PROCESS FOR PRODUCING A HIGH GLOSS COATED PAPER

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This application is a continuation-in-part of copending application for "Coated Paper and Process for Making the Same," Serial No. 48,497, filed August 9, 1960, and now abandoned.

This invention relates to coated paper, and more particularly to a process especially adapted for imparting flatness, high gloss finishes, and improved printing qualities to coated paper.

The general objects of this invention are to provide a smooth and preferably high gloss finish for coated paper, to improve the printing qualities of such papers, and to accomplish these things at lower cost by reducing the number of steps required and by increasing the production speeds.

Hitherto, the desired quality has been available by the well known "cast coating" process, but cast coating is comparatively slow and costly and is not suitable for simultaneously finishing both sides of the paper. Conventionally coated and super-calendered papers may be produced at high speed with a consequently lower cost, but the rigorous calendering treatment drastically reduces their opacity, brightness and bulk, and the process, as performed, is not capable of rendering the surface sufficiently smooth and flat to compare with cast coated surfaces.

The process described in the Hart Patent No. 2,919,205 which we call "Thermofoil" avoids many of the disadvantages of calendering. In "Thermofoil" a gelled coating containing water is pressed against a hot roll (greater than 212° F.) and held against it as by using a relatively broad pressure nip for a sufficient length of time to drive the water from the surface of the coating into the body stock. This action brings about a very marked smoothing of the surface, but it too has certain disadvantages. The best results are obtained when the temperature is relatively high, but this limits the speed of operation because the coating will explode at such temperature if it is not held in the nip long enough for a major portion of the water at the surface of the coating to be driven inwardly toward the body stock. "Thermofoil" has other operational limitations which make it difficult to use in direct sequence with the paper machine. To some extent the present invention and "Thermofoil" overlap as regards their objects and even as to their results; however, the present invention is considerably more versatile and may be regarded generally as an improvement over "Thermofoil."

The present invention stems from our discovery that papers very closely approaching the quality of cast coated papers can be produced at high speed and without a hot finishing roll if four basic precautions are taken. First, the coating and body stock combination must be sufficiently in density and thickness that subsequent calendering will develop substantially no unevenness in density therein. Second, the coating must be essentially flat and smooth across its top surface. Third, the combination of adhesive binder and pigment in the coating must be relatively malleable. And fourth, the adhesive must be sufficiently set at the surface of the coating so that during roll finishing the coating does not stick to the roll.

However obvious these four precautions might seem at first glance, two factors relating to them should be considered. In the first place, prior to our discoveries described in our above said copending application, we know of no teaching that the simultaneous use of all four of these precautions is highly desirable. Secondly, the four said precautions have hitherto been extremely difficult, if not impossible, to obtain simultaneously with economically feasible adhesives in the coating such as casein, soy protein and the like. In the past, the required uniform density, smoothness and flatness have been available only by cast coating and blade coating techniques. Transfer roll coating leaves uneven stipple or "roll" marks on the paper, and "slip knife" coatings are not flat because they follow the contour of the body stock which is relatively uneven. Cast coating, of course, is too expensive, and blade coating, although economically feasible, has other serious drawbacks. With blade coating techniques the amount of coating to be applied to the paper is difficult to vary and control. Streaking is also a major problem with blade coating. Coatings contain on the other hand, even though blade coating can provide the required smoothness, flatness and uniform density, conventional coatings are not sufficiently malleable for any significant improvement over conventional high quality super-calendered papers without the "Thermofoil" hot roll treatment, unless they are wet enough to be essentially soft and flowable. However, when such coatings are that wet, they cannot be roll finished at high speeds because then they stick to the finishing roll.

Accordingly a more detailed object of our invention is to provide a process whereby the above-stated four basic precautions may be met simultaneously in the production of a coated sheet.

