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COATED DRYING ELEMENT

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ABSTRACT OF THE DISCLOSURE

A flexible, liquid permeable, drying element, such as a thin coating, containing an organic desiccant, typically with a synthetic, polymeric binding agent, is used for removing a liquid, such as water, from a permeable solid, such as from one or more layers of a photographic element containing water. For instance, a thin coating of an organic desiccant, such as a mixture of ethylene oxide polymers, removes a large percentage of the water from a wet photographic emulsion layer. An inorganic desiccant and/or other addenda can be present in the thin coating.

This invention relates to removing liquids from permeable solid materials containing such liquids. In one of its aspects, it relates to removing diffusible liquid, such as water, from liquid permeable solid materials, such as a moist layer of a photographic element. In another of its aspects, it relates to drying a moist colloid coating by contacting the moist coating with a supported or unsupported coating containing an organic desiccant.

Two methods have generally been employed heretofore for removing liquids from permeable solids containing such liquids. In one method, liquid is removed by evaporation, for example, by a combination of heating the solid and/or reducing the pressure around the solid material. In the second method, the solid material is immersed in an extractant, such as removing moisture from a moist photographic element by immersing the moist element in an extractant as set out in U.S. Pat. 2,150,757—Bodine, issued Mar. 14, 1939.

These methods have not been satisfactory in many cases, especially for removing moisture from photographic elements, since they require costly equipment, such as apparatus for forcing heated air over the solid material, require excessive time, often leave undesirable residue on the solid dried, make the elements susceptible to accumulation of dust, and/or cause undesirable changes in the material dried.

In the case of photographic elements, it has been usual practice to process such elements after exposure in solutions or processing baths which produce a wet or moist product. It has been necessary in such cases to wait, often for many minutes, for the film, paper, or the like, to dry before further processing or handling, such as contact printing, can be carried out. This time can be reduced by forced air drying at elevated temperatures but this method has not been entirely satisfactory for removing diffusible liquid from a photographic element in a matter of seconds without undesired effects to the element.

Drying of photographic elements processed without use of conventional processing baths and where inspection of the processed element as soon as possible is desirable has been especially important. For example, in aerial reconnaissance, in radiology, and the like, it is necessary to have the processed photographic element in dry condition as soon as possible to determine results, to determine whether another exposure should be made, and/or for other purposes. One method which has been advantageous in decreasing the time from exposure to finished product, without the use of conventional processing baths, employs a wet or moist absorbent web containing processing compounds, typically a monobath, which is contacted with the exposed element for a desired length of time. This method and means for carrying out the method are set out, for example, in U.S. Pat. 3,179,517—Tregillus et al., issued Apr. 20, 1965. One disadvantage of this method, however, is that the resulting processed photographic element is moist, as in other processes, after the film and web are separated and usually must be dried in some manner. Efforts to dry such a photographic element have included application of a powdered inorganic drying agent, such as barium oxide, calcium chloride, activated alumina, and the like, dusted over the surface of the moist element or located on the surface opposite the film of a protective porous web which is contacted with the moist film. This is disclosed in British Pat. 1,012,391, issued Dec. 8, 1965. In the case where the inorganic drying agent is dusted over the surface of the moist photographic element, undesired adherence of the inorganic drying agent to the surface of the element can occur. On the other hand, when the moist photographic element is contacted with a semi-permeable membrane which in turn is contacted with an inorganic drying agent, additional means can be required for contacting the semi-permeable membrane with the inorganic drying agent and removal of moisture can be less efficient than in the case of direct contact of the inorganic drying agent with the moist element.

No process or means has been completely satisfactory heretofore for eliminating the costly air drying steps and apparatus employed for removing moisture or other liquids from a moist layer of a photographic element with direct contact of drying means on the layer.

Accordingly, an object of the invention is to provide novel means for rapidly removing liquid, such as water, from a permeable solid, such as a layer of a photographic element, containing such liquid without undesired changes in the solid.

Another object is to provide a novel composition for removing a liquid, such as water, from a permeable solid, such as a photographic emulsion coating, by contact of the composition with the permeable solid.

A further object is the provision of a means for rapidly removing diffusible liquid, such as water, from a photographic element without leaving undesirable residue on and/or in the element.

