United States Patent Office 3,655,608
Patented Apr. 11, 1972

3,655,608

PAPER COATING COMPOSITIONS AND PAPER THEREWITH

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No Drawing. Filed Jan. 7, 1969, Ser. No. 789,616
Int. Cl. C08g 51/02, 51/04, 51/06
U.S. Cl. 260—37 N 36 Claims

ABSTRACT OF THE DISCLOSURE

A process by which paper coating pigments are treated with a hydroxyl- or hydrogen-reactive organic chemical and subsequently combined with a polymerizable binder material to form a uniform, high-pigment-content, thixotropic water-free coating composition to be applied to paper, film, or web materials to produce a smooth coated product with superior properties, and the product thereof.

BACKGROUND

Pigmented coatings are applied to paper stock for the purpose of providing an improved surface finish suitable for printing. The coating formulations generally used are aqueous systems containing relatively large proportions of water. Coating with such an aqueous system involves mechanical complexity and increased cost because of the necessity for removing the water to dry the product to an acceptable moisture content.

High quality coated paper for printing must meet a number of requirements dictated by the nature of the printing process. Thus, the requirements are somewhat different depending on whether the printing is to be done by offset, gravure or letterpress methods. For example, paper for offset printing generally must have higher moisture resistance than paper for letterpress or gravure printing because the paper is moistened incident to the offset printing process. In general, however, coated printing paper must be smooth and level, dimensionally stable, strong, moisture resistant, resistant to "picking" or pulling up of coating or fibers by contact with a tacky inked surface, resistant to blistering when heat is used to speed up drying of the ink, and above all, it must accept ink uniformly without absorbing it excessively. In addition, such properties as opacity, gloss and color are imparted by the coating; requirements for these vary widely depending on the desired appearance of the finished printed matter but they must be uniform throughout a particular stock.

An uncoated paper surface is not completely smooth but contains higher and lower areas since the thickness of the felted cellulose fibers varies from point to point. The magnitude of these variations in thickness is reduced by the smoothing effect of calendering. However, if the paper is again moistened with water, the cellulose fibers tend to swell and "spring back," increasing the magnitude of the variations. To create a smooth and level printing surface, the coating must fill in all of the low areas of the paper; while, to provide a uniform surface for ink reception, the coating must also cover the fibers in the high areas. When a paper is moistened by application of an aqueous coating, the magnitude of the surface irregularities is increased and a larger amount of coating must be applied to create a uniform surface.

Non-aqueous materials suitable for the binder or adhesive component of a coating formulation are generally thick viscous liquids in the form in which they are applied. When combined with the higher proportions of filler or pigment, the viscosity is further increased to a point where it is not mechanically possible to apply the required smooth, uniform coating at economically practical speeds by conventional coating techniques.

Coating webs with polymerizable organic materials to prepare the surface thereof for printing has been accomplished according to Brown et al. (U.S. Pat. 3,279,424). Brown et al. apply a polymerizable material (with necessary catalyst) directed to a web. After smoothing the surface of the polymerizable material, said material is subjected to elevated temperature to effect polymerization. The "pot life" of the polymerizable material is a critical factor in such a procedure and precautions must be continually taken to avoid premature polymerization. Moreover, Brown et al. are not concerned with the problem of heavy pigment loading in the applied coating.

Although Winchester (U.S. Pat. 3,240,619) applies plural coatings to a substrate, he is not concerned with the preparation of printing papers, but with printing over a dried first coating prior to the application of a second coating. His substrate is wallboard.

Polymeric materials are generally inherently non-receptive to most inks. Coatings containing large proportions of polymeric binder thus fail to meet requirements for uniform and controlled ink receptivity.

In the coating of paper, the use of non-aqueous coatings with high solids concentrations has many apparent advantages. Unfortunately, it has not heretofore been possible to employ such coatings because otherwise suitable high-solids mixtures were thick and pasty, difficult to mix uniformly, difficult to pump or transport to the coating applicator, and difficult or impossible to spread over the paper surface in the required thin, level, and uniform layer. These problems have now been overcome.

Whereas pigments coated from most aqueous systems form moisture sensitive films prone by their hydrophilic nature to be easily redissolved or broken, the films or bonds from many polymers of organic nature are not easily affected as proved by wet rub tests. A further advantage of high pigment loading and a co-acting, polymerizable organic binder in the coating composition is the effect on the structure of the uppermost layers of coating, the reversion to a less fluid state of the coating due to thixotropic effects especially in the absence or near absence of solvents. The quick release of any solvents of organic nature, chosen for their high evaporation rates, produces smoother films, smaller pores within the film structure and resin bonding between surface fibers and pigment which is only slightly affected by moisture.

Since employed solvent must be subsequently removed from the coating, the amount of solvent should be kept to a minimum. The cost of binder is so much greater than the cost of filler or pigment that minimizing the proportion of binder is a matter of economics. Moreover, the preparation of a lighter weight high quality paper, particularly for books and magazines, has a further economic impact in view of the ever-rising mailing costs, which are of material significance.

SUMMARY

The present invention is directed to stronger and/or lighter weight coated paper with improved printability

and methods of preparing same. It is particularly concerned with high quality publication grades for offset, gravure and letterpress printing. However, readily available variations or modifications result in products suitable for copying papers, technical papers, barrier papers and newsprint.

The binder employed develops its properties as a result of chemical polymerization, which may be a final polymerization, cross-linking or curing of prepolymer. Although it is preferred that the final polymer be thermostable, either thermoplastic or thermosettable resin binders may be employed. Due to the chemical nature of the polymeric materials, the process is further characterized by being effected in a non-aqueous system.

According to the invention, pigment (used herein in the sense to include finely divided but not necessarily inorganic solids for admixture with binder regardless of whether or not the solids have tinctorial value), is first treated with an optimum amount, by weight, of a hydrogen- and/or hydroxyl-reactive chemical. Water reactive or hydrogen- or hydroxyl-reactive organic chemicals are suitable for the purpose. Examples are isocyanates, diisocyanates, silanes, Grignard reagents, etc.

Organic solvents may be included in the treatment but a special and unexpected feature is that treating the dry pigment in the absence of solvent, though solvent was heretofore ordinarily employed with a hydrogen- and/or hydroxyl-reactive chemical, results in the high solids content desirable for uniform coating and otherwise impossible unless solvent is subsequently removed after the treatment.

