

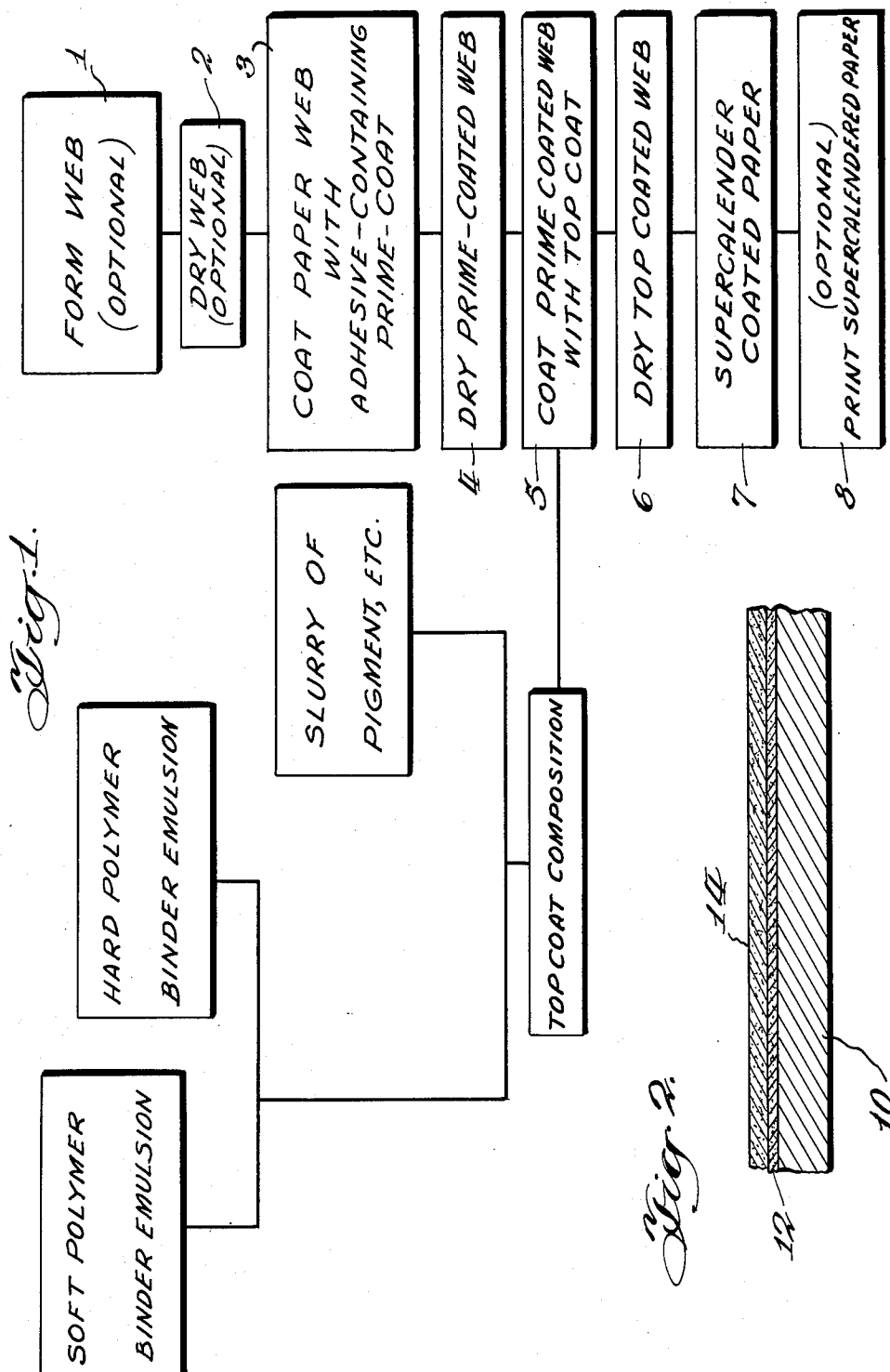
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MANUFACTURE OF CELLULOSIC PRODUCT

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MANUFACTURE OF CELLULOSIC PRODUCT
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This invention relates to the production of coated paper and particularly to the production of coated and supercalendered paper having high gloss characteristics and wherein the high gloss coating forms an overcoat over a prime coat on the paper web.