The invention accordingly, comprises means, compositions and processes for rapidly removing liquid from a permeable solid material containing such liquid by contacting, preferably directly contacting, such permeable solid material with a flexible, liquid permeable, drying element comprising a solid coating containing an organic desiccant, without leaving undesirable residue and without adverse effects to the solid material.

One embodiment of the invention, accordingly, comprises a flexible, liquid permeable, drying element comprising an organic desiccant in a synthetic polymeric binding agent different from said organic desiccant, e.g. having higher molecular weight or being different in composition.

This flexible, liquid permeable, drying element has the properties of (a) removing liquid from a permeable solid material containing such liquid when the drying element and permeable solid material are in contact, and (b) after contact leaving little residue on the permeable solid material.

Another embodiment comprises a flexible, liquid permeable, drying element which is a substrate having on at least one surface a thin, adherent, liquid permeable coating of an organic desiccant in a synthetic polymeric binding agent different from said organic desiccant.

A drying element of the invention typically has the property of transferring no more than about 20 milligrams per square foot of both said organic desiccant and said binding agent to a wet gelatin coating upon contact with said coating for up to about 60 seconds. It also typically has the property of removing at least about 60%, for instance, more than about 85%, by weight of water from a wet gelatin layer coated on a substrate upon contacting said layer for a period of no more than about 60 seconds with said drying element.

For instance, a drying element according to the invention can comprise a support, typically a flexible support, having a solid, polymeric coating comprising an organic desiccant, which is a poly(alkylene oxide), with a polymeric binding agent different, e.g. having higher molecular weight or being different in composition, from said organic desiccant. An especially useful drying element, according to the invention, comprises a flexible support having a solid, polymeric coating comprising a poly(ethylene oxide) having an average molecular weight of about 190 to about 20,000 with a high molecular weight poly(ethylene oxide) binder, e.g. having an average molecular weight of about 100,000 to about 5,000,000 or more. An especially useful drying element according to the invention comprising a flexible support, such as paper or a polyethylene terephthalate film, having a thin adherent coating of about 10% by weight poly(ethylene oxide) having an average molecular weight of about 6000 to about 7500 with about 90% by weight of high molecular weight poly (ethylene oxide) e.g. having an average molecular weight of about 100,000 to about 5,000,000, can remove at least about 90% by weight of the water from a moist gelatin layer coated on a substrate upon contacting said layer for a period of no more than about 60 seconds with said drying element.

The material comprising the organic desiccant and/or binder, if one is used, need not be present only on the surface of the support, if one is employed. It can be present in and/or on the support. For example, part of the organic desiccant in the case of a poly(alkylene oxide) and/or binder can be present in the support. The entire amount of these materials can be in the support or the entire amount can be on the surface of the support if desired. Also, if desired, one or more of such materials can be coated on one or more sides of a support, including the edges in the case of paper or film, for instance.

In some cases, a coating, according to the invention, has sufficient strength that a support is not needed. Accordingly, the word coating as employed herein is intended to include both supported and unsupported coatings. Unsupported coatings include, for example, self-supporting webs, sheets, films, tape, and the like. Use of a support is often advantageous, serving as a reservoir for liquid removed from the permeable solid. For instance, a paper support coated with a polymeric coating according to the invention can hold a significant amount of moisture more than the coating alone.

Any suitable coating thickness can be employed. The coating thickness can vary over a wide range depending upon the material to be dried, the composition of the coating, the type of support if one is employed, the amount and type of liquid to be removed from the permeable solid material, and the like. A suitable thickness comprises about 0.001 millimeter to about 1.0 millimeter, typically about 0.01 to about 0.5 millimeter, but a thickness outside this range can be used.

A wide range of binders can be employed in and/or on the drying elements of the invention. In general, any binding agent can be employed with the organic desiccant of the invention which provides a solid coating, under ambient conditions, and which does not adversely affect the properties of the drying element, e.g. does not hinder liquid removal properties of the drying element and leaves little or no undesirable residue on the material from which liquid is removed.

The binder can be a desiccant. That is, if desired, both the organic desiccant and the binder can effect removal of liquid from a permeable solid containing such liquid.

