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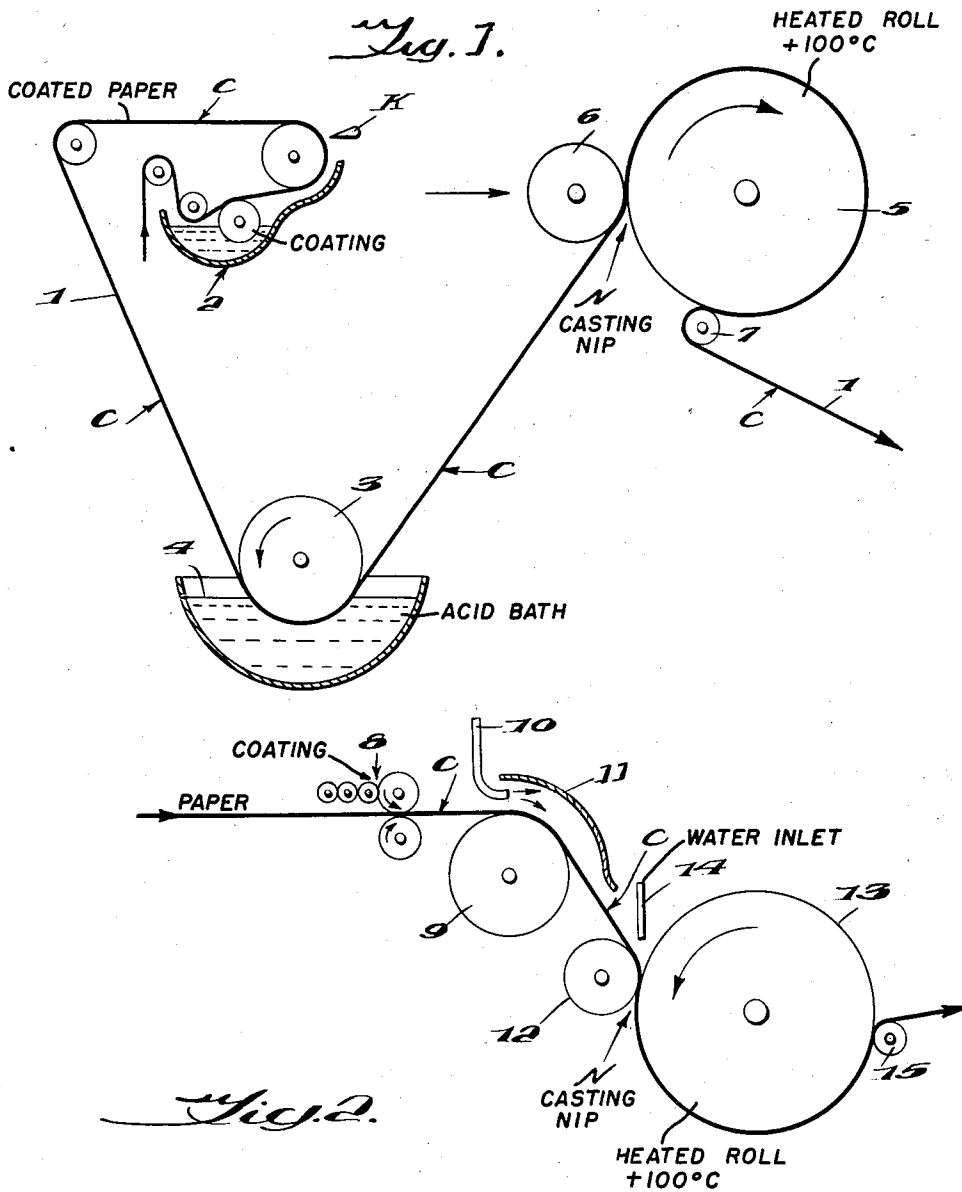
R. T. HART

2,919,205

PROCESS FOR FINISHING COATED PAPER

Filed Sept. 18, 1956

3 Sheets-Sheet 1



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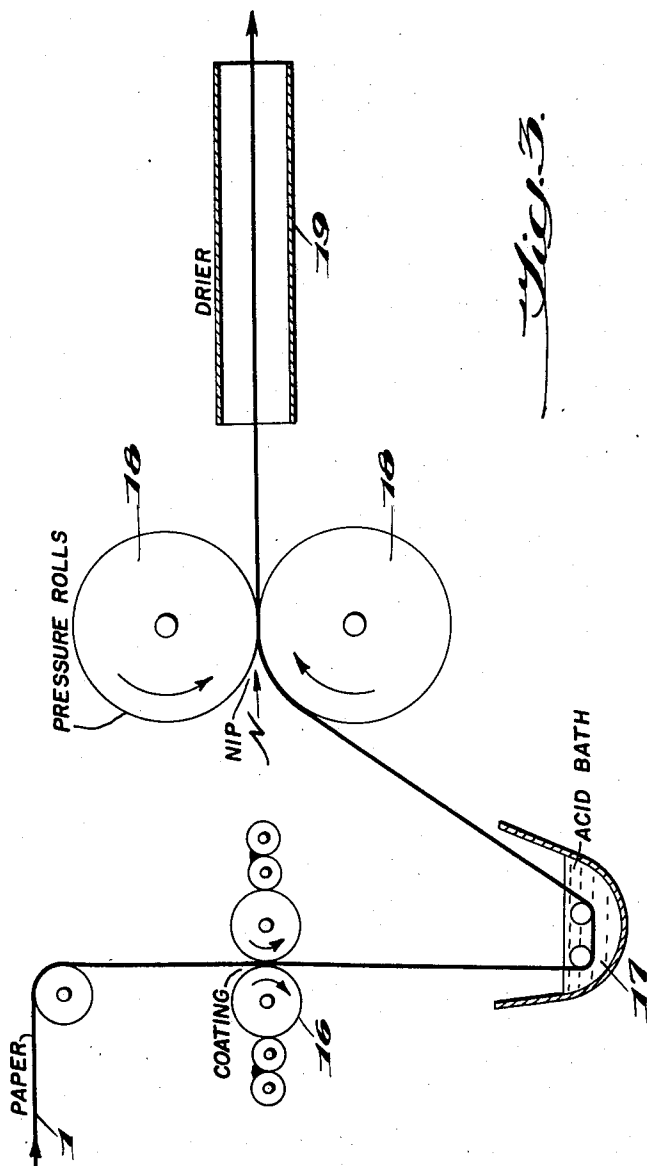


Fig. 3.