High gloss paper is conventionally produced by cast coating procedures; in this process the web with the coating composition thereon is directed over a highly polished drying drum, and the coated, dried paper acquires the high mirror finish of the drum. Such procedure is relatively costly as the speed of casting is quite slow. The procedure results, however, in smooth coatings having a gloss in the high 80's which is desirable for certain applications, particularly advertising material, brochures, and the like.

The usual machine produced coated papers are supercalendered after the coating is dried in order to produce a good level printing surface but such papers commonly lack the high gloss characteristics of cast coated papers even when such coatings include soft polymeric materials as a binder constituent.

One known coating procedure involves the use in emulsion form of a soft acrylic polymeric binder material including an acid which produces carboxylate groups; such soft polymeric materials include the acrylates of methyl, ethyl, propyl, and butyl, while the acids may be acrylic or methacrylic, for example. Such acid is present to the extent of about 4-7% by weight in the copolymer and is asserted to bond with cellulosic fibers. These copolymers are more than sufficiently soft to adequately provide for surrounding of pigment particles of a coating composition by the copolymer and, accordingly, hardening monomers, such as those of the lower alkyl methacrylates, may be included in minor proportion by weight. Such materials are described, for example, in United States Patent 2,790,735.

It has been found that interpolymers such as this coating tripolymer formed of hard, soft, and acid monomers is difficult to employ where it is desirable to achieve a high gloss and where the material is to pass through a hot supercalender. Such coating, when subjected to a hot calendering operation, tends to adhere to the calender and, accordingly, it is customary to employ room temperatures for these calendering operations. Even then the calendering operation is marginal. In such tripolymers the minimum film-forming temperature is usually maintained low to provide for ease of film forming at low temperature but this normally tends to thermoplasticize the coating to such a degree, that on calendering, the material becomes tacky. The coating is then spoiled.

I have found that, if a coating composition containing the usual pigment and other coating ingredients has incorporated therein a binder which includes a soft interpolymer or tripolymer as noted above, together with the addition of a large proportion of a hardness producing homopolymer, a high gloss coating composition operable on the supercalender at normal supercalendering temperatures is attained. Such coating, of itself, has relatively poor bonding properties to paper but is readily adhered to a prime coat carried on the web. The relationship of the hard homopolymer to the tripolymer by weight in the binder is critical within limits; the preferred binder contains about 40% by weight (dry weight

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basis) of the tripolymer combination and may vary from about 35-50%. Thus, the hardness producing homopolymer may vary from about 50-65% by weight in the binder of the top coating of the product. Above about 65% of the hardness producing homopolymer the binder does not coalesce properly in the wet coating as drying takes place. When the hard homopolymer is less than 50% by weight, sticking to a hot supercalender occurs.

Additionally, the soft interpolymer should have a second order transition temperature between about -10°C . and $+10^{\circ}\text{C}$. This transition temperature, termed the T_1 value, is found by plotting the modulus of rigidity against temperature; it is defined in Patent No. 2,790,735 in connection with suitable soft interpolymers and, as noted in that patent, a convenient method for determining modulus of rigidity and transition temperature is described by I. Williamson, British Plastics 23, 87-90, 102 (September 1950). The T_1 value here referred to is that determined at 300 kg./cm.².

The combination of soft interpolymer and homopolymer preferably exhibits a somewhat higher T_1 which may be as high as 40°C .

I have additionally found that the quality or rattle of the paper sheet or web may be improved by appropriate selection of the prime coat which should include adhesives such as starch or protein; any starch or protein in the top coat, however, causes a decrease in gloss.

The prime coat may be applied to the web by any of a number of conventional procedures. This prime coat penetrates the interstices of the web to some extent, bonds to the fibers, and provides a level surface for the top coat. The level surface of the prime coat provides for adequate flow of the top coat as the top coat is applied; additionally, the prime coat strengthens the web, tends to hold the subsequently applied top coat on the web surface, provides for excellent pick resistance of the coating from the web, and is itself preferably so formulated as to bond well to a pigment-containing top coat.

The absence of adhesives such as starch or protein in the top coat further leads to the attainment of high gloss on the supercalender; and the leveling and holdout action of the prime coat on the top coat provide for ease of finishing of the top coat at normal supercalender temperatures and pressures.

