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PAPER TREATING SOLUTION OF AN ALPHA-OLEFIN/MALEIC ANHYDRIDE COPOLYMER AND A BISULFITE

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This invention relates to the production of aqueous basic solutions of synthetic resins which are especially adapted for use as paper treatment chemicals, and to paper treated with such solutions. More particularly, this invention provides improved aqueous basic solutions of synthetic resins for treating paper and paper products, paper products treated with said improved aqueous basic synthetic resin solutions, and processes for improving the color stability of the synthetic resin treated paper upon oven aging of the paper as is evidenced by the lower brightness loss in papers treated with the compositions of this invention.

In the past, paper producers have applied to formed paper many different chemicals in an effort to obtain paper which was more translucent or less opaque so that the paper could be used for various purposes, e.g., as engineering tracing papers, as reproduction or copy paper and for packaging purposes. In reproduction systems the need for translucency or "transparency" as it is loosely termed in the paper making art, is related to the speed of graphic copying by such processes as diazo, thermographic, or silver halide processes in which visual, ultraviolet and/or infrared light is passed through the translucent paper to produce a copy. The copy may be on a separate sensitized sheet or directly on the translucent sheet. In packaging applications, the need for translucency is to permit viewing of the packaged items by the purchaser; however, strength and barrier properties must be imparted simultaneously. The role of the translucentizing chemical therefore may involve considerably more than translucency; for some applications it may be desirable to impart barrier properties such as resistance to penetration by grease and oil and by vapors and gases. For other purposes, papers having good release properties are desired, e.g., for packaging tacky and pressure sensitive materials such as uncured rubber stocks, and for backings for labels and paper and cloth adhesive tapes. Treated papers of this invention can be used for these purposes.

Most chemicals applied to paper to impart translucency, barrier, and/or release properties to the treated paper have previously been applied from non-aqueous solvents which required that the application be accomplished off the paper making machine in a secondary operation and hence, required more handling of the paper. The use of non-aqueous solvent techniques is not desirable because of flammability or toxicity of the solvent or both. There is a basic market need to produce paper having translucency, barrier, and/or release properties on the paper making machine using conventional equipment.

Water solutions of high molecular weight polymers have been applied to paper. However, high polymer solutions are usually too viscous for efficient application. They do not penetrate the base sheet sufficiently to reduce the opacity as desired and their use requires slower machine speed. The opacity of paper and extent of reduction of opacity in a given paper is spoken of in the TAPPI standard T 425 *m*–60 in terms of a contrast-ratio. This contrast-ratio method of determining the opacity of paper is defined as 100 times the ratio of the diffuse reflectance, R_B, of a specimen backed with a black body of not more than 0.005 reflectance, to the diffuse reflectance, R_W of the same paper specimen backed with a white body having an absolute reflectance of 0.89 the reflectance of freshly deposited magnesium oxide; $C_{0.89}=100(R_B/R_W)$. Thus, the contrast ratio is 100% for perfectly opaque paper, and is only a few percent for a perfectly transparent sheet.

Besides lowering the opacity of paper, to be acceptable to the paper maker the given chemical applied to paper must not only penetrate into and fill up the pores of the paper quickly but it must not substantially reduce the good tensile and internal tear strengths, or the folding endurance of the base sheet. Further, the chemical resin must be one which does not migrate from the base sheet to adjacently held absorbent material. It must not cause "blocking" or sticking together of treated paper when it is rolled up or stacked sheet upon sheet. Also the treated paper must still be receptive to ink and ink eradicators. The treated paper must also be receptive to pencil marks which can easily be erased leaving no images. The treated sheet should also be translucent to light in the near ultraviolet and blue region of the light spectrum (actinic region for diazo reproduction systems) and also be translucent to near infrared radiation for use of the treated paper in other applications such as the thermographic reproduction methods, a representative example of which is the "Thermofax" technique of reproduction. The treated paper thus obtained must also be reworkable to recover the "broke" in the beater.

To obtain treated paper meeting all of these requirements in an efficient and economical manner to be commercially significant is understandably a difficult standard for a paper treatment chemical.

Briefly, this invention provides improved compositions for accomplishing the above stated objectives. The compositions of this invention may be described as (1) an aqueous solution of an aliphatic alkene alpha-olefin/maleic anhydride copolymer having an olefin to maleic anhydride molar ratio of from about 1:1 to about 1:1.9 and an average molecular weight of from about 1000 to about 10,000, the alpha-olefins having from about 6 to about 24 carbon atoms and having dissolved therein (2) a minor amount (generally not over about 10%) based on the weight of the polymer solids, of an alkali metal bisulfite or alkali metal sulfite. The alkali metal of the salt preferably has an atomic weight of from about 22.9 to about 39, that is, it is preferably either sodium or potassium.