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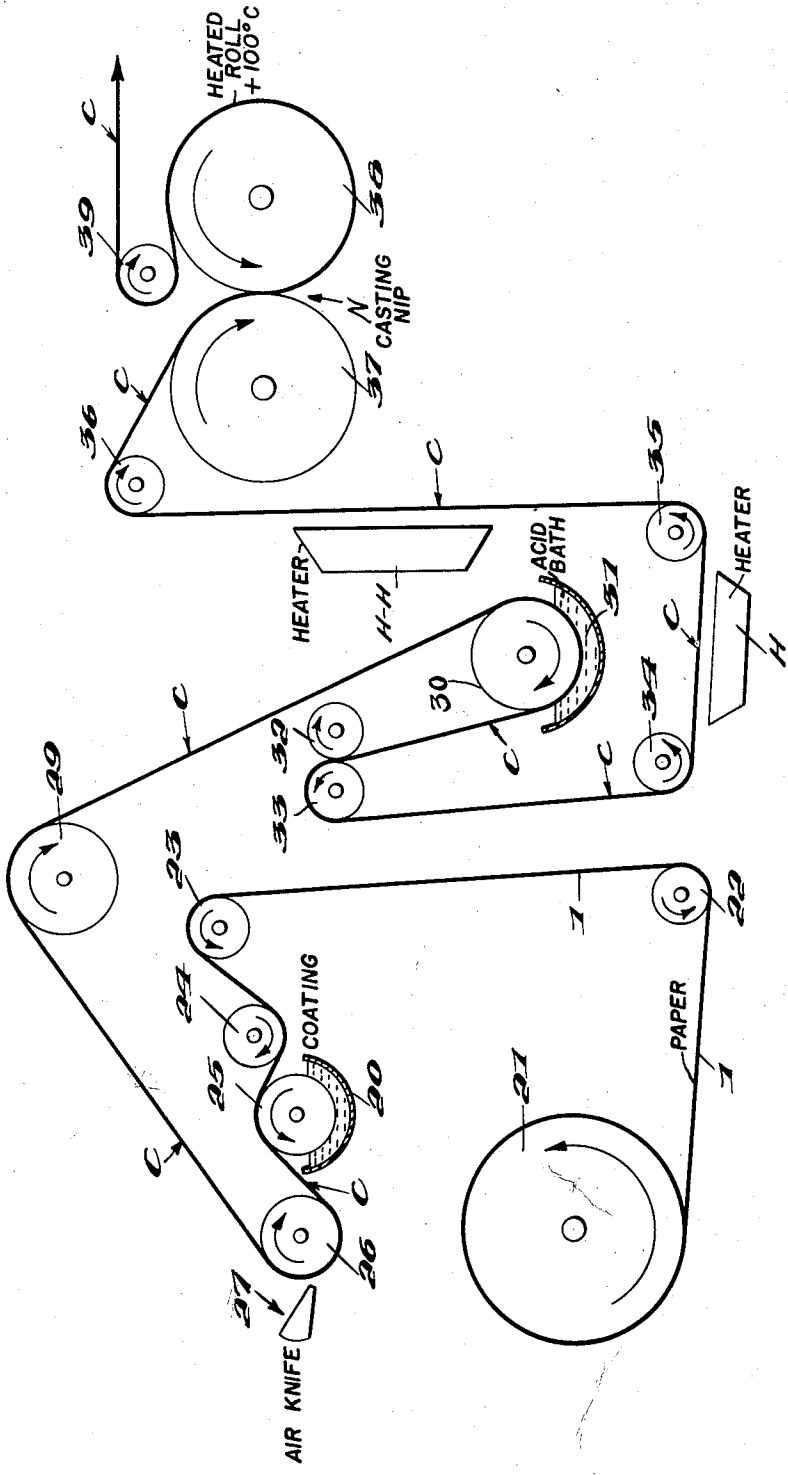
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Fig. 4.



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PROCESS FOR FINISHING COATED PAPER

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13 Claims. (Cl. 117—64)

This invention relates generally to the manufacture of coating compositions and coated paper, and particularly to the manufacture of a mineral-coated paper which optionally has a protein adhesive, but without being limited to any specific adhesive. As one aspect of the invention in making a coated paper, a finishing roll or drum is used, said roll or drum being kept above normal room temperature, to serve as a drying roll. The finishing roll has a highly polished metal surface. In some cases, the finishing roll is maintained at a temperature above 100° C. in an atmosphere of air which is at normal pressure of about 760 mm. of mercury, so that the water in the aqueous coating of the paper web is changed to steam by close contact with the hot roll. In some cases, there is a violent evolution of steam from the aqueous coating, and such violent evolution of steam would disrupt a layer of ordinary fluid aqueous mineral-coating. According to this invention, the aqueous coating, at the time of its contact with the hot roll, is sufficiently coherent so that it is not disrupted by the violent evolution of steam. In order to provide such coherence, the initial aqueous, mineral-coating may be of the usual low-coherent type, and such initial coating may be gelled to provide the necessary coherence, prior to contacting said coating with the finishing roll.

The term "drum-finished" or "roll-finished" paper includes cast-surfaced coated paper, but also includes coated paper which is not cast-surfaced coated paper. When coated paper is made by the cast-surfaced coating method, the wet mineral coating has initial low coherence. While the wet mineral-coating is in said initial low state of coherence, said wet mineral-coating is applied, in the old cast-surfaced coating method, to a hot and revolving casting-drum, thus evaporating the water from the coating and paper web to about 5% by weight of the coated paper, without any longitudinal or lateral slip between the casting-drum and the coated paper web. The drying of the coated paper web to about 5% of moisture, is evidenced by a sudden and sharp lateral contraction of the coated paper web relative to the drum in a direction parallel to the axis of the drum. This sharp lateral contraction is often evidenced by a sharp, popping sound, and such sharp lateral contraction is one distinguishing characteristic of cast-coating. Also as far as I know, the casting-drum in the cast-coating method has always been kept at a temperature below 100° C., as at 85°–90° C., and there has been a long arc of contact between the casting-drum and the coated web, so that the water vapor was gently evolved and could escape gradually through the paper web, without disrupting the mineral coating. Such drying temperature below 100° C., has been another characteristic of cast-surfaced coating.

Drum-finishing or roll-finishing is not to be confused with a process in which a layer of wet coating is brought into contact with a deformable surface such as a thick layer of deformable or flowable grease carried by a support.

Ordinarily, a chromium finishing surface is covered by

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an extremely thin, non-liquid film of oil or grease adsorbed from the atmosphere. This film may be a factor in the easy release of the drum-finished coated paper from the chromium surface. To be sure that the film will not be worn away during continuous running it is sometimes found advantageous to provide a small quantity of soap or of oil in the paper-coating or to apply a dilute soap solution to the chromium surface. The very thin adsorbed film is very different in its action from a thick liquid oil or grease film.

According to an aspect of the present invention, as later explained, the original aqueous coating mixture may be gelled by means of an aqueous solution of a gelling agent. In such case, the paper web and its coating layer may be acidic at the finishing roll. In such case, the paper web shrinks laterally while the coating is in contact with the finishing roll, so that the process is not cast-coating and the resultant coated paper is not cast-coated or cast-surfaced coated paper.

In another case, the paper web and its coating may be alkaline while in contact with the finishing drum. In such case, if there is sufficient alkalinity, the coated web will not slip relative to the finishing roll until the coated web is substantially dry, and the process is cast-coating. Thus, the paper body stock may be alkaline and the acidic gelling agent may be formic acid, which has about the same boiling point as water. In such case, the formic acid may be evaporated in or close to the nip, and there may be sufficient reserve alkalinity in the paper base of the coated web to result in cast-coating.

In either case, whether the process is or is not cast-coating, I may use a finishing-roll which is kept at a temperature above 100° C., as 120° C.–150° C., which is wholly novel.

As later more fully disclosed, the original aqueous coating mixture, in addition to casein or other organic adhesive, may include a metal compound, complex, or chelate, which is decomposed by an acidic agent. However, in some cases, the original aqueous mineral-coating mixture may be free from such metal complex, and may include casein or other protein adhesive or other adhesive which is dispersible in alkaline water. In such case, I can use an acidic agent to regenerate the dispersed adhesive into original water-insoluble or water-non-dispersible state, and use a finishing-roll which is heated above 100° C., as 120° C. If the metal complex is omitted, the temperature of the finishing roll is usually lower than if such metal complex is used.

Thus, one object of the invention is to effect evaporation of water from a wet coated web by heating said web above 100° C., while under pressure and then releasing said pressure to permit rapid vaporization of said water.

Another object is to produce gelling or a substantial increase in cohesiveness of a wet layer of aqueous mineral-coating composition upon a supporting paper web, prior to completing the drying thereof, by chemical reaction upon an organic adhesive material contained in said coating composition.

Another object is to produce mineral-coated paper by drying the coating at a temperature substantially above 100° C.

Another object is to produce mineral-coated paper with a surface which is not a mirror-image of the surface against which it is finished.

Another object is to provide a process of producing coated paper by bringing the wet coating on a paper web into adherent contact with a finishing surface and thereafter forcibly removing the coated paper from the finishing surface before the coating is substantially dry.

Another object is to produce gelling of a layer of aqueous coating composition on a paper web to such a degree

that the said coating will not be liquefied by subsequent heating. Other objects of the invention are later stated herein.

Ordinarily, when a wet web of paper is passed around a drying cylinder or drum heated above 100° C., a layer of steam forms between said drum and said wet web, preventing absolute contact of the two. Up to the time that substantially all the water has been evaporated from the web, the temperature of the web itself normally never rises materially above 100° C. Consequently, even when a very hot drum is used, it normally takes a considerable length of time to dry a wet web of paper.

