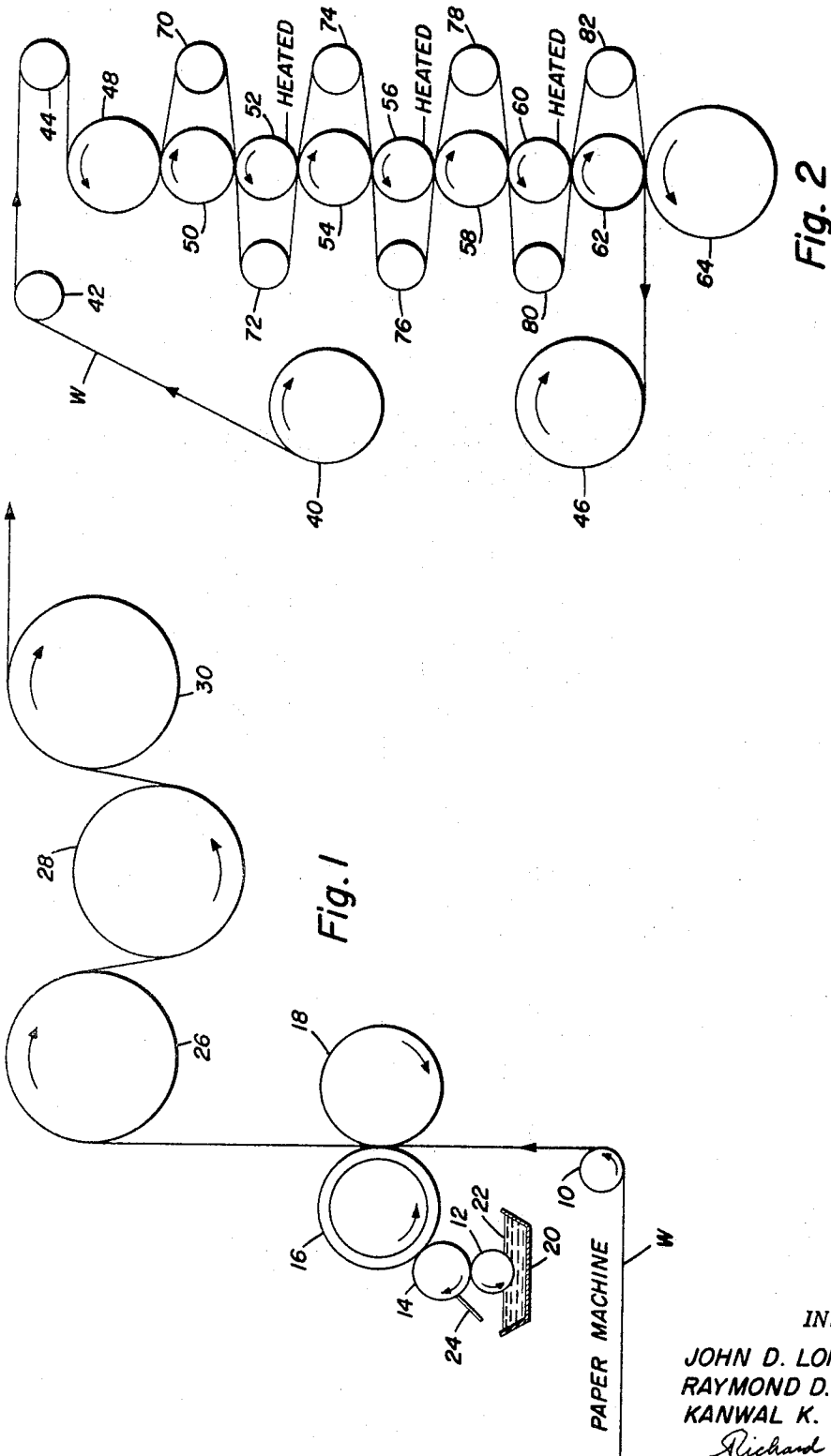


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 PREPARATION OF COATED PAPER HAVING HIGH GLOSS
 AND HIGH WET RUB RESISTANCE
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PREPARATION OF COATED PAPER HAVING HIGH GLOSS AND HIGH WET RUB RESISTANCE

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ABSTRACT OF THE DISCLOSURE

Coated paper, having a high gloss and having a wet rub resistance suitable for printing by offset lithography, is prepared by applying an alkaline coating containing starch and glyoxal to paper, drying the paper, and finishing the paper by passing it through at least one heated nip on a supercalender.

