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COATED CELLULOSIC PRODUCTS AND METHOD FOR PRODUCING THE SAME

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This invention relates to the production of improved cellulosic fabrics, and more particularly to the manufacture of coated, surface-pigmented cellulosic fabric sheets. More specifically, it relates to improved paper-coating compositions, and particularly to the production of white, coated, and surface-pigmented paper-like products.

This application is a continuation-in-part of my co-pending application, Serial No. 258,974, filed on February 28, 1939.

Machine-finished papers produced by forming a dry, calendered web of dispersed paper fibers in which sizing material and/or fillers such as clay, titanium oxide, etc. are present or absent, exhibit many desirable properties, particularly in respect to high bulk value, etc. Because of their relatively rough surface, these products are not adapted for use in printing. Whenever paper having a smooth surface and useful for half-tone printing or the like is desired, it is customary to coat the base material with an aqueous composition which contains a mineral material and an adhesive such as casein, gelatine, starch, etc. Two distinct types of mineral-coated papers exist:

(1) Coated paper
(2) Surface-pigmented paper

"Coated paper" usually has a coating in the amount of about two pounds or more of mineral material per side per 1,000 square feet of paper, applied to a previously dried web which after drying is calendered to present a paper surface substantially entirely covered with an adhesive/mineral material layer. "Surface-pigmented paper" usually has a coating in the amount of about one pound or less of mineral material per side per 1,000 square feet of paper. The coating is ordinarily applied to a partially dried paper web on the paper making machine, following which the surface-pigmented paper is dried and calendered. The resultant product comprises a paper web containing pigment and adhesive substantially entirely located in the minute surface depressions of the paper.

"Coated paper," properly calendered, has a much smoother surface than uncoated paper and comprises a uniform receptor for printing ink. Thus, an ordinary grade of coated paper affords a more faithful reproduction of the subject printed than the best grades of uncoated, super-calendered paper. "Coated paper" is limited in its applications, however, because of its heavy weight and high cost per unit area. "Surface pigmented paper," on the other hand, retains the greater bulk, lighter weight, and other advantages of machine-finished papers. In addition, it possesses improved printing properties and desired higher brightness and opacity.

Mineral materials which are usually employed in paper coating processes comprise extenders having indices of refraction less than about 1.65, such as clay, satin white, calcium carbonate and barium sulfate, and/or various types of high strength pigments having indices of refraction greater than about 2.0, such as titanium oxide, zinc sulfide, zinc oxide, etc. Calcium sulfate has been considered undesirable for use in paper manufacture because of the objectionable characteristic of this extender to lower the color or whiteness of the resultant product (U. S. Patent 2,060,824). Said clay, satin white, calcium carbonate, barium sulfate, etc., extenders are relatively cheap and are widely employed, particularly in the manufacture of coated paper. These extenders are relatively low in opacifying and brightening power, however, and therefore must be used in relatively large quantities to provide the paper with requisite opacity and brightness characteristics. Use of these large amounts is very disadvantageous, especially in surface-pigmented papers carrying relatively small amounts of coating materials. High strength pigments, such as mentioned, produce coated, surface-pigmented papers possessing relatively high opacity and brightness. In most instances, however, their excessive cost renders use of such pigments for the purpose prohibitive. It has been proposed to employ extended forms of these pigments, utilizing such extenders as those mentioned, to obtain improved quality at practicable costs. However, paper products of unsatisfactory brightness and opacity invariably result. In some instances, in fact, their properties in the latter respects are even lower than those of comparable filled machine-finished papers. This is especially true in instances of surface pigmented papers. Thus, in U. S. Patent 1,938,949 the manufacture of white opaque waxed paper by a process which comprises coating the paper with certain types of pigments suspended in a casein size vehicle is proposed. However, surface-pigmented printing papers prepared at practicable costs, in accordance with the teachings of said patent, will be found undesirably deficient in opacity and brightness, and also will fail to provide a matte surface having good printing qualities. Similarly, U. S. Patent 2,047,220 proposes the preparation of coating

compositions comprising titanium dioxide extended with calcium sulfate in aqueous solutions of salts of deacetylated chitin. Such coating compositions, however, set to gels on standing and therefore become unfitted for use in coating sheeted cellulosic fabrics. Also, U. S. Patent 2,106,709 discloses a process for coating paper wherein an aqueous starch composition and a filler (pigment material) is applied to the surface of paper. The resultant product calenders to a very high gloss finish. Such finishes are objectionable because of their high gloss and glare. Furthermore, said process does not produce a paper which has a desired matte surface and excellent printing properties.

It is also well known, as disclosed in U. S. Patents 1,682,292, 2,093,463, 2,111,272, and 2,148,951, that alkali salts of carboxyalkyl ethers or acid esters of polymeric carbohydrates or polyvinyl alcohols act as binders or fixing agents in coating compositions, or as thickening agents in textile printing. However, when employed in requisite amounts as adhesives for pigment materials, the relatively high cost of said compounds renders their use prohibitive in many instances. Furthermore, when calcium sulfate is employed in such compositions, undesirably high viscosities result, and, as a consequence a satisfactory coating medium fails to materialize in many instances.

In my concurrently-filed application, Serial No. 315,167 a process is described for producing coating compositions and the products resulting from their use, particularly surface-pigmented, sheeted cellulosic fabrics, such as surface-pigmented paper, of excellent opacity, brightness, and printing properties and which exhibit a relatively smooth matte surface free from objectionable gloss and glare. In its preferred embodiment, said process contemplates surface-pigmenting paper or other sheeted cellulosic fabric with an oxidized elastic starch, aqueous coating composition containing as an essential ingredient thereof anhydrite of specific particle size and other definite characteristics, or a blended mixture of such anhydrite with a prime pigment, such as titanium oxide, etc.