A way has now been found to hasten the drying of wet paper webs. The wet web is pressed by means of an impervious backing means against a heated surface having a temperature substantially above 100° C. e.g. 120-150° C., the external pressure applied being greater than the pressure of steam at the temperature of said heated surface. In consequence the entire web may be heated substantially to the temperature of said heated surface. When the heated web is thereafter exposed to reduced, e.g. atmospheric, pressure a large portion of the water vaporizes practically instantaneously. If the water is a minor component of the web, as it is in the case of coated paper, substantially all the water may almost instantaneously vaporize into steam.

In the production of mineral-coated paper, an aqueous composition containing mineral pigment, adhesive matter, and a considerable proportion, often over 50%, of water is applied to the surface of a paper web or base. The layer of coating when first applied may be quite fluid, and in any case lacks any substantial degree of cohesiveness. In most cases before the coated surface can be touched, the layer of coating must become set or firm enough to withstand contact with other objects without being marked or marred by such contact. Ordinarily, setting or firming of the coating layer is accomplished by removal of water from the coating, as by absorption thereof into the paper base, or by evaporation into the surrounding atmosphere or both.

Thus, in the production of two-side-coated paper on the usual converting type of paper-coating machines it is customary to float the freshly coated paper, for a considerable distance, upon jets of air which are directed against the under side of the coated web, in order to allow the coating to become set or firm enough to permit contact with some mechanical conveyor without being damaged thereby. Obviously such procedure is bound to impose a severe limitation upon the speed at which such coated paper can be produced.

When "machine-coated" paper is made and coated in a single continuous process on a papermaking machine, the speed must be relatively high and the coated web must come into contact with the first of a series of drying cylinders or drums within a short time after the coating is applied to the web. Consequently, in machine-coating, special precautions must normally be taken to ensure rapid setting of the coating layer. Generally an absorptive paper base is used and it is coated with a coating composition of less than 50% water content. As a result, enough water is quickly absorbed from the coating by the absorptive paper base, so that the coated paper can in a short time be safely brought into contact with the drying cylinders. Nevertheless in order to avoid troublesome sticking of the coating to the first few drying cylinders, it is customary to keep those cylinders at a temperature only slightly above room temperature, so that in fact those cylinders have little or no effect in evaporating water from the coated paper web.

The one instance where the surface of the coating has been not only permitted but has been required to come into contact with a solid object, while still in a fluid or very wet condition, has been the production of cast-surfaced mineral-coated paper. In making such paper the layer of coating upon a paper web, while still very wet

either from water originally contained in the coating composition or from aqueous liquid subsequently applied thereto, is pressed into intimate contact with a heated polished finishing surface such as a chromium-plated casting cylinder or drum. As above noted the wet surface of the coating adheres to the polished finishing surface of the casting-drum and holds the web in non-slipping contact therewith until the coating is substantially dry, whereupon the contractile stresses set up in the web by drying become sufficiently great to cause the substantially dry web to release itself from the finishing surface by a sharp lateral contraction. All evaporation occurring while the paper is in such contact obviously must take place from the reverse side of the web and such evaporation is slow because it has hitherto always been found infeasible to operate with a finishing surface having its temperature as high as 100° C. For, it has been found that when a layer of fluid coating composition having normal cohesiveness is brought against a surface heated to 100° C. or higher the resulting rapid evolution of steam converts the layer of coating largely to a froth-like condition and spoils the product.

It has now been found, as one expedient, that a layer of fluid coating on a paper web can, by suitable chemical action, be gelled or converted to a condition of very substantial cohesiveness while still containing a good proportion of water. After being gelled the layer of coating can, while still wet, be brought into contact with solid objects without being damaged, and it can be dried at a higher temperature than is suitable for the non-gelled or fluid initial coating layer. Such gelation of the wet layer of coating is advantageous in each of the three categories of machine-coating, conversion coating, and roll-finished coating, which roll-finished coating, as above mentioned, may or may not be cast-surfaced coating.

In general, it may be said that gelation of a layer of aqueous coating composition containing an adhesive on a paper web, may be brought about by the inclusion in the coating composition of a complex metal compound which is not reactive with the adhesive, and reacting said complex compound in situ to produce a substance which is capable of causing gelation of said adhesive.

After the coating layer has been gelled, even though it still remains very wet, it can stand a considerable amount of abuse without being damaged thereby. For instance, it can come into contact with rolls or other mechanical conveyors, or it can be dried against drying surfaces having temperatures considerably higher than can be used when the coating has not been gelled. As a consequence the time required for drying can be materially decreased.

Whereas, as has been pointed out previously, in the old and conventional processes of making cast-surfaced coated papers it has been found necessary to keep the temperature of the finishing surface below 100° C. in order to avoid spoiling the coating, when a gelled coating is used, the wet coating can be pressed against a drum or roll having a temperature in the range of 120-150° C. The coated face of the wet web is pressed against the finishing surface by a backing roll, the pressure being higher than the steam pressure corresponding to the temperature of the finishing surface. In the pressure nip, the whole coated web may become heated to a temperature above 100° C. and approaching that of the roll or drum. As the coated web emerges from the nip a large portion of the water contained therein practically instantaneously vaporizes into steam, i.e. substantially all the water in many cases when the water content is relatively low. If some water is left after the initial instantaneous or explosive vaporization, it quickly evaporates at the high temperatures to which it is exposed. As a result it is found possible, when using a gelled coating as described, to produce high-quality roll-finished coated paper at the same speed on a finishing roll 30 inches in diameter, as has been possible under previous conventional

cast-coating methods, when using a finishing drum about 12 feet in diameter. Conversely by using a finishing drum larger than 30 inches in diameter, higher production speeds can be attained than have been feasible in the past. Hence the invention makes possible an important reduction in the cost of producing roll-finished coated paper having a surface gloss which is substantially equal to that of the finishing surface against which it is dried. Such paper is substantially identical in appearance to the best present-day commercial cast-surfaced coated papers.

It is entirely possible, by using such pre-gelled coating, to make such high-gloss paper, while gradually contracting the coated paper web laterally in contact with the finishing roll, thus eliminating the abrupt contraction which is a distinguishing feature of cast-coating as heretofore practiced.

The invention also makes possible an entirely new type of roll-finished coated paper, a product which has the extreme levelness of surface and the superlative printing surface characteristic of prior cast-surfaced coated papers, but whose surface is not a mirror-image of the finishing surface. The known cast-surfaced coated papers of commerce have surfaces which are substantially mirror-images of the finishing surfaces against which they have been dried. Since, to date, the only finishing surfaces commercially successful for producing cast-surfaced coated papers have been highly polished surfaces, especially polished chromium-plated surfaces, the commercial cast-surfaced coated papers available at present invariably have an extremely high specular or mirror-like gloss, far higher than that which can be produced by super-calendering, which is the commonly used process for producing glossy coated paper other than cast-surfaced coated paper.

The gloss of coated paper is commonly measured on a standard instrument, designated as the Bausch & Lomb glossmeter. A gloss value of 100, as measured on said instrument, corresponds to a smooth and polished metal mirror surface. The best cast-surfaced coated papers presently available have gloss values approaching 100. The range of 80 to 100 may be considered to embrace the entire range of gloss values which may be shown by commercial cast-surfaced coated papers now considered satisfactory by the trade. On the other hand an 80 gloss is hardly ever, if ever, attained by a supercalendered mineral-coated paper. The best of such supercalendered glossy-coated papers commonly have gloss values between 60 and 75. The supercalendering process compacts and densifies the layer of coating on a coated paper. The surface produced may be an excellent printing surface but it is somewhat inferior to the surface of high-quality cast-surfaced coated paper in its ability to reproduce printed matter faithfully.

Because of its lower gloss value, the appearance of supercalendered coated paper is less striking than that of current cast-surfaced coated papers. But its lower gloss actually makes it more suitable for typed matter and detailed printed matter which must be studied carefully, because the lower gloss is less tiring to the observer's eyes.