The organic desiccant can, but need not be, the same as the binder. For instance, in the case of poly(ethylene oxide), if the poly(ethylene oxide) is sufficiently solid, e.g. has sufficiently high molecular weight, under ambient conditions, it need not be employed in combination with a binder, such as a poly(ethylene oxide) having an average molecular weight of about 100,000 to about 5,000,000. In this case, the organic desiccant can be used alone without a binder.

If a poly(ethylene oxide) having an average molecular weight of about 190 to about 20,000 is employed as the organic desiccant according to the invention, it is usually desirable, and often necessary to employ a binder therewith, such as a binder which is a poly(ethylene oxide) having an average molecular weight of about 100,000 to about 5,000,000. The presence of the binder can aid in prevention of transfer of undesired residue to the material from which liquid is removed, such as transfer of undesired concentrations of poly(ethylene oxide) to a layer of a photographic element from which water is removed. It can also aid in the removal of liquid.

The binder can be employed in any suitable concentration depending on the components of the drying element, the support, if one is employed, the material from which liquid is to be removed, the conditions under which liquid is to be removed, and the like. Usually about 10% by weight to about 95% by weight binder in a coating according to the invention is sufficient. In the case of a coating containing about 10% by weight of a poly(ethylene oxide) having an average molecular weight of about 6000 to about 7500 about 90% by weight of a poly(ethylene oxide) having an average molecular weight of about 100,000 to about 5,000,000 is especially suitable as a binder where moisture is to be removed from a moist layer of a photographic element.

Typical binders include polymeric binders, for example, natural and synthetic polymers. Polymers as employed herein include homopolymers, copolymers, terpolymers, and other polymeric materials as well as mixtures thereof. It includes polymeric materials which are cross-linked with monomeric and/or polymeric materials. Mixtures of two or more binders can be employed in a wide range of ratios. The polymeric binder must be sufficiently solid and must have sufficient film forming properties to form coatings with an organic desiccant according to the invention.

Examples of typical binders include natural and syn thetic resins, such as poly(ethylene oxide) having an average molecular weight of about 100,000 to about 5,000,000; polyvinyl alcohol; poly(acrylic acid esters), e.g., poly(methylmethacrylate); carboxyl derivatives of cellulose; vegetable gums; cellulose esters; polyvinyl ethers; and silicones.

Examples of suitable materials which can be employed in the practice of the invention as binders and/or as organic desiccants are disclosed, for example, in French Pat. 1,482,699, issued Apr. 17, 1967. Specific examples of materials which can be employed in the practice of the invention as binders and/or as organic desiccants, depending on the properties described, are as follows:

(1) Poly(ethylene oxide), usually available as mixtures having an average molecular weight of about 900 to about 20,000. Compounds of this type are available under the trade name, Carbowax, from Union Carbide Corporation, New York, N.Y.

(2) Poly(ethylene oxide, having a molecular weight of at least about 100,000 and having a narrow melting point range, e.g. about 65° C. Compounds of this type are commercially available under the trade name, Polyox, from Union Carbide Corporation, New York, N.Y.

(3) Poly(acrylamide) and related polyamides, such as those having an average molecular weight of at least about 900, e.g. 900 to 5000.

(4) Polyvinylpyrrolidones, such as those having an average molecular weight of at least about 900, e.g. about 900 to about 40,000 or more.

(5) Alkylene oxide-silicone copolymers. Compounds of this type are available from the Union Carbide Corporation, New York, N.Y. under the trade name, Silicone Polymers L–250, L–530, and the like.

(6) Ethylene oxide-propylene oxide copolymers in which the ethylene oxide comprises at least 40% by weight of the copolymer, such as those having an average molecular weight of at least about 900, e.g. about 900 to about 20,000. Compounds of this type are available under the trade name Pluronic from Wyandotte Chemical Company, Wyandotte, Mich.

(7) Polyvinyl glycols, such as those having an average molecular weight of at least about 900, e.g. about 900 to 9,000.

(8) Urethane resins, such as those having an average molecular weight of at least about 900. Compounds of this type are available, for instance, from the Dow Chemical Company, Midland, Mich. under the trade name, Voranol.