The top coat itself is applied to the prime coated web by conventional coating processes. Preferably, a reverse roll coater, an air knife, or the like is employed. Reverse roll coating in which a rotating roll or rod removes from the prime coated web an excess of top coat composition previously applied by an applicator is effective to provide an exceptionally fine coating lay with the top coat materials now described.

As already noted, the top coat includes polymer binder materials having widely differing characteristics. Most suitably, the polymer binder materials are combined in emulsion form to produce the composite binder which is then formulated with the remaining constituents of the top coat. The polymer materials in mixture form are compatible and display specific adhesion to prime coats employing pigments such as clay, titanium dioxide, calcium carbonate, hydrated alumina, and the like.

The soft monomer of the interpolymer is preferably an alkyl acrylate in which the alkyl group has from 1 to 4 carbon atoms; copolymerized with such a monomer may be a polymerizable unsaturated carboxylic acid and in which the unsaturation is a double bond, or ethylenic linkage; and a hardening monomer of an alkyl methacrylate in which the alkyl group may have from 1 to 4 carbon atoms.

Examples of the soft monomers are alkyl acrylates such as the esters of primary alcohols including methyl,

ethyl, propyl and butyl acrylates; and esters of secondary alkanols such as isopropyl acrylate and isobutyl acrylate.

Examples of mono-unsaturated ethylenic carboxylic acids are: acrylic acid, methacrylic acid, itaconic acid, aconitic acid, maleic acid, fumaric acid, and the like.

Examples of hardening monomers for use in the tri-polymer are: the alkyl methacrylates such as the methyl, ethyl, and propyl.

Typical interpolymer or copolymer systems of the first emulsion include:

	Percent
Ethyl acrylate.....	77
Methyl methacrylate.....	18
Methacrylic acid.....	5
$T_1=+6^{\circ}\text{C.}$	
Ethyl acrylate.....	92
Methyl methacrylate.....	4
Methacrylic acid.....	4
$T_1=-8^{\circ}\text{C.}$	
Ethyl acrylate.....	87
Methyl methacrylate.....	8
Methacrylic acid.....	5
$T_1=-3^{\circ}\text{C.}$	
Butyl acrylate.....	75
Acrylonitrile.....	22
Itaconic acid.....	3
$T_1=-10^{\circ}\text{C.}$	

Techniques for polymerizing the foregoing monomers into the copolymer are further illustrated in Patents Nos. 2,795,564; 2,760,886; 2,790,736; and 2,790,735. The copolymer dispersions which may contain 30-50% resin solids may be made by any of the known emulsion copolymerization procedures, preferably by mixing the several monomers in the desired proportions into an aqueous solution of an anionic or a nonionic dispersing or emulsifying agent. Specific examples of suitable anionic and nonionic emulsifying or dispersing agents and catalysts are set forth hereinafter and are designated in the patents mentioned above.

A second emulsion includes the polymerized hardening monomer. Such monomer preferably is methyl methacrylate. The solids content of such dispersion also is suitably in the range of 30-50% resin solids.

The two emulsions are mixed together to form the binder and then combined with other constituents of the top coating composition as described hereinafter.

In addition to hardness, the composite binder must impart other desirable characteristics to the coating such as a suitable minimum film-forming temperature, coalescence and drying at conventional temperatures utilized in papermaking and coating operations, a capacity for application at high speeds common to a papermaking machine, suitable viscosity at relatively high solids, and maximum bonding to the prime coated web; and it must itself bond well to the pigment particles of the top coating.

I have found that, if at least 50% by weight of the solids content of the binder mixture is produced from polymerized hardening monomer introduced by the second emulsion, the results desired may be achieved—that is, a paper gloss of at least 87 and a coating which may be easily supercalendered at normal temperatures and pressures. The polymerized hardening monomer may form 65% by weight of the binder; above about this limit difficulty is encountered with forming a coating composition film having continuity. Below about 50% there is a tendency of the coating to adhere to the supercalender. This results in an inferior coated surface. Along with this adhering, picking may occur on the supercalender. Optimum conditions for the high gloss supercalender coating are a combination of 60% of the polymerized hardened monomer and 40% by weight of the tripolymer.

It appears that combination in the emulsion form per-

mits the use of the relatively large quantity of the polymerized hardening monomer in the coating composition. This factor, and the effect of the underlying prime coat, provides for the achievement of the desired coating, comparable to a cast coated sheet.

