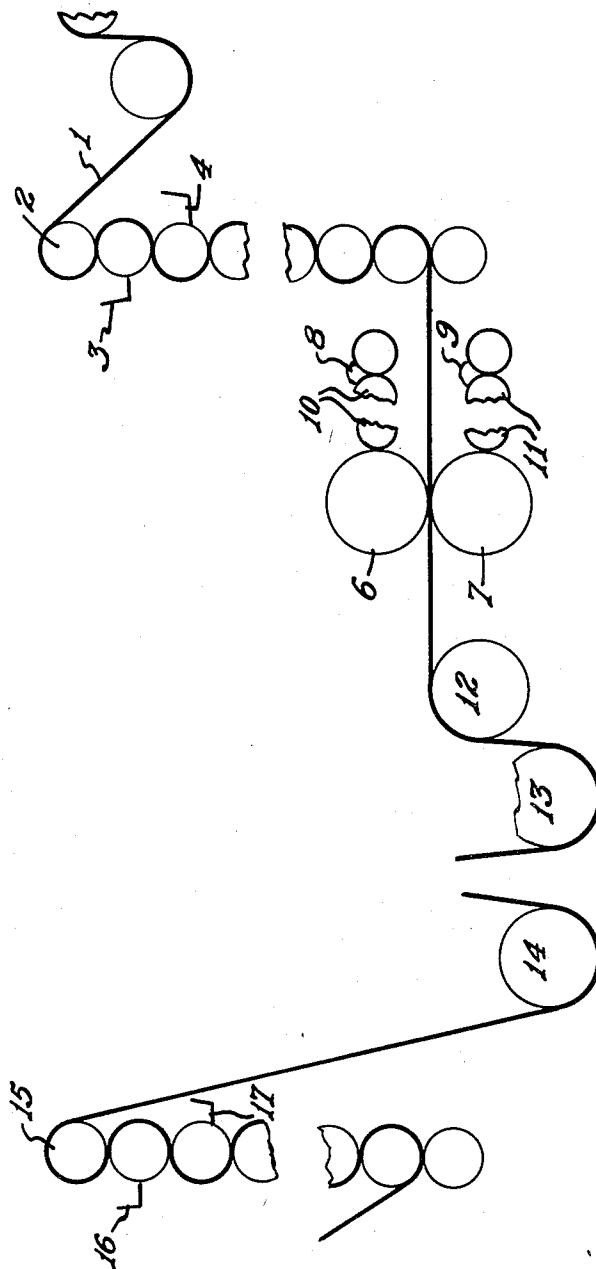


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MANUFACTURE OF WATER FINISHED BOARD HAVING AN
INSOLUBILIZED PROTEIN-MINERAL COATING THEREON
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MANUFACTURE OF WATER FINISHED BOARD HAVING AN INSOLUBILIZED PROTEIN-MIN- ERAL COATING THEREON

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Our invention relates to the coating of paper or paperboard with mineral substances in a suitable binder for the purpose of imparting appearance and printing qualities which the uncoated product does not possess. Our coated paperboard is converted into folding cartons, boxes, signs, etc. Casein has hitherto been suggested as a binder for mineral coatings on paper and board; and it has been known that casein as a binder can be insolubilized by water solutions of metallic salts and some acids. These solutions are acidic in nature. Paper makers' alum, aluminum sulphate, is effective, as is sulphuric acid. This is true for proteins in general, such as protein from soya beans, from animal glue, etc., which sometimes are used to replace part of the casein for reasons of economy or for special effects. For example, if a mineral coating composition having casein as a binder has been imposed and smoothed, as by brushes or rollers, on the surface of paper or board, and dried, then the moistening of that surface with a water solution of alum followed by a drying of it insolubilizes the casein and waterproofs the coated surface to the extent of making it at least resistant to wet rubbing. Such products have also been calendered for improvement in their surface characteristics; but attempts to give them a water finish have been disappointing. If a water finishing procedure is applied before the insolubilizing of the coating, the coating becomes softened during the operation and tends to pick off on the calender rolls with consequent impairment of the finish. Moreover, the subsequent application of a water solution of acidic substance for the insolubilizing of the casein will impair whatever measure of surface smoothness is attained in the water finishing attempt. On the other hand, if a water finishing procedure is applied after the insolubilizing step described above, there will be insufficient softening of the binder to enable the attaining of a satisfactory water finish.