(9) Polyacryloxy sulfonic acids, such as those having an average molecular weight of at least about 900. Compounds of this type can remove water from layers of a photographic element, i.e. they can be an organic desiccant and/or a binder according to the invention.

(10) Vinyl ether-maleic anhydride copolymers, such as those having an average molecular weight of at least about 900. Compounds of this type are available from General Aniline and Film Corporation, New York, N.Y., under the trade name, Gantrez Resin AN–119.

(11) Copolymers of acrylamide with 2-acetoacetoxyethyl methacrylate, e.g. those containing 90% by weight acrylamide.

While various polymeric coatings can be used for removing diffusible liquid according to the invention, especially poly(ethylene oxide), having an average molecular weight of about 190 to about 5,000,000 are especially suitable, for instance, (a) alone, (b) as a binder, (c) part of a mixture of binders or (d) part of a mixture of drying agents and binders.

High molecular weight poly(alkylene oxide) as employed herein means such compounds having an average molecular weight well above 20,000, e.g. above the highest average molecular weight of poly(ethylene oxide) sold under the trade name, Carbowax, by the Union Carbide Corporation, New York, N.Y., and typically at least about 100,000, e.g. about 100,000 to about 500,000 or more.

Highly crystalline, as employed herein, means that the polymer in the solid state has a sharp melting point, e.g. about 65° C. for high molecular weight poly(ethylene oxides). The degree of crystallinity can typically be measured using nuclear magnetic resonance techniques.

A coating of the invention can contain an inorganic desiccant. Any suitable inorganic desiccant can be employed which does not adversely affect the material dried, does not leave an undesirable residue and does not adversely affect the removal of liquid by the coating of the invention. For example, the inorganic desiccant set out in British Pat. 1,012,391 or inorganic drying agents known in the art as molecular sieve materials can be employed in combination with an organic desiccant of the invention. Suitable molecular sieve materials are described, for example, in an article by Rene Petit (University of Paris), in Chim. Anal. (Paris), vol. 47, No. 12, pp. 643 to 656 (1965).

The addition of molecular sieve materials according to the invention can produce an advantageous reduction in possible undesirable adhesion of a coating of the invention to the materials from which diffusible liquid is to be removed. For example, the addition of a crystalline alumino silicate molecular sieve material to a coating of the invention can produce a pronounced decrease in adhesion of a coating of the invention to a photographic element. The concentration of inorganic desiccant and/or method of preparation of a coating according to the invention containing an inorganic desiccant can vary depending upon components in the coating, the material to be dried, the type of support, if one is employed, and the like. In general, less than about 90% by weight, e.g. about 0.01% to about 50% by weight of the total coating is inorganic drying agent. The inorganic drying agent can be admixed in a coating composition before coating on a suitable support, if one is employed, can be applied to or prepared in the support before application of other components of the coating can be applied in a separate layer or can be applied in any suitable manner.

The invention is useful for drying and/or removing diffusible liquid from a wide range of permeable solid materials containing such liquid. For instance, the elements, compositions and processes of the invention can be used for drying or removing liquid from:

(a) textile fibers and/or fabrics, such as removing moisture from moist natural or synthetic fibers;
(b) coatings of various types, such as removing moisture from a moist gelatino coating; or
(c) inked or printed surfaces, such as surfaces where ordinary ink blotters are useful.

In removing diffusible liquids from such materials, it is important that the material to be dried be intimately contacted with the materials according to the invention which effect removal of the liquid.

A semi-permeable membrane material, such as a thin sheet of cellophane, can be used between the permeable material from which diffusible liquid is to be removed and a coating according to the invention, if desired. The semi-permeable membrane material can be applied to the permeable material to be dried and/or to the coating according to the invention. The semipermeable membrane can also prevent undesired transfer of materials to a coating of the invention or to the support containing the coating.

A coating according to the invention can be employed more than once. For instance, a single solid coating comprising a mixture of a poly(ethylene oxide) having a molecular weight of about 190 to about 20,000 with poly(ethylene oxide) having an average molecular weight of 100,000 to 5,000,000, about 1.0 to about 4.0 mils thick on a paper support can be employed for removing more than 90% by weight of the water from at least six pieces of moist photographic film using a contact time of less than two minutes for each piece of film.