Another special and unexpected feature is that the treatment of dry pigment with the hydrogen- and/or hydroxyl-reactive organic chemical results in a product which is readily dispersible in a suitable binder without aggregation and with a manifold reduction in viscosity. The resultant binder/pigment admixture is capable of having a solids content in excess of 75% by weight and still having sufficient homogeneity and fluidity for applying a uniform thin coating on paper. For example, the viscosity of a 25% dispersion of a treated pigment was 11 cps., while the viscosity of an otherwise identical dispersion of an untreated pigment was 1,680 cps. (This effect is obtained with common paper-coating pigments, such as various types of clay, titanium dioxides and silicas, and with typical mixtures of paper-coating pigments. The choice of a particular water reactive chemical depends on the nature or composition of the polymeric binder and other constituents of the coating color and on comparative economics; the amount or proportion of the chemical required varies with its chemical structure.)

The polymeric binder inherently contributes to the moisture resistance, strength and dimensional stability. While the binder securely bonds the pigment particles together and to the paper surface, it leaves a uniformly ink-receptive pigment (high quality printing) surface in view of the high proportion of pigment compared to that of polymeric binder. This is accomplished in part by employing a non-aqueous solvent in the coating mixture which dissolves the prepolymeric binder material and thus distributes it uniformly and in intimate contact with the pigment particles. Use of a non-aqueous system permits production of a smooth and level printing surface without applying large amounts of coating. With a non-aqueous system an increase in magnitude of surface irregularities is avoided and a smaller amount of coating is sufficient to give a uniform and level surface. Coatings of from one to two pounds per side per ream (3300 square feet) produce a coated paper equal or superior in smoothness to those produced by conventional aqueous coatings running from 6 to 10 pounds per side per ream.

The process overcomes difficulties which have heretofore prevented the use of polymeric thermostable binders in the production of high quality printing papers.

Loss of dissolved binder into the paper web is minimized through the use of a coating mixture or coating color with high solids content, i.e. with a small proportion of solvent. This not only reduces the strike-in to acceptable limits, but is economically desirable because of the reduction in the amount of solvent which must be removed from the coated paper after application of the pigment. This economy is further accentuated by the use of organic solvents instead of water, since these solvents have much lower latent heat of vaporization and are removed with an expenditure of less heat energy than the same amount of water.

Coating formulations of this invention involve:

(a) A binder which obtains its binding properties as a result of a polymerization reaction or a condensation reaction.

(b) Formulations which provide a good printable surface at low coating weights by incorporating a high proportion of pigment (compared to binder) in a non-aqueous system in which the binder dissolves in the solvent used.

(c) Formulations which can be applied at high solids concentrations by treating the dispersoid, i.e. pigment, in such a manner as to produce highly fluid dispersions.

The unique nature of these coating formulations requires the use of special processing equipment and techniques. The pigment is applied to the paper by an applicator device, such as that described by Nagler (U.S. Pat. 3,518,964) which permits close control of the rate of application and uniformity of distribution of the high solids coating while preventing loss of volatile organic solvents and permitting continuous recirculation of the coating material. Different, and much simplified, drying facilities are used in comparison with those required for conventional lower-solids aqueous coating. For both economic and hygienic reasons facilities for recovery and re-use of the organic solvents are desirable. Glossing rolls, buffers, burnishers, calender stacks, etc., may be used as desired for producing a variety of surface finishes on the coated product.

In general, the process equipment for producing high quality coated paper by this process is less complex and appreciably less expensive to operate than conventional off-machine coaters. The process can be used on webs of a width or operating at a speed at least equal to the capabilities of conventional equipment for producing coated paper of comparable quality.

The invention involves two distinct phases which combine and cooperate with each other to provide a highly desired result. The first phase comprises admixing or treating pigment with, e.g., a water-reacting organic compound to render the pigment more easily dispersible. Although this can be effected in an organic solvent (as seen from U.S. Pat. 3,156,576), a materially improved result is obtained when the pigment is milled with the water-reacting or hydroxy-reactive organic compound in the absence of solvent. Moreover, a more uniform dispersion of the thus-treated pigment with a materially higher solids content and improved flow characteristics is prepared in this way without having to remove excess solvent.

The second phase comprises admixing the treated pigment with a suitable organic binder to form a coating composition, applying a uniform thin layer of the coating composition to one or both sides of paper sheet and thus preparing a smooth, light-weight paper with excellent printing and physical properties. The resulting paper is also part of said second phase.

An object of this invention is to prepare coated paper with a non-aqueous coating composition having a high solids content. A further object is to provide such a coating composition which is homogenous and which has good flow characteristics under conditions suitable for application to paper. Another object is to provide a light-weight coated paper having the physical properties and ink receptivity of the highest grade heavy-weight printing papers. It is also an object that the produced paper be capable of printing and handling on conventional printing machinery without reducing the speed thereof. A still further object

is to alter the nature of those pigments which form heavy paste-like dispersions with resinous binders so that homogenous thixotropic coating compositions may be prepared in lieu thereof. Other objects will be apparent from the description and examples which follow.

DETAILS

Extremely light coating weights of non-aqueous, high solids, volatile solvent, pigmented coating dispersions are applied to substrates varying from foil to paper with an applicator that gives smooth coating lays with a minimum of solvent loss. Coating speeds can be in the same range, e.g. from 500 to 5,000, preferably from 1,500 to 3,000 feet per minute (f.p.m.) as with conventional water-based conversion coaters. The coating machine requires less drying capacity than for water-based coatings in view of the low solvent content, e.g. 5 to 30 percent by weight, of the coating dispersions. This results in a reduction in capital cost for drying equipment and reduced heat energy requirements for drying.

By applying only 4 or less pounds (normally in the range of 1 to 2 pounds) of the non-aqueous coating dispersion per ream side, printing paper surface characteristics are obtained which are at least equal to those of papers that are conventionally coated with from 6 to 10 pounds per ream side of water-based coatings. The elimination of the adverse effect of water (excluded from said non-aqueous coating dispersions) on the surface smoothness of paper is a major factor. Water causes base paper surface to be roughened by fiber swelling, requiring a larger weight of coating to fill the surface valleys. The lower coating weight also means a reduction in the amount of required coater drying capacity.

Many conventional water-based coated sheets require a super-calender treatment to achieve desired surface smoothness or surface gloss. The need for such calendering is eliminated with this process since the smoothness of the base paper is not impaired by solvent coatings as in the case of water dispersions. The elimination of the supercalendering operation leads to a further reduction in the cost of finished paper. Brush polishing apparatus may be installed directly on the solvent coater to attain any required degree of gloss.