The present invention makes possible, for the first time, the production of a drum-finished coated paper whose surface is not a mirror-image of the finishing surface, but which is comparable in appearance to the best grades of commercial supercalendered glossy coated paper. The product, however, unlike supercalendered paper, has an undensified coating and it possesses superior printing qualities characteristic of known cast-surfaced coated papers which do possess mirror-like surfaces.

According to one feature of the present invention, there is applied to the surface of a moving web of paper a layer of aqueous coating composition containing an adhesive substance capable of being gelled or insolubilized by a metal ion, and also containing a compound of a

metal which has said metal ion in an inhibited phase in which said metal ion is not reactive with said adhesive but said metal compound is capable of being converted in situ to a form in which its metal ion is released to react with and gel said adhesive. Thereafter, the layer of coating, while still wet, is treated to cause release of metal ion which thereupon reacts with the adhesive and causes gelation of the layer of coating. Thereafter the gelled coating layer, though still wet, can be handled without being marred or disfigured by contact with solid objects.

As above noted, the invention here described makes possible the production of roll-finished coated paper at running speeds several hundred percent higher than have previously been possible in making cast-surfaced coated papers.

The invention makes possible almost instantaneous drying of a coated paper, to produce a finished coated paper comparable in appearance to a high quality cast-surfaced coated paper, but which need not be a cast-surfaced coated paper. In experiments in which paper having a gelled wet layer of coating thereon was slowly dried against a polished chrome-plated roll it was observed that it was possible for the wet coated web to shrink laterally and gradually from the time it was applied to the roll to the time it was completely dried. That is, in some cases the coated surface did not remain in non-slipping adhesive contact with the drum as required by the usual definition of cast-surfaced coated paper, but slipped continuously on the drum surface during the drying process. Yet the finished coated paper product was indistinguishable from usual cast-surfaced coated paper by casual examination. Careful examination showed that the product was free from the minute release pattern flaws which are sometimes visible in cast-surfaced coated papers.

Moreover it has been found that the coated paper can be pulled away from the surface of the roll while the gelled coating is still wet, due to the high cohesion of the gelled coating and due to the reduced inherent adhesion of the gelled coating to the finishing roll.

A new non-mirror-image coated paper is made by bringing the coated surface of a wet coated web having a wet coating layer thereon into contact with a finishing surface, and thereafter, before the coating has become substantially dry, forcibly removing the coating layer of the coated web from said finishing surface. Previously, in making cast-surfaced coated paper, and as above noted, it has been impossible to remove the coated paper from adhesive contact with the finishing surface before the paper and coating had become substantially dry, because only when substantially dry did the coating layer become sufficiently cohesive so that it could be pulled away from its contact with the finishing surface without being split or damaged in the process. In one aspect, the present invention depends upon chemically reacting certain constituents of the coating layer while the layer is still wet, whereby the cohesiveness of the wet layer is very markedly increased without removal of water. At the same time the chemically reacted coating layer appears to have its adhesiveness to the finishing surface somewhat decreased. Thus the coated paper can be pulled away from a moderately heated finishing surface while still wet within a period of from considerably less than 1 second to somewhat less than 4 seconds after it has made contact with the finishing surface, to yield a product, which has a coating with a non-mirror-like surface. Even in the case where a very hot casting-drum is used it is still possible to pull the web away therefrom before the coating has become substantially dry, so that the resulting surface of the coating after subsequent drying will not be a mirror-image of the finishing-roll surface. This is true, especially, if little or no external pressure is used to force the wet coating of the wet web against the finishing surface. Or the coated paper can be dried at high temperature as

previously described and can be substantially completely dried in a period of equal length, i.e. less than 1 to somewhat less than 4 seconds to yield a product having a surface which has a mirror-like gloss substantially as high as that of the finishing surface. In conventional processes now in commercial use for making cast-surfaced coated papers, the time of contact with the heated finishing surface usually lies in the range of 10 to 30 seconds.

Aqueous coating compositions containing adhesive substances such as certain proteins or other organic adhesives which are coagulated by ions of metals having a valence greater than one, may include among their constituents a complex compound of such a metal which compound does not ionize to yield an appreciable quantity of simple ions of the metal and, after the composition has been applied to the paper, the said complex compound may be decomposed to set free said metal ions, which then react with said adhesive substance to coagulate the same, and so cause a substantial increase in cohesiveness of the coating composition. My copending application Ser. No. 466,942, now U.S. Patent No. 2,849,334, discloses inclusion in aqueous compositions containing protein such as casein and soy protein, of a soluble chelate of a multivalent metal, such as a complex made by mixing alum and tartaric acid in an ammoniacal aqueous medium. The chelate compound does not affect the protein, but when the chelate compound is broken down by a decrease in the pH value of the aqueous composition, caused by removal of ammonia from the system, the aluminum ion thus released reacts with and coagulates the protein. Under the conditions disclosed in said copending application, the coagulation and drying of the coating occur substantially simultaneously, with production of a water-insoluble coating layer, but normally without development of any substantial degree of cohesiveness in the coating layer while still substantially wet. By taking the same wet coating layer and removing ammonia therefrom while still keeping the coating wet, however, a very cohesive, gelled, wet coating layer results, which can be quickly dried at high temperature as previously described to yield a mirror-like surface; or which can, if desired, be applied to a roll or drum which is at a lower temperature, say about 80° C. and forcibly removed therefrom before becoming substantially dry, the drying being completed elsewhere, to produce a coated paper not having a mirror-like surface.

The desired removal of ammonia may be accomplished by neutralization, as by passing the surface of the wet coating layer through a bath of acidified water, as a 1% solution of acid for example. Alternatively, the ammonia may be driven off while still keeping the coating wet, by heating the coated web below the boiling point of water, while the surface is exposed to an atmosphere saturated with water vapor. When an acid bath is used to neutralize the alkalinity of the coating or to depress the pH thereof to decompose the chelate compound, fixed alkali, such as caustic soda or caustic potash, can be used in place of ammonia. Such fixed alkali, of course, cannot be removed by volatilization.

Although apparently any multivalent metal may be used to insolubilize a protein such as casein, for obvious reasons the preferred metals are those of which the salts are colorless or practically colorless. Such metals include aluminum, tin, and zirconium. Aluminum salts are the cheapest of these and are usually satisfactorily effective. If color is not objectionable, ferric salts are both cheap and effective.

There are, of course, a great number of known chelating agents. These may be typified by the hydroxycarboxylic acids, such as tartaric acid and citric acid and their salts. Of these, tartaric acid and its salts appear to be as satisfactory as any of the readily available chelating agents.

While multivalent metal ions are preferred because of their quicker insolubilizing action on proteins as well as their pronounced effect in decreasing the adhesion of the protein to the casting or finishing surface, nevertheless such reactive divalent metals may be used as can be formed into non-reactive chelate compounds or into complex amines with ammonia. Such divalent metals are usually satisfactorily effective if they are released from their non-reactive complexes in the coating, by treatment of the coated sheet with acid as previously mentioned. Cadmium, cobalt, copper, nickel, and zinc are examples of such usable divalent metals. Of these zinc is preferred because it is colorless, although it is usually considered that zinc is not quite as effective as the multivalent metal, aluminum.

The invention will be further described with reference to the accompanying drawings which diagrammatically illustrate apparatus for carrying out three different embodiments.

Referring to the drawings:

Fig. 1 is a diagrammatic illustration of apparatus suitable for carrying out the process of Examples 1, 2, 3, 7, 9, 10 and 11;

Fig. 2 is a diagrammatic illustration of apparatus suitable for carrying out the process of Examples 4 and 5;

Fig. 3 is a diagrammatic illustration of apparatus suitable for carrying out the process of Example 6; and

Fig. 4 is a diagrammatic illustration of apparatus which is suitable for carrying out the process of Example 8.

The apparatus illustrated in Figs. 1 to 4 will be described in detail in the following specific examples.

In the following illustrative specific examples, the units are by weight.