In general, any diffusible liquid can be removed from a permeable solid according to the invention which is more strongly attracted to a drying element of the invention than said permeable solid when the drying element and permeable solid are intimately contacted. Suitable diffusible liquids include, for example, water, methanol, liquid lower alkyl amines, such as ethyl amine, and lower alkanol amines, such as ethanol amine and propanol amine.

The theory by which diffusible liquids are removed according to the invention is not understood. However, it is believed that in the case of a poly(ethylene oxide), the diffusible liquid forms hydrogen bonds with the poly(ethylene oxide). Hydrogen bonding between materials is described, for example, in The Hydrogen Bond by Pimental and McClellan, W. H. Freeman and Company, San Francisco, 1960.

Various addenda can be present in and/or on the coating and/or a support, if one is employed, according to the invention, especially those known to be beneficial in photographic elements, compositions and processes. The materials from which the diffusible liquid is removed can also contain such addenda. The types of addenda and suitable concentrations can be determined by those skilled in the art. Suitable addenda include, for example, hardeners, such as those set out in British Pat. 974,317; buffers, such as various sulfonamides and boraxes; coating aids; plasticizers; speed-increasing addenda; stabilizing agents and the like.

It has also been found that various sugars, e.g. sucrose and dextrose, can be included in a coating of the invention. The amount which is suitable can vary depending on the coating components, the solid material from which liquid is to be removed, and the like. For example, a composition which can be employed for preparing a coating for drying a moist photographic element comprises about 1 to about 1000 grams of sucrose and/or dextrose per liter of coating composition.

In contacting material from which liquid is to be removed and a solid coating containing an organic desiccant according to the invention a wide range of pressure can be employed. It is not necessary, and often undesirable, to employ high pressure in contacting the materials according to the invention, e.g. pressures of more than about 50 kilograms per square centimeter can be undesired. Any suitable means can be employed for contacting the materials, e.g. in the case of a photographic element it is suitable to pass the photographic element and the drying element of the invention between rollers, or to place the photographic element on a stationary solid surface and press the drying element onto the element.

The time required for removal of diffusible liquid from a peremable solid can vary depending on many factors, such as the material to be dried, the amount and type of liquid to be removed, the components of the coating employed for removing the liquid, and the like. In general, coatings according to the invention can remove a diffusible liquid from a permeable solid, such as a layer of a photographic element, containing the liquid in less than about 120 seconds, e.g. about 1 to about 60 seconds. For instance, a typical coating according to the invention comprising a mixture of a poly(ethylene oxide) having a molecular weight of about 6000 to 7500 with a high molecular weight, highly crystalline poly(ethylene oxide) can remove more than 90% of the water in a moist photographic element under ambient conditions, e.g. a temperature of about 20° C. to about 30° C., in less than 60 seconds, and usually in a fraction of a second up to 15 seconds. If necessary, however, longer time of contact between the drying element of the invention and the material from which liquid is to be removed can be employed.

The temperatures, pressures, and humidities which are suitable for use according to the invention can vary over wide ranges. Usually ambient temperature, pressure and humidity are suitable; however, in some cases it can be desirable to use and/or store the coatings of the invention under controlled conditions, for example, to avoid unnecessary premature take-up of moisture from the air when the coating is to be employed to remove water from a moist photographic element under conditions of high humidity and/or temperature, e.g. under tropical conditions.

A drying element of the invention can be stored and/or packaged in any suitable container, e.g. in foil and/or plastic wrappers, which are air and/or moisture tight, before use.

Any support, if one is employed, can be used for a coating of the invention and such a support can be in any suitable shape or form. These include those commonly employed in the photographic art, such as films, including cellulose acetate films, polyester films, such as polyethylene terephthalate films, polyvinyl acetal films, polystryrene films, polycarbonate films, and related materials, papers, e.g. paper supports coated with resinous materials e.g., coated with polyethylene, polypropylene, and/or ethylene-butene copolymers, glass, fabrics, metal and the like. Supports in the form of webs or tapes can be used, for example. Supports which act as a reservoir for diffusible liquid removed are especially suitable. For this reason, absorbent fibrous materials formed from, for example, textile or glass fibers, paper and/or similar water absorbent supports can be especially useful.