The top coating composition, it has been found, is sensitive to the introduction, as already noted, of adhesive materials. In some instances, as in reverse roll coating operations, it is desirable to employ a coating of relatively high solids; a suspending or thickening agent is then employed—such should, however, be present only in trace quantity—0.1 to 0.3% on the weight of the pigment to avoid loss of gloss. Agents such as the water-sensitive gums including the gel forming synthetic hydrophilic colloids, typical of which is carboxypolyethylene, a vinyl polymer with active carboxyl groups and a commercial form of which is Carbopol 934, a synthetic polycarboxylic acid and a product of B. F. Goodrich Chemical Company; Acrysol thickeners such as an aqueous solution of sodium polyacrylate serve the purpose when introduced in about the same small proportion. The thickener must be such that it will maintain the ingredients of the coating composition suspended in stable condition under the action of high shearing stresses exerted by coating equipment during the formation of the coating and in its application to the prime coated web.

The invention will be more fully understood by reference to the following detailed description, examples, and accompanying drawings wherein:

FIG. 1 is a flow diagram illustrating the steps of producing coated paper in accordance with this invention; and

FIG. 2 is a diagrammatic and greatly enlarged representation of a section of coated paper of the present invention illustrating a web coated on one side.

The product is produced on a papermaking machine in accordance with a preferred embodiment of the invention as illustrated in the flow diagram, FIG. 1. While coating on one side only of the web is illustrated, it will be understood that it is conventional to apply coating to both sides of the paper. The web 10 (FIG. 2) is formed in conventional manner (step 1) and dried (step 2), and a prime coat 12 is applied (step 3) thereto. This prime coat penetrates the web interstices, and the adhesive of the prime coat bonds the particles of pigment to each other as well as to the cellulosic paper fibers. The prime coated web is then dried (step 4) in the continuous operation of the papermaking machine. Such operation is conventional. The formation of the web and drying of the web (steps 1 and 2) are optional in the process of the invention as they may take place independently of the coating steps.

It is also conventional to double coat webs on each side. The dried prime coated web in this instance has a second coat 14 applied thereto as illustrated by step 5. Such second coat might, of course, be applied on an off-the-machine coater after the prime coat has been dried, the web rolled up, and cooled.

As indicated in the drawing, the coating composition of step 5 includes an admixture of the soft interpolymer (tripolymer, for example) and the hardening homopolymer with other coating composition constituents. The top coat is dried on the prime coated web (step 6) and then is supercalendered (step 7). Such supercalendering is necessary to raise the gloss to desired levels.

The final step 8 of printing the supercalendered paper is optional as indicated in the drawing; printing paper, however, is the desired objective of the process of invention.

In the following examples which are illustrative of the present invention, the parts are by dry weight unless otherwise noted.

Example I

In a preferred specific embodiment the invention is practiced by treating a relatively heavy basis weight paper

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with a first coat, followed by the high gloss coating. The coating applications may be by on-or-off the machine coating equipment.

Thus, a web formed of 25% sulfite short fiber pulp, 35% short fiber kraft, and 40% of long fiber kraft pulp by weight may be formed on the conventional Fourdrinier wire, dried, and smoothed to form a 50-pound uncoated sheet or web. Speed of formation is about 1000 feet per minute.

This web is then coated on its opposed sides with a coating composition compounded by conventional methods and of a formulation such as:

Clay (premium predispersed kaolin)-----	100
Starch (white dextrin)-----	22
Sodium hexametaphosphate-----	0.1
Sodium hydroxide-----	0.1
Water to give solids of 55%.	

The viscosity of such coating is about 40 poises at 50° C. This coating composition is applied to the web by a roll coating procedure to provide 6-7 pounds coating on each side.

Other adhesives including protein may be substituted for the starch; such adhesive should demonstrate a specific adherence to cellulose.

This prime coat weight may be as low as 3.5 or 4 pounds per side in some applications but then the binder (starch) content of the coating is preferably increased to about 35% based on the weight of the clay. The important function of this base or prime coat is to penetrate the web and to provide a kind of tie ply to the paper web for the top coat as well as to impart strength to the sheet.

