

[54] **ARTICLE HAVING A HYDROPHILIC COLLOID LAYER ADHESIVELY BONDED TO A HYDROPHOBIC POLYMER SUPPORT**

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[51] Int. Cl. .... **G03c 1/94**

[58] Field of Search ..... **96/87 R, 67, 29 L, 85, 96/1 R**

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[57] **ABSTRACT**

An article is disclosed characterized by a hydrophobic polymer support and a supported portion having a surface comprising a hydrophilic colloid layer which is bonded to the support by an adhesive layer containing an inorganic oxide such as silicon oxide, aluminum oxide, magnesium oxide, tantalum oxide, titanium oxide, boron-silicon oxide, and mixtures thereof. The article can be a photographic article including a radiation sensitive material such as silver halide.

**11 Claims, 3 Drawing Figures**

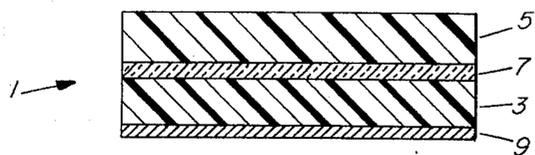


FIG. 1

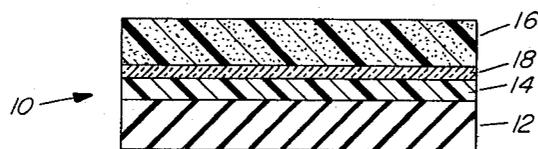


FIG. 2

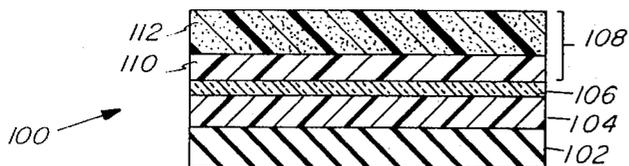


FIG. 3

**ARTICLE HAVING A HYDROPHILIC COLLOID LAYER ADHESIVELY BONDED TO A HYDROPHOBIC POLYMER SUPPORT**

This invention relates to improving the adhesion of hydrophilic colloid layers to hydrophobic support surfaces. In one aspect, this invention relates to articles having a hydrophilic colloid layer and a hydrophobic support surface which are bonded by an interposed inorganic oxide adhesive layer, for example, a metal oxide adhesive layer. In another aspect, this invention relates to a photographic article in which a hydrophilic colloid layer of a radiation sensitive portion of the article is bonded to a hydrophobic support surface using an inorganic oxide subbing or adhesive layer.

It has been recognized that colloid layers which are hydrophilic in nature in order to be uniformly permeable to aqueous solutions utilized in photographic processing, do not readily or uniformly bond to hydrophobic polymer supports with the tenacity that is frequently desired. Since the majority of the photographic supports, principally film and resin coated paper supports, utilized with such hydrophilic colloid layers are hydrophobic, it is common practice to treat the surface of these supports so that they present a hydrophilic surface for receipt of the colloid layer to be bonded.

For example, in the case of polyethylene terephthalate films, which exhibit a comparatively marked degree of hydrophobicity, one approach to achieving the desired tenacious bonding of a hydrophilic colloid such as gelatin to the film is to deposit on the polyester film a comparatively complex terpolymer subbing layer containing dissimilar monomeric units which promote adherence between the hydrophobic and the hydrophilic materials. The terpolymer firmly and uniformly adheres to hydrophobic polyethylene terephthalate film surfaces and also to hydrophilic gelatin surfaces and in this way a reliable and strong indirect bond is achieved between the gelatin and the film.

A principal disadvantage of such subbing layers is that they are complex and hence add significantly to the time and cost of photographic article manufacture. The complexity is reflected both in bonding layer preparation and control, particularly where complex polymers are utilized, and in achieving compatibility with radiation-sensitive article portions. Compatibility with the radiation-sensitive materials and addenda normally associated with photographic articles is particularly demanding. Also, the subbing layers must be compatible with the processing solutions brought into contact with the radiation-sensitive articles after exposure.

While common photographic film supports are typically hydrophobic and do not adhere well to hydrophilic colloids, it has been observed that such supports are, with respect to certain types of coatings, excessively adherent. For example, metal anti-static layers have been employed in photographic articles in the past. However, when a metal anti-static layer is vacuum deposited onto a film support and the coated film wound in reel form in the vacuum chamber before exposure to air, the metal frequently will adhere to both adjacent film surfaces. When this occurs the metal may cause "blocking"—i.e. prevent unwinding of the reel or, if unwinding is in fact accomplished, the metal coating may be partially and randomly transferred to the opposite surface of the polymer support.