A drying element and/or process of the invention is useful for rapidly removing diffusible liquid from a wide variety of photographic elements containing such liquid. For example, it can be used for removing water from any suitable photographic element in a moist condition.

Photographic elements employed in the practice of the invention contain a layer comprising any of the known water permeable binding materials suitable for photographic purposes. These include, for example, gelatin, cellulose derivatives, polymerized vinyl compounds, as well as mixtures of such binding agents. These binding agents can contain water insoluble polymers, such as polymerized ethylentically unsaturated compounds, e.g. polymers of acrylates and methacrylates.

The photographic elements which can be dried according to the invention include, among others, those which contain a photographic silver salt emulsion, e.g. a silver halide gelatino emulsion layer, or a non-silver halide emulsion. These can be non-spectrally sensitized emulsions, such as X-ray type emulsions, or they can be orthochromatic, panchromatic, infrared sensitive, and the like emulsions containing spectral sensitizing dyes, such as described in U.S. Pats. 2,526,632 and 2,503,776. Spectral sensitizers which can be used include cyanines, merocyanines, styryls and hemicyanines.

For example, the invention can be employed for removing diffusible liquid, such as water, from layers of photographic elements used for color photography, e.g. it can be used for drying films and/or prints used in color photography, such as emulsions containing color-forming couplers or emulsions developed by solutions containing couplers or other color generating materials; emulsions of the mixed-packet type, such as described in U.S. Pat. 2,698,794 of Godowsky, issued Jan. 9, 1955; or emulsions of the mixed grain type, such as described in U.S. Pat. 2,592,243 of Carroll and Hanson.

The drying element and/or processes of the invention can be used in processing emulsions intended for use in diffusion transfer processes which utilize undeveloped silver salts in the non-image areas of the negative to form a positive by dissolving the undeveloped silver salts and precipitating them on a receiving layer in close proximity to the original silver salt emulsion layer. Such processes are described, for example, in U.S. Pat. 3,020,155 of Yackel et al., issued Feb. 6, 1962; U.S. Pats. 2,584,029, issued Jan. 29, 1952; 2,698,236, issued Dec. 28, 1954; and 2,543,181, issued Feb. 27, 1951, of E. H. Land and U.S. Pat. 2,352,014 of Rott, issued June 20, 1944. The invention can also be used in color transfer processes which utilize the diffusion transfer of developer, coupler or dye, from a light sensitive layer to a second layer, such as described in U.S. Pat. 2,559,643 of Land, issued July 10, 1951; U.S. Pat. 2,698,798, issued Jan. 4, 1955; U.S. Pat. 2,756,142 of Yutzy, issued July 24, 1956; U.S. Pat. 3,252,-915 of Weyerts et al., issued May 31, 1966; and U.S. Pat. 3,227,550 of Whitman et al., issued Jan. 4, 1966.

The invention can be used in processing emulsions used in lithography, preparation of direct prints, or in colloid transfer processes as well as in processing of elements using monobath processes, such as described in U.S. Pat. 2,875,048 of Haist et al., issued Feb. 24, 1959, and web-type processing such as described in U.S. Pat. 3,179,517 of Tregillus et al. It can also be used in so-called stabilization processing, such as processing an element containing an incorporated developer through an activator bath containing a thiocyanate stabilizer, as described, for example, in British Pat. 1,061,892, issued Mar. 15, 1967, or in an article titled "Stabilization Processing of Films and Papers" by H. D. Russel, E. C. Yackel and J. S. Bruce, P.S.A. Journal, August 1950, pages 59–62.

The drying elements and/or processes of the invention can be employed in the production of layers of liquid permeable solid materials. For instance, the flexible, liquid permeable, drying elements and processes of the invention can be employed in the production of layers of unexposed photographic elements which require removal of water and/or other suitable liquid at some stage. A typical process according to the invention for the production of a layer of a photographic element accordingly comprises applying a hydrophilic colloid coating to a substrate, the resulting coating containing water and/or other suitable liquid, and subsequently contacting the hydrophilic colloid coating with a flexible, liquid permeable, drying element comprising an organic desiccant, to remove a substantial portion of the water and/or other suitable liquid from the hydrophilic colloid coating.

