately follows the heated drier rolls of the paperboard machine, and which precedes the mechanism by which the mineral coating mixture is imprinted upon the paperboard or paper web. An exemplary coating mixture comprises as its chief ingredients, finely divided clay, cooked starch, synthetic resin for insolubilizing the starch, and water. Basic processes are described in the patents hereinabove referred to, and the present invention is not limited to specific formulae either for the plasticizing solution or for the mineral coating mixture.

In the general practice of my invention, the mineral coating mixture containing the starch binder to be waterproofed is blended with a minor proportion of suitable resin such as urea-formaldehyde, and is then coated upon the web of paper or board immediately after the web has received a plasticizing treatment on a stack of breaker calender rolls. The plasticizing substance may be a starch solution, a polyvinyl alcohol solution, solutions containing blends of such substances, or of other plasticizers in water; and I apply a catalyst either along with such a plasticizing solution or separately on the calender rolls, but in either event, prior to the imprinting of the mineral coating mixture on the web surface or surfaces. An exemplary acidic catalytic agent is ammonium chloride which acts rapidly when brought into contact with the mineral coating mixture to insolubilize the mixture on the surface of the web by a mechanism which is not

fully understood. Ammonium chloride is exemplary only of acidic catalysts which may be employed, and in general acids themselves, and salts which provide an acid reaction upon hydrolysis are generally available. To name a few, I may use ammonium oxalate, ammonium phosphate, ammonium sulphate, aluminum sulphate, tannic acid, and similar substances, my preference being for salts having an acid reaction.

Being highly acid in nature, the catalyst even when in admixture with the plasticizing solution used to pretreat the board by application from the water boxes on the stack of polished steel calender rolls, rapidly attacks the rolls to corrode and pit their surfaces, destroying their polished condition. In many cases the corrosion after a few weeks of operation becomes sufficient to render the rolls worthless as a means for smoothing the surfaces of the web, whereupon they must be removed from the calender stack and reground and polished.

In solving the problem of alleviating this corrosive condition, I have found that it is possible to maintain an alkaline condition of the solution containing the catalyst as it is applied by the calender box to the surface of the moving web, but to provide for a rapid transformation of the alkaline condition to an acidic one in which the catalyst becomes active on the surface of the web substantially immediately after the web has emerged from the stack of calender rolls and in most instances before it enters the coating unit. Thus at the point where the mineral coating mixture applied by the coating unit should start to become insolubilized, it will be contacted by an active acid catalyst. In paper mill machinery customarily employed for coating felted webs by the imprinting process, in which the web is substantially completely dried before being treated for the application of the coating, the time element available for converting the catalyst solution from an alkaline to an acidic condition is very short, being in the nature of a few seconds or less. It is an object of my invention to effect the conversion, without the necessity of adding treatment units to the paper machine; and it will be recalled that in the general process to which this invention is addressed, the coating mixture should be applied to the surface of the web while it is still in a plasticized condition, thus precluding the use of intermediate heat treating devices which result in a complete drying of the web surfaces.

In a typical starch solution used to pretreat the paper surface as set forth in the several patents and applications referred to above, the catalyst, such for example as ammonium chloride, will depress the pH to around 6 and even lower. This is sufficiently low to cause the corrosive effect above described on the metal calender rolls. I have found that by the addition of a small amount of removable alkaline substance it is possible to raise the pH of the catalyst solution to a point definitely on the alkaline side, and that this buffers the corrosive effect of the solution upon the metal calender rolls. A satisfactory buffering effect is achieved as soon as the pH of the catalyst solution rises so as to be slightly beyond neutral. In actual practice I add sufficient alkaline substances to bring the pH to around 7.8; but less or more of it may be employed and the advantages of the invention obtained.