In our said prior and copending application, we showed one way of doing this. It comprises applying to a paper base an essentially smooth and uniformly dense coating containing mineral pigment and conventional casein (or similar protein). The uniform density and flatness are achieved by blade coating. After the base coating is applied, a top coating is applied containing as a binder a relatively malleable casein, which we refer to as SPC. (By this we mean casein or equivalent protein which has been peptized in a relatively concentrated solution of a salt slightly above the iso-electric point of the casein.) The resulting combination is an extremely smooth, uniformly dense product which may be calendered to a high finish approximating cast coated papers in many respects.

A second way of achieving these same basic conditions is to apply SPC to a paper base and while it is still extremely moist to squeeze it against a flat, smooth finishing surface. We will henceforth refer to this as giving the coated paper a "wet squeeze." It will be understood that the effect of the wet squeeze is to give the paper a flat surface without simultaneously compacting or densifying the paper non-uniformly beneath its surface as is the case with calendering. The disadvantage of wet squeezing in the past has been that coatings containing economically feasible adhesives, such as casein, have stuck to the finishing drum during wet squeezing to such a degree that high speed operations have been practically impossible. With our invention we have learned that if the wet SPC coating is treated with an acidic multivalent metal ion insolubilizer, such as alum, in a distance in advance of the wet squeeze to permit the alum to set up the surface of the coating, it may thereafter be finished by high speed wet squeezing without any tendency of sticking to the smoothing roll. The product resulting from the wet squeeze is to all intents and purposes, the same as the product we described in our above-stated copending application because the SPC coating is
malleable and having been given a wet squeeze, it is uniform in density and may be calendered thereafter to an extremely high smoothness and gloss approaching cast coating in appearance and quality. Even very light weight coatings give excellent results equaling in many cases the appearance of full weight conventional coatings.

A third way that the same basic conditions may be met is by applying to the paper a conventional coating composition containing mineral pigment and a proteinaceous adhesive therefor which has been pectinated in the conventional alkaline medium. We will refer to this as malleable as well. As we understand it, alkaline clay is actually chemically combined with the pectizing agent, and in the case where the agent is ammonia water, an ammonium caseinate is formed. If the alkaline casein coating is treated with an acid while it is in a sufficiently wet condition for the acid to invade the coating and essentially release the ammonium ion from the caseinate, we have found that the resulting casein is substantially malleable after drying in the same way that SPC is. In addition, we have found that if such an acid treated coating is also treated with alum, it may be "wet squeezed" without sticking to the roll, and will remain malleable thereafter.

Still another way to accomplish the above results is to apply a conventional alkaline casein coating to a paper base by means of conventional blade coating techniques, and thereafter to treat the coating with acid sufficiently to free the casein within the coating, and thereby render the coating sufficiently malleable for later roll treatment after it has been dried. In this latter case, as with the process described in our above copending application, the alum treatment is not necessary because the coating surface is dried, and this drying action in itself sets up the surface of the coating sufficiently to prevent the same from being wrinkled or finishing surface.

We wish it also to be understood that we consider the high speed "wet squeeze" technique disclosed herein to be novel and inventive in and of itself independently of later treatment which the paper may or may not receive, and we intend to claim it broadly herein. As we have stated above, blade coating has serious drawbacks in that it tends towards streaking and is limited as regards the quantity of coating which may be applied to the paper. However, it produces a far more uniform, flat and smooth surface than other economically equivalent techniques. By our wet squeeze technique, however, we achieve all of the benefits of blade coating without the disadvantages.

Controlling the quantity of coating applied is no problem in our process, because it can be done either by air knife or transfer roll techniques. Streaking is no problem because the smoothing is done by pressing the coating against a polished finishing drum. The only problem with our wet squeeze technique is to maintain malleability in the coating and to prevent it from sticking to the drum at high speed. We maintain the malleability by making sure that the protein adhesive is free in the coating. This is done by acid treatment of alkaline casein, or by pectinating the casein the first place in an acid medium (SPC). The sticking is prevented by treatment with a multivalent metal ion insolubilizer, but due to the low pH of the free casein, it does not readily ionize, and therefore, its cross linking tendency is inhibited. Thus malleability remains even after the anti-sticking treatment. These steps are carried out while the coating is wet sufficiently far in advance of the wet squeeze nip to set the surface of the coating up enough both to hold together and to release at high speed finishing conditions of, for instance, greater than 900 feet per minute. Since the smoothing is done with the coating in an extremely moist condition, the coating material flows laterally as may be required to accomplish the smoothing and the resultant product is not only flat and smooth superficially, but it is uniformly dense internally. These characteristics are highly beneficial and produce an extremely attractive printing surface.