A wide range of coating methods and conditions can be employed for preparing the coatings from which liquids, e.g. water, can be removed according to the invention. In general, coating methods, compositions, and conditions commonly employed in the photographic art can be employed.

A typical method for production of a raw photographic emulsion layer comprises applying a coating of a photographic emulsion to a substrate, setting the resulting coating, such as by chilling or fuming with ammonia in the case of gelatino emulsion coatings, and contacting the resulting coating with a flexible, liquid permeable, drying element comprising an organic desiccant. For instance, a raw, wet, photographic emulsion coating can be contacted with a solid, flexible, coating comprising an organic desiccant, such as contacted with a supported or unsupported coating containing a poly(ethylene oxide) and/or one of the organic desiccants described, to remove a substantial portion of the water from the raw photographic emulsion coating.

The raw photographic emulsion coating can be contacted using essentially the same conditions and time of contact as employed for contacting exposed and processed, wet photographic elements to effect removal of water.

One of the useful characteristics of a coating of the invention is that in removing diffusible liquid from a permeable solid, certain solid materials dissolved in the diffusible liquid are also substantially removed from the permeable solid. For example, certain compounds in a photographic element containing a diffusible liquid can be removed from the element with the diffusible liquid according to the invention. These compounds in the case of a photographic element processed with one or more aqueous processing solutions, e.g. a monobath, a stabilizer bath or a bath causing some of the compounds in the element to become water soluble, such as silver halide solvents, are usually water soluble. When the moist element containing such compounds is contacted with a drying element according to the invention these compounds are removed from the element with the water removed. For instance, in processing a photographic element using web processing techniques as set out, for example, in U.S. Pat. 3,179,517 of Tregillus et al., certain processing agents are present in the moist processed element. A significant amount of these processing agents and other water soluble compounds formed in processing, such as a water soluble complex formed between unexposed silver halide and a silver halide solvent, are removed from the element when a coating according to the invention is contacted with the moist processed element. The concentrations and types of compounds removed from the moist photographic element can vary over a wide range and will depend on many factors such as the type of element, the type of processing carried out, the coating according to the invention employed, and the like.

A wide variety of coating compositions and means for applying them can be employed for preparing the coatings of the invention. In general, any composition, coating means or coating process which provides an adherent coating, having the desired thickness, the desired amounts of components, and the desired liquid removal properties can be employed. It is often advantageous to employ an organic solvent in the coating composition. Any organic solvent is suitable which provides the desired coating and can be selected by those skilled in the coating art. Aqueous solvents have been found especially useful, such as mixtures of water and a water miscible alcohol, e.g. methanol or acetonitrile.

An especially suitable coating composition comprises a mixture of:

(a) About 80% to about 90% by weight of the total composition solvent, comprising about 10% to about 20% by volume water and about 80% to about 90% by volume water miscible organic solvent, e.g. water miscible alcohol such as methanol, and

(b) About 10% to about 20% by weight of the total composition solids soluble in the said solvent comprising about 50% to 100% by weight water soluble, high molecular weight, highly crystalline poly(alkylene oxide), e.g. poly(ethylene oxide), and 0% to 50% by weight poly(alkylene oxide) having a molecular weight of about 190 to about 20,000, e.g. poly(ethylene oxide). For example, a coating composition within the scope of this embodiment comprises a mixture of:

(1) About 85% by weight solvent comprising about 15% by volume water and about 85% by volume methanol, and

(2) About 15% by weight solids, comprising about 10% by weight poly(ethylene oxide) having an average molecular weight of about 6000 to 7500 and a high molecular weight, highly crystalline poly(ethylene oxide). Such compositions are typically viscous mixtures.

Another embodiment of the invention is in a process for removing a diffusible liquid from a permeable solid containing said liquid by contacting said permeable solid with a solid material which removes said liquid from said permeable solid, the improvement comprising contacting said permeable solid with a flexible, liquid permeable, drying element comprising a solid coating containing an organic desiccant.