While a highly improved, coated or surface-pigmented product results from the process described in said co-pending application, the calcium sulfate-containing coating compositions employed therein, due to the inherent nature of said calcium sulfate, exhibit relatively high viscosities, especially when the anhydrite and pigment content of said coating is in relatively high or concentrated state. While to some extent this disadvantage of high visconsity is relatively minor when relatively light-weight coatings are to be applied to a cellulosic fabric, or when coatings containing relatively minor proportions of calcium sulfate are utilized, difficulty arises when application of coating compositions containing relatively large and excess concentrations of calcium sulfate is attempted. Thus, when applying a given coating in the nip of squeeze rolls, the weight of coating to be applied is governed by the concentration of the coating composition and the spaced relationship or distance between such squeeze rolls. Since the rolls cannot be spacedly disposed far apart without causing formation of undesired, non-uniform, streaky coatings, relatively heavy coatings can only be obtained by increasing the pigment/adhesive content of such composition. This increase in many instances results in a coating composition of such viscous character as to be wholly unsatisfactory for producing a uniform coating on a given sheet. Accordingly, there exists a definite limit on the weight of the calcium sulfate which may be present in the coating composition. Similarly, in applying these calcium sulfate coatings to fiber board by means of press rolls, the volume of coating applied, and hence the weight thereof, is so limited that desired whitening and brightening effects cannot be obtained from application of a single coating. Furthermore, when said coating compositions are applied in large amounts, as with a brush coater, etc., drying costs markedly and objectionably increase. This for the reason that in order to obtain compositions of correct brushing viscosity, the water content thereof must be increased considerably over that of comparable prior art coating compositions.

It is among the objects of this invention to overcome these and other disadvantages in cellulosic fabric production and to provide an improved type of coated, sheeted cellulosic composition. An additional object is to provide improved coating compositions adapted for use in the manufacture of surface-pigmented, sheeted cellulosic fabrics, such as paper. A further and particular object involves the provision of a useful aqueous calcium sulfate-containing coating composition of desirably non-viscous character, even when the calcium sulfate or anhydrite/pigment content thereof is in relatively high concentration. A specific object of the invention is to provide a process which will afford production and use of a coating composition having a relatively high anhydrite and/or prime pigment concentration and yet normally remain in satisfactory fluid or viscous condition to enable its ready application to all types of cellulosic fabrics. A further and particular object includes the reduction of the viscosity of aqueous adhesive cellulosic fabric coating and surface-pigmenting compositions containing calcium sulfate, and particularly anhydrite of specific particle size and other characteristics to be hereinafter set forth. Further and additional objects of the invention will become apparent from the ensuing description.

These and additional objects are attainable in my invention, which broadly comprises incorporating as an essential ingredient in cellulosic fabric coating compositions containing an adhesive and calcium sulfate (and particularly the anhydrite variety thereof) a water-dispersible alkali salt of carboxyalkyl ethers or acid esters of polymeric carbohydrates or polyvinyl alcohols, whereby calcium sulfate, either alone or as an extender for a prime or base pigment substance, may be employed in such compositions in relatively high concentrations.

In a more restricted embodiment, the invention comprises incorporating in paper coating compositions containing starch or casein and pigment-useful anhydrite, blended or unblended with a prime white pigment, relatively small amounts of a water-dispersible alkali metal salt of carboxyalkyl ethers or acid esters of polymeric carbohydrates or polyvinyl alcohols.

In a specific and preferred embodiment, the invention comprises incorporating as an essential ingredient in an aqueous paper coating composition in which is present an oxidized, elastic starch and anhydrite of particular particle size and pigmentary characteristics, a relatively small amount of a water-soluble alkali salt of a carboxyalkyl ether of a modified or degraded starch,

as distinguished from an unmodified, or water-insoluble, variety thereof.

Before undertaking a more detailed description of the invention to enable its more complete understanding, an explanation of the descriptive terminology herein employed and useful methods for determining the same will now be briefly outlined.

"Reflectance" is the ratio of light reflected from the sample to be tested to light reflected from standard fumed MgO under conditions of equal and essentially diffused illumination and as viewed from a direction normal to the surface of the sample. Values are determined and reported corresponding to noon sunlight illumination and to the spectral region centering at 459 millimicrons, in the blue region.

The values of reflectance, as used herein, were measured by use of the Priest reflectometer which is essentially that described as the Priest-Lange reflectometer in the "American Enameler" for August 1933, pp. 3–4.

The samples and standard are illuminated diffusely and viewed at right angles to their respective surfaces. The illumination is approximately completely diffused except for the viewing hole, 4 cm. in diameter, located about 15 cm. from the sample. The gradings are obtained by illuminating the sphere wall, from which the sample is illuminated, with gas-filled incandescent lamps and viewing the sample and standard through a piece of Corning daylight glass (melt of 1925) of suitable density for the noon sunlight grading, or a suitable blue filter for the blue region grading.

The brightness of each sample illuminated in this way was determined relative to that of magnesium oxide by a Martens photometer according to standard procedure.

The samples were prepared for test by pressing the dry pigment into a trough, using fine ground plate glass to form a flat-matte surface.

"Oil-absorption" is the amount of oil, in grams, required to wet 100 grams of pigment.

"Particle size," as herein employed, refers to the "frequency particle size average" which a pigment or extender may exhibit, and may be described as the number weighted average diameter thereof.

Convenient methods for determining oil absorption and particle size values are more particularly described in the previously issued United States patent to Hall et al. 2,125,342, dated August 2, 1938; such described methods being the ones used for determining the oil absorption and particle size determinations employed in the instant invention.

"Consistency" or apparent viscosity comprises the resistance of a material to flow at any point on a stress-flow curve. The consistencies of the aqueous coating compositions herein described were determined on the modified Stormer viscometer, designed primarily for the determination of the consistency of paints, which is described at page 1273, Perry's Chemical Engineers' Handbook, published 1934 by McGraw-Hill Book Company, such determinations being made by the method described at pp. 1276–1277 of said book, utilizing the standard curve illustrated on page 1276.