A primary object of our invention is the provision of an inexpensive but highly effective procedure for the formation of a water finished insolubilized casein coating on paper or board.

Other important objects of our invention have to do with the provision of improved casein coated paper or board.

These and other objects of our invention, which will be set forth hereinafter or will be apparent to one skilled in the art upon reading these specifications, we accomplish by that procedure and in that product of which we shall now describe an exemplary embodiment. Reference is made to the accompanying drawing wherein is shown in diagrammatic form the elements of an apparatus with which our procedure may be carried on.

Briefly, in the practice of our invention, we have found that under certain circumstances hereinafter outlined, it is possible to manufacture coated paper or board in which the coating binder is an insolubilized casein, resistant to moisture and wet rubbing, the product having at the same time all of the desirable qualities of a water finished coated sheet, by a procedure which involves simultaneous water finishing and insolubilizing.

In Patent No. 2,419,207, issued April 22, 1947, in the name of Harry C. Fisher, one of the applicants herein, there is described a process for the manufacture of coated paper and board in which the felted web, after drying on the machine, has its surface or surfaces subjected to a so-called plasticizing treatment. This treat-

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ment involves passing the web through a breaker stack of calenders and imposing upon one or both surfaces, by means of water boxes on the calender rolls, a plasticizing solution, the surface characteristics of the web being thus modified to a condition peculiarly favorable for the acceptance of a thin imprinted coating of mineral coating substance in a suitable binder. The surface preparation is the combined result of mechanical work exerted by the calender rolls and conditions brought about by the plasticizing solution itself; and the mineral coating should be imposed upon the plasticized surface or surfaces during a persistence of the plasticizing effect. When this is done, a coating suspension consisting of suitable finely divided mineral coating substances in a solution of a binder, the mixture having a printable consistency or body, may be imprinted upon the web in an exceedingly thin layer, the web then being dried and recalendered. Coatings produced in this way are inexpensive because of the minimum quantity of materials involved and because they are produced coincident with the paper or board making process; and the coated paper or board is of exceptional quality and has great appearance value.

The plasticizing solution is, as set forth in the above mentioned patent, usually a water solution of starch or polyvinyl alcohol, or both. In the practice of the present invention, we employ the same types of plasticizing solutions and in the same way. The coating compositions consist essentially in a water suspension of suitable, usually mineral, coating substances of sufficient opacity and desirable color, and a binder which not only assists in the dispersion of the coating substances in the water vehicle, but also binds the coating substances together and to the web surfaces when the imprinted coating has been dried. The specific nature of the coating substances forms no limitation on this invention, and they may consist of or comprise any of those materials which have hitherto been used in the art for coating paper and board. Among other binders which may be employed in accordance with the above entitled patent for the coating composition, is starch. Very beautiful sheets having a soft matte finish are produced, but unless the aforesaid starchy binder is insolubilized, the sheets will not be resistant to wet rubbing.

