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SYNTHETIC RESIN COATED PAPER

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This invention relates to coated paper and more particularly to paper having a gloss coating and useful wherever a paper product having a high gloss finish which greatly improves its appearance and reduces moisture vapor transmission is useful, particularly for display purposes, as for the fabrication of containers, and wherever a paper or paper board having a highly glossed finish of reduced moisture vapor transmission is desired.

This application is a continuation-in-part of my prior and copending application, Serial No. 54,211, filed October 12, 1948, now abandoned.

Heretofore paper (which term is used herein to include both ordinary paper of a high flexibility and paper board, such as cardboard or the like) has been provided with a glossy finish by various methods. One of these methods involves laying a sheet of preformed transparent foil of thermoplastic material over the paper and applying heat and pressure to cause the foil to adhere to the paper. The product made in this manner is subject to the objections of the great expense of manufacture and the marked tendency of the applied foil layer to separate from the paper base upon handling and use. Another method involves the application of a solution of a resinous thermoplastic polymer in a volatile organic solvent to the paper base followed by removal of the solvent by drying. However, the product of this method has been unsatisfactory in that the resinous solution penetrates into the paper to an objectionable extent with the result that the flexibility of the product is impaired. Furthermore, the product has been unduly expensive. Other methods of providing paper with glossy resinous finishes has been proposed, but so far as I am aware, none of them has been suitable for use on a large commercial scale. The result is that the industry has not heretofore had available a glossed paper product sufficiently cheap to be used widely, for example in magazine production and in container manufacture, and possessing the necessary combination of physical properties adapting it to such large-scale usage.

My invention resides in the discovery that a glossed paper product meeting the requirements for wide commercial utilization may be obtained by providing on one or both surfaces of the paper a thin, continuous, flexible, transparent coating of polymeric material selected from the group consisting of a resinous copolymer of styrene and acrylonitrile in proportions of from 65 to 80% by weight of styrene and correspondingly from 35 to 20% by weight of acrylonitrile and mixtures

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of from 50 to 95% by weight of said resinous copolymer and correspondingly from 50 to 5% by weight of a rubbery copolymer of butadiene-1,3 and acrylonitrile, the coating being manifested as a highly glossed film tenaciously adherent to the surface of the paper and the amount of the coating ranging from 0.1 to 3.0 pounds of said polymeric material per 1000 square feet of coated surface. So far as I am aware, paper has never been successfully commercially glossed with such a small amount of polymeric material. At the same time the coated paper product of my invention is distinguished by its excellent flexibility, absence of taste, odor or flavor, markedly reduced moisture vapor transmission, absence of any tendency of the glossy coating to separate from the paper base, freedom from any tendency to block (by which is meant solidification of a plurality of superimposed coated sheets into a block at ordinary or moderately elevated temperature), high resistance to oil and grease, good abrasion- and scuff-resistance, and good chemical resistance and resistance to sunshine. Where the glossed coating of my invention is applied over paper which has been printed or lithographed with colored inks, the glossy coating exerts a very definite protective effect upon the colored inks, protecting them from fading upon exposure to light.

The resin used in the practice of my invention is a copolymer of monomers consisting essentially of styrene and acrylonitrile. I have obtained unusually successful results with a resinous copolymer of 70% by weight of styrene and 30% by weight of acrylonitrile. While, as previously indicated, such a resinous copolymer of styrene and acrylonitrile can be the sole polymeric material in the glossed coating, even better results are obtained, particularly where very high flexibility of the coating is desired, as in coating paperboard to give a product particularly suitable for manufacture of folded containers where the glossed paperboard product of my invention is subject to being bent sharply during fabrication of the container with the result that the coating is stressed, by incorporating with such a resinous copolymer of styrene and acrylonitrile a rubbery copolymer of monomers consisting essentially of butadiene-1,3 and acrylonitrile. This not only markedly increases the flexibility of the coating but also imparts higher resistance to transmission of moisture vapor.

The resinous styrene-acrylonitrile copolymer and the rubbery butadiene-acrylonitrile copolymer are completely compatible with each other

so that in the glossed film they form a mutual solid solution in one another.