Prior to this invention it has been recognized that vapor deposited inorganic oxides are, like vapor depos-

ited metals, readily adherent to glass and plastic surfaces. It has also been recognized that certain vapor deposited inorganic oxides may in turn receive vapor deposited overlayers, such as vapor deposited metal oxide, metal halide and metal overlayers, and thereby bond any such overlayer to a support. For example, Agfa British Pat. No. 1,066,944, published Apr. 26, 1967, teaches using certain vapor deposited metal oxides as adhesives for vapor deposited metal halides.

Such vapor deposited overlayers, however, differ markedly in physical properties from hydrophilic colloids. In addition to being hydrophilic, which in itself renders the colloids difficult to bond to hydrophobic surfaces, hydrophilic colloids also ingest water when brought into contact with aqueous solutions, such as photographic processing solutions. The ingestion of water creates substantial dimensional changes in the hydrophilic colloid and/or large internal stresses, particularly at a bonding interface. For example, a hydrophilic colloid layer may ingest a quantity of water several times its original weight leading to doubling, tripling or greater increase in its original thickness. When a hydrophilic colloid is deposited directly on a hydrophobic support, it can be sloughed from the support on swelling of the layer during exposure to aqueous solutions. Accordingly the art has heretofore generally utilized terpolymers as above noted as subbing layers to facilitate adhesion of hydrophilic colloid layers to hydrophobic support surfaces.

It is an object of this invention to provide an article in which the bonding of an article portion presenting a surface comprised of a hydrophilic colloid to a hydrophobic polymer support surface is achieved using an interposed adhesive layer that is of low cost and complexity.

It is another object to provide a photographic article having a radiation sensitive portion comprising a hydrophilic colloid layer which is bonded to a hydrophobic polymer support surface by means of an interposed subbing layer that is relatively inert and insoluble in the course of photographic processing and also that is compatible with radiation sensitive materials and addenda.

It is still another object to provide a photographic article bearing a metal layer that is protected against blocking by an inorganic oxide layer positioned on a major surface of the support opposite to the metal layer.

These and other objects of this invention are accomplished in one aspect by an article comprising a support having a hydrophobic polymer supporting surface, a hydrophilic colloid layer and an adhesive layer which is contiguous to the supporting surface and the hydrophilic colloid layer and is bonded to each. The adhesive layer comprises an inorganic oxide selected from the group consisting of silicon oxide, aluminum oxide, tantalum oxide, magnesium oxide, titanium oxide and mixtures thereof. In a preferred form the article contains a radiation-sensitive material. A metal layer can be associated with a surface of the support from which the subbing layer is absent.

In accordance with this invention it has been found that a hydrophilic colloid layer can be firmly bonded to a hydrophobic polymer supporting surface by means of an inorganic oxide adhesive layer which is contiguous to the supporting surface and to the hydrophilic colloid layer. Such adhesive layers (commonly referred to as subbing layers in the photographic arts) are binderless

layers which consist essentially of inorganic metal oxide and are capable of bonding directly and tenaciously to both hydrophilic colloid layers and to hydrophobic polymeric support surfaces to perform the function heretofore performed by considerably more complex polymer layers. The term "binderless layer" refers to a layer that is substantially free of organic adhesive materials and refers particularly to the absence of those organic adhesive and binder materials commonly utilized in the photographic arts, such as natural and synthetic polymeric binders and colloidal vehicles. The binderless adhesive layer may be formed of crystalline or amorphous inorganic oxides. In a preferred form the adhesive layer is a glass.

It is a surprising feature of this invention that the hydrophilic colloid remains tenaciously bonded by the inorganic oxide to the hydrophobic support surface when the article is immersed in colloid swelling aqueous solutions and when the article is subjected to mechanical flexure of the support and colloid. In the course of processing after exposure, photographic articles bearing radiation-sensitive colloid layers are often brought into association with alkaline, acid and/or neutral aqueous solutions in accordance with procedures well known to those skilled in the art. In the course of such processing the colloid layer, being water permeable, ingests appreciable quantities of aqueous solution, and the increase in volume of the emulsion layer can produce marked dimensional changes and/or internal stresses. The inorganic oxide layer utilized in the practice of this invention remains comparatively stable during such photographic processing. Furthermore, despite dimensional changes and stresses produced during photographic processing a colloid layer is rendered highly adherent by an inorganic oxide layer even when subjected to mechanical stress, as, for example, when binding a colloid layer to a flexible support that is wound or repeatedly flexed.