Although we do not intend to limit the scope of this invention to any specific theoretical basis, we believe that the acid treatment we use represses ionization of the casein molecule and so inhibits the more complete cross linking of the protein which occurs when an alkaline caseinate is treated with a multivalent metal ion insolubilizer, such as alum. In this way the rigidity which results from the drying of caseinates especially multivalent metal caseinates is avoided while sufficient cohesiveness for high speed operation is attained. The surface is set up enough to avoid sticking to the smoothing roll. We believe also that the same mechanism takes place when SPC is used. In both processes there is present an acidic substance in proportion sufficient to insure that a substantial portion of the protein is at or near its isoelectric point. This results in maintaining the protein in its uncombined relatively insoluble, thermoplastic state thereby giving it the desired malleability. This is what we intend to convey herein when we use the term essentially "free" casein or protein.

The most readily apparent, and perhaps significant, features of our invention are the facts that we have provided for the first time a process by means of which coated paper may be finished with quality closely approaching cast coated quality at such high speeds and with sufficient simplicity of control of the process that the process may be placed in direct sequence with the papermaking machine. The economical advantages of our success in this achievement need no further elaboration.

Further objects and features of our invention will be understood and appreciated from the following detailed description of a preferred embodiment of our invention, selected for purposes of illustration, and shown in the accompanying drawings in which:

FIG. 1 is a flow diagram of an embodiment of our invention which involves in sequence with a paper machine, application of a conventional alkaline casein coating by means of a blade coater, followed by drying, subsequent application of an SPC coating by an air knife coater, drying and calendering; FIG. 2 is a flow diagram of an embodiment of our invention which involves in sequence with a paper machine, applying to the paper an SPC coating by means of an air knife coater, and while the coating is still wet passing it through an alum bath, subsequently wet squeezing and drying it and calendering it;

FIG. 3 is a flow diagram of an embodiment of our invention which involves in sequence with a paper machine, applying a conventional alkaline casein coating to the paper by means of an air knife coater, subsequently passing the paper while still wet through a bath of acid and insolubilizer and thereafter wet squeezing, drying and calendering the paper;

FIG. 4 is a flow diagram of an embodiment of our invention which involves in sequence with a paper machine, applying to the paper a conventional alkaline casein coating by means of a blade coater, subsequently passing the paper while still wet through an acid bath, drying the paper and calendering the same.

In carrying out the various embodiments of our invention, the flow diagrams of which appear in FIGS. 1-4, the paper is formed on a conventional paper machine and will usually have applied to it a size coat prior to any specific treatments discussed herein. A suitable body stock may comprise bleached chemical fibers including 40% soft wood and 60% hard wood fibers, and having a weight of 48 pounds per ream. It may also contain approximately 15% clay or carbonate filler having been retained in the sheet by the use of a manugulcan retention agent and sized by means of a small percentage of a ketene dimer.

The size coat may be applied by a squeeze roll coater or size press and includes a clear size solution which may contain one of several substances as follows: (a) starch
and water, (b) ammoniacal casein, (c) ammoniacal soy bean protein or the like. These clear size solutions contain about 8% solids in solution and are applied to the paper at a weight of about 1 pound per ream. We have also used a small amount of wax in these clear size solutions; i.e., 2 pounds of emulsified sperrnaceti wax to about 700 pounds of the above said starch or protein. Other waxes or equivalent materials are also suitable for increasing the water "build up" of the body stock when such is desirable. We have also used in place of the above said clear size solution a sizing composition comprising approximately 100 parts by weight of the above said starch or protein to about 50 parts by weight of mineral pigment such as clay or calcium carbonate, 35 parts by weight of starch or protein, and a small percentage of a ketene dimer. These latter ingredients are mixed in a slurry representing approximately 32% solids and applied to the paper at a weight of about 2 pounds per ream. Another sizing combination we have used with success comprises approximately 100 parts by weight of mineral pigment such as clay or calcium carbonate, 35 parts by weight of starch or protein, and a small percentage of a ketene dimer. These latter ingredients are mixed in a slurry representing approximately 32% solids and applied to the paper at a weight of about 4 pounds per ream (500 sheets, 25 x 38 inches in size).