A key to the subject coating development is the preparation of flowable, non-aqueous essentially homogeneous coating dispersions having from about 10 to 25 percent by weight of binder based on the weight of the pigment and a total solids content of from about 60 to 95, preferably from about 70 to 80, percent by weight based on the total weight of the coating dispersion. Smooth, opaque, coatings for printing paper application are achieved at lower cost with coating dispersions having such high levels of pigmentation. The higher pigment loading in such non-aqueous dispersion permits lower total coating weights without sacrificing strength or printability.

After polymerization of the binder, the coating becomes resistant to most solvents and acids and bases. A high degree of oil resistance is attained, and this can be further improved by increasing the binder to pigment ratio in the coating composition. The subject invention is preferred for use in the preparation of printing paper wherein pigment solids comprise at least 50 percent by weight of the coating composition, but can be advantageously employed, e.g., for barrier coated (high solvent holdout) papers where the pigment solids comprise 35 to 50 percent by weight of said composition, or even for papers prepared with a lower pigment loading in the coating composition. The coated paper has improved dimensional stability over wide ranges of relative humidity in view of the water-insolubility of the coating. By varying the proportions of the reactants which form the binder of the coating, the coating hardness may be changed from rigid to very flexible.

The coating dispersions of this invention are useful in preparing (a) water, oil and chemical resistant papers or films, (b) smooth surfaces without supercalendering, (c) matte or glossy surfaces, (d) soft to hard films, (e) unique characteristics due to reaction with a precoat on base paper, (f) printing papers of superior ink holdout, (g) strong, lightweight printing papers, (h) high gloss label or decorative papers, (i) barrier papers, (j) special copy papers, (k) varnish label papers, (l) adhesive-coated paper, (m) adhesive-coated films, (n) higher bulk printing papers due to the elimination of supercalendering, and (o) carbonizing paper.

Pigment

Pigments for the preparation of printing papers constitute a recognized class including, but not limited to, such mineral pigments as kaolin clay, bentonite, fuller's earth, calcium carbonate, titanium dioxide, silicas, barium sulfate and other finely divided mineral substances used as opacifiers and/or fillers in various types of surface coatings. Many of these pigments are difficult to wet with non-aqueous liquids. Extensive mixing and comminution are required to obtain effective dispersal in non-aqueous vehicles; even then there is a tendency for the pigment particles to form undesirably large aggregates of individual particles and to separate out of the dispersion by settling rapidly. However, virtually any pigment or colorant, organic, e.g. Quinacridone Red and Phthalocyanine Blue, or inorganic, which can be prepared in finely divided form (having an average diameter of from about 0.2 to 5 microns) can be employed in the preparation of the coating dispersion.

In concentrations in excess of about 50 percent by weight in organic media those pigments, e.g. kaolin clay, titanium dioxide and colloidal silica, which form heavy non-homogenous pastes having poor flow characteristics, can be altered by a relatively small proportion, e.g. from 0.1 to 20 percent by weight, of a hydroxy-reactive, active hydrogen-reactive or water-reactive organic chemical so that they form thixotropic dispersions in the same organic media at even higher concentrations. These thixotropic dispersions can be made homogenous and of sufficient fluidity for coating paper in a thin smooth coat.

This effect is still obtained on pigments specially dried to remove all adsorbed moisture before treatment with the hydrogen- and/or hydroxyl-reactive agents.

The pigment employed can be a single pigment or a combination of two or more pigments. When a combination of untreated pigments is employed, a thick paste-like dispersion may result when at least one of the combination is such (if used alone) as would produce a paste-like dispersion in organic media.

Hydrogen- and/or hydroxy-reactive compounds

Hydrogen- and/or hydroxy-reactive organic compounds constitute an established class, as reflected from U.S. Pat. 3,156,576. All such compounds, e.g. monoisocyanates (hexylisocyanate, octadecylisocyanate and others enumerated in U.S. Pat. 2,789,919), di- and polyisocyanates (hexamethyl diisocyanate, toluene di-isocyanate, benzene di-isocyanate and equivalent isothiocyanates), water-reactive halosilanes (hexadecylchlorosilane) and polyhalosilanes having from 1 to 16 carbon atoms, and water-reactive organometallic compounds (phenyl magnesium bromide), are useful in appropriately modifying the troublesome pigments. (Water-reactive compounds are those which are hydrogen- and/or hydroxy-reactive.) Of the reactive agents ethyleneimines appear least effective; some other hydrogen- and/or hydroxy-reactive compound is thus to be preferred.

It is preferred to select for pigment treatment a hydroxy-reactive organic compound which is also reactive with the binder to form a polymer. When the hydroxy-reactive compound is a di-isocyanate, the preferred binder thus contains a polyalcohol, e.g. 1,3-propylene glycol, a polyether, e.g. polyethylene ether glycol, or a poly-

ester, e.g. diethylene glycol/adipic acid polyester. Other illustrative combinations are:

Hydrogen- and/or hydroxy-reactive compounds	Binder Component
Isocyanate e.g. toluene isocyanate.	Prepolmers of polyesters and poly ethers reacted with diisocy-nates.
Diisocyanate e.g. toluene diisocy-anate; 4,4'-biphenylene diisocy-anate; 2,8-chrysene diicosyanate, diphenylmethane diisocyanate; 2,7-fluorene diisocyanate; isopro-penyl diisocyanate; 1,4-naphtha-lene diisocyanate.	Examples—diols, triols, alkyd resins (including maleic acid; adipic acid; phthalic anhydride; and adipic, maleic, etc., acid condensates*), and pentaery-thritol prepolymers.
Polyisocyanates e.g. 4,4',4''-triphen-ylmethane; triisocyanate (PAPI®).	Diols, e.g. polyoxypropylene derivatives of propylene glycols;
Trialkylmonosilane e.g. trimethylsi-lane.	Triols, e.g. polyoxypropylene derivatives of glycerine or polyoxypropylene deriva-tives of trimethylol propane;
Alkylmonochorosilane e.g. methyl-chlorosilane.	Polyesters or alkyds, e.g. pre-pared from glycerine and/ or ethylene glycol reacted with adipic acid or phthalic
Trialkyl monochlorosilanes e.g. tri-methylchlorosilane.	anhydride wherein the total moles of acid and/or anhy-dride equals N and the total moles of glycol equal (N+1).
Amino organosilanes e.g. silyl-methylamine; N-methylsilyla-mine.	Acrylic resins, e.g. copolymers of ethyl acrylate and methyl meth-acrylate.
Dichlorosilanes e.g. ethylbenzyldi-chlorosilane.	Epoxy resins, e.g. condensates of epichlorohydrin and bisphenol A.
Trichlorosilanes e.g. methyltrichlo-rosilane; vinyltrichlorosilane.	Phenolic resins, e.g. reaction of phenol and formaldehyde, acid or base catalyzed.
Metal alkyls e.g. triethyl Alumi-num.	Urea resins, e.g. condensates of urea and formaldehyde under action of acid or base catalysts.
Metal aryls e.g. tetraphenyl tin.	Melamine resins, e.g. condensates of melamine and formaldehyde under action of acid or base catalysts.
Metal alkylhalides e.g. diethyl alu-minum chloride.	Polyvinyl acetates, e.g. reaction products of vinyl acetate by polymerization.
Metal aryl halides e.g. diphenyl aluminum chloride.	Polyvinyl alcohol, e.g. polyvinyl acetate hydrolyzation products.
Grignard reagents e.g. alkyl mag-nesium halide; methyl magnesi-um bromide; ethyl magnesium chloride; aryl magnesium halide; phenyl magnesium chloride.	Polyamide resins, e.g. copolymers of adipic acid and hexamethyl-enediamine (Nylon 6, 6) or-ε caprolactam polymerization product (Nylon 6).
Ethyl zinc chloride.	
Phenyl zinc chloride.	
Vinylbenzene ammonium chloride.	
A vinyl monomer, such as meth-acrylate, in a redox system.	
A vinyl monomer, such as methyl-methacrylate.	