It is a surprising feature of this invention that not only does the inorganic oxide layer serve as an excellent adhesive between the hydrophobic polymer surface and the hydrophilic colloid surface, but, additionally, this layer may be relied upon to prevent undesired adhesion of a metal to the support surface. For example, it has been observed that where a metal layer is deposited on a hydrophobic polymer film support and the film is wound on a reel prior to allowing the metal surface to become oxidized, the metal will adhere to both adjacent surface of the film. This may lead to blocking, preventing unwinding of the film, or the metal may adhere randomly to the opposite surfaces of the film. To cite a specific example, in vacuum depositing a metal anti-static coating onto a film surface in an evacuated enclosure, it is necessary, in order to coat appreciable lengths of film, to wind the film from one reel to another during coating and before air exposure occurs. The resulting adhesion and/or partial transfer of the metal anti-static coating to the opposite surface of the film upon unwinding poses a substantial difficulty. Where an inorganic oxide layer is formed on one major surface of the film, a freshly deposited metal layer on the opposite surface of the film will not transfer to the adjacent inorganic oxide surface on winding and will not adhere to the metal oxide surface so as to prevent unwinding of the film. In comparing colloid coated films with and without inorganic oxide bonding layers provided according to this invention, similar improve-

ments in preventing the colloid layer from being pulled away by the metal layer are obtained with those films having inorganic oxide bonding layers.

In the articles of this invention the overall thickness of the adhesive layer can be widely varied. To the extent that the layer is formed so thin that it does not fully cover the support surface the advantages of this invention may be at least partially diminished. At the same time, for many photographic applications it is desirable to limit the layer thickness employed so that the optical density of the photographic article is not objectionably increased. For many applications and photographic applications particularly layer thicknesses of from 10 to 1000 angstroms are desirable, with thicknesses of from 50 to 500 angstroms being preferred. Binderless adhesive (or subbing) layers consisting essentially of inorganic oxide according to this invention may be readily formed by conventional vacuum vapor deposition procedures as well as by other techniques generally known to those skilled in the art.

Adhesive layers employed in the practice of this invention are prepared from inorganic oxides. Oxides of silicon, such as silicon monoxide and silicon dioxide, are preferred inorganic oxides, since they are substantially water insoluble and chemically inert in photographic processing and use environments and are essentially transparent. Silicon oxides are also preferred since they can be vapor deposited by heating to vaporization temperatures that are low as compared to those required for vaporizing the other inorganic oxides utilized in the practice of this invention. Aluminum oxide, boron-silicon oxide, magnesium oxide, tantalum oxide and titanium oxide as well as mixtures thereof are particularly suited to the practice of this invention.

The inorganic oxide adhesive layer may be utilized on any hydrophobic supporting surface. Typical hydrophobic polymers which form supporting surfaces according to this invention include cellulose esters such as cellulose nitrate and cellulose acetate; poly(vinyl acetal) polymers, polycarbonates, polyesters such as polymeric, linear polyesters of bifunctional saturated and unsaturated aliphatic and aromatic dicarboxylic acids condensed with bifunctional polyhydroxy organic compounds such as polyhydroxy alcohols—e. g. polyesters of alkylene glycol and/or glycerol with terephthalic, isophthalic, adipic, maleic, fumaric and/or azelaic acid; polyhalohydrocarbons such as polyvinyl chloride; and polymeric hydrocarbons, such as polystyrene and polyolefins, particularly polymers of olefins having from 2 to 20 carbon atoms. The above polymers may be utilized in the form of flexible films or other unitary supports or may be utilized as coatings on metal, glass, paper and polymer supports. A preferred class of coated supports is alpha-olefin resin coated paper supports, such as paper supports coated with polyethylene, polypropylene, ethylene-butene copolymers and the like.