Our process may be carried out in any one of four different ways which will be referred to respectively as Methods 1, 2, 3 and 4.

**METHOD #1**

Method #1 is depicted diagrammatically in FIG. 1 and is more specifically described in our above said pending application. Essentially Method #1 comprises applying a conventional alkaline casein coating to a paper web, drying it, thereafter applying an SPC coating over the conventional coating by means of an air knife coater (or transfer roll coater), drying the same, and subsequently calendering the same. In FIG. 1 we have shown the sequence for applying the coating to one side only of the web, but it will be understood that the coating may be applied to both sides simultaneously or in sequence by a duplication in reversal of the elements shown. This manner of showing a single coating is repeated throughout all of the embodiments described and in each case it will be understood that coatings may be duplicated on the opposite side of the sheet by additional equipment.

**Intermediate coat for Method #1**

The intermediate coating in Method #1 is applied by a trailing blade coater which results in an extremely flat and smooth surface having highly uniform water absorency. Coatings used with success with parts by weight dry are as follows: (Examples A-C)

**EXAMPLE A**

<table>
<thead>
<tr>
<th>Parts</th>
<th>Coating clay</th>
<th>Soy protein dispersed in water with ammonium hydroxide and urea</th>
<th>Styrene butadiene latex</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td></td>
<td>approximately 14</td>
<td>5</td>
</tr>
</tbody>
</table>

These ingredients were mixed in a water slurry to between 55-62% solids and applied to the paper at approximately 5 pounds per ream per side.

**EXAMPLE B**

<table>
<thead>
<tr>
<th>Parts</th>
<th>Premium English clay</th>
<th>High grade coating calcium carbonate</th>
<th>Soy protein dispersed in water with ammonium hydroxide and urea</th>
<th>Styrene butadiene latex (as above)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td></td>
<td></td>
<td>approximately 14</td>
<td>5</td>
</tr>
</tbody>
</table>

These ingredients were mixed in a water slurry to between 55-62% solids and applied to the paper at a weight of 5 pounds per ream per side.

**EXAMPLE C**

<table>
<thead>
<tr>
<th>Parts</th>
<th>Calcium carbonate</th>
<th>Conventional clay</th>
<th>Modified starch adhesive dispersed in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td></td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

These ingredients were likewise mixed in a water slurry to between 55-62% solids and applied to the paper at a weight of about 5 pounds per ream per side.

**The top coat for Method #1**

Turning now to the application of the SPC top coat in Method #1, we have employed the following examples D through F with success (parts by dry weight given):

**EXAMPLE D**

<table>
<thead>
<tr>
<th>Parts</th>
<th>Premium English clay</th>
<th>Casein (peptized in approximately 3 parts ammonium nitrate, 1½ parts dicyandiamide and 50 parts water)</th>
<th>Styrene butadiene latex</th>
<th>Tributylphosphate</th>
<th>Tallow soap</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td></td>
<td></td>
<td>4</td>
<td></td>
<td>½</td>
</tr>
</tbody>
</table>

The clp was dispersed in water with tetrasodium pyrophosphate (½ % on clay) as a dispersant giving a 50% solids slurry.

The casein was peptized by adding casein, soap and tributylphosphate to an aqueous solution of the ammonium nitrate and dicyandiamide and heating to 60-65° C. for 15 minutes until thoroughly dispersed. The clay slurry was then added to the peptized casein solution with vigorous agitation. Then the latex was added to the above mixture.

This composition had a pH of approximately 5.6. It was applied to the paper by an air knife coater at a weight of approximately 10 pounds per ream per side.