The base coated web is dried to a water content of 5% or less before application of the top coat. The following formulation may be employed for the top coat, the quantities being on a dry weight basis:

Clay (premium predispersed kaolin)-----	100
Titanium dioxide-----	20
Acrylic homopolymer (polymethyl methacrylate)-	11.2
Acrylic interpolymers-----	7.5
(Ethyl acrylate—83)	
(Methyl methacrylate—13)	
(Methacrylic acid—4) ($T_1 = +1$)	
Thickening agent (high mol. wgt. polyacrylic acid)-----	0.148
Sodium hexametaphosphate-----	0.16
Sodium hydroxide-----	0.11
Water sufficient to make solids of 64.9%.	
pH-----	7.5
Viscosity, 11.8 poises at 50° C. at 100 r.p.m. with #6 spindle (1180 centipoises).	
Coat weight, 13 pounds per side.	

The prime coated web to which this top coat is applied has a basis weight of about 64 pounds (25" x 38" x 500 sheets).

To prepare the top coat formulation, the thickener is dissolved in water to provide a clear solution; this solution is added to a kneader, and the dispersant, sodium hexametaphosphate, introduced. The pigment is then added to the solution to form a slurry while stirring at room temperature; the slurry is opaque and creamy and preferably as much as possible of the pigment (clay and titanium dioxide) is added at this time—usually enough to make the solids content of the slurry about 75% by weight. Sodium hydroxide in a solution form (1-5%) is then added to neutralize the mentioned thickener—this alkali addition helps to thicken the slurry and aids in drying of ink subsequently applied to the finished paper. The remaining water and pigment are then added and mixing continues for 20 to 30 minutes. The binder is then added; the binder is added in mixed form, that is, the binder is formulated by simply mixing physically together emulsions containing the relatively soft tripolymer and the polymerized hardening monomer; then the binder admixture is added to the main batch.

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The tripolymer aqueous dispersion is obtained by the emulsion polymerization of a mixture of 83 parts by weight of ethyl acrylate, 13 parts by weight of methyl methacrylate, and 4 parts of methacrylic acid in about 100 parts of water in the presence of about 6 parts of a *t*-octylphenoxypolyethoxy ethanol containing about 30 oxyethylene units and small amounts of ammonium persulfate and sodium hydrosulfite as catalyst. After polymerization, the pH is adjusted to about 6.5. The T_1 of such interpolymers is about 1° C. A similar commercial emulsion suitable for the purpose is provided as Rhoplex B-15 by Rohm & Haas Company, Washington Square, Philadelphia 5, Pennsylvania. Also, with the same top coat formulation given above except for an acrylic interpolymers of 85 parts of ethyl acrylate, 10 parts of methyl methacrylate and 5 parts of acrylic acid having a T_1 of about -5° C., similar results are obtained.

The dispersion of the hardening monomer is formed by the emulsion polymerization of about 55 parts by weight of methyl methacrylate in about 100 parts of water in the presence of about 5 parts of sodium lauryl sulfate and small amounts of potassium persulfate and sodium meta-bisulfite as catalyst. After polymerization, alkali, such as sodium hydroxide, is added to adjust the pH to about 8.5.

These two emulsions are mixed at room temperature and combined in the coating composition as described above.

The weight of top coating applied to each side may be about 13 pounds per side for the 50-pound uncoated sheet. The top coating is applied in excess to the web and subjected to the action of a rod rotating reversely to web movement to remove the excess while the web is supported on a backing roll.

Wetting of the prime coat by the aqueous top coat composition causes the two coatings to become intimately united.

The web with the prime and top coats thereon is dried at about 350° F. air temperature in a high velocity air dryer. Such drying is an important step to achieve adequate bonding of the top coating. The drying temperature may suitably be as low as 300° F. but should not exceed 450° F. air temperature. Too low a temperature of drying as well as too high a rate of drying at a high temperature tends to result in poor bonding of pigment in the top coating and of poor top coat bonding to the prime coat.

Drying may be carried out on a heated drum dryer. In such instance the temperature of the drum is suitably lower than that for the high velocity air dryer. Drum temperatures in the range of 250° F. to about 325° F. have been the most satisfactory.