*Refer to Synthetic Resins for Coating, Rohm & Haas Company, Resinous Products Division, Philadelphia, Pennsylvania, 1953.

Copolymers prepared from these monomer and prepolymer combinations are known. For the purpose of this invention a sufficient amount, e.g. up to 20 percent by weight based on the weight of the pigment, of hydrogen- and/or hydroxyl-reactive component must be admixed with the pigment both to modify said pigment and to provide additional reactive sites to polymerize with the binder component to form a resin. (The term "resin," as used herein, encompasses both natural and synthetic products and includes elastomers.)

When a hydrogen- and/or hydroxy reactive compound of higher functionality (any organic compound containing at least two active hydrogen-containing groups as determined by the Zerewitinoff method) reacts with the binder to form a polymer, higher pigment solids can be attained than with a hydroxy-reactive component, e.g. monoisocyanate, which reacts, but at lower functionality to produce poorer properties.

For example, the preferred hydroxy reactive component with a urethane type binder is a polyfunctional isocyanate of the formula

$$(OCN)_n—R—(NCO)_m$$

wherein

R may be aromatic, e.g. 2,4-tolylene diisocyanate; aliphatic, e.g. ethylene diisocyanate and hexamethylene-1,6-diisocyanate; cycloaliphatic, e.g. cyclohexylene-2,4-diisocyanate; mixed aliphatic and aromatic, e.g. p,p',p''-triphenylmethane triisocyanate; diaromatic, e.g. 3,3'-dichloro - 4,4' - biphenylene diisocyanate and p-phenylene diisocyanate; or heterocyclic, e.g. furfurylidene diisocyanate; and each of

m and *n* is either 1 or 2.

(R may, but need not necessarily, be a hydrocarbon radical; its molecular weight, however, must be in the range from 14 to 2,000, inclusive.) Such isocyanates are well-known and are further exemplified, e.g. by U.S. Pat. No. 3,180,852 and U.S. Pat. No. 3,218,215.

When the hydroxy-reactive component contains two or more isocyanate groups, these may be partially blocked. Suitable blocking agents and the method of preparing blocked isocyanates are well known (Saunders and Frisch, "Polyurethanes—Chemistry and Technology," Part I, pages 118 to 121, 463 and 464, Interscience Publishers, 1962). The need for only partial blocking is apparent since the purpose of the component is to modify the pigment. However, when a di- or polyisocyanate or isocyanate prepolymer is employed in the binder, it may be completely blocked, and stable over long periods at ordinary temperatures and moistures.

Pigment treatment

In order to obtain the highest pigment solids content in a coating dispersion, the pigment is treated with from 0.1 to 20, preferably from about 2 to 10, percent by weight, based on the weight of pigment solids, of a hydrogen- and/or a hydroxy-reactive organic compound in the absence of any solvent. This is referred to as a "dry" treatment. Such dry treatment is advantageously effected in any apparatus, e.g. a ball-mill, a rod-mill and a Banbury, for the intimate mixing of solids. Ball-milling a hydroxy-reactive organic compound, e.g. toluene diisocyanate, with a finely-divided pigment, e.g. kaolin clay having an average particle diameter of from 0.2 to 5 microns, for about one hour (venting the ball-mill after about 20 minutes), triturating the milled product to break up any aggregates and ball-milling the triturated product for a further period, e.g. about one hour, results in a modified pigment which can be combined with a suitable binder component, e.g. any of the organic compounds enumerated in U.S. Pat. No. 3,386,944 as capable of reacting with a di- or polyisocyanate to form a polyurethane, to produce a flowable homogenous coating composition. The treated pigment is a soft and friable aggregate which is readily dispersible in the organic binder or a component thereof.

A small percentage, e.g. from about 10 to about 30 percent by weight based on the weight of the modified pigment, of organic solvent is ordinarily incorporated in the coating composition. The organic solvent is inert to each of the coating composition components and is a solvent for the hydroxy-reactive component and all essential binder components. Suitable solvents, e.g., for binder components which react to form urethane resins are mixtures of esters and aromatic hydrocarbons, e.g., butyl acetate/xylene, ethyl acetate/benzene, propyl acetate/toluene, etc. Solvents for the various binder systems are known to those skilled in the art and are selected on the basis of their reciprocal solubility and rate of evaporation.

Although it is possible to admix solvent with the pigment and hydroxy-reactive component during the initial treatment of the pigment, the reduction in viscosity obtained when the thus-treated pigment is incorporated in the binder component is not as great. Moreover, the amount of solvent required for suitable ball-milling is excessive and places a severe limitation on the pigment loading of the coating dispersion prepared therefrom unless excess solvent is removed from the treated pigment. Even with the subsequent removal of solvent, comparable coating dispersions cannot be obtained when solvent is present during milling; the dry treatment results in a superior coating composition.

The binder component

The binder is an adhesive, such as those detailed in the 1968 Modern Plastics Encyclopedia, McGraw-Hill, Inc., New York, 1968, which holds together the pigment, or modified pigment, particles. This adhesive is ordinarily a

synthetic resin, which may be either thermosetting, e.g. polyesters, or thermoplastic, e.g. polyvinylchloride. Although not necessary, it is preferred that the "binder component" react with the hydrogen- and/or hydroxy-reactive component to form the binder. In any case the pigment modified by the hydrogen- and/or hydroxy-reactive component must be compatible, or made compatible, with said binder component.