It has been found that when paper is impregnated or coated with the modified aqueous basic copolymer compositions as described above, and the treated paper thus obtained is dried and aged in an oven in a standard test (105° C. for 72 hours) the color stability of the aged paper is improved. This discovery is important to paper makers who wish to obtain papers having improved translucency, barrier properties such as grease resistance, moisture, vapor and gas resistance, and release properties, which properties may be obtained singly or in combination depending upon the paper base stock to which the resins are applied, while holding or keeping as much as possible the original brightness of the untreated paper.

To obtain translucent paper, the paper base stock used is one which can be impregnated with the aqueous basic solution of the olefin/maleic copolymer composition. It is preferably a porous, waterleaf or slack-sized paper. It should have a relatively low air resistance, preferably below about 200 seconds/100 ml. of air (TAPPI T 460). However, papers having appreciable water resistance due to sizing or low porosity may be impregnated by the "wet pack" method rather than by the more conven-

tional methods such as by the tub or size press application. To obtain treated papers having good release properties it is desirable to keep most of the applied resin on the surface of the paper or board. Thus the paper or board base stock used for this purpose should be substantially resistant to penetration of the aqueous basic solution of the resin by being either sized or of low porosity.

Grease proof paper can be obtained by this invention by impregnating and/or coating any cellulosic base stock such as waterleaf, slack-sized or hard-sized paper of high or low porosity. The base stock used may have pigments or fillers incorporated to obtain a treated paper which retains a substantial amount of opacity. Papers obtained from any of the conventionally prepared pulps may be treated in accordance with this invention, e.g., sulfite, sulfate, rag stock papers, and papers containing pigment fillers such as clay, titanium dioxide etc.

As stated above, the alpha-olefin/maleic anhydride copolymer basic solution used to treat the paper and which is improved by this invention may be one copolymer composition from one terminal alpha-olefin and maleic anhydride; it may also be a copolymer composition prepared from a mixture of terminal alpha-olefins and maleic anhydride; it may also be a mixture of alpha-olefin/maleic anhydride copolymers from the same or different alpha-olefins of different molecular weight such that the average molecular weight of the copolymer composition is from about 1000 to about 10,000 as determined by the Mechrolab Osmometer method.

For this invention the higher alpha-olefins having from 6 to about 24 or more carbon atoms are used to prepare the copolymer resin with maleic anhydride. The alpha-olefin may be a substantially pure single terminal aliphatic alkene alpha-mono-olefin such as 1-hexene, 3-methyl-1-pentene, 2-methyl-1-pentene, 1-heptene, 1-octene, 2-methyl-1-octene, 1-decene, 1-undecene, 1-dodecene, 1,tetradecene, 1-pentadecene 1-octadecene, 1-eicosene, 1-tetracosene, 1-hexacosene, or it may be a particular distillation fractional cut or blend of various straight or branched chained terminal alpha-mono-olefins. Preferred mixtures of alpha-olefins have from about 10 to about 20 carbon atoms in the olefin components. A particularly suitable blend of aliphatic alpha-mono-olefins of this type for use in preparing copolymers for use rendering paper more translucent is a mixture of C_{14} to C_{18} alpha-mono-olefins. These olefins may be obtained from various sources such as from the dehydration of fatty alcohols, from the polymerization of ethylene and/or propylene, from wax cracking products having low diolefin content, say, less than about 1 percent diolefin content.

Although for reasons of cost and availability we prefer to use maleic anhydride for reaction with the aliphatic alpha-olefins described above, it is contemplated that other related materials could also be used, but not necessarily with the same advantageous results. Such materials would include maleic acid, fumaric acid, itaconic acid, citraconic acid, and their esters and anhydrides, such as the half-methyl ester of maleic anhydride.

The low molecular weight alpha-olefin/maleic anhydride copolymers may be prepared by any conventional solvent or non-solvent technique. Usually the alpha-olefin and maleic anhydride are combined in proportions such that the maleic anhydride is in excess relative to the aliphatic olefin, e.g., in olefin:maleic anhydride mole ratios of from 1:1 to about 1:1.9. When a solvent is used the copolymer product obtained usually has a little higher proportion of maleic anhydride than the ratio charged. For example, in one run the olefin:maleic anhydride charge ratio was about 1:1.25. The ratio of the the copolymer obtained in xylene was 1:1.43. When a solvent is not used the copolymer obtained tends to have a reacted mole ratio closer to the mole ratio of the charged olefin and maleic anhydride reactants. We have found that for many applications it is not necessary to remove all of any excess olefin from the copolymer product before it is used in accordance with this invention. We have found that up to about 6% and even higher amounts of olefin do not substantially impair the properties of the treated paper.