This dried coated web is then supercalendered. The supercalender itself was conventional and comprised of alternate steel and paper filled rolls, 8 in number. Super-calendering temperature was about 140° F.; this super-calendering operation has a normal range of 140-160° F. Supercalendering pressure was also normal; the pressure range was about 1000 pounds per lineal inch and may range from as low as 350 pounds to 2000 pounds per lineal inch depending on calender roll diameter. With the coated web sheet moisture is not critical for super-calendering. A gloss of 87 or above can be obtained with less than 1% moisture in the sheet, but some moisture will increase gloss by a point or two. The sheet, however, is calendered without external moisture application.

The total basis weight of this sheet was about 90 pounds per ream (25" x 38" x 500 sheets).

Paper gloss after supercalendering was 89.2 on the wire and 89.9 on the felt side—using a 75° instrument. Such gloss meter is a conventional device commonly employed in gloss measurements.

Tests on the paper made as described gave optimum half-tone and letter press pick values.

Example II

The procedure of Example I is followed, substituting for the quantity of tripolymer 6.55 parts by weight and for the homopolymer 12.15 parts by weight on the dry weight basis. Thus the ratio is about 35 of the soft interpolpolymer to 65 of the homopolymer. The coated paper is essentially the same in quality as produced by Example I.

Example III

The procedure of Example I is followed, substituting for the quantity of interpolpolymer 8.42 parts by weight and for the homopolymer 10.28 parts by weight. This is about a 45 to 55 ratio. The quality of the coated paper is similar to that attained in accordance with Example I.

Example IV

The procedure of Example I is followed except that equal parts by weight of the interpolpolymer and homopolymer are employed, 9.35 by weight of each on a dry basis.

Example V

The procedure of Example I is followed except that the top coating composition is:

Clay (premium predispersed kaolin).....	100
Acrylic homopolymer (methyl methacrylate)....	10.8
Acrylic interpolpolymer (Example I).....	7.2
Thickening agent (carboxypolymethylene).....	0.148
Sodium hexametaphosphate.....	0.16
Sodium hydroxide.....	0.11
Water to make solids of 60.9%.	
Viscosity 2450 centipoises at 50° C.	
pH	6.9

The top coat weight per side is 13.3 pounds. The basis weight of such finished coated sheet is about 90 pounds.

Such sheet, when supercalendered at normal temperatures and pressures, had a paper gloss on each side of 87.4.

It will be noted that the effect of eliminating the titanium dioxide is to slightly reduce the gloss.

Example VI

The procedure of Example I is followed except that the top coating composition is:

Clay (premium predispersed kaolin)	90
Titanium dioxide	10
Rhoplex B-15—a 46% solids aqueous emulsion, a commercial product of Rohm & Haas—solids....	7.5
Rhoplex B-85—a 38% solids, a commercial product of Rohm & Haas—solids	7.5
Thickening agent (Carbopol 934) a synthetic polycarboxylic acid, a product of B. F. Goodrich Chemical Co.....	0.156
Sodium hexametaphosphate	0.1
Sodium hydroxide	0.062
Water to make solids of 65%.	
Viscosity, 1110 centipoises at 50° C.	
pH	6.7

The results of such top coat application are similar to those of Example I; on supercalendering gloss levels of 89-91 were obtained. Half-tone values and print values were optimum.

However, it is to be noted that less alkali was included and the composition was slightly acid—this leads to slower speed of ink drying. However, the commercial binder products work as well on the alkaline side when employed in the composition as indicated in the following example.

Example VII

The procedure of Example I is followed except that the top coating composition contains:

5 Clay (premium predispersed kaolin)	100
Rhoplex B-15—a 46% solids aqueous emulsion, a commercial product of Rohm & Haas Company—solids	10
Rhoplex B-85—a 38% solids aqueous emulsion—a commercial product of Rohm & Haas Company—solids	15
Thickening agent (Carbopol 934)	0.148
Sodium hexametaphosphate	0.10
Sodium hydroxide	0.11
15 Water to make solids of 65%.	
Viscosity, 1200 centipoises at 50° C.	
pH	7.5

Upon supercalendering a web with the above noted top coating at a top coating weight of about 10 pounds per side, a paper gloss of 89-90 is achieved.