The binder component may be a complete binder per se, e.g. polyvinylchloride. Having said binder component react with the hydrogen- and/or hydroxy-reactive component makes it possible to attain greater binding with less resin and a higher total pigment solids in the coating dispersion comopsition.

This component can be a monomer (i.e. an adhesive precursor), a prepolymer or a polymer. Employed polymers can be cross-linked or cured, e.g. catalytically, after admixture with the treated pigment. For stability, these monomers or prepolymers having isocyanate groups can have some or all of said groups blocked.

The particular binder component, per se, is not the essence of the invention. Binders suitable for coating paper are well-known. For the subject invention the binder is organophilic and is in a non-aqueous form.

Coating compositions

The coating compositions are prepared by admixing the modified pigment and binder components with the required amount of a suitable solvent and any catalyst necessary for the polymerization of binder components. Suitable solvents may vary with the binder components and are well-known for the different possible combinations thereof. Required catalysts and amounts needed are also known. Although these are required for the preparation of the final product, they are not of the essence of the invention, except as specifically delineated in the claims.

The mixing of the prepared pigment and other binder component is effected in a high-shear mixer, such as the "Brookfield" counter-rotating blade mixer. With such mixing, even compositions having a 90 percent by weight pigment loading are made fluid enough to apply as a paper coating. Those treated pigments which, in the absence of modification by a hydrogen- and/or a hydroxy-reactive component, would result in only heavy non-aqueous pastes having poor flow characteristics, combine with the binder to form thixotropic dispersions which can be maintained at a fluency sufficient for applying thin coatings thereof on paper. Only the amount of solvent required to obtain a smooth homogeneous non-aqueous dispersion is employed, so that the subsequent removal of excessive amounts of solvent is avoided.

The total amount of binder (hydroxy-reactive component, other binder component and any resin formed therefrom) in the coating composition is preferably from 10 to 25 percent by weight, based on the weight of untreated pigment solids.

An applicator (suitable for viscous thixotropic mixtures) which applies high shear forces to the coating mixture to create high fluidity, limits the residence time of excess coating material on the paper surface to minimize strike-in or penetration of the liquid phase, minimizes solvent loss due to evaporation, and permits recovery and recirculation of surplus coating material is described by Nagler (U.S. Pat. 3,518,964). The coating compositions of this invention may be applied to one or both sides of paper sheet with such an applicator. The thixotropic coating compositions have the additional advantage of becoming stiff as soon as shearing forces are removed and the composition is placed on the paper surface.

In the examples which follow all temperatures are in degrees centigrade (° C.) and all proportions and percentages are on a weight basis unless otherwise specified. The "percentage of binder" is based on the weight of pigment used and not on the weight of the complete system; the "percentage of solids" is based on the weight of those ingredients which remain in the finished coating, i.e. pigment plus binder. Because of the thixotropic nature of the products the viscosity values obtained are affected by the method and duration of mixing, the measurement technique used and other variables. The values reported were those obtained in the particular experiments described; widely different values might be obtained if other conditions varied. The examples are merely illustrative and in no way limit the scope of the invention.

EXAMPLE I

Preparation of pigment—dry treatment

One kilogram of finely divided commercial No. 2 Type Coating Clay (average particle diameter from .2 to 5 microns) was placed in a porcelain ball mill jar together with a sufficient number of hard ceramic grinding rods for effective milling. One hundred grams (10%) of toluene diisocyanate were added, the jar closed and sealed and placed on a roller mill, and milled at ambient temperature (about 20°) for a period of one hour. After approximately twenty minutes the milling was stopped briefly and the mill jar vented to relieve internal gas pressure.

After milling for one hour, the jar was removed from the mill, vented and then opened, the contents removed therefrom onto a No. 30 mesh screen, and passed through the screen in order to break up soft lumps or aggregates which had been formed. Immediately thereafter the thus triturated milled pigment was returned to the mill jar with the grinding rods, resealed, and milling continued for an additional period of one hour. At the end of this period the contents were screened again and stored as treated pigment for future use.

Replacing the No. 2 Type Coating Clay with a like particle size and like weight of either titanium dioxide, fuller's earth, mica, silica, silicates, talc, bentonite, etc. results in a comparably modified pigment. Replacing the toluene diisocyanate with chemically equivalent amounts of any other mono-, di- or polyisocyanate, hexadecylchlorosilane or phenyl magnesium bromide results in the preparation, in the same manner, of a similarly modified pigment. Although the milling was effected at room temperature, the temperature is not critical and can be varied over a considerable range to produce either a liquid or gas phase of the hydrogen- and/or hydroxyl-reacting material for the specified reaction on pigment.

EXAMPLE 2

Dry treatment with a Grignard reagent

One hundred grams of No. 2 coating clay were placed on a No. 00 ball mill jar containing 10 porcelain balls. Thirty-eight and three-tenths (38.3) milliliters of 3 molar phenyl magnesium bromide solution in diethyl ether were added to the jar and milled for two hours. The thus-treated pigment was sifted.

The sifted pigment was then dispersed in 300 grams of xylene by mixing for two minutes with a Brookfield high-shear mixer. The viscosity was measured immediately with a Brookfield viscometer at a spindle speed of 20 r.p.m. Using Spindle No. 1 the viscosity was 20 centipoises (cps.).

EXAMPLE 3

Preparation of pigment—slurry treatment

Following the procedure ("dry" treatment) of Example 1, 500 to 600 grams of xylene, which is the minimum quantity of a suitable non-reactive solvent required to prepare a slurry ("wet" treatment), were added to the initial ball-mill charge. After the milling was completed, the treated pigment slurry could be used in a manner similar to pigment which is subjected to the "dry" treatment, but the percentage of solids in the resulting coating dispersion (treated pigment+binder+solvent) was lower due to the additional solvent present. To obtain a higher pigment loading in the coating dispersion, solvent must

be removed from the slurry-treated pigment prior to incorporation in said coating dispersion. Such removal is effected, e.g., by evaporation or distillation.

EXAMPLE 4

Slurry treatment with a Grignard reagent

One hundred (100) grams of No. 2 coating clay, 300 grams of xylene and 40 milliliters of 3 molar phenyl magnesium bromide in diethylether were placed in a No. 00 ball-mill jar containing 10 porcelain balls and milled for 24 hours. The resulting milled slurry showed a viscosity (Brookfield viscometer using a No. 1 spindle at 20 r.p.m.) of 39 cps.