To obtain the low molecular weight desired for this invention it is convenient to prepare the copolymer by conducting the reaction using a dialkyl peroxide as an initiator or catalyst, a chain transfer agent and a reaction temperature sufficient to provide a reasonably short initiator or catalyst half-life so that the polymerization may take place in reasonably short periods of time. Generally with dialkyl peroxides temperatures on the order of from about 130° C. to about 160° C. are used, although the temperature may vary from about 120° C. to about 170° C., depending upon the conditions used. With di-tert-butyl peroxide as initiator or catalyst, and xylene as chain transfer agent and solvent, temperatures of about 140°–155° C. are preferred with higher carbon content olefins (over about 10 carbon atoms average). Reaction times will vary from about 0.5 hour to several hours depending upon the temperature used, whether a solvent is used, etc.

In order to obtain a copolymer product which has a low enough viscosity for use in accordance with this invention it is desirable to include in the polymerization reaction mixture a chain transfer agent to control the average chain length of the copolymer. Any material which serves to limit the growth of the polymer chain or to transfer polymerizing moieties to monomers such that the average molecular weight range of the resulting copolymer product is from about 1000 to about 10,000 may be used. Examples of such chain transfer agents include cumene, the xylenes, alkyl and polyalkylbenzenes (e.g., diisopropylbenzene) which contain at least one hydrogen alpha to the benzene ring, dialkyl ethers such as dimethyl ether, diethyl ether, and saturated aliphatic esters, ketones, aldehydes, mercaptan and other similar compounds having a hydrogen alpha to an activating group. Those in the art are aware of chain transfer agents which may be used. Some chain transfer agents serve as a diluent for the reaction mixture. However, the average molecular weight of the alpha-olefin/maleic anhydride copolymer may also be controlled in the absence of a chain transfer agent or diluent or solvent by conducting the polymerization at higher temperatures, e.g., 160° C. to 180° C. The polymerization should be conducted in an inert substantially oxygen free atmosphere. This may be done by conducting the polymerization under an inert gaseous atmosphere such as nitrogen, carbon dioxide, or methane vapor, or refluxing solvent vapor.

When the polymerization is completed, the reaction mixture is usually stripped to remove at least a part of any unreacted alpha-olefin or maleic anhydride. Usually under the conditions used unreacted olefin is present to some extent. The reaction mixture is usually stripped or evaporated, preferably under reduced pressure to remove by-products such as tert-butanol when di-tert-butyl peroxide was used as the initiator, acetone, diluent or solvent, chain transfer agent etc., and some unreacted olefin. This is desirably accomplished at temperatures sufficiently high to keep the crude product in the liquid state but not high enough to cause any substantial decomposition. Generally temperatures of from about 160° C. to about 225° C., under vacuum down to about 50 millimeters of Hg pressure or lower are used. The resin product which remains as residue may then be poured or otherwise emptied from the reaction vessel, and upon cooling to room temperature it solidifies to a vitreous glassy material which can be crushed or ground easily to any convenient particle size.

These alpha-olefin/maleic anhydride copolymers are water soluble in the basic side of the pH range. Any

alkaline reacting material which produces water soluble salts, amides, or mixed amide-salts of the copolymer composition may be used to make aqueous solutions of the copolymer. Examples include ammonia, ammonium hydroxide, ammonium acetate, the hydroxide of alkali metals having atomic weights of from about 22.9 to about 39, such as sodium hydroxide, sodium oxide, sodium carbonate, sodium propionate, potassium hydroxide, potassium carbonate, etc., so long as the concentration of the base used is low enough to avoid precipitation of the polymer from aqueous media. Organic bases such as the heterocyclic amines e.g., pyridine, morpholine, picoline, the trialkylamines such as triethylamine, tributylamine, the alkylenediamines, and polyalkylenetriamines such as ethylenediamine, diethylenetriamine, tripropylenetetramine may also be used. However, the preferred basic solubilizing agents are ammonia, ammonium hydroxide, and alkali metal hydroxide such as sodium hydroxide and mixtures of ammonium hydroxide with such alkali metal hydroxide. When ammonium hydroxide is used, the preferred practice is to slurry the pulverized solid resin into most (say, 75–90%) of the required amount of water to obtain the desired percent solids solution and while stirring add the required amount of concentrated ammonium hydroxide to effect solution by heating somewhat. A convenient amount of ammonium hydroxide to use is between about 0.5 and 0.6 ml. of concentrated (28%) ammonium hydroxide per gram of resin used. The percent solids in the solutions can be adjusted by adding water. The pH should be kept above about 7.5 to 8.5 for the higher solids content (15% to 25%) solutions to prevent precipitation.