The hydrophilic layer to be adhesively bonded to the hydrophobic polymeric support surface can be formed from one or more hydrophilic, water permeable colloid forming substances including both naturally occurring substances such as, for example, proteins such as gelatin and gelatin derivatives; cellulose derivatives; polysaccharides such as dextran, gum arabic and the like and synthetic polymer substances, such as water soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

The hydrophilic colloids utilized can also contain other synthetic polymeric compounds such as those which increase the dimensional stability of the colloid layers. Suitable synthetic polymers include those described, for example, in Nottorf U.S. Pat. No. 3,142,568, issued July 28, 1964; White U.S. Pat. No. 3,193,386, issued July 6, 1965; Houck et al. U.S. Pat. No. 3,062,674, issued Nov. 6, 1962; Houck et al. U.S. Pat. No. 3,220,844, issued Nov. 30, 1965; Ream et al. U.S. Pat. No. 3,287,289 issued Nov. 22, 1966; and Dykstra U.S. Pat. No. 3,411,911 issued Nov. 19, 1968. Particularly effective are those water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have cross-linking sites which facilitate hardening or curing described in Smith U.S. Pat. No. 3,488,708, issued Jan. 6, 1970, and those having recurring sulfobetaine units as described in Dykstra Canadian Pat. No. 774,054.

The hydrophilic colloid can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes and blocked aldehydes described in Allen et al. U.S. Pat. No. 3,232,764, issued Feb. 1, 1966, ketones, carboxylic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfonyl ethers as described in Burness et al. U.S. Pat. No. 3,539,644 issued Nov. 10, 1970, active haolgen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguargum and the like.

Where the article formed is employed in forming an image by exposure to activating radiation that portion of the article to be bonded to the support will contain in or on it a radiation-sensitive material. This material may be panchromatic or orthochromatic material, sensitive only to X-rays or sensitive to selected portions of the electromagnetic spectrum. In one form of the invention the radiation-sensitive portion of the photographic article can contain a single, unitary hydrophilic colloid layer having dispersed therein the radiation-sensitive material together with photographic addenda to form a photographic emulsion layer or coating having a hydrophilic colloid surface. In alternative forms the radiation-sensitive portion of the article can comprise a plurality of layers with the radiation-sensitive material or materials being contained in some or all of the layers, but not necessarily in the hydrophilic colloid layer immediately adjacent the inorganic oxide subbing layer. For example, as is characteristic of color photography, a plurality of layers can be present sensitized within separate segments of the visible spectrum. While each of the layers can comprise a hydrophilic colloid photographic emulsion coating or layer, it is recognized that only the bonding surface of the radiation sensitive portion of the article need be comprised of hydrophilic colloid in order to achieve the objectives of this invention. Suitable hydrophilic colloid layers which can be bonded to a hydrophobic support surface but which contain no radiation-sensitive material, such as silver halide, when coated include, for example, antihalation layers, nucleated chemical transfer receiving layers, dye-mordant layers and the like.

Suitable radiation-sensitive materials which can be employed in practicing this invention are sensitive to electromagnetic radiation and include such diverse materials as silver salts, zinc oxide, photosensitive polycarbonate resins and the like. Silver halides are preferred

radiation-sensitive materials and are preferably associated with a colloid or synthetic polymer dispersion vehicle to form an emulsion coating or layer. Silver halide emulsions can comprise, for example, silver chloride, silver bromide, silver bromiodide, silver chlorobromide, silver chloriodide, silver chlorobromiodide crystals or mixtures thereof. The emulsions can be coarse or fine grain emulsions and can be prepared by a variety of techniques, e.g. single jet emulsions such as those described in Trivelli and Smith *The Photographic Journal*, Vol. LXXIX, May, 1939 (pp. 330-338), double jet emulsions such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al. U.S. Pat. No. 2,222,264, issued Nov. 19, 1940; Illingsworth U.S. Pat. No. 3,320,069, issued May 16, 1967, and McBride U.S. Pat. No. 3,271,157, issued Sept. 6, 1966. Negative type emulsions can be made, as well as direct positive emulsions as described in Leermakers U.S. Pat. No. 2,184,013, issued Dec. 19, 1939; Kendall et al. U.S. Pat. No. 2,541,472, issued Feb. 13, 1951; Schouwenaars British Pat. No. 723,019, issued Feb. 2, 1955; Illingsworth et al. French Pat. No. 1,520,821, issued Mar. 4, 1968, Illingsworth U.S. Pat. No. 3,501,307, issued Mar. 17, 1970; Ives U.S. Pat. No. 2,563,785, issued Aug. 7, 1951. Knott et al. U.S. Pat. No. 2,456,953, issued Dec. 21, 1948 and Land U.S. Pat. No. 2,861,885, issued Nov. 25, 1958.