The resinous copolymer of styrene and acrylonitrile may be prepared by the aqueous emulsion polymerization of styrene and of acrylonitrile as disclosed in U. S. Patent No. 2,140,048, in the presence of an emulsifying agent and a polymerization catalyst. The customary regulators or modifiers used in making Buna N synthetic rubber may be included, such as those of the mercaptan or other type. Following polymerization the resulting latex is stripped in known manner to remove any unreacted monomers and is then ready for direct use in making the coated paper product of my invention.

The rubbery copolymer of butadiene and acrylonitrile is a well-known synthetic rubber of the type commonly designated as Buna N. Its manufacture is well-known, it also being made by aqueous emulsion polymerization. Following polymerization and stripping the resulting latex is suitable for use directly in admixture with the above-described styrene-acrylonitrile resin latex. The relative proportions of butadiene and acrylonitrile employed in the monomeric charge may vary within the known limits which give a rubbery elastic copolymer Generally the rubbery copolymer comprises between 50 and 75% of combined butadiene and correspondingly between 50 and 25% of combined acrylonitrile.

The relative proportions of the resinous copolymer of styrene and acrylonitrile and of the rubbery copolymer of butadiene-1,3 and acrylonitrile may vary widely depending upon the properties desired. However, I prefer to employ between 50 and 95% by weight of the resinous copolymer and correspondingly from 50 to 5% by weight of the rubbery copolymer, these percentages being based upon the sum of the resinous copolymer and the rubbery copolymer. I usually prefer to effect the intermixture of the rubbery copolymer with the resinous copolymer by simply blending a latex of the butadiene-acrylonitrile rubbery copolymer with a latex of the resinous styrene-acrylonitrile copolymer in the indicated proportions after which the resulting mixture is applied to the paper, dried and calendered in the manner described in detail below.

The coated paper of my invention is prepared by applying to the paper an aqueous dispersion of the amorphous thermoplastic resinous or resinous and rubbery material in an amount such that the weight of solids, i. e., of polymeric resinous or resinous and rubbery material, applied ranges from 0.1 to 3.0 pounds per 1000 square feet of coated surface followed by drying to remove the water and set the polymeric material on the paper in the form of discrete particles adhered to the surface of the paper and constituting a discontinuous film, and hot calendering of the solids deposited from the aqueous dispersion to effect glossing by converting the solid discrete polymeric particles to a continuous film manifested predominantly as a surface film. One method of effecting the production of the product of my invention is described in my copending application Serial No. 769,046, filed August 16, 1947, now Pat. No. 2 554,662 issued May 29, 1951, in accordance with which the paper after being coated with the aqueous resin dispersion is dried at a temperature ranging from 20° C. to 60° C. above the second order transition temperature of the resinous polymer, after which the dried coated surface of the paper is pressed against a heated surface, typically by subjecting the coated paper to an even-speed calendering operation in a calender having a highly polished (preferably mirror-finish chromium-plated) heated roll in contact with the coated surface of the paper, at a temperature ranging from 40° C. to 80° C. above the second order transition temperature of the resinous polymer whereby the resin particles on the surface of the paper are converted to a thin, continuous, strongly adherent coating, whereupon the hot glossed product is stripped at the latter temperature from the heated surface.

When using a dispersion wherein the polymeric material consists of a 70% styrene-30% acrylonitrile copolymer resin having a second order transition temperature of approximately 95° C., I have obtained very excellent results by drying the coated paper at a temperature of from 145° to 155° C. followed by glossing by contacting under pressure with a highly polished (mirror-finished chromium-plated) calender roll at a temperature ranging from 135° to 150° C. These temperatures have reference to the actual temperature to which the coated paper is heated. The drying is carried out while the coated paper is not in contact with any solid material, i. e., while it is in a heated gaseous atmosphere. The temperature to which the mirror-finished chromium-plated calender roll used for glossing is heated will vary with the speed at which the glossing is conducted. For example, when employing relatively low glossing speeds, say, when passing the coated dried paper through the calender at lineal speeds of the order of 60 feet per minute, the glossing roll may be heated to a temperature of say 135° C. whereas when operating at higher lineal paper speeds, say of the order of 300 to 350 feet per minute, the glossing roll often must be heated to a temperature of the order of 150° to 160° or even higher in order to bring the paper and its coating to within the temperature limits given.