When an alkali metal hydroxide is used as the basic solubilizing agent it is recommended that the pulverized resin be added to the heated (50°–60° C.) aqueous solution of the base. We prefer to use about 0.15 to about 0.30 g. of sodium hydroxide per gram of resin solids, although lower and higher amounts may be used. Gross excesses of sodium hydroxide, however, should be avoided to prevent precipitation of polymer solids from the solution. When mixtures of sodium and ammonium hydroxides are being used the polymer resin solids should be added to the sodium hydroxide solution, and then aqueous ammonium hydroxide can be added to complete solution formation.

The copolymer may also be used in the form of the aqueous basic solutions of its partial amides, such as are formed by reacting the copolymer with anhydrous ammonia, dialkylaminoalkylamines or dialkylaminoalkanols, its partial esters such as the one-half methyl or ethyl esters of the alpha-olefin maleic anhydride copolymer, etc., and in the form of basic quaternary salts of the copolymer by reacting the amide formed from reaction of a dialkylaminoalkylamine with the copolymer with quaternizing materials such as dimethyl sulfate and the like.

The alkali metal bisulfite or alkali metal sulfite may be incorporated into the copolymer solution by any known method. The alkali metal bisulfite may be mixed with the dried pulverized-copolymer solids in suitable minor proportions before the copolymer is dissolved in the aqueous medium and the dried mixture of the copolymer and the alkali metal bisulfite or sulfite may be added as such to the aqueous medium. Alternatively, the dried copolymer and the alkali metal bisulfite or sulfite salt may be added separately to the aqueous medium. It is preferred to first dissolve a given weight amount of copolymer solids in an aqueous basic medium and then to add the minor proportion, preferably from about 0.1% to about 5% of the salt based on the weight of polymer to the dissolved copolymer solution thus obtained.

The bisulfite and/or sulfite ions may be provided to the copolymer solution in any other convenient form also such as in the free acid form or as liquid SO_2 so long as a basic pH is maintained, or as the salts with other metals such as lithium, rubidium, cesium, etc. so long as the amount of the salt used is not enough to precipitate the copolymer from solution. However, these materials are not preferred because of handling, availability, and cost considerations.

It is preferred to combine the alkali metal bisulfite or sulfite salt with aqueous alkali metal hydroxide solutions of the copolymer to obtain optimum color stability in the treated paper. It has been found, however, that the compositions of this invention dissolved in ammonia and amine containing bases such as ammonium hydroxide possess substantial advantage over aqueous ammoniacal solutions of the copolymer which do not contain the alkali metal bisulfite or sulfite. The compositions of this invention so dissolved show substantial resistance to liquid phase corrosion when the solution is held in copper based alloy equipment. This is important since in the absence of the alkali metal bisulfite or sulfite, the ammoniacal solution of the copolymer upon standing turns blue and when colored solutions applied to paper, the paper is discolored. When used to prevent discoloration of ammoniacal solution of the copolymer amounts ranging as low as about 0.01 to 1% are generally sufficient.

The aqueous basic copolymer composition solution thus obtained may be applied to paper as such or there may be incorporated into the aqueous solution other additives or modifiers before it is applied to the paper. Such materials which may be found desirable include antifoaming agents and/or defoaming agents, e.g., trialkyl phosphates such as tributyl phosphate, sulfonated tallow waxes, liquid fatty acid mineral oils, as well as various commercial materials sold for their anti-foaming or defoaming properties such as Hercules "Defoamer 831," "Nopco KFS," "Napco 1497–V," General Electric Antifoam 60, and Dow Corning Antifoam A in amounts ranging from a few parts per million to about 0.5 or 1 percent based on the weight of the copolymer resin of antifoaming or defoaming agent. The aqueous basic copolymer solutions may also be extended, blended with, or used to modify other paper chemicals before being applied to paper. For example these copolymers either dry or in their aqueous basic solutions may be blended with such materials as starch, modified starches such as oxidized starch, enzyme converted starch, starch ethers, British gums, dextrins, and the like, casein etc. when it is desired to improve the water resistance of the coating on paper. Amounts of such additional modifying agents may vary up to about 98% by weight of the copolymer resin composition applied to paper in an aqueous basic medium.