BRIEF SUMMARY OF THE INVENTION

This invention relates to paper and to a method of preparing paper having a coating thereon which contains starch as the binder or adhesive for the mineral pigment in the coating. It has long been known in the art that paper bearing a coating which contains casein as the binder for the mineral pigment can be printed by offset lithography because a casein coating has good wet rub resistance and is not washed from the paper during the printing operation. It has also been known that less expensive starch coated papers do not perform well when printed by offset lithography because starch coatings have little wet rub resistance and will pile when printed on an offset press. One method used to gain wet rub resistance is to cationize the starch, but this greatly increases the price of the starch. Another method has been to treat starch with a dialdehyde, such as glyoxal, in an acid medium and cure the glyoxal by passing the starch-glyoxal coated sheet over the conventional dryer drums found on a paper machine. This latter treatment has never been completely successful to the extent of providing a starch coated sheet which can be printed on an offset press. This is so because inks used in the printing of fine printing papers demand that the coating on the paper be alkaline in order to facilitate ink drying.

The art has also recognized the fact that if very high gloss is desired on a coated paper, the coating should be cast on a highly polished chromium drum, to provide a coated surface having a mirror finish. Those coated papers which are not cast coated are usually supercalendered to obtain a glossy finish, but the gloss, in the past, has not been as high as that of a cast coated paper.

We have discovered that the properties of excellent wet rub resistance and high gloss can be afforded to paper bearing an alkaline starch-mineral pigment-glyoxal coating if the coated paper, after being dried on the paper machine, is processed by passing it through a supercalender which contains at least one heated nip. The heat from the heated calender rolls further enhances the glyoxal-starch cross-linking reaction, to provide a wet rub resistance as good as the more expensive casein coated papers. That such cross-linking takes place to form a stronger adhesive for the coating is evidenced by the fact that wax pick, as measured by Dennison waxes, is at least about 2 numbers higher after the hot supercalender treatment than before it. Additionally, the heat from the heated calender rolls, unexpectedly, produces a glossy surface on the starch-mineral pigment-glyoxal coating that substantially resembles a cast coated sur-

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face. Paper, made according to the present invention, finds great utility as label paper because it exhibits high gloss, good wet rub resistance, and a varnish holdout superior to presently known label papers. This paper also finds great utility in the cigarette package industry where a washproof package is demanded so that coating will not come off the package when it is subjected to moisture in one form or another as the result of personal handling or accident.

The coating employed in the present invention comprises cooked starch, glyoxal, and mineral pigment. The starch may be oxidized or enzyme converted, but preferably is an ethylated starch. The mineral pigments may be any of the various pigments normally found in conventional paper coatings, such as kaolins, sulfates, or titanium dioxide. A small amount of butadiene styrene latex may be included in the coating to add adhesive strength to the coating.

The pH of the coating is preferably adjusted to about 7.0 to 7.5 in order to meet the requirements for best coating application and to provide the alkalinity needed to facilitate drying of the ink when the paper is printed. The selection of the alkali for pH adjustment is rather critical. If a volatile alkali, such as ammonium hydroxide, is used, a coating color pH of above 9.0 must be maintained since some of the ammonia evaporates when the coated paper is dried. However, at a pH of 9.0 or above, the efficiency of glyoxal to insolubilize starch is reduced greatly and the viscosity of the coating becomes so great (in excess of 500,000 centipoises, Brookfield, 20 r.p.m., 100° F.) that the coating cannot be handled. To overcome these problems, we have found the use of non-volatile alkalies to be best for pH adjustment. Sodium hydroxide has been found suitable for this purpose and, unexpectedly, the efficiency of glyoxal has been found to be higher at a fixed pH in the presence of sodium hydroxide than in the presence of ammonium hydroxide. The stability of sodium hydroxide is such that we have found that a coating, having a pH adjusted to 7.3 with sodium hydroxide, when applied to paper produces a sheet surface pH of about 7.4 as measured according to the G.P.O. Standard Test for Surface pH of Coated Lithographic Papers.