In accordance with such methods, the coating composition to be tested is stirred thoroughly in a pint vessel to make sure that all pigment is in suspension. The coating composition-containing vessel is then placed on the stand of the instrument, such stand being raised until the surface of the coating composition within the container rises to the mark on the spatula-like blades. Weights are applied and readings taken until a reading falls between 24 and 36 seconds per 100 revolutions of spatulas. This reading is spotted on the chart and translated into consistency by dropping vertically to the horizontal scale. The consistency determination comprises a superimposed arbitrary scale in which the numeral 10 represents the consistency of a medium-bodied paint, 9K to 3K progressively thicker coating composition and 9N to 3N progressively thinner compositions.

Having explained the terminology to be employed herein and convenient methods for determining values to be referred to, a more detailed description of the invention will now be undertaken.

In adapting the invention to practice, calcium sulfate, preferably in the form of pigment-useful anhydrite and possessed of specific particle size and other characteristics, is employed in my novel coating composition. While use of anhydrite is preferred, other forms of calcium sulfate, such as gypsum, crown or pearl filler, etc., may also be employed, provided optimum results are not desired or essential. Said anhydrite desirably possesses a reflectance value in the blue region of at least about 0.9, has a frequency particle size average not exceeding about 0.7 micron, and about 90% of its particles are less than about 1.5 microns in diameter. Said calcium sulfate or anhydrite produces a blended pigment having an oil absorption value in the range of from about 12.5 to 37.5 when blended in the proportions of substantially 30 parts by weight of pigment titanium oxide, having an oil absorption value of about 20, with about 70 parts by weight of calcium sulfate. Preferably, however, the anhydrite should have a reflectance in the blue region of at least about 0.95, a frequency particle size average of not more than about 0.5 micron, and at least 90% of the constituent particles thereof are less than about 1 micron in diameter; said calcium sulfate producing a blended pigment having an oil absorption value in the range of from about 25 to about 30 when blended in the proportion of about 30 parts by weight titanium oxide to 70 parts by weight calcium sulfate with a pigment titanium oxide having an oil absorption value of 20.

A suitable and preferred type of calcium sulfate for use in the invention is prepared by resort to special methods and procedures. Thus, a particularly useful and effective method comprises the following: Slaked lime containing 150 grams CaO per liter is gradually added to 60° Bé. sulfuric acid until about 90% of the acid becomes neutralized. The amount of sulfuric acid used is sufficient to produce about 1400 pounds of precipitated calcium sulfate. During precipitation, the temperature rises relatively rapidly to approximately 120° C. and then gradually decreases. The temperature is held close to substantially the boiling point during the operation, and the reaction mass is maintained at such temperature, accompanied by continued and thorough agitation, until such time as the slurry becomes substantially free from acicular crystals of gypsum capable of being observed under the microscope at 400 diameters magnification. The resultant anhydrite slurry is then filtered and washed until the filtrate shows a pH of at least about 4. The filter cake is then removed from

the press, repulped in fresh water, and the pH adjusted with a small amount of sodium hydroxide to about 7.5. Thereafter, the slurry is filter pressed and made ready for use, the calcium sulfate or anhydrite product being used either alone or in conjunction with a prime pigment in blended condition. If desired, the calcium sulfate may be suitably calcined prior to use or blending, whereby the same becomes stabilized against hydration. The anhydrite product so obtained will be of excellent white color and possess the desired reflectance, oil absorption, and particle size values referred to.

While the calcium sulfate or anhydrite may be employed in my novel coating compositions in blended or unblended condition, I preferably resort to a blend of the anhydrite with a prime pigment, such as zinc sulfide, lithopone, titanated lithopone, or titanium oxide, preferably the latter, in the proportion of about 30 parts of titanium oxide to 70 parts of anhydrite by weight. I preferably effect blending or mixing of the pigment and anhydrite, while both are in aqueous slurry, agitating the mixture for several hours and until the individual pigment particles become completely dispersed and thoroughly blended. The resultant blended product is then filtered, dried and disintegrated, as by passage through a rotary hammer mill.

The pigment product thus obtained is then preferably mixed with water to which has been added from about 0.1% to about 2%, and preferably about 0.75%, on the basis of the pigment weight, of a water-dispersible alkali salt of a carboxyalkyl ether or acid ester of polymeric carbohydrates or polyvinyl alcohols. A useful and preferred water-dispersible compound comprises a sodium starch glycolate obtained by reacting modified or degraded dextrinized starch with a caustic alkali solution, and subsequently reacting the product of this reaction with sodium chloracetate under such conditions that the dextrinized starch is sufficiently depolymerized and substituted to be rendered water-soluble. Preferably, the resultant aqueous pigment suspension is then suitably incorporated in a coating composition comprising a pigment material, an adhesive (casein, starch, glue, etc.) and water. A preferred type of composition for use in the invention may be conveniently obtained by adding the resultant aqueous pigment suspension with stirring to an aqueous cooked starch solution comprising, say, 20% oxidized tapioca starch, whereby a coating composition consisting of, say, about 10.5% anhydrite, 4.5% pigment titanium oxide, 0.11% sodium starch glycolate, and 5.25% oxidized tapioca starch, results. After preparation of the coating composition, the same may be suitably applied on a paper coating machine to a cellulosic fabric or paper sheet, or directly onto the cellulosic or paper web formed on the paper machine wire. The resultant coated product may be suitably passed through the usual driers and then subjected to calendering, if desired. A convenient, specific method for applying the coating composition comprises passing a web of paper formed on the paper machine wire through driers to reduce its moisture content to about 40 to 60%, or, if desired, to not exceeding about 6%. Said coating may then be applied thereto by suitably immersing the web therein, or passing said web between the nip of two squeeze rolls containing the same and spacedly disposed a definite distance from each other in a horizontal position in the same plane, said nip being kept filled by continuous addition of coating composition. Thereafter, the resultant paper product may be dried on the usual paper machine driers and calendered, if desired.