Example No. 1

Step 1.—Fifteen units of casein were wetted with a solution of 3 units of dicyandiamide (also called cyanoguanidine) in 50 units of water. The dicyandiamide was used to reduce the viscosity of the final coating composition. The wetted casein was mixed with 1.8 units of 28% ammonia water at 50° C. until the casein was colloidally dispersed.

Step 2.—Thirty units of fine-particle calcium carbonate and 70 units of fine-particle coating clay were mixed in a heavy-duty mixer with the dispersion of Step 1, and also with 40 units of water, to provide a thick mixture or mass.

Step 3.—1.4 units of crystalline aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) and 1.0 unit of tartaric acid were dissolved in 30 units of water. To this were added 4 units of 28% ammonia water. The resultant solution of the metal complex or chelate was alkaline to litmus and had a strong odor of ammonia.

Step 4.—The solution of step 3 with mixed with the mixture of step 2, and 0.5 unit of a silicone anti-foam agent (Dow's "Anti-Foam A") was added thereto.

Step 5.—12.5 units of a commercial aqueous synthetic latex containing 6 units of styrene-butadiene copolymer were added to the mixture of step 4, as additional, non-protein adhesive.

Step 6.—One unit of melted dimer of hexadecylketene, 0.5 unit of sodium stearate, 0.2 unit of gum ghatti, and 6 units of water at 95° C. were homogenized by passage through a homogenizer to produce a stable aqueous dispersion. This mixture was added to the product of step 5 to complete the aqueous coating composition, in order to impart some water-repellent quality to the finished dried coating as well as to assist clean parting between the casting drum and the coated surface when the latter is pulled away from said drum.

Step 7.—The coating composition of step 6 was applied by means of an air-knife coating machine 2 (Fig. 1) which has an air-knife K to one side C of a well-formed paper web 1 of the type commonly used as base stock for the production of high quality coated paper. The air-

dry weight of the paper base stock was about 210 grams per square meter. Sufficient wet coating composition was applied on face C to form a wet coating layer whose weight was about 26 grams, dry weight, per square meter. The freshly coated web with its coated face C of wet coating outward was run under a roll 3 dipping into a bath 4 of 1% aqueous formic acid to set the coating by making it more cohesive. The wet coating was then run into contact with the surface of a polished chromium-plated cylinder 5 heated to 130° C. against which it was firmly pressed in nip N by a soft rubber roll 6 at a pressure of about 400 pounds per linear inch of the width of the web. As the web emerged from the pressure nip a cloud of steam burst from it. The linear speed of web 1 in Fig. 1 was about 200 feet per minute. The period between the coating step and the application of the acid was about 3 seconds, and the period between the acid bath and the nip N was about 3 seconds. The height of nip N was about 1.5 inches or about 3.8 centimeters. The web was removed from the polished finishing surface of roll 5 at the take-off roll 7 in less than one-half second after its first contact therewith. The coated surface was then substantially dry; it was very resistant to wet-rubbing; and it had a surface gloss which was substantially equal to the gloss of the surface of cylinder 5. The web was then reeled up without further treatment.

It is noted that the acid bath used was dilute formic acid. Dilute mineral acid is also effective, but when such mineral acid is used the web must be further treated to remove therefrom the excess acid picked up by the web. With organic acids such as formic or acetic acids the excess acid is sufficiently volatile at the drying temperature so that the excess is evaporated from the web during the drying process. Formic acid also has the further advantage of causing insolubilization of protein by an action similar to that of formaldehyde.

Example No. 2

Step 1.—Twenty units of casein were wetted with a solution of 4 units of dicyandiamide in 65 units of water. The wetted casein was mixed with 2 units of 28% ammonia water at 50° C. until the casein was colloiddally dispersed.

Step 2.—One hundred units of fine-particle coating clay were mixed in a heavy-duty mixer with the dispersion of step 1, and also with 40 units of water, to provide a thick mixture or mass.

Step 3.—Two units of crystalline aluminum sulfate and 2.9 units of Rochelle salt (sodium potassium tartrate, crystalline) were dissolved in 10 units of water. To this were added 6 units of 28% ammonia water.

Step 4.—The solution of step 3 was mixed with the mixture of step 2.

Step 5.—0.5 unit of a silicone anti-foam agent and 0.5 unit of sodium stearate were dispersed in 6 units of water and added to the mixture of step 4.

Step 6.—16.7 units of aqueous synthetic latex (Dow's 512R) containing 8 units of styrene-butadiene copolymer were added to the mixture of Step 5 to complete the aqueous coating composition.

Step 7.—The coating composition of Step 6 was applied by means of an air-knife coater 2 (Fig. 1) to one side C of a well formed paper web 1 weighing 120 grams per square meter in quantity of wet coating layer equivalent to 24 grams, dry weight, per square meter. The fresh coating layer was then wetted with 2% aqueous formic acid solution in the bath 4 and then firmly roll-pressed into contact with the polished chromium plated finishing surface of the roll 5 at a temperature of 140° C. The web was removed from said finishing surface at the take-off roll 7, in less than a half-second. The coating was substantially dry and its surface was resistant to wet-rubbing and had a mirror-like gloss substantially equal to the gloss of the chromium plated finishing surface.

Example No. 3

A coating composition prepared according to the first six steps of Example 2 was applied by means of an air-knife coater 2 (Fig. 1) to one side C of a sheet of paper-board 1 weighing about 380 grams per square meter, said coating composition left on said web being equivalent to about 30 grams, dry weight, per square meter. The freshly coated web with its coated face or coating layer outward was run under a roll 3 dipping into a bath 4 of 2% aqueous formic acid solution and then roll-pressed by the roll 6 into contact with a polished chromium plated finishing surface of the roll 5 at a temperature of 115° C. After $\frac{1}{10}$ second contact of the coating C with roll 5 beyond nip N, the web was forcibly pulled away from said finishing surface at the take-off roll 7. The coating was still wet when it left the finishing surface and the web was passed through a hot air drying oven (not shown) before it was reeled up. The undensified dry coating and paper had a very flat and level surface which had a gloss of about 72 as measured on a Bausch and Lomb glossmeter.

It will be understood that the take-off roll 7 may be positioned as desired around the circumference of the roll 5 in order to determine the time of contact of the web with the roll 5, beyond the nip N.

Example No. 4

Step 1.—Fifteen units of casein were wetted with a solution of 3 units of dicyandiamide in 50 units of water. The wetted casein was mixed with 1.8 units of 28% ammonia water at 50° C. until the casein was colloiddally dispersed.

Step 2.—Eighty units of fine-particle calcium carbonate and 20 units of fine-particle coating clay were mixed in a heavy-duty mixer with the dispersion of Step 1, and also with 40 units of water to provide a thick mass.

Step 3.—1.4 units of crystalline aluminum sulfate and 1.0 unit of tartaric acid were dissolved in 8 units of water. To this were added 4 units of 28% ammonia water.

Step 4.—The solution of Step 3 was mixed with the mixture of Step 2.

Step 5.—0.5 unit of a silicone anti-foam agent and 0.5 unit of sodium stearate in 6 units of water were added to the mixture of Step 4.

Step 6.—12.5 units of aqueous latex containing 6 units of styrene-butadiene copolymer were added to the mixture of Step 5 to complete the aqueous coating composition.

Step 7.—The aqueous coating composition of Step 6 was applied by means of a roll coater 8 (Fig. 2) to one side C of a paper body-stock 1 weighing about 95 grams per square meter, in amount of wet coating equivalent to 26 grams (dry weight) per square meter. The reverse side of the web was then passed into contact with a cylinder 9 heated to 85° C. while the top or freshly coated side of the web was exposed to air saturated with moisture provided by the steam pipe 10 and hood 11 to avoid excessive loss of moisture from the coating while expelling ammonia therefrom to set the coating by making it more cohesive. The coated surface C was then pressed by the roll 12 at the nip N into contact with a chromium plated drum 13 heated at 75° C., while a trickle of water was continuously fed from the pipe 14 into the entering nip between the coated web and the drum according to the process described in U.S. Patent No. 2,678,890. After about 3 seconds in contact with the finishing surface of drum 13 the coated paper was forcibly pulled away from said finishing surface at the take off roll 15 while the coating was still wet, and the paper was further dried by hot air and then wound up. The dried coated paper had a surface which was not a mirror-image of the finishing surface but instead looked like fine super-

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calendered glossy coated paper. It had a B. & L. gloss of 70. It was not densified like supercalendered paper. It had superlative properties for both letterpress and offset printing processes, and it was wet-rub resistant. The pressure used at the nip on Fig. 2 was the same as in Fig. 1 and the height of nip N in Fig. 2 was the same as in Fig. 1.