The silver halide emulsions employed in the articles of this invention can be sensitized with chemical sensitizers, such as with: reducing compounds; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these.

The photosensitive emulsion coatings or layers can additionally include a variety of conventional addenda both for the colloid and for the radiation-sensitive material. For example, photographic emulsion layers employed according to this invention may include development modifiers, antifoggants and stabilizers, plasticizers and lubricants, brighteners, spectral sensitization agents and color forming materials as set forth in paragraph IV, V, XI, XIV, XV, and XXII, respectively, of *Product Licensing Index*, Vol. 92, December, 1971, publication 9232, pages 107-110.

As previously indicated photographic articles of this invention can be processed with aqueous photographic processing solutions. Photographic articles containing the inorganic oxide subbing layers described herein can also be used in non-aqueous processing—e.g. in so-called dry processing systems. For example, the subbing layers described herein can be used in silver halide containing articles designed for recording print out images as described in Fallesen U.S. Pat. No. 2,369,449 issued Feb. 13, 1945 or Bacon et al. U.S. Pat. No. 3,447,927 issued June 3, 1969; direct print images as described in Hunt U.S. Pat. No. 3,033,682 issued May 8, 1962 and McBride U.S. Pat. No. 3,287,137 issued Nov. 22, 1966; and articles designed for processing with heat, such as in articles containing an oxidation-reduction image-forming combination with a photosensitive metal salt such as a silver salt as described in Sheppard et al. U.S. Pat. No. 1,976,302 issued Oct. 9, 1934; Sorensen et al. U.S. Pat. No. 3,152,904 issued Oct. 13, 1964 and Morgan et al. U.S. Pat. No. 3,457,075 issued July 22, 1969.

A metal anti-static layer can be utilized in the practice of this invention. Such a layer is conveniently

coated on the opposite side of the support on which the radiation-sensitive material is to be coated. Preferred metals for forming anti-static layers on polymeric film supports are chromium, silver, nickel, and aluminum. Typically the metal anti-static layers are kept as thin as is consistent with providing the required surface resistivity characteristics. A metal anti-static layer in order to be effective must generally provide a surface resistivity of less than  $10^{12}$  ohms per square, with surface resistivities of less than  $10^8$  ohms per square being preferred for most photographic applications. To insure that all areas of a photographic article exhibit a surface resistivity of less than  $10^8$  ohms per square, it is generally preferred that the article exhibit an overall surface resistivity of less than  $10^5$  ohms per square. As is well understood by those skilled in the art surface resistivity is determined by measuring the resistance between two parallel electrodes of a given length spaced apart by the same distance along a surface. Since an increase in the length of the electrodes tends to decrease the resistance observed by an amount equal to that by which the resistance would be increased by lengthening the spacing between the electrodes by a like increment, it is apparent that the electrode length and spacing is not material so long as they are identical. Hence the surface resistivity expressed in ohms per square is a resistance measurement taken for the special case in which electrode length and spacing are identical and therefore mutually cancelling parameters.

Metal anti-static layers providing surface resistivities within the above criteria are generally formed having thicknesses of less than 500 angstroms and, preferably, less than 100 angstroms. By limiting the thickness of the metal anti-static layer its optical density is limited and the amount of metal which may enter film processing solutions during film development and processing is limited.

It is, of course, recognized that the photographic article formed according to this invention can, if desired, incorporate anti-static or conducting layers other than or in addition to metal anti-static layers. Such layers can comprise soluble salts, e.g. chlorides, nitrates, etc., ionic polymers such as those described in Minsk U.S. Pat. No. 2,861,056, issued Nov. 18, 1958, and Serman et al. U.S. Pat. No. 3,206,312, issued Sept. 14, 1965, or insoluble inorganic salts such as those described in Trevoy U.S. Pat. No. 3,428,451, issued Feb. 18, 1969.

This invention may be better understood by reference to the drawings, which are each fragmentary sectional views of photographic articles according to this invention. For ease of illustration the various elements of the articles are not drawn to scale.

FIG. 1 illustrates an article 1 comprising a hydrophobic polymer support 3. A hydrophilic colloid coating 5 is located by the support and is adhesively bonded thereto by an inorganic oxide layer 7 according to this invention. An optional metal anti-static layer 9 is bonded to the major surface of the polymer support not bonded to the colloid coating.