**EXAMPLE E**

The same ingredients as the above Example D were employed except that 20% of the clay was replaced by calcium carbonate. The coating procedures and weight of coating applied were the same. The latex ingredient appears to coat the calcium carbonate in such a way as to permit operation at a pH below 7.

**EXAMPLE F**

The same ingredients as Examples D and E next above were employed except that the casein proportion was reduced to 8 parts and the latex proportion was increased to 10 parts.

**The SPC casein in Method #1**

When we refer to SPC, we mean casein or equivalent protein which has been peptized in a relatively concentrated solution of a salt slightly above the iso-electric point of the casein. Suitable examples are as follows (Examples G through J):

**EXAMPLE G**

<table>
<thead>
<tr>
<th>Parts</th>
<th>Water (at 180° F.)</th>
<th>Casein (hydrochloric)</th>
<th>Ammonium nitrate (Aeropl.)</th>
<th>Dicyandiamide (Azile)</th>
<th>Tallow based soap</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td></td>
<td>1</td>
<td>12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These ingredients were agitated until the casein became dispersed. Thereafter they were introduced into the top coat slurry examples set forth above. Upon dilution in the said slurry, the casein precipitated, but in the presence of all these substances with continued agitation, an extremely fine dispersion resulted. The coating was thereafter both malleable, wet-rub resistant and capable of developing a high degree of strength.

**EXAMPLE H**

The ingredients of Example G next above were employed, but the dicyandiamide and soap were left out. It took longer to peptize the casein, but otherwise the adhesive functioned properly.
EXAMPLE 1

The ingredients of Example G next above were employed except that sodium nitrate was used instead of ammonium nitrate. A satisfactory adhesive for use in this invention resulted.

EXAMPLE J

Ammonium chloride was used in Example G next above in place of the ammonium nitrate. A satisfactory adhesive for use in this invention resulted.

SPC should not be limited to the foregoing specific examples because we have found that fluorides, iodides and bromides will work in addition to the nitrates and chlorides. Apparently all that is required is a stable soluble neutral to acidic salt of an alkali metal or ammonium having a monovalent anion, to have such a salt present in solution in a concentration of at least 3% and preferably about 4% to 8% and to subject the mixture to agitation. A possible theoretical explanation for the peptizing action is that the oppositely charged salt ions neutralize the electrostatic forces of the Zwitter ions in the protein molecule, and thereby disperse the casein without actually chemically reacting with it. But it is not necessary to limit the invention to any particular theoretical basis, and when we use the term SPC in the claim, we mean any casein or equivalent proteinaceous adhesive which has been peptized in a concentrated solution of a neutral to acidic salt of an alkali metal or ammonium having a monovalent anion.

Minor ingredients

In all of the above examples for the various coats, minor proportions of conventional anti-fogging agents, dyes, etc., were employed where appropriate and in accordance with well known procedures.

Gloss

When the papers coated in accordance with the foregoing examples were supercalendered, they developed an extremely flat, smooth and glossy finish better than conventional supercalendered letter press papers while at the same time being sufficiently strong for offset printing. The paper has a gloss higher than that of conventional supercalendered coated letter press papers which have a gloss of about 70 as measured by a Bausch & Lomb glossmeter. To the eye (which is even more accurate than the Bausch & Lomb glossmeter for high gloss comparison) the paper has a gloss approaching that of cast coated papers and is considerably more glossy than previously known conventionally calendered papers.