When the aliphatic alkene alpha-olefin/maleic anhydride copolymer, as such or in the form of its ammonium, or alkali metal salts, or its partially amidated-partial salt form, such as the amidated copolymer formed by treating the α-olefin/maleic anhydride copolymer with anhydrous ammonia or a suitable amine and then dissolved in an aqueous medium is extended with or blended into a starch for application to paper, the aqueous basic solution of the copolymer derivative may be added to the dry or wet starch before or after cooking. It may also be applied to paper which has previously been treated with starch compositions. For these applications of the copolymers applied to paper admixed with starch it is preferred that the molecular weight of the copolymer used be kept between about 1000 and 5000, although higher molecular weight copolymer materials up to about 10,000 may also be used if increased viscosities can be tolerated in the paper application procedure used. The final starch-copolymer composition applied to paper should have neutral to basic pH, and should preferably be kept between about 7 to about 10. The amount of starch with which the copolymers may be blended or admixed for application to paper may vary widely depending upon the purpose for which the copolymer is being used, the starch or starch product with which the copolymer is to be ad-

mixed etc. Generally, starch alpha-olefin/maleic copolymer compositions containing from about 1 percent to about 90 percent by weight of the copolymer, based on the weight of the starch, is sufficient for most applications in which the copolymer is applied to paper admixed with starch. When applied to paper admixed with starch to improve the water resistance thereof, maleic anhydride copolymers with alpha-olefins mixtures having from 6 to about 10 carbons atoms are preferred, although the higher carbon content olefins may also be used. For this purpose starch admixed with from 5 to about 15 percent, preferably about 10 percent by weight of the alpha-olefin/maleic anhydride copolymer based on the weight of starch and applied to paper in an aqueous basic reacting system has substantially higher water resistance than paper treated with unmodified starch. Improvements of up to 400 to 1000 percent in water resistance of starch on paper have been obtained in this manner.

These alpha-olefin/maleic anhydride copolymers, and the ammonium, and alkali metal salts and ammoniated amide derivatives thereof may also be used as binder or adhesive modifiers used in pigmented coating compositions for papers to be used in fine printing processes. For example, these copolymers are useful for modifying starch to improve the insolubility characteristics of the starch which is often used as the binder component of what is referred to in the art as a coating color composition wherein pigments such as clay, calcium carbonate, and/or titanium dioxide, among many, are admixed with proportionately smaller amounts of starch, casein, or synthetic resin binders, usually on the order of from about 5 to 15 percent by weight, based on the weight of the total pigment weight. The amount of the alpha-olefin/maleic copolymer product, or derivative thereof, added to the starch used for any such binder purpose will vary depending on the degree of water resistance required and other factors such as the maximum permissible cost of the treated paper thus obtained.

The modified aqueous basic solutions of alpha-olefin/maleic anhydride copolymer compositions of this invention may be applied to any paper, i.e., a prelaid web of paper, by any means known in the art. Application to a web of paper means application to paper which is formed in a web on a paper making machine. This distinguishes this method of application from the application to the paper pulp in the wet-end pulp treating technique. For example, the aqueous solution of the resin may be applied to the base sheet with an applicator, it may be sprayed on the paper, or the paper as it is formed may be passed through the aqueous basic resin solution at a speed adjusted to allow for the desired percent pickup of resin solution. The resin solution may be of any concentration sufficient to allow the paper to be impregnated, surface treated or coated with the desired percentages of resin solution under the conditions applied. For most uses for which the treated paper is intended to be used it is preferred to use resin solutions having from about 10 percent to about 15 percent solids concentration, although for particular uses, and for particular methods of application, solution concentrations having from about 1 percent to about 25 percent solids concentration may be used. The amount of the aqueous basic copolymer applied to the paper to be treated will vary depending upon the type of paper being treated and the object to be accomplished. Generally, amounts of the copolymer resin solution are used to provide the dried treated paper with from about 0.001 percent to about 50 percent resin pickup, based on the weight of the untreated paper. For surface applications and for coating thick substantially non-porous cellulosic paper, the aqueous basic copolymer solution may be applied to the surface of the paper in an amount sufficient to provide the dried treated paper with from about 0.1 to about 25 pounds of resin per 1000 square feet of surface. When relatively porous papers are to be treated to impregnate the interstices of the whole paper web or sheet it is preferred to treat the paper with a sufficient amount of the copolymer resin solution to provide the dry treated paper having from about 0.1 to about 30 percent resin pickup, based on the weight of the untreated paper.

The performances of paper treated with the aqueous basic solution of the alpha-olefin/maleic anhydride resin under various test conditions is further illustrated by the following detailed examples which are meant to illustrate how the polymers may be prepared, and properties of the treated paper and are not intended as limitations on the scope of the invention. The test methods used to determine the performance of the treated papers are described below.