When a dispersion of polymeric material consisting of a mixture of the styrene-acrylonitrile resinous copolymer described above and a butadiene-acrylonitrile rubbery copolymer as described above is used in the practice of my invention, the method of application to obtain the high gloss desired is preferably that shown in my copending application, Serial No. 133,183, filed December 15, 1949, now Pat. No. 2,554,663 issued May 29, 1951, in accordance with which the paper is coated with the aqueous dispersion, is then dried to remove the water and heated at a temperature of from 20° C. to 60° C. above the second order transition temperature (T_2) of the resinous copolymer (while the coated surface is out of contact with any solid surface) to set the polymeric material on the surface, is then fed continuously into the nip of a continuously rotating, heated, hard non-resilient, mirror-finished (preferably chromium-plated) glossing roll and a cooperating continuously rotating resiliently surfaced roll rotating at a speed identical with the glossing roll, so that there is no relative movement whatever in the nip insofar as the coated paper and the two rolls are concerned, with the polymer-coated surface of the paper web in contact with the glossing roll, passing the paper web around the glossing roll in intimate contact therewith and while stationary with respect thereto for a substantial angular distance, preferably at least 180° C., heating the coating to a glossing temperature ranging from

T_2+40° C.—0.4° C. (P) to T_2+80° C.—0.4° C. (P)

where P is the percentage by weight of the butadiene-acrylonitrile rubbery copolymer employed in conjunction with the resinous copolymer, based on the sum of the two copolymers, while the coating is in contact with the glossing roll and by means of the heat and pressure exerted causing the coating to flow into a thin, highly glossed, tenaciously adherent, continuous film on the surface of the paper web, continuously stripping the hot paper web from the heated glossing roll at the end of said angular distance by withdrawing the web tangentially therefrom while the coating is at the temperature to which it was heated by the glossing roll, i. e., without cooling, and continuously passing the stripped web in a straight line, while maintaining the hot coated surface out of contact with any solid surface, until the coating cools to such an extent that its gloss is not injured by bending.

The glossing machine used to produce the product of the present invention is preferably constructed in accordance with my copending application, Serial No. 195,966, filed November 16, 1950.

The above described resinous copolymers of styrene and acrylonitrile and mixtures thereof with butadiene-acrylonitrile rubbery copolymers impart to the resulting highly glossed coating the properties of good abrasion- and scuff-resistance, high resistance to the transmission of moisture vapor, low or no odor, taste or flavor, transparency, good flexibility at the temperature encountered in use, high resistance to oil and grease, good adhesion to the paper, low combustibility, good chemical resistance and resistance to deterioration upon exposure to sunshine. In addition, the coatings obtained are heat-sealable both to themselves and to uncoated paper surfaces. This allows heat-sealing of the coated product during fabrication of containers or the like therefrom.

The proportion of dispersed resinous polymer or of resinous and rubbery polymers in the aqueous dispersion used to prepare the product of my invention will generally range from 25 to 45% by weight and preferably from 30 to 40% by weight.

The amount of the aqueous dispersion of the polymeric material applied to the paper in making the product of my invention is such that from 0.1 to 3.0 pounds of resinous copolymer or of resinous and rubbery copolymers are applied per 1000 square feet of coated paper surface. For many applications the amount may range from 0.5 to 3 pounds per 1000 square feet. However, there are many situations in which amounts ranging from 0.1 to 0.5 pounds per 1000 square feet are used with the production of a highly glossed product. For container stock the amount of solids applied usually is in the upper portion of the broad range, often ranging from 1.5 to 3 pounds per 1000 square feet of surface.