METHOD #2

Method #2 is depicted diagrammatically in FIG. 2 and may be characterized generally as applying an SPC coating to a paper base, subsequently passing the paper while still wet through an alum bath, thereafter wet squeezing the same, drying it and calendering it. The body stock of Method #1 may be employed and the coating composition may be applied to the paper by means of an air knife coater as shown in FIG. 2 or by a transfer roll coater. An example of a coating composition used for this purpose is as follows:

EXAMPLE K

<table>
<thead>
<tr>
<th>Parts</th>
<th>English clay (dispersed in 100 parts water by 0.5 part tetrasodium pyrophosphate)</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dicyandiamide</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Sodium nitrate</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Tallow soap</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Tributyl phosphate</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Styrene butadiene copolymer latex (Dow Latex 512R—dry basis)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Tributyl phosphate</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Dilution water was used to bring the solids to approximately 40%. This coating was applied at 6 pounds per ream (25' x 38"—500) for coating weight by an air knife coater to a 50 pounds per ream surface-sized body stock. Then the freshly coated web was passed through a pressure nip formed by two rolls, consisting of one polished chromium-plated roll and one rubber covered roll. The nip was continuously flooded by a 1-2% solution of papermaker's alum, Al₂(SO₄)₃·18H₂O. The temperature of the chromium surface which contacted the coated side of the web was 250° F. The force applied to give this wet squeeze was of the order of 500 pounds per linear inch. The paper web was run at speeds of 300 feet per minute, and was pulled off the drum with a moisture content that required further drying by conventional mechanical driers. The web was then given a peptizing treatment on a supercalender. The surface finish after calendering was in most respects comparable to that of a high quality coated paper having much higher coating weight.

The alum bath serves the purpose of setting up the coating so that it can be given a wet squeeze without adhering to the drum and for this reason a sufficient length of time is necessary for the reaction to take place prior to actual contact with the chromium surface roll. In the example described, the alum bath is located in the nip at the wet squeeze roll, but in FIG. 2 we have shown the alum bath being located in the nip for high-speed operation in which an appreciably greater length of time is needed for the reaction to take place. It will be understood that the reaction can take place at the wet squeeze nip if the alum bath is sufficiently deep and the throughput speed is slow enough. In addition, the concentration of the alum may be increased in order to speed up the reaction time in the nip. The temperature of 250° F, set forth above may be lowered to below the boiling point of water also for the purpose of increasing speed and excellent results are still obtained. Likewise the coating weights may be increased. Moreover, we have performed the process by drying the paper completely in contact with the chromium drum. Under certain circumstances, and particularly where the coating weights are heavier, for instance in the neighborhood of 10-12 pounds, greatly improved results have been attained. Speeds of greater than 600 E.P.M. have been obtained even with the alum bath at the wet squeeze nip.

METHOD #3

Method #3 is depicted diagrammatically in FIG. 3 and may be characterized generally as applying a conventional alkaline casein coating to the paper, subsequently and while the coating is still wet passing the coating through an acid and alum bath, wet squeezing the paper, drying it and calendering it. More specifically, we have carried out this embodiment with a conventional alkaline coating as follows:

EXAMPLE L

<table>
<thead>
<tr>
<th>Parts</th>
<th>Dry English clay as a slurry at 55%</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tetrasodium pyrophosphate dispersant</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Casein</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Dicyandiamide</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Ammonium hydroxide commercial concentrated (54% NH₄OH)</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>Soap—tallow based</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Dow Latex 512R</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Defoamer (tributylphosphate)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Together with water sufficient for 40% solids</td>
<td></td>
</tr>
</tbody>
</table>

This coating was prepared in a conventional manner in that the clay was dispersed with the tetrasodium pyrophosphate in water to make a 55% solids slurry. The casein, dicyandiamide, soap, tributylphosphate and ammonium hydroxide were added to water and the mixture heated under agitation until the casein had dispersed into a colloidal solution. The clay slurry and casein solution were
then mixed together, the latex emulsion added and the mixture stirred until a smooth homogeneous coating composition was obtained. After dilution to 40% solids, the coating composition was applied by an air knife coater, applying 10 pounds dry weight per ream to one side of a surface-sized paper web. The web, while wrapped tightly around a roll, was immediately run through an aqueous bath containing 2% formic acid and 2% paper makers' alum, immersing it so that the coated side only came in contact with the said setting solution. The web was then passed through the wet squeegee nip. The results of Method #3 are similar to the two methods previously described. The coating, after the wet squeegee, is extremely smooth and flat and sufficiently malleable to produce, by calendering alone, an extremely high finish comparable to cast coating in appearance and printing quality. Method #3 (also Method #4) may be carried out with other acids if their quantity is regulated so that the free acid does not remain in the sheet so as to weaken it. Conceptually any acid will work, but due to the practical difficulty of accurate regulation to avoid a free acid residue in the sheet, we prefer to use volatile acids such as formic or acetic acids. Also other multivalent metal ion insolvibilizers may be used (in Methods #2 and #3) of the same general nature as alum. Thus acidic salts of any metal other than alkali metals will work, for instance, iron, copper, nickel, chromium, tin, zinc, zirconium, aluminum, and the like. In Method #3, as with the other methods described, exact location of the application of the acid and alum is not critical. It may be applied at the wet squeegee nip if the process is proceeding slow enough for the reactions thereof to take place, or may be applied in advance of the wet squeegee nip when high speeds require such.