When paper is wetted and then dried, the expansion-contraction cycle causes the resulting sheet to be cockled or wrinkled. To avoid cockle the sheet must be dried under tension. The following treating method is a convenient way to impregnate sheets and dry them under tension. The resulting sheets are cockle free.

The sheets were treated as follows to obtain uniform samples.

A. A rigid aluminum plate, larger in size than the sheet to be treated, is liberally coated with resin solution by means of a paint brush.

B. The sheet to be treated is applied to the prepared aluminum plate by contacting one edge initially, and then the flexed sheet is "rolled" slowly into complete contact with the plate. Simultaneously more resin solution is applied to the top of the sheet with the brush, using transverse strokes. Care is exercised to avoid uneven expansion and wrinkling of the sheet.

C. The wet paper sheet is covered with a sheet of polyethylene (2 mil) and the "sandwich" thus formed is passed through the rolls of a wringer.

D. The polyethylene sheet is immediately peeled off.

E. The sheet of impregnated paper is carefully peeled from the plate and laid on TAPPI blotter paper. A small amount of glue, such as "Elmer's Glue-All," is placed on the circumference of an aluminum frame. With the glue side facing the impregnated sheet, the frame is laid on the sheet and pressed with mild pressure causing the sheet to adhere to the frame. (The frame has inside dimensions of 7" x 8" and outside dimensions of 9" x 10" and was designed to treat 9" x 10" sheets.)

F. The frame and treated paper are placed on a photo drier with the paper side up and in contact with the canvas. Drying time is three minutes at 205° F. (surface temperature of dryer).

G. The frame and paper are removed from the drier. The paper is then cut out of the frame and conditioned in a standard humidity-temperature room overnight prior to testing. The frame is immediately soaked in warm water to loosen the paper adhering to the frame.

When sheets are treated by the "wet pack" method, treating solution is brushed onto each sheet as it is stacked on the one under it. Excess solution is left between each layer. The wet sheets are stored between glass plates, the entire unit being sealed in flexible plastic containers such as "Saran Wrap" to prevent drying of the treating solution along the edges. After the desired amount of "wet packing" (3 to 16 hours) the sheets are peeled from the stack and dressed through the wringer and dried as described in the sequence above. The results reported here were obtained on sheets wet packed for 16 hours.

TEST METHODS

The test methods used to evaluate the base stock and treated sheets are listed below along with explaining notes where necessary. Samples were conditioned according to TAPPI T402 *m*–49 before testing.

A. *Basis weight.*—This is determined by weighing 8 to 12 die cut sheets having dimensions of 6 x 7 inches or 4 x 7 inches. The results were converted to grams per square meter using information contained in TAPPI T410 *os*–61.

B. *Thickness.*—TAPPI T411 *m*–44.

C. *Percent pickup.*—This was determined as follows:

$$\text{Percent Pickup} = \frac{\text{weight of dried treated sheet} - \text{weight of untreated sheet}}{\text{weight of untreated sheet}} \times 100$$

D. *Opacity.*—TAPPI T425 *m*–60 using a Bausch and Lomb Opacimeter (Cat. #33–88–22) equipped with a white body having a reflectance of 89%. Instead of reporting opacity as percent, it is reported in numerically equivalent "points." This was done to avoid confusion when using the terms "opacity reduction" and "opacity increase."

E. *Oil leakage.*—This is a modification of the method given in Federal Spec. UU–P–561*e* par. 4.3.5. The test sheet was placed between a sheet of bond paper and a sheet of tablet paper. These were placed on a flat surface under a pressure of 0.05 p.s.i. The bond and tablet papers were inspected after 48 hours to determine if the additive had migrated from the test sheet. Rating: pass or fail.

F. *Oven aging test.*—This test is described in UU–P–561*e* par. 4.3.3. Test sheets were hung in a Fisher Scientific Company forced draft Isotemp oven for 72 hours. The oven temperature was 100° C. Opacity of the sheet was determined before and after aging. Change in color of the sheet was determined by visual inspection.

G. *Fadeometer test (UU–P–561e par. 4.3.6).*—Samples were exposed to ultraviolet radiation for 10 hours in a type FDA–R Fadeometer. Opacity of the test sheet was determined before and after exposure. Change in color of the sheet was determined by visual inspection.

H. *Folding resistance, M.I.T.—Modified TAPPI T423 m–50.*—The test specimens were ½ x 6 inch strips cut with their long dimension in machine direction. A one-kilogram sample loading was applied. The numbers given are double folds required to sever the specimen.