Example No. 5

The procedure described in the foregoing Example 4 was repeated excepting only that the coated web was held in contact with the finishing surface until it was substantially dry. This procedure yields a surface on the coating which has a gloss substantially equal to the gloss of the finishing surface.

It may be pointed out that in the case of Example 4 it is not absolutely necessary to supply moisture to the atmosphere while preheating the coated web, because by careful attention during the preheating period the coating can be set without excessive loss of moisture therefrom even in a dry atmosphere. If too much moisture is lost during the setting period the coating cannot be satisfactorily molded against the finishing drum. If the loss of moisture is only slightly too great introduction of ammonia into the water used in the nip at the drum will usually yield satisfactory casting results.

The degree of drying of the coating depends upon the temperature of the finishing drum, the time of contact therewith, the weight of coating applied, and the particular body stock used. If the drying goes to substantial completion on the drum, as in Example 5, the finished product has a surface which has a gloss substantially equal to the gloss of the drum's surface. But since the coating composition used can be gelled and so develop high cohesiveness while it is still wet, the coating can be pulled away from the drum surface before it becomes substantially dry, as in Example 4. Subsequent drying by other means yields a flat and level surface but one which is not mirror-like. If the coating is very wet when it is pulled away from the finishing drum it will have practically no gloss after it has become dry. When the coating is less wet when it is pulled away from the finishing surface the gloss of the final dry product increases with the degree of dryness at the time of removal from the finishing surface.

Example No. 6

Step 1.—Sixteen units of casein were wetted with a solution of 3 units of dicyandiamide in 50 units of water and then mixed with 2 units of 28% ammonia water at 50° C. until the casein was colloiddally dispersed.

Step 2.—One hundred units of fine-particle coating clay were mixed in a heavy-duty mixer with the dispersion of Step 1 and also with 40 units of water.

Step 3.—1.6 units of crystalline aluminum sulfate and 2.3 units of Rochelle salt were dissolved in 10 units of water and to this were added 5 units of 28% ammonia water.

Step 4.—The solution of Step 3 was mixed with the mixture of Step 2.

Step 5.—0.5 unit of tributyl phosphate (foam dispersant) and 0.5 unit of sodium stearate in 6 units of water were added to the mixture of Step 4 to complete the aqueous coating composition.

Step 6.—The coating composition of Step 5 was applied by means of a transfer-roll coating machine 16 (Fig. 3) to both sides of a paper web 1 weighing about 80 grams per square meter, in quantity equivalent to 18 grams, dry weight, per square meter on each side of the web. The coated web was then run through a bath 17 of 1% aqueous formic acid to set the coating by making it more cohesive and the wet sheet was then run between a pair of press rolls 18 of non-deflecting type having polished chromium plated surfaces. The coating having been made cohesive by passing through the acid bath 75

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pulled away cleanly from the press rolls and the web was thereafter dried, either by hot air in the tunnel 19 or optionally by conventional paper-machine drying cylinders (not shown). The dried web had a very flat and level surface without appreciable gloss. It was an excellent printing surface, however. The web was thereafter passed through a conventional supercalender to develop a high gloss while retaining most of its excellent printing properties. The time interval between bath 17 and the nip N between rolls 18—18 is at least one second.

Example No. 7

This example illustrates the use of a zinc-ammonia complex. Thus, in place of the solution of Step 3 of Example No. 2, I can substitute a solution of 1.5 units of zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) dissolved in 6 units of water with 3 units of 28% ammonia water. This produces a zinc-ammonia complex which is soluble in the ammonia water, and said zinc-ammonia complex is non-reactive with casein. With this change, Example No. 2 can be followed. However, it is highly preferable to use a complex of a metal which is ordinarily at least trivalent.

Although in preceding Examples 1 to 7 casein has been used as the gelable adhesive, it should be understood that the casein may be replaced in whole or in part by other organic adhesives which are gelable by the particular metal ion released in the coating layer. For instance, an equal weight of soy protein can be substituted for the casein in any of Examples 1 to 7.

Example No. 8

This example illustrates the use of the apparatus of Fig. 4, which is superior to and can replace the apparatus of Fig. 1.

The apparatus of Fig. 4 can be used either in cast coating or in non-cast coating, to make any of the previously described types of paper; by suitably selecting the factors.

As in the other examples an invariable procedure cannot be stated because the factors may vary, such as the thickness and porosity of the paper stock, the percentage of solids and water in the initial coating composition, speed of the web, temperature of the driers, and the number of driers.

Hence, only typical working examples are given.

The uncoated paper web 1 is withdrawn from reel 21, or from any source and is fed at 200 feet per minute. This paper web or body stock weighs about 21.2 grams per square meter, air dry, with about 5% of water by weight. This web 1 is led around rolls 22, 23, 24, 25 and 26. In this example, the roll 25 transfers coating composition equivalent to about 14.2 grams per square meter, dry weight, from the coating pan 20 to the coated face C.

In this example, the coating machine is of the air-knife type, which has an air knife 27. In using the air-knife coating machine, the coating composition may contain 44% of solids and 56% of water by weight. By using a different type of coating machine, such as the transfer-roll coater, the coating composition may have as much as 70% of solids and 30% of water by weight, with much greater viscosity than the coating composition which is applied by the air-knife machine illustrated in Fig. 4.

In Fig. 4, as only one example and without limitation thereto, the linear speed of the web through the machine may be 200 feet per minute. In this specific example, with a coating composition identical to that of Example 2 except that it has 44% of solids and 56% of water, the coated web has 22% by weight of water, immediately after passing beyond the air-knife 27.

The coated paper passes over roll 29 and then under and around the roll 30, which dips into an acid solution

in a pan 31. In this example, the acid solution is a one percent aqueous solution of formic acid, at room temperature of 20° C.-30° C. The invention is not limited to this temperature, or to the other specific illustrative details mentioned thereon.

In this example, the time between the coating station and the application of the acid at roll 30, is about three seconds. During this short period of three seconds, the coating composition which has 56% of water does not substantially penetrate the paper body stock 1, if such body stock is properly selected to have suitable low absorption.

If the coating composition has a relatively low percentage of solids such as 44% of solids, such composition is of a gelable type. This gelable type may be according to the previous examples, but is not limited thereto. The gelling of the low-solids coating composition at gelling station 30-31, increases the viscosity of the original low-solids coating composition, so that the gelled layer of coating composition has low penetration into suitably selected body stock 1. In this example, acid is used at the gelling station 30-31, but the invention applies to the use of any gelling action or gelling agent, depending on the composition of the original coating mixture, which is of the mineral-coating type.

If the original coating composition has high viscosity, due to a large percentage of solids, said coating composition need not be gelled.

In this specific example, in which a low-solids, gelable coating composition is applied by the air-knife coating machine, the coated web 1, immediately after leaving the acid bath 31, has 52% by weight of water, calculated on the weight of the paper stock and gelled coating.

The coated web is passed between squeeze rolls 33 and 32, which reduce the percentage of water to 25%. The roll 33 has a chromium face, and roll 32 is made of soft rubber. The squeeze rolls 33 and 32 help to maintain proper tension on the web.

The coated web is then passed around rolls 34, 35, 36, and through heating zones H and HH, where radiant heat is used to reduce the percentage of water to 15% by weight at roll 36. Heat is not necessarily applied anterior the dryer H, and all operations anterior to dryer H may optionally be at room temperature of 20° C.-30° C.