The coating is applied to a moving web of paper in known manner, such as by a conventional knurled roll coater. The coating is preferably applied at a coat weight varying from about 8 to 11 pounds of coating per side per ream of paper (500 sheets, 25 x 38 inches). The coated paper is then dried on the paper machine by conventional drying means, such as dryer drums heated with steam to a temperature between about 140° to 210° F.

The coated and dried paper is then supercalendered to further cure the glyoxal-starch coating and to gloss the coated surface of the paper. As is well known in the industry, a supercalender is a vertical stack of calender rolls constructed so that the stack is comprised of alternate chilled iron and soft rolls. The soft rolls generally are comprised of compressed cotton or paper, or they may be comprised of plastic materials. The paper is passed between the alternating hard and soft rolls to increase the smoothness and gloss of the paper. If the supercalender is a double finish stack, two soft or two hard rolls may be adjacent each other so that the web is treated on both sides. A double finish supercalender can be used in practicing the present invention.

In the process of this invention, at least one of the hard, metal rolls of the supercalender is heated with steam to a temperature between about 180° to 325° F., and preferably to a temperature between about 185° to 230° F. Any number of the metal rolls in the supercalender may be so heated. In actual practice, a nine

roll supercalender, containing five metal rolls alternating with four soft rolls, has been employed, and the three intermediate metal rolls have been steam heated. It is obvious that a supercalender may contain more or less than five metal and four soft rolls and that means other than steam may be employed to heat, either directly or indirectly, the desired number of metal rolls. The temperature to which the metal rolls are heated may vary as long as the rolls are hot enough to produce the desired glossing and curing effects but not so hot as to damage the paper. Also, for purposes of the present invention, the supercalender may be an integral part of the paper machine or, preferably, it may be an off-machine supercalender.

Paper made according to the preferred embodiment of this invention will exhibit a B & L gloss of about 85 or higher, a gloss usually found only on cast coated papers. It is believed that this unexpected high gloss is partly the result of flow of the coating which becomes plasticized when the coated paper passes through the heated nips formed by the supercalender rolls. It is also believed that the high gloss is due in part to the rather low ratio of parts adhesive to parts pigment in the coating. For example, the preferred coatings comprise, by weight, no more than about 15% starch on total pigment when about 13% glyoxal on starch is used.

BRIEF DESCRIPTION OF THE DRAWING

FIGURE 1 is a diagrammatic illustration of an embodiment of the present invention showing in sequence with a paper machine the application of a coating according to this invention, followed by drying of the coated paper by conventional dryer drums.

FIGURE 2 is a diagrammatic side view of a supercalender which includes heated metal rolls.

DETAILED DESCRIPTION

In the practice of the present invention, a traveling web of paper W, formed at the wet end of a paper machine and dried, passes under guide roll 10 and advances into a knurled roll coater comprised of furnish roll 12, knurled roll 14, applicator roll 16, and backing roll 18. Furnish roll 12 revolves in pan 20 which contains the starch-mineral pigment-glyoxal coating 22. Furnish roll 12 picks up coating 22 from the pan 20 and carries the coating on its periphery to the knurled roll 14. The knurled roll 14 is the metering device in this type of coater. Knurled roll 14 is an engraved roll, having numerous indentations in the form of cells or cups which become filled with the coating transferred from the furnish roll 12 to the knurled roll 14. Doctor blade 24 bears against knurled roll 14 and meters excess coating from the roll. The applicator roll 16 is a resilient roll, such as a rubber roll, and it lifts or pulls a portion of the coating from the cells in the knurled roll and then transfers the coating to the traveling web W, to coat the web W as it passes between the applicator roll 16 and the backing roll 18.

After passing through the knurled roll coater, the coated traveling web is dried by any suitable means, such as by passing partially around each of the dryer drums 26, 28, and 30. Drums 26, 28, and 30 are heated, preferably by steam, to temperatures between about 140° and 210° F. The coated and dried web of paper is then finished according to the present invention either by passing directly through a supercalender which is an integral part of the paper machine or by being wound up at the reel end of the paper machine and finished on an off-machine supercalender. The latter procedure is the preferred embodiment of the invention, but the invention is not limited thereto.