I. *Tensile breaking strength—TAPPI T404 os–61.*—The strips were one inch wide and cut in machine direction. The distance between clamps was 4 inches. Rate of jaw separation was 0.5 inch/minute. The instrument was a table model Instron.

J. *Air resistance—(Gurley-Hill porosity)—TAPPI T460 m–49.*—The time in seconds for passage of 100 ml. of air was measured.

K. *Ink penetration.*—This was run at 35° C. with ink adjusted to a pH of 1.5. Time, in seconds, for ink to penetrate through the sheet was measured.

L. *Pencil erasure.*—The paper is placed on a drawing board equipped with a standard drawing board cover and a pencil mark made with a black graphite 2H lead pencil. The mark is erased with an "Eberhard Faber 101" eraser. The paper is rated chiefly on mark removal; but also on linting and smudging. "5" indicates complete mark removal with no linting or smudging, "0" indicates a completely unsatisfactory result due to linting, smudging, or image retention.

M. *Ink reception.*—With an "Esterbrook" pen equipped with a #2558 point and using "Sheaffer's" Permanent Blue Black #232 ink the test sheet is written upon. The marks are inspected for skipping and feathering. If neither is present the sheet is rated "OK."

N. *Ink eradication.*—The mark made with "Sheaffer's" ink for the ink reception test is eradicated with "Carter's" "Rytoff." The eradicator is applied to the mark and allowed to stand 20 seconds. It is then blotted

and allowed to stand an additional 20 seconds. The area is then inspected for mark removal. Complete removal is rated "5"; completely unsatisfactory removal is rated "0". When the test area had dried it is written upon with pen and ink; if no feathering occurs it is rated "5"; extensive feathering is rated "0."

O. *India ink reception.*—With a ruling pen, lines of black waterproof ink ("Higgins India") are drawn on the sheet. The lines are inspected for skipping and feathering. If neither is present, the sheet is rated "OK."

P. *Internal tearing resistance—TAPPI T414 m–49.*—The long dimension of the sample was cut in machine direction and then torn across the machine direction.

Q. *Stiffness.*—Stiffness was determined with a Gurley Stiffness Tester. The test sheet was flexed along the machine direction axis.

Example 1

A mixed olefin/maleic anhydride copolymer was prepared as follows:

To a 22 liter flask equipped with stirrer, thermometer, reflux condenser, nitrogen inlet tube, and additional funnel there was added 4500 g. (20.0 moles) of a commercially available C_{14}–C_{18} mixed aliphatic alkene alpha-olefin, and about one-half of 5309 g. (50.0 moles) of mixed xylenes. The flask was purged with nitrogen while the mixture was heated to about 140° C. over about 1 hour. Then about one-half of 131.6 g. (0.9 mole) of di-tert-butyl peroxide was added to the flask and addition of a solution of maleic anhydride and the other half of the di-tert-butyl peroxide dissolved in the other half of the xylene was added from the addition funnel over about 60 minutes while controlling the temperature at from 140° C. to about 145° C. Tert-butanol distillation was noted after about 45 minutes of addition. The mixture was held at 136°–140° for 2 hours and then xylene was stripped out of the reaction mixture over a 133 minute period at temperatures of from 138° C. up to about 170° C. The pressure was dropped to a final pressure of 40 mm. as the temperature increased. Total distillate including tert-butanol was 5530 g. The viscous yellow resin polymer which remained as residue weighed 7015 g. was poured into storage containers. Upon cooling it solidified to a yellow-colored brittle glass. It was pulverized sufficiently to pass through a 20 mesh screen. The copolymer had a specific viscosity of 0.24 as measured on a 4% solution in methylethylketone at 25° C. The average molecular weight was 2095.

The liquid product obtained from these reactants before cooling had a density of about 0.77 g./ml. (6.4 lbs./gal.) at 170° C. It had a melting point of about 110° C. Approximate viscosities of the resin product at various temperatures are:

Temperature (° C.):	Viscosity (stokes)
150	170
160	117
170	79
180	43

The pulverized copolymer solid was added to a stirred, heated (50°–60° C.) aqueous solution of sodium hydroxide containing about 0.23 g. of sodium hydroxide for each g. of copolymer resin. Heating was continued to 80° C. until all the resin particles were dissolved. To portions of this solution there was added 2% and 3%, based on the weight of the polymer solids, of sodium bisulfite. When complete dissolution was effected, the aqueous basic solution of the mixed alpha-olefin-maleic anhydride copolymer containing the sodium bisulfite was applied to a paper stock having the characteristics described in column 1 which was a control. The effects of the chemical treatment are summarized in columns 2, 3, and 4.