In the finished coating the soft copolymer or interpolpolymer tends to surround the pigment particles and to retain them positioned with a degree of plasticity to give a smooth surface on supercalendering. The admixed hard polymer particles dispersed throughout the coating are of lesser effect in aiding the retention of the pigment particles, and the hard polymer would itself be quite ineffective as the sole binder material. However, when well dispersed in the coating, the hard particles, when present as described, achieve a high gloss and the overall sheet gloss is uniform and high, in excess of 87 as already noted. The flow of the softer, more thermoplastic material under supercalendering pressures and temperatures aids the attainment of this high uniform gloss; in the appropriate proportion the thermoplastic softer material is not adversely affected by the calender temperature and pressure, and picking at the calender is avoided.

Similarly, the picking factor is excellent when the paper is subjected to tacky letterpress or offset inks. The smooth gloss surface exhibits high ink holdout characteristic of coatings formulated with all soft copolymer or interpolpolymer as binder.

Print test results on the high gloss paper produced in accordance with the invention are comparable to results achieved with a high quality cast coated paper. Four-color reproductions, monotone half-tones and gloss instrument measurements made on commercially produced prints indicated that the paper quality is comparable for the cast coated and machine produced paper of this invention. Ink drying and coating pick even using inks which were quite tacky were entirely satisfactory. Registry in the printing operation was also good.

The specific embodiments described have all included a thickener in the top coating in what is substantially trace amounts. The thickener is employed for the purpose of achieving optimum rheological properties in the coating for blade, rod, and reverse roll coating applications. It may be eliminated when the coating is applied by other methods such as dipping or air knife.

The clay and other pigments may be any conventional material which is well dispersed in the composition to provide for adequate coating application, drying and supercalendering.

The web itself suitably has a basis weight (25" x 38" x 500 sheets) of at least 40 pounds uncoated and about 70 pounds coated; usually the upper limit of the coated sheet is a basis weight of about 120 pounds. Conventionally, the type of printing paper under consideration is coated on both sides and has a basis weight of 80 to about 100 pounds.

While the prime coat need not contain pigment, it is highly desirable that a considerable quantity of clay be present to aid in the attainment of a smooth prime coated surface. Clay in the top coating is essential. It is desirable that in each coating the clay form the dominant por-

tion by weight on a dry basis. Clay in the prime coat not only provides for increased adherence of the top coating, but the clay is receptive to the action of polar groups in the top coating to further improve adhesion.

It will be understood that this invention is susceptible to modification in order to adapt to different usages and conditions and, accordingly, it is desired to comprehend such modifications within the invention as may fall within the scope of the appended claims.

What is claimed is:

1. A coated and supercalendered printing paper having a paper gloss in excess of 87 and comprising a web of cellulosic fibers, a top coating on said web having the noted gloss characteristic, said top coating including a soft acrylic interpolymers having a specific adherence to polar groups and having a T_1 value of between about -10°C. and $+10^\circ\text{C.}$, a pigment, and methyl methacrylate physically admixed with the interpolymers and pigment and present in the top coating to at least the same extent by weight as the interpolymers, and a prime coat containing a major proportion by weight of a pigment and an adhesive which has a specific adherence to said web and to said top coat, said prime coat penetrating, coating and bonding the fibers of the web and providing a smooth surface to which the top coat is bonded, the top coat being thereby bonded to the web, said top coat being present on said web in a greater proportion by weight than said prime coat.

2. A coated and supercalendered paper product having a paper gloss in excess of 87 comprising a web of cellulosic fibers, a prime coat containing an adhesive having a specific adherence to said fibers, said prime coat penetrating and coating said web and bonding fibers of the web together, and a top coating on said prime coated web, said top coating comprising:

(a) a finely divided pigment having a predominant portion of clay; and

(b) a binder comprising for each 100 parts of clay between about 12 and 25 parts by weight of an admixture of

(1) an interpolymers having a T_1 value of between about -10°C. and $+10^\circ\text{C.}$ and which includes a water-insoluble copolymer of at least one lower alkyl acrylate in which the alkyl group has from 1 to 4 carbon atoms with an acid or amide to the extent of between about 0.5% to about 7.0% by weight and selected from the group consisting of methacrylic acid, acrylic acid, itaconic acid, maleic acid, fumaric acid, or amides of these acids and with a small proportion of an alkyl methacrylate; and

(2) a homopolymer which includes methyl methacrylate hardening monomer, said methyl methacrylate being present to the extent of between about 50 to 65% by weight of the admixture.