EXAMPLE 5

Effects of different moisture-reactive reagents—slurry treatment

Each of two identical No. 00 ball-mill jars (each containing 10 porcelain balls) was charged with 200 grams of No. 2 coating clay in "as received" condition. To one of said ball-mills (A) 20 grams (10 percent by weight) toluene diisocyanate (TDI) were added; to the other (B) 20 grams of hexadecylchlorosilane

$$[H_3C—(CH_2)_{15}—SiCl_3]$$

were added.

Two hundred (200) grams of a mixture of one part n-butylacetate to three parts of xylene ("BAX Solvent 13") were added to each jar to obtain a 50 percent solids slurry. Both jars were sealed and milled for one hour. Upon venting, a copious discharge of hot hydrogen chloride gas was obtained from B; a moderate discharge of gas from A. The jars were resealed and milling continued for eighteen hours.

Thereafter, 100 grams of each slurry were transferred to separate 400 milliliter beakers, and 100 grams of BAX–13 Solvent added to each beaker to botain 25 percent-solids slurries. Each such slurry was mixed for two minutes on a Brookfield high-shear mixer and the respective viscosities measured immediately with a Brookfield viscometer, using Spindle No. 1 at a speed of 20 r.p.m. A viscosity of 244 cps. was obtained for A and 32 cps. for B.

Replacing the BAX–13 Solvent with any other non-reactive solvent yields essentially the same results. In view of the high proportion of solvent required to form millable slurries and the fact that the presence of such an amount of solvent makes it impossible to attain the desired high percentage of solids in a coating composition prepared therefrom, the dry treatment is preferred for the preparation of coating compositions.

Replacing the hexadecylchlorosilane with water-reactive silanes having shorter alkane chains, e.g. from 1 to 15 or, preferably, 10 or less carbons, yields comparable results at a more competitive cost.

EXAMPLE 6

Binder preparation

A resin pot reaction vessel was charged with 55.1 grams of commercial toluene diisocyanate (NIAX Isocyanate TDI) and 200 grams of a solvent (BAX–13) consisting of a mixture of one part of polyurethane-grade n-butyl acetate and three parts of xylene. [The resin pot is equipped with a mechanical stirrer, and fitted with a dropping funnel, a reflux condenser with drying tube, a thermometer, and a connection to a source of positive dry nitrogen gas flow which blankets the contents and exhausts through the drying tube at the top of the reflux condenser. Means for external heating and for external cooling are provided.]

Eighty-six and nine-tenths (86.9) grams of polypropylene glycol diol having an average molecular weight of approximately 1,000 and an average hydroxyl number of approximately 110 (NIAX Polyol PPG–1025) was mixed with 58.0 grams of polyether triol having an approximate average molecular weight of 700 and an average hydroxyl number of about 235 (NIAX Polyol LHT–240), and the resulting admixture placed in the dropping funnel of the reactor vessel.

A flow of dry nitrogen gas was established through the apparatus, the mechanical stirrer turned on and cold water circulated through the reflux condenser. The polyol mixture in the dropping funnel was dropped into the stirred mixture of toluene diisocyanate and solvent at such rate that the temperature of the reaction mixture due to the ensuing exothermic reaction did not exceed 30°.

After the addition of the polyol mixture was completed and the exothermic reaction subsided, the reaction vessel was externally heated to bring the temperature of the material therein gradually to approximately 75°, and maintained at that temperature for from three to five hours with constant stirring.

The urethane binder thus prepared had a diol/triol ratio of 60:40, an isocyanate/hydroxyl ratio of approximately 1.5:1 and a 50% binder solids concentration. The materials employed were commercial products of Union Carbide; approximately equivalent materials are manufactured by other suppliers. The binder thus prepared may be stored for extended periods for future use, provided that exposure to moisture is avoided.

EXAMPLE 7

Percentage of hydroxy-reactive component employed

The viscosity of the final coating color decreases as the percentage of hydroxyl- or hydrogen-reactive organic compound used in the pigment treatment is increased. In this example each of the coating dispersions was identical except for the pigment treatment. The stated viscosities were determined by "Brookfield Viscometer." Treatment of the pigment was effected according to the procedure of Example 1 with toluene diisocyanate (TDI) as the hydroxy-reactive compound.

To one kilogram of No. 2 clay pigment (as further defined in the following table), 571.4 grams of binder (prepared according to Example 6), 428.55 grams of BAX–13 solvent and 0.714 gram of stannous octoate catalyst (0.25 percent based on binder solids) were added and the resulting mixture blended for five minutes with a "Brookfield" counter-rotating blade mixer. [The binder has 50 percent by weight resin solids, an average hydroxyl number of 162 and an isocyanate:hydroxyl ratio of 1.5:1.]

Viscosities obtained with varied pigment treatments are given in the following table.

Pigment treatment:	Viscosity (centipoises)
Untreated, as received	1,960
Treated with 2.5% TDI	113
Treated with 5.0% TDI	87
Treated with 7.5% TDI	74
Treated with 10.0% TDI	41

In a related experiment, a series of coating dispersions with various percentages of pigment solids were prepared in the same manner with each of the treated pigments defined in the above table. The percentage of solids was plotted against the viscosity of the resulting dispersion, and the percentage of pigment solids at each treatment level which resulted in a uniform viscosity of approximately 600 cps. determined.

The data are:

Pigment treatment:	Percent solids
Treated with 10% TDI	70
Treated with 7.5% TDI	67.5
Treated with 5.0% TDI	64
Treated with 2.5% TDI	58

For useful coating dispersions, the hydrogen- and/or hydroxyl-reactive compound with which the pigment is treated can vary from 0.1 to 20 percent by weight based on the weight of the pigment solids.

EXAMPLE 8

Preparation of coating mixture using polyurethane binder

Four hundred grams of binder prepared according to Example 6, 314.3 grams of BAX–13 solvent (described previously) and 0.5 gram of stannous octoate catalyst (0.25% based on binder solids) were added to one kilogram of treated pigment prepared according to Example 1 and the resulting mixture blended by stirring for five minutes with the "Brookfield' counter-rotating high-shear blade mixer.

The proportions stated yielded a coating color (coating dispersion) with a total solids content of 70%, a binder content of 20%, and having a viscosity of approximately 600 centipoises, as determined by "Brookfield Viscometer" using the No. 2 spindle at a speed of 20 r.p.m.