In a copending application of Harry C. Fisher and Brainard E. Sooy, Serial No. 738,722, filed April 1, 1947, and entitled Improvements in Colored Coated Board, now Patent No. 2,515,340, there are described certain procedures for insolubilizing a starchy binder. One of these procedures involves the incorporation of a thermosetting resin in the coating composition, and the use of a catalyst for the resin in the plasticizing solution. A somewhat similar technique, namely the incorporation in the plasticizing solution of the acidic substances serving to insolubilize the casein binder of the coating, is not fully effective in the present invention to attain the purposes set forth above, although it may be employed in connection with the other steps hereinafter set forth for a specific purpose, if desired. To mix the acidic substance with a coating composition containing casein as a binder also will not attain the objects of this invention because the insolubilizing reaction will be accomplished prior to the time the web reaches the water finishing apparatus, especially since after the coating imprinting step, it is necessary to dry the coating to a relatively hard condition before calendering the web. In addition, mixing the insolubilizing substance with a casein-bearing coating composition prior to the time of the imposition of the composition on the web, results in a premature hardening of the composition in coating reservoirs and in picking of the coating on the imprinting rolls. Since, as will be explained later, we insolubilize surface layers only of the casein coating on the web, an equivalent amount of acidic substance added to the web coating mixture would be insufficient to insolubilize all of it, even if a coating mixture of usable properties remained, which it does not.

We have found that if the surface or surfaces of a web of paper or board are first plasticized, as hereinabove described, and then, during a persistence of the plasticizing effect, are coated by imprinting upon them a thin layer of coating composition containing, say, mineral coating substances and a casein binder, the coating

being then dried, it becomes possible to calender the coated stock and attain concurrently an insolubilization of the casein binder and waterproofing of the mineral coating and a very high degree of water finish of coated surface by imposing upon the coated surface or surfaces of the web on the finishing calender stacks, and by the usual water boxes, a water solution of alum or other suitable metallic salt or other acidic substances in lieu of the conventional water or water solution of starch or the like. If desired, the acidic substances can be dissolved in the water solution of starch or other compatible substance commonly used to water finish a paper surface on the calender stack and this will not seriously detract from the waterproofness of the insolubilized coating because the actual amount of starch thus imposed on the casein surface is very small. However, any advantage in the obtaining of special surface effects, as in the printing of the coated surface with inks, may be unimportant because similar printed effects can be obtained by changing the composition of the casein-mineral coating mixture.

By a thin imprinted coating, we mean a coating imprinted upon the plasticized surface and having a thickness, after calendering, of substantially a few tenths of one one-thousandth of an inch, or a coating having a dry weight lying in the range between substantially one and four pounds per thousand square feet of paper surface. The lower limit of substantially one pound dry weight represents the smallest amount of coating that can be imposed with complete coverage of the paper surface; the upper limit of substantially four pounds represents the largest amount of coating it is practical to imprint and yet obtain a commercially smooth coated surface. Naturally these quantities of coating are subject to considerable variations dictated by the quality of paper surface, of coating mixture and of imprinting machinery. The insolubilizing effect described herein is not limited to casein mineral coatings with this coverage and thickness. The preparation of the surface or surfaces of the web by the plasticizing treatment is the thing which enables us to produce a satisfactorily coated web with such very thin layers of coating composition; while the action on the water finishing calender stack hereinafter described is in turn dependent upon the treatment of a very thin layer of casein-bound mineral substance. However, we do not exclude the use of our insolubilizing and finishing process on coatings imposed on a plasticized paper surface by any method whatsoever providing that the coaction of smoothing and insolubilizing of the coating occurs during persistence of the plasticizing effect.

Referring to the drawing, we have shown a web 1 as it comes from the end of the paperboard machine passing through a breaker stack of calender rolls 2. A plasticizing solution, as hereinabove described, is applied to a surface or both surfaces of the web 1 by means of water boxes 3 and 4. A greater number of water boxes may be employed if desired. The mechanical work exerted on the surfaces of the web 1 by the calender rolls 2 in the presence of the plasticizing solution smooths and plasticizes surface portions of the web fitting them for the smooth reception of the imprinted coating. The coating is imprinted upon the web by means of imprinting rollers 6 or 7, or both, being fed with the coating composition 8 or 9 by transfer rolls 10 or 11. As above indicated, the imprinting is accomplished during a persistence of the plasticizing effect and usually before the complete elimination by evaporation of the water vehicle of the plasticizing solution. The coated web, passing beyond the imprinting rollers, is preferably carried around a series of heated drying rolls 12, 13 and 14 (which may be multiplied as desired to produce an adequate drying effect), and then is passed through a second set of calendering rolls 15, which is a water finishing calender stack and is provided with one or more water boxes 16 and 17. Additional calender stacks may be used.