Various alkaline substances may be employed with entire success. Triethanolamine is an example of an organic substance with an alkaline reaction capable of being removed under the conditions presently to be outlined. The least expensive and most available alkaline substance is ammonium hydroxide, which I employ in current practice. It is required that the alkaline substance be capable of being dissolved into the solution of catalyst without precipitating it. Thus an alkaline substance with an ion common to the acid catalyst is preferred, e. g. ammonium hydroxide as the alkaline substance and ammonium chloride as the acid catalyst which can exist together in a common solution in water.

The heat resident in the moving web suffices to drive off the ammonia once the web has left the point of application of the catalyst solution, with the result that the catalyst-treated surface of the web rapidly reassumes its acidic condition. Depending upon the speed of motion of the web, its thickness, the resident heat in it from the paper machine driers, and perhaps weather conditions tending to mild or hot temperatures at the finishing end of the board machine, the free ammonia will be driven off of the treated surface or surfaces in periods of time which are variable but are always short. In normal operations the reactivation of the catalyst occurs well ahead of the coating point; but if the complete removal of the alkaline substance is delayed until after the coating is applied, it will occur during the heating of the web on the after-driers as hereinafter described. In either event the removal of the alkaline substance restores the catalyst to a condition of activity necessary for insolubilizing the starch-resin mixture.

In the drawing I have indicated diagrammatically apparatus which may be placed at the end of the driers of a paper or paperboard machine. The rolls **1** are the final drier rolls, and the web **2** passes thence through a stack of breaker calender rolls **3**. Water boxes such as those indicated at **4** and **5** may be used to flow liquid material onto the web as it passes around the calender rolls; and it will be noted from the position of these boxes that they are arranged to apply materials to opposite sides of the web where this is desired. Other boxes as at *4a* and *5a* may, however, be arranged to apply increments of liquid materials to the same side of the web.

Imprinting rolls for imposing a coating mixture of high solids content on one or both sides of the web as desired are indicated at **6**. I prefer to employ in connection with each of the imprinting rolls **6** a series of distributing rolls **7** which rotate against each other and some of which may be caused to oscillate endwise. The coating mixture, which is relatively heavy in consistency, may be imposed on gate rolls at the ends of the series as indicated at **8**.

From the imprinting point the web preferably travels through a drier section having rolls **9** and thence to a calender stack **10** for calendering the dried product.

The plasticizing solution will be applied to the web surface or surfaces by one or more of the water boxes used in connection with the breaker calender stock 3. Any of the plasticizing solutions taught in any of the patents referred to above may be employed; and the precise nature of the plasticizing solution does not form a limitation on this invention excepting as set forth in the appended claims. In a typical pretreating water solution, 250 gallons of it may contain 70 pounds of chlorinated starch and 6 pounds of dispersed or emulsified wax. If the catalyst is to be incorporated in the plasticizing solution, I add a proper quantity of suitable catalyst, say, 150 pounds of ammonium chloride. In instances where the plasticizing effect of the surface of the web is to be increased, the amount of chlorinated starch may be increased, as for example to 140 or 210 pounds. Multiples of 70 pounds of starch are practically useful in this example as representing so-called single, double and triple concentrations and so on.

The particular solution set forth above has a pH of 6 and is highly corrosive to the polished steel surfaces of the calender rolls. In following the teachings of this invention I add to such a solution from ¾ to one pound of ammonium hydroxide solution of 28% strength. This increases the pH to around 7.8 which is definitely alkaline and very much less corrosive. Whereas the polished steel calender rolls corrode rapidly in contact with a solution such as the one set forth above but without the ammonia the addition of the ammonia so buffered the solution that corrosion was not observable after several months of continuous operation. Since in the average board mill it is not customary to run one grade of board

continuously, it is not possible to give definite times for the increase in the life of the metal calender rolls under the practice of the present invention. It is sufficient to point out that in customary operations the employment of the invention indefinitely prolongs the life of the calender rolls and essentially renders corrosion a nugatory factor in the paper mill operations.