If an off-machine supercalender is employed, the coated and dried web of paper W is led from the unwinder roll 40 over guide rolls 42 and 44, and is fed into and through the supercalender stack and is rewound on roll 46, all as is shown in FIGURE 2. The supercalender, for purposes of

illustration, comprises metal rolls 48, 52, 56, 60, and 64 which are alternated with soft rolls 50, 54, 58, and 62. At least one of the metal rolls is heated to a temperature between about 180° and 325° F., and in the preferred embodiment where a nine roll supercalender is employed, as shown in FIGURE 2, three metal rolls 52, 56, and 60 are heated. These rolls are preferably heated by supplying their hollow interiors with steam, but other means for heating the rolls, directly or indirectly, may be used. Fly rolls 70, 72, 74, 76, 78, 80, and 82 are preferably used to help keep air out of the nips between calender rolls, but their use is not essential.

If the supercalender is an integral part of the paper machine, the coated and dried web may be led from the final paper machine dryer drums directly to the supercalender. In such an instance, the passage of the web through the supercalender may be identical to that shown in FIGURE 2, or the web may enter the supercalender by passing into a nip between two rolls, as, for example, between rolls 48 and 50.

The pressures to which the supercalender is loaded may be varied from about 1500 to 1900 pounds per lineal inch at the bottom nip, with the preferred pressures ranging from about 1550 to 1650 pounds per lineal inch at the bottom nip.

If the paper or paperboard web has been coated on only one side, the coated side of the web is preferably placed against the hard, metal rolls of the supercalender, i.e., the soft rolls press the coated surface of the web against the hard rolls as the web passes through the supercalender. If the web has been coated on both sides, the felt side of the web is preferably placed next to the hard rolls.

A better understanding of the invention will be apparent from the following detailed examples.

Examples 1 and 2

A coating, with parts by weight dry, was prepared as follows:

	Parts
Coating clay -----	3400
Titanium dioxide -----	200
Sodium hydroxide -----	8
Starch -----	325
Latex, butadiene-styrene -----	340
Glyoxal -----	43

The clay, titanium dioxide, and sodium hydroxide, along with soap and sodium hexametaphosphate as dispersants, were placed in a mixer. The starch, which was an ethylated starch, was cooked at 25% solids in water, at a temperature of about 195° F. for about 10 minutes. The cooked starch was added to the mixer and brought to a knead, with sufficient water, with the other ingredients for about 20 minutes, to form a clay-starch slurry. Water was then added to the slurry to adjust the solids content to about 62%, and then the latex was added and mixed into the slurry. Finally, the glyoxal (40% solution in water) was added to and mixed into the slurry, to form a paper coating. The temperature of the coating at this point was about 100° F., the pH was about 7.1, the Brookfield viscosity at 20 r.p.m. using a No. 5 spindle was 6075, and the solids content was about 61.6%.

The above coating was applied by a knurled roll coater to paper having a basis weight of about 50 pounds per ream at a coat weight of about 10.5 pounds per ream. The coated paper was dried by passing it over dryer drums heated with steam to about 140° to 180° F. The paper was taken from the paper machine and calendered on an off-machine supercalender.

Part of the coated paper was calendered with the supercalender in a normal condition in which none of metal calender rolls was purposely heated, and the rolls ran at a temperature of about 140° F. Part of the coated paper was calendered according to the present invention, with the three intermediate metal rolls of the super-

calender heated with 50 p.s.i. steam to elevated temperatures ranging from 206° to 220° F. In all instances, the coated side of the web was against the metal rolls of the supercalender and the supercalender was loaded to a pressure of about 1600 pounds per lineal inch at the bottom nip. The following data on the calendered paper was gathered:

	Example 1, cold calendered	Example 2, hot calendered
B & L gloss.....	70.0	90.0
B & L opacity.....	90.0	90.0
K & N ink receptivity.....	20.0	14.0
Gurley porosity.....	9,840	17,250
Bekk smoothness.....	1,250	2,560
Dennison wax pick.....	8	10
G. E. brightness.....	79.6	79.0

It can be seen that the starch-glyoxal-mineral pigment coating exhibited extremely high gloss values when the hot supercalender was employed. It is to be noted, for comparison purposes, that conventional washproof paper coated with a coating containing casein as the binder had a B & L gloss of only about 65 when cold supercalendered and a gloss of about 81 when hot supercalendered. It is apparent that the coating containing glyoxal gives an advantage in gloss, and that the glyoxal containing coating, when treated on a hot supercalender, gives an even higher gloss in the range of cast coated papers. Further, the improved wax pick indicates that additional cross-linking between the starch and glyoxal occurred as a result of the hot supercalendering treatment.