It will be understood that the coated web reaching the water finishing calender stack is characterized by a casein binder or protein binder or binder component which is not insolubilized and which, while in a relatively dry condition, is capable of being softened by water. If in order to secure a water finish water alone were applied to the coated surface portions of the web on the calender stack 15 by means of the water boxes 16 and 17, no useful result would be attained since the binder of the coating would be so softened by the water

that the coating would pick off on the calender rolls, fouling them, redepositing the removed coating sporadically on the sheet surfaces and to all intents and purposes ruining the coated paper or board. We have discovered, however, that when, instead of water in the boxes 16 and 17, we employ a solution of acidic substance capable of insolubilizing the casein, a peculiar action results. Although a softening of the binder occurs due to the action of the water vehicle of the acidic solution, as demonstrated by the actual smoothed surface of coating produced, the insolubilizing proceeds at such a rate relative to the softening action as to prevent picking. The surface finishing action depends upon the employment of a layer of coating composition that is not too thick because, the insolubilizing effect being largely confined to the outer portion of the layer of coating, too thick a layer of coating leaves too much coating substance interior of the layer not insolubilized and still susceptible to softening by water. As hereinafter disclosed, the additional use of acidic substance in the plasticizing solution employed on the breaker stack of calenders insolubilizes that portion of the subsequently imposed layer of coating adjacent the paper surfaces, whereby a reduction in the amount of coating layer, not insolubilized, can be obtained. With very thin layers of coating, complete or substantially complete insolubilization of the entire layer of coating results. We have no reason to believe that the insolubilizing action is not coextensive with the actual penetration of the coating. The insolubilizing action does not prevent such a softening of the coating composition as will permit the attainment of a high degree of water finish, although we have found that a completion of the insolubilizing action prior to the water finishing treatment will not give a good water finish.

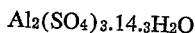
In the water boxes 16 and 17, we prefer to employ substantially a 4% solution of dry alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, or a solution in the range substantially from 2% to 6%. Expressed otherwise, the acidic solution employed should have strength substantially in the range from one-fifth to three-fifths normal. Considerable variation in the strength of the solution is permissible. The limitations are, first, that in applying the solution by means of the water boxes on the calender stack and in the light of the squeeze action of the calender rolls, each water box is capable of treating the coating with only a limited quantity of solution. While, depending upon the number of rolls in the calender stack, a plurality of boxes may be employed to treat the same coated surface of the web, there is a limit to the number of water boxes which can be so used (the web may become too dense or too damp), and the strength of the solution should be such that the web will be treated with an adequate amount of acidic substance to produce the desired resistance to wet rubbing. An excess amount of acidic substance does not seem to be harmful per se, since the solution is applied substantially at the nip of the rolls which do the calendering, and the softening action proceeds concurrently with the insolubilizing action. We have not encountered a condition in which an excess of the acidic substance produces so rapid an insolubilizing effect as to preclude the attainment of the objects of this invention. On the other hand, an excess of acidic substance over that required to produce wet rubbing resistance is undesirable from the cost standpoint, and in the case of acidic substances which have an initial odor but lose it upon drying, is undesirable for other reasons.