The invention is likewise not restricted to particular coating mixtures excepting to the extent that such mixtures require for the desired results an active acidic catalyst as hereinabove set forth. For example, I may employ as a coating mixture a water dispersion containing around or greater than 50% solids principally starch binder and clay, together with a resin which will react with the starch under the influence of the catalyst to insolubilize the coating. As an example, the resin may be used in the form of a urea-formaldehyde syrup containing 70% of resin solids to 30% of water, and added to the coating mixture in amounts of from approximately 2 to approximately 25% by weight of the mixture.

While I have contemplated mixing the catalyst with the plasticizing solution for the web surfaces, it may be applied separately in solution as by the additional water boxes *4a* or *5a* of the drawing, together with the removable alkali.

As set forth in Patent 2,515,340 referred to above, it is possible to employ a procedure in which the resin is imposed on the web surface or surfaces along with or at the time of the imposition of the plasticizing solution. In this event corrosion of the rolls of the breaker calender stack **3** is not encountered. The catalyst then will be added in admixture with the coating substance; but a buffering of the catalyst is possible under these circumstances to prevent corrosion of the imprinting mechanism because, as explained above, it is possible to employ the heat of the drier rolls **9** to remove the alkali after the imposition of the coating. There is little need to do this when the several rolls of the imprinting mechanism in contact with the coating mixture are rubber covered and therefore are not subject to metallic corrosion. Nevertheless my process may be employed in this manner, also. It is further possible within the scope of my invention to apply a plasticizing solution containing the resin by means of certain water boxes on the stack **3** after which the buffered catalyst may be applied on the same stack by means of other water boxes.

The application of the teachings of my Patent 2,370,344 wherein a coloring agent which subsequently affects the coating is imposed on the web along with the plasticizing solution, does not alter the operation of the teachings hereof. Further, the teachings of this invention may be practiced in the formation of colored coated board along with the teachings of Patent 2,515,340.

Modifications may be made in my invention without departing from the spirit of it. Having thus described my invention in certain exemplary embodiments, what I claim as new and desire to secure by Letters Patent is:

1. In a process of making coated webs of paper and board characterized first by plasticizing the surface of the web by imposing thereon a plasticizing solution on a breaker stack of calenders acting to work the web surface, and second by imprinting a high solids mineral coating mixture on the prepared surface of the web while it is still in plasticized condition, the steps of including in the plasticizing solution an acid catalyst and a heat removable alkaline substance to raise its pH above 7, the said coating mixture having a starch binder, and including in said coating mixture a resin capable of being catalyzed by said acidic catalyst upon removal of said removable alkaline substance by heat, and producing removal of said removable alkali.

2. The process claimed in claim 1 wherein said removable alkaline substance is ammonium hydroxide.

3. The process claimed in claim 1 wherein said removable alkaline substance is ammonium hydroxide and wherein said removal is effected by heat resident in said web to a sufficient extent to raise the pH to at least 7 prior to the imposition of the coating on the surface of said web.

4. In a process of producing webs of coated paper and board involving the initial application of a plasticizing solution containing an acidic catalyst to the web surface on a breaker stack of calender rolls followed by the imprinting of a mineral coating mixture containing a starch binder and a reactive resin, the steps of protecting the said calender rolls from corrosion by said acidic catalyst by raising the pH of the plasticizing solution to a value above neutral with ammonium hydroxide followed by driving the ammonia off the surface of said web by heat after the web has passed beyond said calender breaker stack.

5. The process of claim 4 wherein a coloring matter is imposed on the surface of the said web.

6. The process of claim 4 wherein a coloring matter is imposed on the surface of the said web, along with the said plasticizing solution.

7. The process of claim 4 wherein a coloring matter is imposed on the surface of the said web, along with said mineral coating mixture.

References Cited in the file of this patent

UNITED STATES PATENTS

2,419,207	Fisher	Apr. 22, 1947
2,433,680	Backman	Dec. 30, 1947
2,515,340	Fisher	July 18, 1950