FIG. 2 illustrates a photographic article 10 in which a dielectric support 12 is provided with a hydrophobic polymer layer 14 adjacent one major surface. A radiation-sensitive hydrophilic colloid coating 16 containing radiation-sensitive material is adhesively bonded to the hydrophobic polymer layer by an inorganic oxide layer 18.

FIG. 3 illustrates a photographic article 100 in which a dielectric support 102 is provided with a hydrophobic polymer layer 104 adjacent one major surface. An inorganic oxide layer 106 bonds a radiation-sensitive portion 108 of the article to the hydrophobic polymer surface presented by the layer 104. The radiation-sensitive portion 108 is comprised of a hydrophilic colloid layer 110, which is as coated substantially free of radiation-sensitive materials, and a radiation-sensitive emulsion layer 112, which overlies the layer 110.

To further illustrate the invention the following examples are included:

#### EXAMPLE 1

To illustrate the non-blocking characteristics of the inorganic oxide coatings of this invention and to prepare supports protected against blocking for use in subsequent comparisons a glass is deposited on one major surface of several rolls of polyethylene terephthalate film support in the following manner: A roll of support is loaded into a conventional vacuum roll coater, and a boro-silicon oxide coating is deposited by placing a boro-silicon oxide (i.e. borosilicate) glass available as Code 8329 glass (manufactured by Jena Glaswerk Schott and Gen., Mainz, West Germany) in the crucible of an electron beam heated vapor source. The vacuum chamber is closed and pumped down to a pressure of  $7.2 \times 10^{-5}$  Torr. The glass is heated in an electron beam until it is evaporating at a high rate. Shutters protecting the support from the vapor are opened and the support is drawn through the vapor stream at a rate such that the boro-silicon oxide glass coating that condenses on the support forms a film of less than 100 angstroms thick. After coating, the source is cooled, the pressure in the chamber raised to atmospheric pressure, and the coated roll reloaded in the system so that all subsequent coatings are made on the side opposite the glass coating. This first glass coating is non-blocking and is provided to assure direct comparability of later coatings. It should be recognized that oxides of silicon, titanium, tantalum, aluminum and magnesium are also non-blocking and can be deposited singly or in combination in place of the glass layer.

#### EXAMPLE 2

In order to compare the qualities of inorganic oxide, metal and terpolymer subbing layers in promoting the adhesion of hydrophilic colloid layers to hydrophobic polymer film supporting surfaces, to the support surfaces opposite the non-blocking glass layers several adhesive coatings, as designated in Table I, are deposited using the above vacuum vapor deposition procedure. As indicated in Table I one roll is coated with boro-silicon oxide on both major surfaces and, for purposes of comparison, aluminum, nickel and silicon dioxide are deposited on glass coated rolls of the support. Layer parameters are set forth in Table I.

TABLE I

Layer	Thickness	Net Optical Density
Nickel	40A	0.21
Aluminum	100	0.41
Silicon monoxide	250	0.00
Boro-silicon oxide	100	0.00
Silicon dioxide	50	0.00

The net optical densities are determined using an optical densitometer; the net optical densities in each instance being the difference between the optical densities of otherwise identical coated and uncoated supports. It can be seen that the inorganic oxide layers are advantageous in failing to significantly add to the optical density of the articles.

The supports having the coatings described in the above Table I are stored in rolls for two weeks under ambient conditions and then overcoated with a gelatin silver bromiodide photographic emulsion at a coverage equivalent to 400 mg of silver/ft<sup>2</sup>. In addition, film supports of uncoated polyethylene terephthalate and polyethylene terephthalate coated with a conventional subbing layer formed of a terpolymer of methyl acrylate, vinylidene chloride and acrylic acid are similarly overcoated with this emulsion.

The dry, unprocessed photographic emulsion adheres very poorly to the unsubbed support and flakes off when the support is flexed or twisted. This effect does not appear on any of the articles which are provided with a layer interposed between the support and the photographic emulsion coating. This indicates that prior to processing each of the interposed layers to some extent improves the bond between the support and the hydrophilic emulsion coating.