The coated paper from Example 2, which had been hot supercalendered, was tested at the end of five days for wet rub resistance. A sample of the paper having a size of about 4 inches in diameter was cut and securely placed in a disc on the revolving platform of a Taber Abraser. Ten milliliters of distilled water poured on the sample and the platform of the Taber instrument was motor driven to rotate the platform. A one-inch nylon brush contacted the surface of the sample as it was driven through 35 revolutions. The bristles of the brush were then washed over the specimen, and the disc and sample were drained into a container. The disc and sample were washed with enough water to give a 25 ml. volume in the container.

The diluted material was checked for percent transmittance on a Beckman Spectrophotometer having the wave length scale set at 450. The instrument was set to read 100% transmittance for distilled water. The diluted sample material had a reading of about 90%. Further tests have shown that casein coated washproof papers exhibit a transmittance of between about 90 and 100%. Conventional starch coated papers exhibit a zero transmittance, and papers coated with a starch-glyoxal coating but which are cold supercalendered, as in Example 1, exhibit a transmittance of only about 50% or below. It is apparent that the clearer the test sample, the higher the percent transmittance reading and the higher the wet rub resistance of the coated paper, i.e., a 100% transmittance indicates excellent wet rub resistance and a zero reading indicates very poor resistance. It can be seen from above that the product of the present invention has a wet rub resistance substantially equal to that of casein coated papers.

The paper from Example 2 was printed on an offset multicolored press, and the paper printed successfully without causing any piling of pigment on the press. A paper, without sufficient wet rub resistance, causes piling on the presses and makes an extended press run nearly impossible.

From the above description, it can be seen that a novel paper product has been produced. For the first time, a

product comprising a paper substrate bearing an alkaline coating containing starch and glyoxal has been produced which has a gloss in the cast coated range and a wet rub resistance substantially equivalent to paper coated with a casein-containing coating. Tests have shown that a B & L gloss of at least about 85 can be produced when paper is coated and treated in the manner according to the present invention.

While certain preferred embodiments of the invention have been illustrated and described in detail, it is to be understood that changes may be made therein and the invention practiced in other forms. It is not, therefore, our intention to limit the patent to the specific details described, but to cover the invention broadly in whatever form its principles may be utilized.

We claim:

1. In the method of producing paper which involves the steps of applying to at least one surface of a traveling web of paper an aqueous coating containing starch, mineral pigment, and glyoxal, drying the coated paper, and passing the coated paper between the rolls of a supercalender comprising alternate metal and soft rolls, said supercalender rolls being loaded to pressures between 1500-1900 pounds per lineal inch as measured at the bottom nip, the improvement for producing a high gloss on the coated surface of the paper and for producing a coated surface having a high wet rub resistance which comprises adjusting the pH of the coating to at least about 7.0 with a non-volatile alkali before the coating is applied to the traveling web, heating at least one of the metal rolls of the supercalender to a temperature between about 180° and 325° F., and pressing a coated surface of the web against the metal rolls of the supercalender with the soft rolls of the super calender.

2. The method according to claim 1 in which the non-volatile alkali is sodium hydroxide.

3. In the method of producing paper which involves the steps of applying to at least one surface of a traveling web of paper an aqueous coating comprising starch, a paper coating grade mineral pigment, and glyoxal, drying the coated paper, and passing the coated paper between the rolls of a supercalender comprising alternate metal and soft rolls, the improvement for producing a high gloss on the coated surface of the paper and for producing a coated surface having a high wet rub resistance which comprises adjusting the pH of the coating to at least about 7.0 with a non-volatile alkali before the coating is applied to the traveling web, heating to temperatures between about 185° to 230° F. a plurality of the metal rolls of the supercalender stack, said supercalender stack being loaded to pressures between about 1550 to 1650 pounds per lineal inch as measured at the bottom nip, and pressing a coated surface of the web against the metal rolls of the supercalender with the soft rolls of the supercalender.

4. The method according to claim 3 in which the non-volatile alkali is sodium hydroxide.

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