In order that the invention may be more clearly understood, the following illustrative examples are given, which are not to be taken as in limitation of the underlying concepts of the invention:

Example I

100 grams of a blended pigment of 25 oil absorption value, comprising 70% anhydrite (having a reflectance in the blue region of 0.96, a frequency particle size average of 0.5 micron and 95% of its particles being not greater than 1.5 microns in diameter) and 30% pigment titanium dioxide (having a reflectance in the blue region of 0.94, a frequency particle size average of 0.5 micron and 95% of its particles being not greater than 1.5 microns in diameter), was mixed accompanied by stirring with 225 grams of an aqueous solution containing 0.8 gram water-soluble sodium starch glycolate had by reacting a dextrinized tapioca starch with sodium hydroxide solution and then with sodium chloracetate. 40 grams tapioca starch, containing 0.75% barium peroxide, was mixed with 160 grams water, heated with stirring to about 50° C., and held at that temperature for one-half hour being stirred continuously. It was then heated with stirring to 90° C. and allowed to cool. Water was then added to said starch solution in sufficient amount to make up evaporation losses, and 175 grams of the resultant 20% starch solution was then mixed with the aforementioned blended pigment/sodium starch glycolate/water slurry. A coating composition comprising 10.5% anhydrite, 4.5% pigment titanium dioxide, 1.12% sodium starch glycolate and 5.25% oxidized tapioca starch, resulted. Said coating composition had a low consistency of 7.8N, as measured on the above-described Stormer viscometer.

Example II

A similar blended pigment/oxidized tapioca starch coating composition was prepared in exactly the same manner as that of Example I, being identical in all respects, save that it contained no sodium starch glycolate. When similarly tested, it was determined to have a consistency value of 9.6N, which is undesirably high for certain paper and similar coating applications.

Example III

An aqueous casein paper coating composition containing 4.91% of alkali solubilized casein and 35.09% of a blended pigment comprising 30% pigment titanium dioxide and 70% anhydrite, having a reflectance in the blue region of 0.96, an oil absorption of 25, a frequency particle size average of 0.5 micron and with 90% of its particles not greater than 1 micron in diameter, was conventionally prepared. This composition had a Stormer viscometer of 5.1N, and in a Ford type viscosity cup, equipped with #4 orifice, as illustrated on page 585 of the 8th (January 1937) edition of "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors" by Henry A. Gardner, gave a viscosity reading of 19.4 seconds.

An aqueous casein paper coating composition, identical with that of the next preceding paragraph save that 0.75% (based on the weight of the blended pigment) of a sodium starch gly-

colate prepared from a dextrinized tapioca starch was added thereto, was employed. The resultant composition exhibited a much lower viscosity, giving a reading of 3.4N on the Stormer viscometer and 14.2 seconds with the Ford type viscosity cup.

Example IV

A casein coating composition similar in all respects to that of Example III hereof, but having an increased pigment content, consisting of 36.84% of the blended pigment of Example III, 5.16% of alkali solubilized casein, and 0.28% of sodium starch glycolate, exhibited a lower viscosity than the more dilute, untreated coating composition. Such treated composition gave viscosity readings of 4.6N on the Stormer viscometer and 15.5 seconds on the Ford type viscosity cup.

While in Example II above, I have referred to a consistency of 9.6*N* as rendering the coating composition nonuseful for certain paper and similar applications, it will be understood that the specificity of the viscosity or consistency is variable, and will largely depend upon the intended or desired use, as well as the character of product sought to be obtained.

Although sodium starch glycolate, one useful and preferred type of agent in my invention, has been employed in the above examples, other agents, as indicated, may also be employed herein. In general, use is contemplated of the water-soluble alkali salts of polymeric polyhydroxy compounds such as the carboxyalkyl ethers or acid esters of polymeric carbohydrates or polyvinyl alcohols. Included among specific examples of such compounds may be mentioned the ammonium, sodium, potassium or rubidium cellulose or starch glycolates; the like alkali or alkali metal salts of the glycolic acid ethers of polyvinyl alcohols; the ammonium, sodium, potassium or rubidium salts of the phthalic acid esters of cellulose or starch; or the like alkali or alkali metal salts of phthalic acid esters of polyvinyl alcohols, etc.

Because of the superior results which accrue, I prefer to employ agents of the aforementioned class which are plaster of Paris stabilizers. The latter term includes all alkali polymeric polyhydroxy compounds from the group consisting of carboxyalkyl ethers and acid esters of carbohydrates and polyvinyl alcohols which function to prevent hydration of plaster of Paris upon being stirred in water under the relatively severe conditions to be now alluded to. Thus, to determine whether or not such compounds are stabilizing agents, 50 grams of plaster of Paris containing from 6.0% to 6.5% H_2O by weight is added to 200 grams of water at a temperature of 25° C. containing 0.5 gram of the agent under test. The resultant mixture is agitated vigorously for 1 hour by stirring in a suitable agitator or high speed mixer. The resulting suspension is then filtered and dried to constant weight at 60° C. If, after such treatment, the plaster of Paris contains less than 7.0% H_2O by weight, the agent added to the aqueous slurry is denominated a "plaster of Paris stabilizer."

As stated, the preferred agent comprises water-soluble alkali metal cellulose or starch glycolate, particularly the latter, and the sodium starch glycolates prepared from a modified starch, such as dextrinized or degraded starch, the modified carbohydrate being readily obtained from starch by oxidation or by hydrolysis due to the action of dilute acids, diatase, ferments or heating, etc. Preferably, the relatively highly water-soluble alkali metal salts of carboxyalkyl ethers of starch or cellulose are employed, which exhibit solubility values equalling substantially that of an alkali metal glycolate of dextrinized starch, such as sodium starch glycolate, or, for example, that prepared from commercial "#3 white dextrine." It is to be understood that the salts of the glycolic acid ethers of starch used in my invention should preferably give solutions in which the starch granules are substantially completely broken down or dispersed. The salts of the glycolic acid ethers of starch which, when mixed with water give dispersions which are still principally in granular form, such as those produced from raw potato starch at a low degree of etherification, are for the purposes of this invention classed as water-insoluble. Specific examples of starches useful for the preparation of such starch glycolate include arrow root, tapioca, potato and corn starches previously subjected to an oxidation action with, for example, chlorine, barium peroxide, etc. and the acid hydrolyzed starches, enzyme-treated starches, or the like.