Formulation involves only combining selected proportions of the several components to yield the desired product. The percentage of binder depends on the nature of the pigment and the properties required in the resulting coated paper. It is economically desirable to employ the lowest practical proportion of binder and, accordingly, the highest practical proportion of pigment. Although the example illustrated a coating dispersion with 70 percent pigment solids and with a binder content of 20 percent, the pigment solids can readily be increased to 80 or 85 percent and the amount of binder can vary from 10 to 25 percent, based on the weight on the pigment solids.

EXAMPLE 9

Preparation of coating mixture using polyester binder

Ninty (90) parts by weight of a 70/30 alkyd resin/styrene polyester molding resin (MFG 3482M, Molded Fiberglass Corporation) were mixed with a solution of 0.8 PHR (parts by weight per hundred parts by weight of resin) of benzoyl peroxide (catalyst) in 10 parts by weight of styrene to form a binder.

Twenty (20) parts by weight of the above binder were mixed with 51.4 parts by weight of methyl ethyl ketone, and 100 parts by weight of a treated pigment prepared as in Example 1 were dispersed therein. The resulting coating mixture had a viscosity of approximately 1500 cps.

This coating mixture can be employed in the same manner as the Polyurethane system of Example 8. Similar considerations of formulation apply.

EXAMPLE 10

Coating application

The coating mixture of Example 8 was applied with an applicator (described by Nagler in U.S. Pat. 3,518,964 to one side of a stock "Thorcote" size press pigmented printing paper (manufactured by Bergstrom Paper Company) having a nominal 50-pound basis weight. The coating weight and quality are controlled by variations of web speed, doctor blade pressure, coating solids, etc. Coating weights can be varied over a considerable range, e.g. from less than one pound to more than six pounds per ream-side a convenient range is from 0.4 to 6, preferably from 0.6 to 3, pounds per ream-side (3,300 square feet per ream-side). For this example the web speed was 120 feet per minute; the doctor blade pressure, 30 p.s.i.g.; and the pumping rate about one gallon per minute.

The following comparative data (the properties cited are understood throughout the industry and the test methods were, except as noted, as specified by TAPPI or ASTM standards) provide a comparison between coated "Thorcote" prepared according to this example and a high quality commercial trailing blade coated over size press pigmented printing paper, "Mounte Matte" (manufactured by the Northwest Paper Co., subsidiary of Potlatch Forests, Inc.)

	Coated "Thorcote"	"Mountie Matte"
Basis weight	50.2 lb./ream [1]	53.2 lb./ream.
Caliper	3.15 mils	3.40 mils.
Coating weight (by difference)	0.6 lb./ream/side	6 b./ream/side [2].
K&N brightness before wiping [3,4]	81.4/—	84.5/83.0.
K&N brightness after wiping	57.2/—	43.5/44.0.
K&N difference	24.2/—	41.0/39.0.
K&N ink holdout (visual)	Good	Good.
Porosity	3,516 seconds	1,160 seconds.
Ink flotation [5]	350–400 seconds	70 seconds.
Mineral oil absorption	625 seconds	170 seconds.
Smoothness (Sheffield)	54/—	68/82.
Wet rub	Better	Good.
Letterpress printing	Excellent	Excellent.
Glare	22/—	36/36.
Brightness	81.4	84.5.
Opacity	93.5	94.0.
Wax pick	12/—	8/10.

[1] 3,300 square feet per ream.
[2] Estimated from data available.
[3] Measured by G.E. Brightness Meter.
[4] Felt side/wire side ("Thorcote" coating was on felt side only).
[5] Mineral oil used instead of castor oil.

These results show the coated "Thorcote" to be superior to the high quality commercial product with respect to K&N difference, ink flotation, oil absorption, smoothness, wet rub resistance, glare, and pick resistance, with a coating approximately one-tenth as heavy. The slightly lower values for brightness and opacity are probably due to the fact that the pigment used in coating the "Thorcote" is No. 2 clay, rather than a brighter clay or a mixture of pigments.

EXAMPLE 11

Effect of variations in binder formulation

Coating the same stock "Thorcote" paper as in Example 10 with coating compositions varying from that of Example 8 only in the proportions of diol and triol polyols in the binder illustrates the potential range of properties obtained even by minor changes in binder composition. Comparative data are presented in the following table.

With increased proportions of triols, the binder becomes more extensively cross-linked and tends to produce a harder coating; as the proportion of diols increased, there is less cross-linking during polymerization of the binder and hence the coating tends to be softer and slightly elastomeric. The K&N difference improves with increasing triol content, while the wet rub resistance decreases. Lowest porosity is obtained with high diol content; lowest oil absorption with high triol content; etc. As would be expected, glare opacity and brightness show little change, since the type and proportion of pigment is the same in all of these coatings.

Still further ranges of variations in properties and different combinations of properties can be obtained by substituting other triols and diols in the binder composition.

Properties of coated paper can be varied in other ways as well. With the same binder system the isocyanate/hydroxyl ratio can be altered. Binder systems based on different polymers, thermoplastic or thermosetting, can be employed. Different pigments and combinations of pigments can alter the properties as well.

The use of an uncatalyzed isocyanate-terminated prepolymer in the binder is a preferred embodiment. As there are presently no commercially used non-aqueous coating compositions for high-grade printing papers, the subject invention opens new avenues of development.

"THORCOTE" COATED WITH COMPOSITIONS VARYING IN DIOL/TRIOL RATIO

	100% triol; 0% diol	80% triol; 20% diol	60% triol; 40% diol	40% triol; 60% diol	20% triol; 80% diol	0% triol; 100% diol
Basis weight, lb./ream	50.6	50.8	51.2	50.2	51.4	50.4.
Caliper, mils	3.20	3.20	3.20	3.15	3.10	3.05.
Coating weight, lb./ream side	1.0	1.2	1.6	0.6	1.8	0.8.
K&N difference, G.E. brightness	20.9	25.2	22.0	24.2	27.3	27.3.
K&N ink holdout, visual	Best	Less	Less	Less	Less	Poorest.
Porosity, seconds	3,912	3,696	2,168	3,516	3,760	4,656.
Ink flotation, seconds				350-400	75	80.
Oil absorption, seconds	725	750	590	625	525	525.
Smoothness, Sheffield	58	60	58	54	48	50.
Wet rub resistance	Fair	Good	Good	Better	Best	Better.
Letterpress printing	Uneven lay.	Uneven lay.	Very good	Excellent	Good	Good.
Glare	21	24	21	22	18	22.
Opacity	93.2	93.2	93.2	93.5	93.2	93.5.
Brightness	81.1	80.9	81.4	81.4	81.1	80.7.
Wax pick	10	13	10	12	10	10.