The coated web is then passed through nip N between the resilient, rubber-covered roll 37, and finishing roll 38, which has a highly polished metal surface of chromium or other metal.

Roll 38 is kept at 120° C.-150° C., so that the water in web 1 is heated above 100° C. in nip N, and the resultant steam is quickly released beyond nip N. The height of nip N is about 1.5 inches. The web is removed from roll 38 at roll 39, after contacting with roll 38 through any selected arc. When the coated web is removed from roll 38, it may be air dry, with 5% of water by weight.

This method will not result in a high gloss surface, because the percentage of water in the coating C has been reduced to 15% by weight, prior to contact with roll 38, in order to provide a coating of low plasticity, which will not conform wholly to the mirror surface of roll 38.

Due to the relatively low pressure used in the nip N in Fig. 4, the resultant sheet is not transparentized or crushed or weakened. The increase in flatness of the coating results in better printing.

The plasticity of the coating layer as it enters the nip of Fig. 4, will depend, to some extent, upon the composition of the original coating mixture, in addition to the percentage of water. The specific figure of 15% by weight of water, relates to the use of the gelable compositions of Examples 1-6, and in conjunction with the subsequent use of a gelling agent.

If it is desired to use the embodiment illustrated by Fig. 4 to make a high-gloss paper, the removal of mois-

ture is regulated so that the web and coating have a sufficiently large percentage of water anterior the nip N of Fig. 4.

Example No. 9

Step 1.—Fifteen units of a styrene-maleic anhydride adduct (Scriptite 50 made by Monsanto Chemical Company) were dissolved in 60 units of an aqueous solution containing 2.1 units of dissolved ammonia.

Step 2.—One hundred units of fine-particle coating clay were mixed with 54 units of water and the solution of Step 1.

Step 3.—1.5 units of hydrated aluminum sulfate, 0.75 unit of tartaric acid, 9 units of water, and 2.5 units of 28% ammonia water were mixed together and added to the composition of Step 2.

Step 4.—The composition of Step 3 was applied by means of an air-knife coater 2 (Fig. 1) to one side of a paper body-stock 1 weighing about 67 grams per square meter in amount equivalent to 18 grams, dry weight, per square meter. The freshly coated surface was then wet with 1% aqueous formic acid solution in the bath 4 and then was firmly roll-pressed into contact with the polished chromium plated finishing surface of the roll 5 at a temperature of 140° C. The web was removed from said finishing surface at the take off roll 7 in less than a half-second. The coating was substantially dry and its surface was resistant to wet-rubbing and had a gloss comparable to that of the polished chromium plated finishing surface.

The styrene-maleic anhydride adducts are fully described in a textbook entitled "Styrene, Its Polymers, Copolymers and Derivatives," by Boudner and Boyer, published in 1952 by Reinhold Publishing Corporation. The maleic anhydride may be replaced by the anhydrides of other unsaturated, dicarboxylic acids.

It is noted that when an original ungelled coating composition is gelled, such gelling results in a reaction between an adhesive in the original coating composition and an ion of a gelling agent, thus resulting in a new compound or in a new complex.

For some purposes, the coating composition can include water-soluble polyvinyl alcohol, which is reactive with an alkaline gelling agent, such as ammonium borate. Such water-soluble polyvinyl alcohol is exemplified by "Elvanol," which is a satisfactory binder in mineral-coating compositions. This "Elvanol" and its use in coating mixtures are described in "Vinyl Products Bulletin, V6-555" published by E. I. du Pont de Nemours & Company, Inc. Hence the invention includes the use of alkaline and acid gelling agents and also includes the use of protein and non-protein adhesives.

Another system includes the use of polyvinyl methyl ether-maleic anhydride adduct in the original coating composition, and releasing aluminum ions from an aqueous solution of an aluminum chelate as the gelling agent.

Another system includes the use of vinyl acetate copolymer, soluble in aqueous alkaline solution, known as "Elvadex" Vinyl Polymer, in the original coating composition, and releasing heavy metal ions as the gelling agent. This "Elvadex" Vinyl Polymer and its use in paper coating are described in "Vinyl Products Bulletin V16-654" published by E. I. du Pont de Nemours & Company.

Another system includes the use of water-dispersible terpolymers of styrene-butadiene-acrylonitrile, such, for example, as the one manufactured and sold by the United States Rubber Company as "Nitrex 2625." These are combined with a metal chelate, such as the combination described above of an aluminum salt and tartaric acid in the presence of ammonia. This combination adhesive is gelled with an aqueous solution of formic acid.

These systems use water-soluble adhesives which have vinyl groups.

Example No. 10

Step 1.—Fifteen units of casein were wetted with a solution of 3 units of dicyandiamide in 50 units of water. The dicyandiamide was used to reduce the viscosity of the final coating composition. The wetted casein was mixed with 1.8 units of 28% ammonia water at 50° C. until the casein was colloiddally dispersed.

Step 2.—One hundred units of fine-particle coating clay were mixed in a heavy-duty mixer with the dispersion of Step 1, and also with 40 units of water, to provide a thick mixture or mass.

Step 3.—0.5 unit of a silicone anti-foam agent and 0.5 unit of sodium stearate were dispersed in 6 units of water and added to the mixture of Step 2.

Step 4.—12.5 units of a commercial aqueous synthetic latex containing 6 units of styrene-butadiene copolymer were added to the mixture of Step 3, as additional, non-protein adhesive.

Step 5.—The composition of Step 4 was diluted by addition of 54 units of water. It was then applied by means of an air-knife coating machine 2 (Fig. 1) to one side of a well-formed paper web 1 having a weight of about 67 grams per square meter in quantity equivalent to 20 grams, dry weight, per square meter. The freshly coated web with its coated face outward was run about a roll 3 dipping into a bath 4 of 2% aqueous solution of ammonium bisulfate (NH_4HSO_4) to gel the coating. It was then run into contact with the surface of a polished chromium-plated cylinder or drum 5 heated to 120° C. against which it was firmly pressed by a soft rubber roll 6 at a pressure of about 380 pounds per linear inch of the width of the web. The web was removed from the finishing surface at take-off roll 7 in less than one second after its first contact therewith. The coated surface was then substantially dry and had a gloss substantially equal to that of the finishing surface.

The foregoing Example 10 illustrates a method in which the original aqueous mineral coating mixture does not contain a metal chelate or complex. The ammonium bisulfate solution is acidic and regenerates the casein, in water-insoluble and viscous gel state, from the original alkaline mineral coating composition. As above noted, in this case, the finishing roll is used at a lower temperature than when a chelate complex is used.

In the foregoing examples, if the acid gelling agent is used, and the paper web and its coating are kept acid in the nip, the coated paper will gradually contract while in contact with the polished metal drum 5 or 13 or 38, up to the respective stripping roll, thus evidencing that the process is not cast-coating and that the resultant product is not cast-surfaced coated paper.

Example No. 11

Step 1.—17.5 units of casein were wetted with a solution of 3.5 units of dicyandiamide in 70 units of water. The wetted casein was mixed with 2 units of 28% ammonia water at 50° C. until the casein was colloiddally dispersed.

Step 2.—One hundred units of fine-particle coating clay were mixed with the dispersion of Step 1, and also with 60 units of water to form a smooth slurry.

Step 3.—One unit of sodium aluminate (NaAlO_2) was dissolved in 9 units of water and added to the composition of Step 2.

Step 4.—0.5 unit of a silicone anti-foam agent and 0.5 unit of sodium stearate were dispersed in 6 units of water and added to the mixture of Step 3.

Step 5.—14.5 units of aqueous synthetic latex containing 7 units of styrene-butadiene copolymer were added to the mixture of Step 4 to complete the aqueous coating composition.