The optimum amount of agent utilizable in the invention is readily determined by trial, such amount being variable with the type of agent, the type and previous history of the calcium sulfate, the proportions of the pigment material to adhesive, the type and previous history of said adhesive, the total solids content of the coating composition, the type of coating or surface-pigmenting equipment being utilized, and the use requirements of the finished, sheeted cellulosic fabric. Usually, only relatively small amounts of the treating agent need be employed. Thus, when employing sodium starch glycolate, the preferred agent, appreciable effects result when the agent is employed in relatively minor quantity, say, as low as about 0.1% and to as high as about 2%, based on the weight of the pigment present. Optimum beneficial results accrue when the amount of agent employed ranges from about 0.5% to about 1.0%, based on the weight of the pigment material.

While various forms of calcium sulfate may be utilized in the invention, to procure optimum benefits herein I preferably resort to use of anhydrite which exhibits certain desired pigmentary properties, particularly in respect to particle size and other values. Thus, the anhydrite most preferred for use in the invention exhibits a frequency particle size average of not more than about 0.7 micron and preferably not to exceed about 0.6 micron, while said frequency particle size average is preferably not greater than about 0.5 micron. At least 90% of the particles thereof should have diameters of less than about 1.5 microns, and preferably should have diameters of less than about 1.3 microns. For optimum benefits, 90% of said particles should have diameters of less than substantially 1 micron. Also, the anhydrite should have a reflectance in the blue region of not less than about 0.9, and preferably not less than about 0.95. The oil absorption value of said anhydrite is determined by blending the same with a prime pigment, preferably titanium oxide. Thus, when blended, for example, with titanium oxide having an oil absorption value of 20, in the proportion of 30 parts by weight titanium oxide to 70 parts by weight anhydrite, the blended product should have an oil absorption value in the range of from about 12.5 to about 37.5, and preferably from about 21.5

to about 32.5, an optimum value being in the range of from about 25 to about 30. Accordingly, the calcium sulfate oil absorption values given herein and contemplated by the appended claims are the numerical values obtained from a blend of such pigment titanium oxide and calcium sulfate.

While the calcium sulfate contemplated for use in the invention may be employed as the sole pigmenting material for the coating composition, preferably, and in order to procure optimum benefits hereunder, a blended form of pigment is employed, comprising about 20 to about 40% of a prime pigment such as zinc sulfide, lithopone, titanated lithopones, and preferably titanium oxide, and from about 80 to 60% of calcium sulfate, and preferably anhydrite. The anhydrite and pigment may be mechanically or otherwise blended in aqueous or dry state with the prime pigment. A highly useful proportion consists of, say, 30 parts of TiO_2 to about 70 parts of anhydrite, both figures being by weight. Blends of calcium sulfate and pigment in varying proportions and in which the calcium sulfate is in higher or lower percentage amounts are also employable.

In general, and to insure obtainment of a relatively matte appearance in the final product, a relatively high oil absorption pigment, particularly one which preferably exhibits an oil absorption value of at least about 15.25, as determined by the test mentioned, is employed for blending with the calcium sulfate. Whatever the oil absorption of the prime pigment, the blended product preferably exhibits an oil absorption value of at least about 12.5, and, to insure optimum results and the provision of a matte appearance, at least about 21.5. A particularly useful blended product comprises one exhibiting an oil absorption value of the order of about 30 and preferably not less than about 21.5. A product of the latter type results when my special anhydrite is mixed with pigment titanium oxide having an oil absorption value of not less than substantially 20, and calcination of said anhydrite is effected at a temperature of not more than about 850° C. prior to or subsequent to blending with the prime pigment. Should a product exhibiting an oil absorption value of less than about 22.5, but not less than about 12.5, be desired, the anhydrite may be mixed with the titanium oxide and calcination thereof to a temperature not exceeding about 925° C. effected prior or subsequent to blending, or said reduction in oil absorption may be effected by milling the same in pulverizing mills such as ring roll mills, edge runner mills, pebble mills, buhrstone mills, and the like.

A particuarly useful and effective type of prime pigment for blending with calcium sulfate employed in the invention comprises one of requisite opacifying and brightening power, particularly titanium oxide having a frequency particle size average of not more than about 0.5 micron and at least 90% of its particles being less than about 1.5 microns in diameter, and preferably less than about 1 micron in diameter. Said prime pigment also possesses an oil absorption value of not less than about 15.25, and preferably not less than about 20. Said pigment also exhibits a reflectance value of at least 0.94 and is substantially free from colored impurities. It must be of requisite crystalline nature, such as results by development through heat treatment of precipitated hydrous titanium oxide, as distinguished from more or less colloidal or amorphous products which lack requisite opacifying and brightening power. Convenient methods for obtaining such a highly useful titanium oxide pigment comprise processes described in the following United States Patents: Reissue 18,854, 1,851,487 and 1,892,693. The term "prime pigment," as employed herein and in the appended claims, includes those white pigments such as titanium oxide, extended titanium oxide pigment, antimony oxide, titanates of divalent metals, lithopone, titanated lithopone, zinc oxide, zinc sulfide, zirconium oxide, zirconium silicate, and the like, having a refractive index of at least about 1.8, whose pigment properties have been developed by calcination, autoclaving, or other treatment, as by the processes of U. S. Patents 1,704,483, 1,892,693, 1,977,583, 2,006,259, and the like.

The blended product must also exhibit a frequency particle size average of not more than about 0.5 micron. Preferably, it exhibits a frequency particle size average of not more than about 0.4 micron, and substantially not more than about 0.3 micron. At least 90% of the particles thereof must have diameters of less than about 1.5 microns, and for optimum results 90% of the particles of the blended product should have diameters of less than about 1.3 microns, and preferably should have diameters of less than substantially 1 micron. Additionally, said blended pigment should have a reflectance value in the blue region of at least about 0.9 and preferably not less than about 0.95. Furthermore, said blended product must exhibit an oil absorption value in the range of from about 12.5 to about 37.5. For optimum results said oil absorption value should be in the range of from about 21.5 to about 32.5, and preferably should be in the range of from about 25 to about 30.