Base Used for Solution Prep.	Control [1]	NaOH	NaOH	NaOH
Percent Sodium Bisulfite			2	3
Percent Pickup of Dissolved Solid	None	23.4	24.8	24.4
Opacity, B/L points	75.6	54.2	53.8	54.0
Basis Weight, g./m.^{2}	56.1	69.4	70.0	69.9
(17" x 22"—500 sheets), lbs.	14.9	18.5	18.6	18.6
Thickness, mils	3.60	3.62	3.71	3.71
Air Resistance, sec./100 ml.	13	74	83	79
Ink Penetration, seconds	<1	135	120	110
Tensile, MD lbs./inch width	19.2	24.7	26.6	27.4
Internal Tear, CD, grams	59.4	50.3	51.9	51.4
M.I.T. Fold, MD, Double Folds	58	40	49	53
Stiffness (Gurley), MD, mg.	68.1	95.9	91.7	98.7
Oven Aging, 72 hours, 100° C.:				
Opacity Increase, B/L points	1.0	2.2	1.5	1.5
Brightness Loss, points	8.0	13.0	11.0	10.5
Oil Leakage		Pass	Pass	Pass
Fadeometer, 10 Hours:				
Opacity Increase, Points	0.5	1.5	1.0	1.5
Color Change	None	None	None	None
Pencil Erasure		5	5	5
Ink Reception		OK	OK	OK
Ink Eradication		5-3	5-2	5-1
India Ink Reception		OK	OK	OK

[1] Treated with distilled water.

These data show a substantial reduction in the amount of brightness loss upon accelerated oven aging when the paper is treated with aqueous basic solutions of the copolymer containing a minor amount of the alkali metal bisulfite.

Example 2

To 10.0 g. portions of a mixed alpha-olefin/maleic anhydride copolymer, prepared as described in Example 1, there was added 40–45 g. of distilled water. While agitating the mixture ammonia solution equivalent to 0.402 ml. of 28% ammonium hydroxide per gram of copolymer was added. The mixture was stirred at room temperature for 10 minutes and then heated to 60°–70° C. and held at that temperature for 20 minutes. The pH of the aqueous ammoniacal copolymer solution was 7.7. The polymer solids content of the solution was adjusted to 15% polymer solids content.

Similar solutions to that above were prepared except that to one such solution there was added about 0.3 percent by weight of sodium bisulfite, based on the weight of the polymer solids.

Such aqueous ammoniacal copolymer solutions, i.e., with and without the sodium bisulfite therein each of which solutions was originally clear, and slightly more yellow than distilled water were allowed to stand with pieces of copper wire immersed therein. After 3 days in contact with copper, the aqueous ammoniacal copolymer solution containing the sodium bisulfite had developed no more color than a similar ammoniacal copolymer control solution not in contact with copper, whereas the aqueous ammoniacal copolymer solution which did not contain the sodium bisulfite developed a definite blue color.

I claim:

1. A composition comprising (1) an aqueous basic solution of an aliphatic alkene alpha-olefin/maleic anhydride copolymer having an olefin to maleic anhydride molar ratio of from about 1:1 to about 1:1.9 and an average molecular weight of from about 1000 to about 10,000, the alpha-olefins having from 6 to about 24 carbon atoms, and (2) from about 0.01 percent to about 5%, based on the copolymer content, of an alkali metal salt of an anion selected from the group consisting of bisulfite and sulfite.

2. A composition as described in claim **1** wherein in the aqueous basic solution of the alpha-olefin/maleic anhydride copolymer (1) the alpha-olefin used to prepare the copolymer is a mixture of alpha-olefins having from about 10 to about 20 carbon atoms, and the basic material used to solubilize the copolymer in water is selected from the group consisting of ammonia, ammonium hydroxide, alkali metal hydroxides and mixtures thereof, the alkali metal of said alkali metal hydroxides having an atomic weight of from about 22.9 to about 39, and the alkali metal salt (2) is sodium bisulfite.

3. A composition as described in claim **2** wherein in the aqueous solution of the alpha-olefin/maleic anhydride copolymer (1) the alpha-olefin used to prepare the copolymer is a mixture of alpha-olefins having from about 14 to about 18 carbon atoms, and the basic material used to solubilize the copolymer in water is an alkali metal hydroxide, the alkali metal of which has an atomic weight of from about 22.9 to about 39, and the alkali metal salt (2) is sodium bisulfite.

4. Paper treated with a composition as described in claim **1.**

5. Paper treated with a composition as described in claim **2.**

6. Paper treated with a composition as described in claim **3.**

No references cited.

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