What is claimed is:

1. In a pigment coating composition which has sufficient fluidity for applying a uniformly thin pigment coating on a paper surface, the improvement wherein the composition is a non-aqueous homogeneous intimate admixture of binder with pigment/organic chemical, the binder of which is an organic polymeric adhesive or a monomer or prepolymer precursor thereof, the pigment/organic chemical of which is, per se, a non-aqueous soft and friable aggregate essentially free from solvent for the organic chemical, the pigment of the pigment/organic chemical is a finely divided pigment, the organic chemical is a hydrogen- and/or hydroxyl-reactive organic chemical, and the pigment solids of the pigment/organic chemical comprise at least 35 percent by weight of the composition.

2. A composition according to claim 1 wherein the pigment is in organic and the organic chemical comprises at most 20 percent by weight based on the weight of said pigment.

3. A composition according to claim 1 wherein the pigment is clay having an average particle diameter of from 0.2 to 5 microns.

4. A composition according to claim 1 wherein the organic chemical comprises from 0.1 to 20 percent by weight, based on the weight of the pigment, said organic chemical being at least one member selected from the group consisting of an isocyanate, a diisocyanate, a polyisocyanate, a haloalkylsilane, a polyhalosilane having from 1 to 16 carbon atoms and a Grignard reagent.

5. A composition according to claim 4 wherein the organic chemical comprises a haloalkylsilane.

6. A composition according to claim 4 wherein the organic chemical comprises a polyhalosilane having from 1 to 16 carbon atoms.

7. A composition according to claim 6 wherein the polyhalosilane is hexadecyltrichlorosilane.

8. A composition according to claim 4 wherein the organic chemical comprises a Grignard reagent.

9. A composition according to claim 8 wherein the Grignard reagent is methyl magnesium bromide.

10. A composition according to claim 8 wherein the Grignard reagent is phenyl magnesium bromide.

11. A composition according to claim 4 wherein the organic chemical is a diisocyanate.

12. A composition according to claim 11 wherein the diisocyanate is toluene diisocyanate.

13. A product according to claim 1 wherein the pigment is inorganic material which, in the absence of intimate treatment with the organic chemical, generally forms heavy non-homogeneous pastes having poor flow characteristics when admixed in an amount in excess of 50 percent by weight with an organic liquid medium.

14. A pigment coating composition according to claim 29 wherein the binder is a resinous binder and the coating composition is a thixotropic dispersion.

15. A coating composition according to claim 14 wherein the binder is only partially polymerized.

16. A coating composition according to claim 14 wherein the resinous binder is thermosettable.

17. A coating composition according to claim 14 wherein the resinous binder is thermoplastic.

18. A non-aqueous, homogeneous binder/pigment/organic chemical composition according to claim 1 wherein the binder is an organic resin, and the pigment solids comprise at least 70 percent by weight of the composition.

19. Paper coated with a composition according to claim 1 wherein the binder is resinous, the coated paper being essentially free from moisture sensitivity.

20. Coated paper according to claim 19 wherein pigment solids comprise from 35 to 50 percent by weight of said coating.

21. Coated paper according to claim 19 wherein pigment solids comprise in excess of 50 percent by weight of said coating.

22. Coated paper according to claim 19 wherein pigment solids comprise at least 70 percent by weight of said coating.

23. Paper according to claim 19 wherein the resinous binder is polyurethane.

24. Paper according to claim 19 wherein said coating weighs from 0.4 to 6 pounds per ream side.

25. Paper according to claim 19 wherein said coating weighs from 0.6 to 3 pounds per ream side.

26. The use of a non-aqueous coating dispersion to obtain lighter-weight high-grade printing paper according to claim 19.

27. The use of a composition according to claim 1 to reduce the weight of quality printing paper.

28. The use according to claim 27 wherein the pigments/organic chemical prepared in the absence of solvent for the organic chemical.

29. A composition according to claim 1 wherein the pigment solids comprise at least 50 percent by weight of the composition.

30. A non-aqueous, homogeneous binder/pigment/organic chemical composition, according to claim 1, the pigment/organic chemical of which is a non-aqueous product which is free from solvent for the organic chemical.

31. A non-aqueous, homogeneous binder/pigment/organic chemical composition according to claim 1 consisting essentially of binder and pigment/organic chemical.

32. A composition according to claim 2 which is a dispersion wherein the binder is from about 10 to 25 percent by weight based on the weight of pigment in the pigment/organic chemical.

33. A composition according to claim 2 wherein the amount of binder is not substantially more than that required to obtain the sufficient fluidity, to bond particles of the pigment together and to bond the pigment to the paper surface.

34. A composition according to claim 2 wherein the binder is one which derives its binding properties from polymerization or condensation.

35. High-grade printing paper according to claim 35.

36. Coated paper according to claim 19 having a uniformly ink-receptive pigment surface.

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U.S. Cl. X.R.

106—308 N; 117—76 P; 260—41

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,655,608 Dated April 11th, 1972

Inventor(s) KARL R. GUENTHER and DONALD G. HAVEKOST

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 4, "Middletown" should read --Middleton--. Column 2, line 13, "directed" should read --directly--. Column 6, line 59, "diisocyanate," should read --di-isocyanate,--; lines 66 to 69, delete "Of the reactive ... to be preferred.". Column 7, line 8, "diicosyanate," should read --diisocyanate,--; line 30, "magnesium halide;" should read --magnesium halide; phenyl magnesium bromide;--; lines 33 to 35, in table, delete last four lines "A vinyl monomer .... methylmethacrylate." in the left column; line 53, "hydroxy reactive" should read --hydroxy-reactive--. Column 8, line 27, "and" should read --or--. Column 11, line 37, "botain" should read --obtain--. Column 13, line 58, "3,518,964" should read --3,518,964)--; lines 66 to 68, "per ream-side a ... ream-side)." should read --per ream-side (3,300 square feet per ream-side). A convenient range is from 0.4 to 6, preferably from 0.6 to 3, pounds per ream-side.--. Column 14, lines 1 and 2, "trailing blade ... printing paper" should read --printing paper trailing blade coated over size press pigmented base--; line 17, "flotation^{5}" should read --flotation--; line 18, "absorption" should read --absorption^{5}--. Column 15, claim 2, line 2, "in organic" should read --inorganic--; claim 13, line 1, "product" should read --composition--. Column 16, claim 28, line 2, "ments/organic chemical prepared" should read --ment/organic chemical is prepared--; claim 30, line 2, "composition," should read --composition--; claim 35, line 1, "35." should read --19.--.

Signed and sealed this 9th day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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