As stated, blending of the prime pigment and the anhydrite can be effected in any desired manner, provided a most thorough distribution of one component throughout the mass of the other is effected. While this can be effected in a dry state, in most instances it is more convenient to resort to wet blending. In most processes the titanium oxide and anhydrite are obtained in the form of an aqueous slurry which before being available for use needs only dewatering and crushing to break up the lumps formed during drying. Such aqueous slurries are entirely suited for blending. The slurries may be mixed with thorough agitation, such agitation being preferably continued for several hours and until the individual pigment particles become completely dispersed and thoroughly blended. The blended mixture is then filtered, dried, and the dry cakes disintegrated.

The adhesive composition which is preferably employed in effecting paper coating comprises an oxidized elastic starch, more specifically defined as a root or tuber starch, such as arrow root, tapioca and potato starches, and the like, previously subjected to mild oxidation, such as by application of barium peroxide, chlorine, sodium peroxide, etc. Oxidized tapioca starch comprises a preferred oxidized elastic starch in the invention because of its ready availability and the superior results which its use induces. Other types of oxidized starches are also contemplated, as for example, chlorinated corn starches, etc. Also, acid-treated and unmodified starches may be used in certain instances, as may casein size, and to advantage, particularly in the manufacture of coated paper or in cases where substantial water-resistance is desired. Also, other

adhesives which are soluble in aqueous media and relatively inert toward calcium sulfate, and do not react therewith to form gels, including glue, dextrin, gum arabic, gum tragacanth, or the like, may be used. Generally, I may employ as adhesives for the pigmenting materials various types of film-forming materials, soluble in aqueous media. These comprise (*a*) cellulose derivatives, such as methyl cellulose, glycol cellulose; or (*b*) polymeric basic materials soluble in the form of their salts with acids, such as diethyl amino ethyl methacrylate, dimethyl amino ethyl methacrylate, dimethyl amino methyl zein, piperidyl methyl zein, cellulose derivatives containing basic groups soluble in dilute acids, e. g., diethyl amine ethyl cellulose; (*c*) water-soluble resins and salts of resins containing carboxyl groups, such as polymethacryl amide; (*d*) water-soluble proteins, including gliadin, glycinin, edestin, casein, vegetable caseins, e. g., soya bean casein, gelatin, glue, egg albumen, blood albumen; (*e*) natural gums, including gum gatti, gum shiraz, gum Madagascar, etc.

While the proportion of adhesive to pigment material in the coating compositions of the instant invention may be varied, as desired, I have found that the beneficial effects thereof, particularly highest opacity and brightness per unit cost and the provision of a matte surface having excellent printing properties, only result when the amount of adhesive present is less than the amount of pigment material. Ordinarily, the weight of adhesive should not exceed about 60% of that of the pigment material. Optimum results accrue when the weight of adhesive is not greater than substantially 40% of that of the pigment material. While increased opacifying and brightening effects result with even lower percentages of adhesive, too low a percentage results in coatings which dust off or become picked off during subsequent printing operations. A useful minimum amount comprises about 10% of adhesive above the weight of the pigment material present. While this comprises a preferred minimum ratio, the utilizable minimum of adhesive can be readily determined by trial and depends somewhat upon the oil absorption of the pigment, the type and previous history of the adhesive, the physical characteristics of the paper to be coated, and the use requirements of the finished paper.

The optimum percentage of water to be employed in the coating compositions of the invention is also best determined by trial and likewise depends on the proportion of pigment material to adhesive, the oil absorption of the pigment, the type and previous history of the adhesive, the type of coating or surface-pigmenting equipment employed, and the use requirements of the finished paper. Coating compositions comprising from about 40 to about 98% water have been advantageously employed in the invention, although optimum results accrue with compositions containing from about 50% to about 90% of water, and preferably from about 60% to about 85% of water.

The novel coating compositions of this invention may be conventionally applied to one or both sides of the paper and in any suitable manner. When employed for surface pigmentation, they may, for example, be applied by passing the paper down between the nip of coating rolls containing the coating composition, or by passing the paper through a vat containing the same, and thereafter removing the excess composition by operation of squeeze rolls. When employed for paper coating, said compositions may be applied by brush or roll coaters, or by any other methods well known in the art. After coating or surface-pigmenting papers with said compositions, the same may be dried in accordance with conventional procedures. After leaving the coating or squeeze rolls, the surface-pigmented papers may, for example, be passed directly to conventional paper making machine driers or to specially-constructed air tunnel driers, or a combination thereof. After leaving brush or roll coaters, the coated papers may be air or tunnel dried, as desired, or in any other manner.

By use of the novel treating agent of my invention, one may utilize higher pigment concentrations in paper coating compositions, while at the same time maintaining satisfactory conditions of fluidity or viscosity in said compositions. Moreover, it permits formulation of coating compositions which are normally fluid and do not require heating prior to or during use. Furthermore, the surface-pigmented and coated cellulosic fabrics, and particularly paper, which are obtained from this invention possess many advantages not exhibited in prior cellulosic fabric coatings. For example, when the calcium sulfate employed, or the blend thereof with prime pigment, has an oil absorption value in excess of about 21.5, the surface-pigmented paper product obtained will exhibit unexpectedly improved opacity and brightness substantially equal to or surpassing that resulting when such papers are surface pigmented with an equal weight per unit area of a comparable aqueous coating composition containing a prime pigment alone, such as titanium oxide, as the sole pigmenting agent. Additionally, my novel product will possess excellent printing properties and a pleasing smooth matte surface, free from objectionable high gloss and glare. In view of the fact that one is permitted to employ relatively high concentrations of pigmenting material in the coating composition, a single application of such coating to the paper will result in a product exhibiting satisfactory opacity and brightness, whereas previously several coatings materially less concentrated in pigment would be required. Thus, a substantial saving in processing and elimination of undesired coating repetition results.