The imposition of acidic solution on the paper surface in such a way that it continually comes into contact with the highly finished steel rolls of the calender stack is repugnant to the established principles of the finishing art, since such solutions tend to attack, roughen and etch the roll surfaces. With solutions in the neighborhood of 4% strength of alum or its equivalent, the corrosion has not been prohibitive. Attack on the rolls may be further minimized by chromium plating them. Chemical buffers may also be employed in our invention as ingredients of the water finishing and insolubilizing solutions. The choice of chemical buffers is somewhat limited in the present invention being confined to substances which will not discolor the acidic solution and for that reason the coated surface. Thus, the metallic chromates, used as inhibitors, have limited usefulness in the acidic solution because they color it yellow. We have successfully employed formalin, adding this substance in the amount of one quart of commercial formalin to 250 gallons of in-

solubilizing solution. The formalin appears to have a measurable effect in retarding chemical attack on the calender stack rolls and has some effect at the same time in hardening the casein.

We have spoken generally of acidic substances as insolubilizers. There is a considerable variety of substances which will serve in this respect, some of which, without limitation, are: ferrous ammonium sulphate, aluminum chloride, potassium bisulphate, and ammonium molybdate as well as solutions of acids as such, including sulphuric, hydrochloric and the like.

Ordinary paper makers' alum (aluminum sulphate) is both inexpensive and entirely satisfactory, and we employ it in our commercial operations. The formula of paper makers' alum of 17% Al_2O_3 content is



We do not regard the specific nature of the acidic substance as a limitation on the invention.

In the practice of our invention the mineral coating mixture comprises the casein adhesive dissolved in water and thoroughly mixed with finely divided mineral matter such as clay. The mixture may contain minor proportions of other substances used to improve the coating. In making up a mixture granulated casein may be soaked in water, then brought into solution by the use of an alkaline substance such as sodium carbonate, sodium hydroxide, borax, ammonia and the like with gentle heat. A small amount of preservative, such as a chlorinated phenol, may be added to prevent the spoiling of the casein. Instead of or in addition to casein, other proteinaceous materials such as alpha protein from soya beans, animal glue, and the like can be employed; but as a practical matter it is generally preferred to use casein alone or as the greater part of the adhesive. A casein solution of pourable consistency is preferably first made up, and will usually contain around 15% of casein by weight. This is mixed with the mineral matter of the coating and the actual quantity of casein in the final casein mineral matter mixture will usually amount to substantially 14% to 16% of the dry mineral solids. These proportions may be departed from, as for example if greater or less porosity of coating is desired.

As indicated, the nature of the coating substance for which the casein is used as a binder does not form a limitation on the invention. An exemplary composition may comprise white coating clay alone or with any desired amount of a white opacifying pigment, such as titanium dioxide. It is within the scope of our invention to replace a white clay or other coating material wholly or in part with finely divided colored mineral or other pigments where a tinted or colored coating is desired.

The coating mixture, formed initially in a blade-type mixing device, usually can be improved by passing it through a disperser, ink grinding mill or the like. A small amount of dispersing and liquefying agent, such as tetrasodium pyrophosphate, sodium silicate, etc., may be incorporated into the mixture. Likewise, a small amount of bodying agent, such as sodium carboxymethyl cellulose, may be dissolved in the solution to improve the body and texture of the mixture. Yet again, a quantity of plasticizing substance, such as ammonium stearate, may be added to improve smoothness, flexibility and slip of the coating on the board.

It has hitherto been proposed in casein coating compositions to replace up to about one-half of the casein with the solids from a synthetic latex comprising an aqueous dispersion of a styrene-butadiene copolymer, vinyl resins, and the like, to give a rubbery feel, a smoother surface and improved folding characteristics. Such a resin will itself increase the water resistance of the clay coating mixture, but even with such compositions the calender treatment with a water solution of acidic substance, e. g. alum, will exercise its waterproofing and waterfinishing effect on the coated surface. In the claims which follow, the term "casein binder" is to be understood as relating to coating compositions of which so much of the adhesive or binder is casein or its proteinaceous equivalents as to require an insolubilizing treatment to attain water resistance and wet rubbing resistance.