3. A method of producing a supercalendered coated paper having a paper gloss in excess of 87, the said method comprising the steps of:

(a) coating a relatively heavy basis weight web of cellulosic fibers with a prime coating composition containing an adhesive having a specific adherence to polar groups to impregnate and bind the fibers together and to provide a smooth coated surface on said web;

(b) drying the coated web;

(c) applying a top coating to said prime coating which is compatible with and bonds to the adhesive-containing prime coating;

(d) applying said top coating in the form of an aqueous dispersion containing a pigment and a binder to the extent of about 12 to 25% by weight of the pigment, said binder containing a physical admixture of

(1) an interpolymers which has adherence to cellulose and has a T_1 value of between about -10°C. and $+10^\circ\text{C.}$; and

(2) a methyl methacrylate homopolymer present to at least the same extent by weight as the interpolymers and which homopolymer normally has little adherence to cellulose;

(e) drying the web with the top coating thereon at a temperature in the range of about $225-450^\circ\text{F.}$; and

(f) supercalendering the web under elevated temperature to a paper gloss of at least 87.

4. A method of producing a supercalendered coated paper having a paper gloss in excess of 87, the said method comprising the steps of:

(a) coating a relatively heavy basis weight web of cellulosic fibers with a prime coating composition containing an adhesive having a specific adherence to polar groups to impregnate and bind the fibers together and to provide a smooth coated surface on said web;

(b) drying the coated web;

(c) applying a top coating to said prime coating which is compatible with and bonds to the adhesive-containing prime coating;

(d) applying said top coating in the form of an aqueous dispersion containing a pigment and a binder to the extent of about 12 to 25% by weight of the pigment, said binder containing a physical admixture of

(1) an interpolymers which has adherence to cellulose and has a T_1 value of between about -10°C. and $+10^\circ\text{C.}$; and

(2) a methyl methacrylate homopolymer present to at least the same extent by weight as the interpolymers and which homopolymer normally has little adherence to cellulose;

(e) drying the web with high velocity heated air at a temperature of between about $300-450^\circ\text{F.}$; and

(f) supercalendering the web under elevated temperature to a paper gloss of at least 87.

5. A method of producing a supercalendered coated paper having a paper gloss in excess of 87, the said method comprising the steps of:

(a) coating a relatively heavy basis weight web of cellulosic fibers with a prime coating composition containing an adhesive having a specific adherence to polar groups to impregnate and bind the fibers together and to provide a smooth coated surface on said web;

(b) drying the coated web;

(c) applying a top coating to said prime coating which is compatible with and bonds to the adhesive-containing prime coating;

(d) applying said top coating in the form of an aqueous dispersion containing a pigment and a binder to the extent of about 12 to 25% by weight of the pigment, said binder containing a physical admixture of

(1) an interpolymers which has adherence to cellulose and has a T_1 value of between about -10°C. and $+10^\circ\text{C.}$; and

(2) a methyl methacrylate homopolymer present to at least the same extent by weight as the interpolymers and which homopolymer normally has little adherence to cellulose;

(e) drum drying the web with the top coating thereon at a temperature in the range of about $250-325^\circ\text{F.}$; and

(f) supercalendering the web under elevated temperature to a paper gloss of at least 87.

6. A method of producing a supercalendered coated paper having a paper gloss in excess of 87, the said method comprising the steps of:

(a) coating a relatively heavy basis weight web of cellulosic fibers with a prime coating composition containing an adhesive having a specific adherence to polar groups to impregnate and bind the fibers together and to provide a smooth coated surface on said web;

(b) drying the coated web;

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- (c) applying a top coating to said prime coating which is compatible with and bonds to the adhesive-containing prime coating;
- (d) applying said top coating in the form of an aqueous dispersion containing a pigment and a binder to the extent of about 12 to 25% by weight of the pigment, said binder containing a physical admixture of
- (1) an interpolymers comprising about 83% by weight of ethyl acrylate, 13% by weight of methyl methacrylate, and about 4% of methacrylic acid, said interpolymers having a T_g value of about $+1^\circ\text{C}$.; and
 - (2) a methyl methacrylate homopolymer present to at least the same extent by weight as the interpolymers and which homopolymer normally has little adherence to cellulose;

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- (e) drying the web with the top coating thereon at a temperature in the range of about $225-450^\circ\text{F}$.; and
- (f) supercalendering the web under elevated temperature to a paper gloss of at least 87.

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