Obviously, the anhydrite or blends of the same with prime pigments may be mixed with other pigment materials, such as natural low-grade extenders, for example, clay and the like, or cheap precipitated extenders such as calcium carbonate, or with other pigment materials, such as barium sulfate, satin white, or the like, to produce desired and specific properties in the resultant coating composition and paper product. While, preferably, no dulling or tinting agents are utilized in the coating compositions of this invention, such mateirals may be added, if desired, and in certain instances where a change in tint or increase in opacity and lower brightness of coated or surface-pigmented cellulosic fabric is sought. Examples of tinting and dulling materials include ultramarine blue, chrome yellow, basic zinc chromate, basic lead chromate, chrome orange, chrome green, barium chromate, iron blue, earth colors such as iron oxide, insoluble dyestuffs such as para red and toluidine red, acid dyestuffs such as pigment scarlet and lithol red, extended colors, carbon black, tinted titanium dioxide, basic color phosphotungstates, vat dyes of the anthraquinone series, azo direct dyestuffs, basic dyes of the

triphenylmethane, azine and thiazine series, and the like, or mixtures thereof.

While the invention has been specifically described in connection with its preferred application to paper production, it will be understood that it is equally applicable to the production of sheeted and laminated cellulosic products generally, such as paper, cardboard, etc. Specific examples of such sheeted cellulosic materials include all types of paper, such as anti-tarnish, bag, Bible, bond, book, catalog, coated, duplex, envelope, ledger, offset, rotogravure, tissue, waxing, wedding and wrapping papers, as well as bristol board, wallboard, bottle caps, boxboard, combination board, newsboard, and patent coated board, etc.

I claim as my invention:

1. A process for producing a coated, sheeted cellulosic fabric comprising applying to said fabric an aqueous adhesive coating composition containing as an essential ingredient pigment anhydrite treated with from about .1 to 2%, based on the pigment, of a water-soluble alkali polymeric polyhydroxy compound from the group consisting of carboxyalkyl ethers and acid esters of carbohydrates and polyvinyl alcohols as a thinning agent for said composition, said anhydrite having a reflectance value in the blue region of not less than about 0.9, a frequency particle size average not exceeding about 0.7 micron, and an oil absorption value ranging from about 12.5 to 37.5, said adhesive being relatively inert towards said anhydrite.

2. A process for producing a coated, sheeted cellulosic fabric comprising applying to said fabric an aqueous adhesive coating composition containing as essential ingredients a blended pigment comprising a prime pigment and calcium sulfate treated with from about .1 to 2%, based on the pigment of a water-soluble alkali polymeric polyhydroxy compound from the group consisting of carboxyalkyl ethers and acid esters of carbohydrates and polyvinyl alcohols as a thinning agent for said composition, said adhesive being relatively inert towards said calcium sulfate and said blended pigment having an oil absorption value in the range of from about 12.5 to 37.5.

3. A process for producing a coated, sheeted cellulosic fabric comprising applying to said fabric an aqueous adhesive coating composition containing as essential ingredients a blended titanium oxide-anhydrite pigment from about .1 to 2%, based on the pigment, of a water-soluble alkali polymeric polyhydroxy compound from the group consisting of carboxyalkyl ethers and acid esters of carbohydrates and polyvinyl alcohols as a thinning agent for said composition, said adhesive being relatively inert towards said anhydrite and the blended pigment having an oil absorption value in the range of from about 12.5 to 37.5.

4. A method for improving aqueous adhesive compositions employed in coating cellulosic fabrics which comprises incorporating in said composition pigment anhydrite treated with from about .1 to 2%, based on the pigment, of a water-soluble alkali metal polymeric polyhydroxy compound from the group consisting of carboxyalkyl ethers and acid esters of carbohydrates and polyvinyl alcohols as a thinning agent for said composition, said anhydrite having an oil absorption value ranging from 12.5 to 37.5 upon blending with a prime pigment, a reflectance value in the blue region of not less than about 0.9, and a frequency particle size average not exceeding about 0.7 microns, with 90% of the particles thereof having diameters of less than about 1.5 microns, and the adhesive component of said composition being substantially non-reactive towards said anhydrite.

5. A method for improving aqueous adhesive compositions employed in coating cellulosic fabrics which comprises incorporating in said composition pigment anhydrite treated with from about .1 to 2%, based on the pigment, of a soluble alkali starch glycolate as a thinning agent for said composition, said anhydrite having an oil absorption value ranging from 12.5 to 37.5, a reflectance value in the blue region of not less than about 0.9, a frequency particle size average not exceeding about 0.7 micron, and 90% of its particles having diameters of less than about 1.5 microns, and the adhesive component of said composition being substantially non-reactive towards said pigment anhydrite.

6. A process for producing an improved coated, sheeted cellulosic fabric which comprises applying to said sheeted fabric an aqueous coating composition containing water, pigment anhydrite, and from about 0.1% to 2% of a water-soluble alkali metal polymeric polyhydroxy compound from the group consisting of carboxyalkyl ethers and acid esters of carbohydrates and polyvinyl alcohols as a thinning agent for said composition, said anhydrite having an oil absorption value ranging from 12.5 to 37.5 upon blending with a prime pigment, and a reflectance value in the blue region of not less than about 0.9, a frequency particle size average not exceeding about 0.7 micron, with 90% of the particles thereof having diameters of less than about 1.5 microns, the adhesive component of said composition being substantially non-reactive towards said anhydrite and present in an amount by weight not exceeding substantially 60% of the amount of pigment material present.

7. A method for producing an improved coated, sheeted cellulosic fabric which comprises applying to said fabric an aqueous coating composition containing water, a pigment material comprising a blend of from about 20 to 40 parts by weight of a prime pigment, and from about 80 to 60 parts by weight of anhydrite, from about .1 to 2%, based on the pigment, of a water-soluble, stabilizing alkali polymeric polyhydroxy compound from the group consisting of carboxyalkyl ethers and acid esters of carbohydrates and polyvinyl alcohols as a thinning agent for said composition, an adhesive substantially non-reactive towards said anhydrite and the latter possessing an oil absorption value ranging from 12.5 to 37.5, a reflectance value in the blue region of not less than about 0.9, a frequency particle size average not exceeding about 0.7 micron, and 90% of the particles of which do not exceed substantially 1.5 microns.