Since the insolubilizing action of an acidic solution applied by means of the water boxes on a finishing stack of calenders extends inwardly from the outer surface of the coating layer and is largely concentrated to that outer surface of the coating, an enhanced degree of moisture

and wet rubbing resistance in the coating can frequently be attained by additionally insolubilizing the under portion of the coating layer, as by incorporating an acidic substance in the plasticizing solution applied to the paper web surface on the breaker stack of calenders. Care must be taken not to insolubilize the entire coating before it reaches the water finish calender stack. We ordinarily use the same concentration and kind of acid substance in the plasticizing solution as in the finishing solution but, of course, can vary it if desired for some particular purpose.

Our invention is not limited to white or to any particular tint or color of coated paper or board. Various colored effects may be attained, as for example, by incorporating a water soluble dye in the plasticizing solution or in the insolubilizing solution, or by incorporating a water soluble dye or water dispersible pigment in the coating composition. In any of such procedures, we have found that the insolubilizing of the casein binder of the coating serves to waterproof the coating per se but that its resistance to color bleeding is specific to the particular coloring or dyeing material used.

By the procedure herein outlined, we produce coated paperboard having a hard, glossy, smoothed, even surface finish excellently adapted to receive printing and in the case of the board, excellent for the conversion into cartons and containers.

Having thus described our invention in an exemplary embodiment, what we claim as new and desire to secure by Letters Patent is:

1. A process of manufacturing a web of coated paper or board which comprises applying to the surface of the web a plasticizable film forming water-borne substance chemically inert to the fibers of the web, and passing the web through a breaker stack of calender rolls to plastically smooth the treated surface, and during a persistence of the said plasticizing effect, imprinting thereon a thin layer of coating composition consisting essentially of mineral substance and protein binder in water, drying the web, and subjecting it to a water finishing treatment by passing it through a stack of metallic finishing calender rolls and applying to the treated surface of the web while passing through said stack a water solution of an insolubilizing substance for the said protein.

2. The process of claim 1 wherein the thickness of the calendered layer of dried insolubilized coating composition is substantially less than one one-thousandth of an inch.

3. The process of claim 1 wherein the coverage of dried coating composition is substantially one to four pounds solids per one thousand square feet of coated surface, and wherein the agent employed in water finishing is a solution of dried crystalline aluminum sulphate having a strength between 2 and 6 per cent by weight.

4. The process of claim 1 wherein the protein binder is casein.

5. The process of claim 1 wherein the binder comprises a blend of protein and resinous substance.

6. The process of claim 1 wherein the coverage of the imprinted layer of coating composition is substantially one to four pounds of dry solids per thousand square feet of coated surface, and wherein the agent employed in water finishing is a solution of acidic insolubilizing substance having a strength of between substantially one-fifth and three-fifths normal, and wherein said agent is applied to coated surface portions of said webs by means of a water box on a calender stack employed in said finishing treatment.

7. The process of claim 1 wherein the coverage of the imprinted layer of coating compositions is substantially one to four pounds dry solids per thousand square feet of coated surface, and wherein the agent employed in water finishing is a solution of acidic insolubilizing substance having a strength between substantially one-fifth and three-fifths normal, and wherein said agent is applied to coated surface portions of said webs by means of water boxes on said finishing stack of calender rolls, said agent being aluminum sulphate.

8. The process claimed in claim 7 including the step of admixing an acidic insolubilizing substance with the plasticizing solution used to treat the web surface before the protein-mineral coating mixture is imprinted thereon.

9. The process claimed in claim 8 in which, in the plasticizing solution the acidic insolubilizing substance has

a strength between substantially one-fifth and three-fifths normal.

10. The process claimed in claim 8 in which a water compatible coloring material forms an ingredient of one at least of the treatment substances applied to said web.

11. The process claimed in claim 7 in which an organic substance of film forming nature is included in the acidic insolubilizing solution applied to the outer coated surface of the web.

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