In some cases the paper may be given a light precoating of a suitable material such as a diluted latex of a styrene-acrylonitrile resinous copolymer of the type described above, diluted say to from 4 to 10% solids, and preferably applied in the water box, in order to reduce the extent of absorption or penetration of the subsequently applied polymer coating into the paper. In this way the polymer coating is caused to be manifested to an even greater extent as a surface coating. The pre-treatment should be such that absorption is not completely prevented since otherwise the adhesion of the glossed polymeric film to the paper base may be seriously reduced. In fact, even when such pre-treatment of the paper is omitted, the penetration of the solids content of the aqueous dispersion into the paper generally does not exceed 20% by weight of the said solids content, this being attributable to the filtering and/or precipitating action of the paper upon the aqueous dispersion whereby the solids content thereof is laid down upon the paper as a separate and distinct film. When the aforementioned pre-treatment is used, the extent of penetration of the aqueous dispersion into the paper will generally range from 1 to 20% by weight of the solids and in most cases will not exceed 10% thereof.

Following is an example of the preparation of the product of my invention in accordance with the best practice now known to me.

Example

There is first prepared an aqueous dispersion of a resinous styrene-acrylonitrile copolymer containing 70% of combined styrene and 30% of combined acrylonitrile. This dispersion is prepared by polymerizing the following recipe:

	Parts by weight
Water	180
Styrene	70
Acrylonitrile	30
Modifier	0.3
$K_2S_2O_8$ (catalyst)	0.6
Duponol ME (sodium lauryl sulfate)	3.5
Daxad 11 (condensation product of formaldehyde and sodium naphthalene sulfonate)	0.5

This recipe is polymerized at 50° C. for 5 to 15 hours and is then stripped, yielding a white latex having a solids (copolymer) content of 36% and a pH of 3.0 to 5.0. With this latex is admixed 0.6 part of Duponol ME and 0.6 part of Daxad 11 per 100 parts of solids content. The resulting latex is then blended with a latex of Buna N which contains approximately 43% of a copolymer of 65% butadiene-1,3 and 35% acrylonitrile, in such proportions that there is present 60% of the resinous styrene-acrylonitrile copolymer and 40% of the butadiene-acrylonitrile copolymer. The Buna N latex was prepared from the following recipe:

	Parts by weight
Water	140
Butadiene	65
Acrylonitrile	35
Duponol ME	3.0
Benzoyl peroxide	0.4
Dodecyl mercaptan	0.5

This recipe is polymerized at 40° C. for 8 hours and then at 65° C. for 5 hours. The latex is then short-stopped followed by stripping whereupon it is blended with the resin latex aforesaid.

The resulting latex blend is applied to paper at a rate corresponding to 1 pound of polymeric material per 1000 square feet of coated surface. The coated paper is then dried at a temperature of 148° C. for 45 seconds to remove substantially all of the water and set the polymeric material, i. e., cause the polymer particles to adhere to the paper and to flow out very slightly without however merging. The thus coated paper is then passed at the rate of 60 feet per minute through the nip of a mirror-finished chromium-plated calender roll and a compressed cotton-surfaced

calender roll with the coated surface of the paper in contact with the chromium-plated roll which is heated to a temperature of 120° C. The paper is allowed to pass half way around the chromium-plated roll and is then stripped therefrom by taking it off in a horizontal plane. The resulting paper has an extremely high gloss and exhibits good resistance to moisture vapor transmission. It is flexible and when sections thereof are stacked under 1 pound per square inch pressure at 170° F. no blocking occurs. Where the paper has been printed with colored inks before applying the coating, the brilliancy of the inks is greatly enhanced by the superposition of the glossy coating and upon exposure of coated samples in the Fadometer for 7 days (which is equivalent to about 7 months in the sunlight), the extent of fading of the inks was very materially reduced, apparently because the gloss reflects the injurious light rays.

The product of my invention is distinguished by its extremely high gloss. In fact the brilliancy of the coated product of my invention exceeds that of any coated paper with which I am familiar the coating of which is laid down from a coating composition. The brilliancy is so great that it cannot be measured upon the present-day glossometer. The only way of obtaining a gloss approaching the gloss of my coated product is to laminate cellophane or similar transparent foil to paper, but my product is not to be compared with such a laminated product since in my product the extent of solids application is much less than could be approached by a laminating process, and moreover in my product the film is laid down directly from a coating composition and is a hot calendered deposit in contrast to a preformed foil. My coating is formed in situ in contact with the paper as distinguished from a product made by laminating a preformed foil to paper.