To illustrate the effects of photographic processing on the adhesion of the emulsion coatings to the supports like-sized strips are cut from the supports having the aluminum, boro-silicon oxide and terpolymer subbing layers. In the first comparison the emulsion coating is scribed to the support with an 0.1 mm stylus and the article is processed under conditions of high agitation as follows: Each emulsion coated support is developed in a buffered aqueous developing solution having a pH of approximately 10 and incorporating equal parts by weight p-methyl aminophenol and hydroquinone for 2 minutes at 23°C, followed by 3 minutes fixation in a sodium thiosulfate containing aqueous fixing bath. Peel is measured in millimeters from the originally scribed line to the remaining adjacent edge of the emulsion. Exemplary results are set forth as Comparison No. 1 in Table II.

In a second comparison, using strips identical to that used in the first comparison, a 1-inch circle of the emulsion coating on each strip is identically washed at 70°C and dried. Thereafter the percent peel from the strip is measured by observing the area within the 1-inch circle from which the emulsion coating has spalled during washing and by calculating this as a percentage of the total circle area. Exemplary results of Comparison No. 2 are set forth in Table II.

TABLE II

Layer	Comparison No. 1 mm peel	Comparison No. 2 % peel
Aluminum	Complete peel	Complete peel
Boro-silicon oxide	4.3	4
Ter-polymer	1.4	1

While the boro-silicon oxide adhesive layer does not bond quite as well as considerably more complex conventional terpolymer subbing layer, it bonds considerably better than the aluminum, which is representative of oxidizable metal layers. At the same time the degree of bonding afforded by the boro-silicon oxide layer

under the stringent conditions provided fully demonstrates its highly adhesive characteristics. In a similar manner, an article can be prepared in which a gelatin layer containing no silver bromiodide is substituted for the gelatin silver bromiodide photographic emulsions employed in this example. Such an article also possesses excellent adhesion characteristics.

## EXAMPLE 3

To illustrate that the inorganic oxide layers employed in the practice of this invention are non-blocking and may be utilized to prevent blocking of metal layers associated with the support, such as anti-static layers, a plain, untreated polyethylene terephthalate film support is coated with an approximately 100 angstrom thick film of silicon monoxide using the equipment and techniques described in Example 1. An additional sample of untreated support is spliced to the metal oxide coated sample and another coating run made in which a nickel film approximately 50 angstroms thick was deposited on the side of the substrate opposite the silicon monoxide film and on one side of the uncoated substrate. When the coated support is unrolled, it is found that the section of support coated with nickel alone blocks badly and the nickel film is partially stripped from the coated surface during unwinding. In that part of the roll which is protected with the silicon monoxide layer, no blocking occurs, and the support is unwound without damaging the nickel film.

What is claimed is:

1. In a photographic article comprising a radiation-sensitive silver salt, a support having a hydrophobic polymer supporting surface, a hydrophilic colloid layer and a subbing layer which is contiguous to said supporting surface and said hydrophilic colloid layer and is bonded to each, the improvement in which said subbing layer is binderless and consists essentially of an inorganic oxide selected from the group consisting of silicon oxide, magnesium oxide, aluminum oxide, tantalum oxide, titanium oxide, boro-silicon oxide and mixtures thereof and is from 10 to 1000 angstroms thick.

2. The invention according to claim 1 in which said support is a polyester film support.

3. The invention according to claim 1 in which said hydrophobic polymer is polyalkylene terephthalate.

4. The invention according to claim 1 in which said support is polyolefin coated paper.

5. The invention according to claim 1 in which said silicon oxide is silicon monoxide or silicon dioxide.

6. The invention according to claim 1 additionally including a metal layer associated with the surface of said support which is opposite from said subbing layer.

7. The invention according to claim 1 in which said subbing layer exhibits a thickness in the range of from 50 to 500 angstroms.

8. In a photographic article comprising a radiation-sensitive silver salt, a flexible hydrophobic polyester film support, a gelatin layer and a subbing layer interposed between and bonded to said film and said gelatin layer, the improvement in which said subbing layer is vapor deposited to a thickness of from 50 to 500 angstroms and comprises a binderless inorganic oxide selected from the group consisting of silicon oxide, magnesium oxide, tantalum oxide, titanium oxide and mixtures thereof.

9. A photographic article according to claim 8 in which said support is polyethylene terephthalate.

10. A photographic article according to claim 8 in which said support is polyethylene terephthalate, said radiation-sensitive material is a silver halide and said inorganic oxide is silicon oxide.

11. A photographic article according to claim 10 in which said silver halide is silver bromochloride.

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