METHOD #4

Method #4 is depicted diagrammatically in FIG. 4 and may be characterized broadly as applying an alkaline casein coat to a paper base by means of a blade coater and subsequently treating the same with an acid bath so as to inhibit the cross linking tendency of the casein molecule, thereby drying the coating and calendering the same. The coating was formulated and the process was carried out in accordance with the following example:

**EXAMPLE M**

<table>
<thead>
<tr>
<th>Parts</th>
<th>100</th>
<th>12</th>
<th>2</th>
<th>5</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>English coating clay (air dry)</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>Casein dispersed in water with ammonia water</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dicyandiamide</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dow Latex 512R</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soap</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Dilution water was employed to reduce the solids content to 57%, and the coating was applied by an air-loaded flexible blade coater to a web of paper. The coated surface was immediately contacted by a 2% aqueous solution of formic acid which was then metered off by an air jet from an air knife after sufficient reaction had taken place. The acid-treated coated web was then dried in a conventional oven at 280°F. Supercalendering gave a superior result due to rendering, by acid treatment, the coating more moldable than when in the alkaline condition.

Since minor variations in the preferred embodiments herein described will be readily apparent to those skilled in the art, it is not our intention to confine the invention to the precise forms herein shown, but rather to limit it in terms of the appended claims.

Having thus described and disclosed preferred embodiments of our invention, what we claim as new and desire to secure by Letters Patent of the United States is:

1. A process for producing a high gloss coated paper comprising coating a uniformly dense cellulosic paper web with a flat smooth wet aqueous coating of a paper-coating-grade mineral pigment and a proteinaceous adhesive therefor which proteinaceous adhesive is in free-form and upon drying is malleable, drying said paper sufficiently to accept calendering and imparting gloss to the coated surface thereon by passage through a narrow roll-finishing nip, said proteinaceous adhesive being selected from the group consisting of casein and soy protein and said coating being a salt peptized protein-mineral pigment slurry prepared by admixing and agitating together in water said proteinaceous adhesive in acidic form and a soluble salt having a cation selected from the group consisting of the alkali metals and ammonium and a monovalent anion, the concentration of said salt in the mixture being in the range of 3 to 8 weight percent and the resulting mixture being maintained near the isoelectric point of said proteinaceous adhesive, and thereafter admixing therewith a slurry of said mineral pigment.

2. The process of claim 1 wherein said coating is applied by a trailing blade coater.

3. The process of claim 1 wherein said process is operated in direct sequence with a paper-making machine operating at speeds in excess of 600 feet per minute.

4. The process of claim 1 wherein said narrow roll finishing nip is one of a series of nips in a supercalender.

5. The process of claim 1 wherein said paper web is sized prior to the application of said coating.

6. The process of claim 1 wherein said paper web is first coated with a conventional alkaline protein-mineral pigment coating.

7. The process of claim 1 wherein said coating while still wet is treated with an aqueous solution of a salt of a multivalent metal ion followed by smoothing of the thus treated coating while still wet by pressing against a smooth finishing surface, the amount of said multivalent metal ion incorporated into said coating being only sufficient to prevent said coating from sticking to said finishing surface.

8. The process of claim 7 wherein said salt of a multivalent metal ion is papermaker's alum.

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