The product of my invention is also distinguished, as mentioned above, by the exceedingly small amount of solids applied to the paper which is in marked contrast to the heavy applications of coating materials which have been considered minimum in the prior art. The product is also distinguished by the small absorption of the coating into the paper, the absorption being just sufficient to effect tenacious adherence of the glossed film to the paper but insufficient to effect impregnation of the paper surface with the resin of an extent which would objectionably increase the cost of the resin or interfere unduly with the flexibility of the paper. The product of my invention is also distinguished by its high resistance to moisture vapor transmission. In a standard test, the glossed paper of my invention allows less than 5 grams of water per 100 square centimeters of surface exposed at 90° F. to an atmosphere of 95% humidity to be transmitted in 24 hours. If the paper is pre-treated with a dilute dispersion as previously described so as to reduce still further penetration of the aqueous dispersion into the paper, the resistance to moisture vapor transmission is increased to such an extent that not more than 2 or 3 grams of water per 24 hours per 100 square centimeters of exposed surface are able to pass in such a standard test.

The product of the present invention is believed to be completely different from any glossed paper product ever heretofore made. If the resinous polymer were applied in the molten state to the paper, it would penetrate into the paper thereby giving rise to an impregnated paper not comparable to the product of the present invention. A product made by lamination of a foil to paper is not comparable with the product of the present invention because it is impractical by the lamination method to apply a preformed film of the thickness contemplated by the present invention. Furthermore, a laminated foil is subject to separation, particularly when the paper is subjected to moisture. Where the resinous polymer is applied in the form of a solution in an organic solvent, excessive penetration of the resin into the paper cannot be avoided and a totally different product results. My product is unique in the small amount of material applied and is also distinguished by the fact that the coating is manifested as a surface film rather than one which penetrates into the paper to such an extent as to decrease the flexibility of the paper. However the coating of my product is tenaciously adherent to the surface of the paper as illustrated by the fact that if pressure sensitive tape is pressed firmly down upon the glossed surface of the paper of my invention and then pulled suddenly therefrom the paper is actually split and is torn away but no separation of the glossy coating from the surface of the paper occurs. In other words, the bond between the glossy coating of my invention and the paper is considerably greater than the bond between the various portions of the paper itself.

It should be explained that the term "continuous" as used herein does not necessarily mean that the film is free from pinholes, but rather denotes that the polymer particles have been merged into one another in the glossing step to form a continuous structure. Thus, generally speaking, the glossed films of my invention do not begin to exhibit complete freedom from pinholes until a level of approximately 1 lb. of polymer per 1000 square feet of coated surface, and manifest freedom from pinholes from that weight of coating up. Similarly, the term "discontinuous" does not necessarily denote the presence of pinholes, because the film as laid down before glossing is free from pinholes when the percentage of butadiene-acrylonitrile rubbery copolymer ranges from 45 to 50% by weight based on the sum of the rubbery copolymer and the resinous styrene-acrylonitrile copolymer; however, in such a film the polymer particles are not merged together to form a continuous homogenous structure. Those skilled in the art will readily appreciate that freedom from pinholes and continuity of structure are not necessarily synonymous.

From the foregoing description many advantages of the product of my invention will be obvious to those skilled in the art. It will be seen that the present invention makes available to the art for the first time a glossed paper product having an extremely high brilliance and good moisture vapor transmission resistance at a level of solids application which is such that the product is commercially feasible in such applications as glossed colored advertisements in magazines and containers for almost any type of product where a paper having a high gloss is desirable. The coating of the present invention can be readily applied over ordinary printing or lithographing with any color of ink and serves to enhance greatly the brilliancy and attractiveness of the printed or lithographed sheet. Many other advantages of the product of my invention will be obvious to workers in the art.