8. A sheeted cellulosic fabric coated with a composition containing calcium sulfate as a pigmenting material, from about .1 to 2% of a water-soluble alkali polymeric polyhydroxy compound from the group consisting of carboxyalkyl ethers and acid esters of carbohydrates and polyvinyl alcohols, as a thinning agent for said composition, and an adhesive which is substantially non-reactive towards said calcium sulfate.

9. A sheeted cellulosic fabric coated with a composition containing anhydrite as a pigmenting material, from about .1 to 2%, based on the pigment, of a water-soluble alkali polymeric poly-

hydroxy compound from the group consisting of carboxyalkyl ethers and acid esters of carbohydrates and polyvinyl alcohols, as a thinning agent for said composition, an adhesive which is substantially non-reactive towards said anhydrite, the anhydrite component of said composition having an oil absorption value ranging from 12.5 to 37.5, a reflectance value in the blue region of not less than about 0.9, a frequency particle size average not exceeding about 0.7 micron, and 90% of the particles thereof having diameters of less than about 1.5 microns.

10. A sheeted cellulosic fabric coated with a composition containing a blend of a prime pigment and anhydrite as a pigmenting material, from about .1 to 2%, based on the pigment, of a water-soluble alkali polymeric polyhydroxy compound from the group consisting of carboxyalkyl ethers and acid esters of carbohydrates and polyvinyl alcohols, as a thinning agent for said composition, an adhesive substantially non-reactive towards said anhydrite present in an amount by weight not exceeding substantially 60% of the amount of said pigment material, the anhydrite component of said composition having an oil absorption value ranging from 12.5 to 37.5, a reflectance value in the blue region of not less than about 0.9, a frequency particle size average not exceeding about 0.7 micron, and 90% of the particles thereof having diameters of less than about 1.5 microns.

11. A sheeted cellulosic fabric coated with a composition containing pigment anhydrite as a pigmenting material, treated with a small amount of a water-soluble alkali starch glycolate as a thinning agent, an adhesive comprising an oxidized elastic starch in an amount by weight not exceeding substantially 60% of the amount of pigment material present, said anhydrite having an oil absorption value upon blending with a prime pigment ranging from 12.5 to 37.5, a reflectance value in the blue region of not less than about 0.9, a frequency particle size average not exceeding about 0.7 micron, and 90% of the particles thereof having diameters below substantially 1.5 microns.

12. A sheeted cellulosic fabric coated with an adhesive composition containing as essential ingredients a blend of from about 20 to 40% of a prime pigment with from about 80 to 60% of anhydrite, said anhydrite in such blended condition having an oil absorption value ranging from 12.5 to 37.5 a reflectance value in the blue region of not less than about 0.9, a frequency particle size average not exceeding about 0.7 micron, and 90% of the particles thereof having diameters of less than about 1.5 microns, an adhesive substantially non-reactive towards said anhydrite present in an amount by weight not exceeding substantially 60% of the amount of pigment material present, and as a thinning agent for said composition from about 0.5 to about 1%, on the basis of the pigment material present, of a water-soluble alkali metal polymeric polyhydroxy compound from the group consisting of carboxyalkyl ethers and acid esters of carbohydrates and polyvinyl alcohols.

13. A sheeted cellulosic fabric coated with an adhesive composition containing as essential ingredients a blend of from about 20 to 40% of pigment titanium oxide with from about 80 to 60% of anhydrite, said anhydrite in such blended condition having an oil absorption value ranging from 12.5 to 37.5, a reflectance value in the blue region of not less than about 0.9, a frequency particle size average not exceeding about 0.7 micron, and 90% of the particles thereof having diameters below substantially 1.5 microns, an adhesive substantially non-reactive towards said anhydrite present in an amount by weight not exceeding substantially 60% of the amount of pigment material present, and as a thinning agent for said composition from about 0.5 to about 1%, on the basis of the pigment material present, of a water-soluble alkali metal polymeric polyhydroxy compound from the group consisting of carboxyalkyl ethers and acid esters of carbohydrates and polyvinyl alcohols.

14. A sheeted cellulosic fabric coated with an adhesive composition containing as essential ingredients a blend of from about 20 to 40% of pigment titanium oxide with from about 80 to 60% of anhydrite, said anhydrite in such blended condition having an oil absorption value ranging from 12.5 to 37.5, a reflectance value in the blue region of not less than about 0.9, a frequency particle size average not exceeding about 0.7 micron, and 90% of the particles thereof having diameters of less than about 1.5 microns, an adhesive substantially non-reactive towards said anhydrite present in an amount by weight not exceeding substantially 60% of the amount of pigment material present, and from about 0.5 to about 1%, on the basis of the pigment material present, of a water-soluble alkali starch glycolate.

15. A paper product coated with an adhesive composition containing as essential ingredients a blend of from 20 to 40% of pigment titanium oxide and from 80 to 60% of pigment anhydrite, the anhydrite in said blend having an oil absorption value ranging from about 21.5 to 32.5, a reflectance value in the blue region of not less than about 0.95, a frequency particle size average not exceeding about 0.6 micron and 90% of the particles thereof having diameters of less than substantially 1.3 microns, from about 0.5% to 1% of a water-soluble alkali starch glycolate as a thinning agent, and an adhesive substantially non-reactive towards said anhydrite present in an amount by weight not exceeding substantially 60% of the amount of pigment material present in said composition.

16. A paper product coated with an adhesive composition containing as essential ingredients a blend of about 30 parts by weight of pigment titanium oxide to about 70 parts by weight of pigment anhydrite, from about .5% to 1% of a thinning agent for said pigment comprising a water-soluble alkali starch glycolate, an adhesive comprising an oxidized elastic starch present in an amount by weight not exceeding substantially 40% of the amount of pigment material present, said pigment material having an oil absorption value in the range of from about 25 to 30, a reflectance value in the blue region of not less than about 0.95, a frequency particle size average not exceeding about 0.3 micron, and 90% of the particles thereof having diameters of less than substantially 1 micron.

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