Step 6.—The coating composition of Step 5 was applied by means of an air-knife coater 2 (Fig. 1) to one side C of a well formed paper web 1 weighing about

65 grams per square meter in quantity of wet coating layer equivalent to 21 grams, dry weight, per square meter. The fresh coating layer was then wetted with 3% aqueous formic acid solution in bath 4, and then was firmly roll-pressed into contact with a polished chrome-plated finishing surface of the roll 5 at a temperature of 120° C., against which it was dried to substantial dryness. The coating was resistant to wet-rubbing and had a mirror-like gloss substantially equal to the gloss of the chrome-plated finishing surface.

While preferred embodiments of this invention have been disclosed, numerous changes, omissions, additions and substitutions can be made without departing from its scope. The invention is further disclosed in the appended claims.

This application is a continuation-in-part of application Ser. No. 559,366, filed January 16, 1956, now abandoned (which in turn was a continuation-in-part of application Ser. No. 466,942, filed November 4, 1954, now U.S. Patent No. 2,849,334).

I claim:

1. A method of treating a web of paper which has a gelled but still plastic mineral coating layer thereon with water at the surface thereof and in a sufficiently plastic state to yield in forming relation to a forming surface, which process includes leading said web through a nip between a pair of turning rolls, the roll which abuts the wet coating layer having a forming surface and being maintained at a temperature of over 100° C. thereby heating the water at said coating surface in said nip to at least 100° C. while substantially preventing the vaporization of water at said coating surface by confining the web in said nip under pressure in excess of the vapor pressure of water at the temperature of said forming surface, and moving said web beyond said nip to produce a flash vaporization of said water, and rendering said wet coating layer sufficiently gelled and cohesive at the time of said flash vaporization to remain smooth and uniform beyond said nip during the flash drying thereof.

2. A method of treating a wet paper web which has a layer of wet, gelled but still plastic mineral coating thereon, the surface of which is sufficiently plastic to yield in forming relation to a forming surface, said method consisting in passing said layer in tight contact with the highly polished surface of a revolving hot roll, while moving said web in the direction of its length and in the direction of rotation of said roll, keeping the temperature of said surface above 100° C. to heat said wet paper web and its wet coating above 100° C. while said coating is in contact with said hot roll, the wet mineral coating which is thus applied being sufficiently gelled and coherent to prevent disruption thereof by the steam which is evolved by the heating of the water in said wet coating to above 100° C.

3. A method which consists in contacting a wet and gelled but still plastic mineral coating on a paper web with a hot revolving, finishing roll, said paper web being moved longitudinally in substantial unison with the circumferential movement of said roll, pressing said coating against said finishing roll in a nip at a pressure sufficient to shape said plastic mineral coating, heating the coated paper web in said nip to above 100° C., said pressure being sufficient substantially to prevent the escape of steam from said wet and plastic coating in said nip, passing said web beyond said nip and permitting steam to escape freely from the heated web beyond said nip, the wet and plastic coating issuing from said nip being sufficiently gelled and coherent to prevent its disruption under pressure of the steam generated in said nip, and drying said coating at least partially by maintaining the contact between said coating and said roll beyond said nip.

4. A method according to claim 3, in which the coated paper is forcibly removed from the finishing roll while it is still wet and is thereafter allowed to shrink during

subsequent drying so that the dried surface does not possess a mirror image of the finishing roll.

5. A method according to claim 3, in which the pressure imposed upon said coated web in said nip is a maximum of 600 pounds per inch of the width of said web.

6. A method according to claim 3, in which the pressure imposed upon said coated web in said nip is insufficient appreciably to densify the body stock of the paper web.

7. Method of making roll-finished coated paper which includes applying to a paper web a layer of aqueous mineral-coating composition containing pigment and an organic binder capable of being gelled, causing gelation of said binder in said layer of aqueous coating without rendering said coating non-plastic, and thereafter while said coating surface is still wet roll-pressing the coated face of the web under positive pressure against a moving polished solid finishing surface having a temperature above 100° C., and releasing said pressure, thereby causing flash evaporation of water from said coating at the point where said pressure is released, and thereafter quickly removing said coated web from said finishing surface, and controlling said gelation to render said coating sufficiently cohesive at the point of said flash evaporation to prevent internal disruption.

8. A method of making coated paper which consists in coating a paper web with a layer of an aqueous, gelable mineral coating composition, gelling said coating without rendering the same non-plastic by contacting it with an aqueous solution of a gelling agent, thus increasing the percentage of water in the coated web; removing water from said coating to regulate the plasticity of the gelled coating to a selected value, thereafter shaping and drying said gelled coating under pressure in contact with a hot finishing roll, the temperature of which is maintained above 100° C., and maintaining said pressure at a value in excess of the vapor pressure of water at the temperature of said hot finishing roll until water in said coating migrates sufficiently from said surface to prevent disruption of said coating when said pressure is released.

9. A method comprising coating a paper web with a gelable mineral coating substance which is relatively soft and moldable when the surface of said coating is wet; gelling at least the surface portion of said coating without rendering it completely non-plastic; thereafter pressing said coated paper against a finishing surface under conditions of moisture, heat and pressure in which said coating surface conforms to said finishing surface; driving moisture from said coating surface into the body of said web without disrupting the smoothness of said coating by simultaneously maintaining the temperature of said finishing surface substantially in excess of 100° C., and pressing said coated paper against said finishing surface in a nip of substantial height at a pressure substantially in excess of the vapor pressure of water at the temperature of said finishing surface; and maintaining said coating in contact with said finishing surface under said pressure until the surface of said coating is substantially dry and sufficiently cohesive to resist disruption from flash evaporation.

10. A method comprising coating a paper web with a gelable water plasticized coating, passing said coated paper with its coated surface in a wet and plastic state through a nip formed between a finishing roll having a polished surface and a pressure roll having a soft but smooth and impervious surface extending in contact a substantial distance around the said finishing roll; driving water from the surface of said coating into said web to dry and harden said coating without disrupting the sur-

face thereof by maintaining the temperature of said polished surface at a value substantially in excess of 100° C. and the pressure in said nip at about 300 lbs. per linear inch, and so holding said coating against said polished surface until the surface of said coating is dry whereby steam does not erupt between said coating surface and said polished surface after release of said pressure, and until said coating is sufficiently set to resist disruption from flash evaporation after said pressure is released.

11. A method comprising coating a paper web with a gelable coating containing a substantial portion of a volatile liquid, said coating also containing a substantial portion of an adhesive which is sufficiently plastic to conform to a finishing surface only so long as said volatile liquid is present in the surface of said coating in said substantial proportion, pressing said coated paper with said liquid so present at the surface of said coating against a finishing surface the temperature of which is substantially higher than the boiling point of said volatile liquid and under a pressure substantially greater than the vapor pressure of said liquid at said temperature of said finishing surface, and maintaining said pressure on said web until a substantial portion of said volatile liquid is evaporated from and driven from said surface into said coating and web whereby said coating is rendered sufficiently non-plastic to resist disruption once said pressure is released.

12. A method comprising coating a paper web with a gelable liquid plasticized coating, driving a liquid which plasticizes said coating into said web from the surface of said coating while said coating is in forming contact with a forming surface by maintaining said surface at a temperature substantially in excess of the normal boiling point of said liquid while pressing said web between said forming surface and a second surface under a pressure in excess of the vapor pressure of said liquid at the temperature of said forming surface, maintaining said pressure until said liquid is no longer at the surface of said coating, releasing said pressure thereafter, and controlling the cohesiveness of said coating to resist disruption from flash evaporation at the moment when said pressure is released.

13. A method comprising coating a paper web with a liquid plasticized gelable coating, gelling said coating, driving a liquid which plasticizes said coating into said web from the surface of said coating while said coating is in forming contact with a forming surface by maintaining said surface at a temperature substantially in excess of the normal boiling point of said liquid while pressing said web between said forming surface and an impervious surface under a pressure in excess of the vapor pressure of said liquid at the temperature of said forming surface, maintaining said pressure until said liquid is no longer at the surface of said coating, thereafter gradually releasing said pressure as by issuing said paper from a nip between a hard roll and a soft roll pressed against said hard roll over a substantial area, and controlling the cohesiveness of said coating to resist disruption from flash evaporation at the moment when said pressure is released.

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