Having thus described my invention, what I claim and desire to protect by Letters Patent is:

1. As a new article of manufacture, paper in sheet form having on a surface thereof a thin continuous flexible transparent coating of polymeric material selected from the group consisting of a resinous copolymer of styrene and acrylonitrile in proportions of from 65 to 80 per cent by weight of styrene and correspondingly from 35 to 20 per cent by weight of acrylonitrile and mixtures of from 50 to 95 per cent by weight of said resinous copolymer and correspondingly from 50 to 5 per cent by weight of a rubbery copolymer of butadiene-1,3 and acrylonitrile, said coating being manifested as a highly glossed film so tenaciously adherent to the surface of the paper that when pressure sensitive adhesive tape is pressed firmly upon the coated surface and then pulled suddenly therefrom the paper is split and no separation of the coating from the surface of the paper occurs, the amount of said coating ranging from 0.1 to 3.0 pounds of polymeric material per 1000 square feet of coated surface, said coating being a hot calendered film formed in situ of the solids deposited by drying from an aqueous dispersion of said polymeric material.

2. As a new article of manufacture, paper in sheet form having on a surface thereof a thin continuous flexible transparent coating of a mixture of a resinous copolymer of styrene and acrylonitrile in proportions of from 65 to 80 per cent by weight of styrene and correspondingly from 35 to 20 per cent by weight of acrylonitrile, and a rubbery copolymer of butadiene-1,3 and acrylonitrile, the relative proportions of said resinous copolymer and of said rubbery copolymer ranging from 50 to 95 per cent by weight of said resinous copolymer and correspondingly from 50 to 5 per cent by weight of said rubbery copolymer, said coating being manifested as a highly glossed film so tenaciously adherent to the surface of the paper that when pressure sensitive adhesive tape is pressed firmly upon the coated surface and then pulled suddenly therefrom the paper is split and no separation of the coating from the surface of the paper occurs, the amount of said coating ranging from 0.1 to 3.0 pounds of said copolymers per 1000 square feet of coated surface, said coating being a hot calendered film formed in situ of the solids deposited by drying from an aqueous dispersion of said resinous and rubbery copolymers.

3. As a new article of manufacture, paper in sheet form having on a surface thereof a thin continuous flexible transparent coating of polymeric material selected from the group consisting of a resinous copolymer of styrene and acrylonitrile in proportions of from 65 to 80 per cent by weight of styrene and correspondingly from 35 to 20 per cent by weight of acrylonitrile and mixtures of from 50 to 95 per cent by weight of said resinous copolymer and correspondingly from 50 to 5 per cent by weight of a rubbery copolymer of butadiene-1,3 and acrylonitrile, said coating being manifested as a highly glossed film so tenaciously adherent to the surface of the paper that when pressure sensitive adhesive tape is pressed firmly upon the coated surface and then pulled suddenly therefrom the paper is split and no separation of the coating from the surface of the paper occurs, the amount of said coating ranging from 0.1 to 3.0 pounds of polymeric material per 1000 square feet of coated surface, said coating being a hot calendered film of the solids deposited by drying from an aqueous dispersion of said polymeric material, the extent of penetration of the solids of said dispersion into the paper not exceeding 20% by weight of the polymeric material content of said dispersion, said coating exhibiting a resistance to moisture vapor transmission equal to not over 5 grams of water per 100 square centimeters per 24 hours when exposed at 90° F. to an atmosphere of at least 95% relative humidity.

4. As a new article of manufacture, paper in sheet form having on a surface thereof a thin continuous flexible transparent coating of a mixture consisting essentially of a resinous copolymer of approximately 70 per cent by weight of styrene and 30 per cent by weight of acrylonitrile and a rubbery copolymer of butadiene-1,3 and acrylonitrile, the relative proportions of said resinous copolymer and of said rubbery copolymer ranging from 50 to 95 per cent by weight of said resinous copolymer and correspondingly from 50 to 5 per cent by weight of said rubbery copolymer, said coating being manifested as a highly glossed film so tenaciously adherent to the surface of the paper that when pressure sensitive adhesive tape is pressed firmly upon the coated surface and then pulled suddenly therefrom the paper is split and no separation of the coating from the paper surface occurs, the amount of said coating ranging from 0.1 to 3.0 pounds of said copolymers per 1000 square feet of coated surface, said coating being a hot calendered film formed in situ of the solids deposited by drying from an aqueous dispersion of said resinous and rubbery copolymers and being bonded directly to the surface of the paper by absorption thereinto of not over 20 per cent by weight of the polymeric material contained in the dispersion.

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No references cited.