According to the invention, any method of and/or means for contacting the permeable solid containing the diffusible liquid and the solid coating of the invention can be used which provides the desired removal of liquid from the permeable solid. A coating of the invention can, for example, be on a flat, vertical, horizontal, or angular surface, on a continuous web, or it can be on a drum or cylinder, such as one which rotates, which contacts the permeable solid, e.g. a moist photographic element. It is important, however, that the method and means employed provide intimate contact. One method which is suitable comprises wrapping a flexible support, e.g. a paper web, coated on one or both sides with a coating according to the invention, on a common core with a moist photographic element, e.g. a roll of moist photographic film.

The amount of solid coating per square foot suitable according to the invention can vary over wide ranges depending on the components of the coating, the material to be dried and the like. A coating consisting of, for example, about 3 grams to about 30 grams, typically about 4 to about 10 grams per square foot, in and/or on a support, if one is used, can be suitable for removing moisture from a moist photographic element.

A typical process within this embodiment comprises removing moisture from a moist photographic element by contacting said element with a solid coating comprising a mixture of a poly(ethylene oxide) having an average molecular weight of about 190 to about 20,000 and a high molecular weight poly(ethylene oxide), e.g. a poly(ethylene oxide) having an average molecular weight of about 100,000 to about 5,000,000. In such a process at least about 60% by weight, and typically at least about 85% by weight, of water is removed from said element in about 1 to about 60 seconds at about 20° C.

For example, moisture can be removed from a moist photographic element by contacting said element for up to about 60 seconds under ambient conditions of temperature, pressure and humidity with a drying element which is a paper or film support having a solid coating comprising a mixture of poly(alkylene oxide) having an average molecular weight of about 190 to about 20,000 with a high molecular weight poly(alkylene oxide) about 0.01 millimeter to about 1.0 millimeter thick to remove at least about 90% by weight of said moisture from said element.

The drying element and processes of the invention are especially useful in a method of processing an exposed photographic element comprising contacting said element with a matrix such as a liquid permeable film or sheet of paper, containing a monobath, such as described in The Monobath Manual by Grant M. Haist, 1966, to produce the desired image and drying the resulting moist element by contacting said element with a solid coating comprising about 10% by weight poly(ethylene oxide) and about 90% by weight polymeric binder, for instance, by contacting said element with a solid coating comprising about 10% by weight poly(ethylene oxide) having an average molecular weight of about 6000 to about 7500 with about 90% by weight of high molecular weight poly(ethylene oxide).

The invention is further illustrated in the following examples. Unless otherwise indicated, percentages employed herein are by weight.

EXAMPLE 1

This example illustrates removing moisture from a processed, moist photographic film according to the invention.

A piece of photographic film containing a medium grain silver bromoiodide gelatino emulsion layer on a polyethylene terephthalate support is exposed imagewise to light. The film is 35 mm. wide and 25.4 centimeters long. The exposed film is processed using conventional silver halide developer and stabilizer baths, i.e. Kodak D–85 developer and Kodak F–5 Fixer. It is then washed for several minutes in water after which water on the surface of the film is removed by wiping.

A so-called drying tape, i.e. a paper support containing a coating according to the invention, is placed in intimate contact with the moist film under room conditions, i.e. about 21° C. and about 50% relative humidity, for 15 seconds by pressing the drying tape on the emulsion side of the film.

The drying tape in this example is a paper support about 0.1 millimeter thick having a 0.114 millimeter solid coating of a mixture of 10% by weight poly(ethylene oxide) having an average molecular weight of about 6000 to 7500 (Carbowax 6000, produced by Union Carbide Corporation, New York, N.Y.) with 90% by weight poly(ethylene oxide) having an average molecular weight of about 600,000 (Polyox WSR–N–3000, produced by Union Carbide Corporation, New York, N.Y.). The coating is prepared by coating a composition consisting of a viscous aqueous methanol solution of the poly(ethylene oxide) compounds on the paper support with a doctor blade.

At least 90% of the moisture is removed from the moist film and no poly(ethylene oxide) residue is observable on the film employing this procedure and coating according to the invention.

EXAMPLE 2

This example illustrates removing moisture from a photographic film according to the invention which is processed using web processing according to U.S. Pat. 3,179,517 of Tregillus et al., issued Ap. 20, 1965.

A processing web is prepared by soaking a hydrolyzed cellulose acetate film support in a 0.1% gold chloride solution for 3 minutes and then in a 0.2% solution of N-methyl-p-aminophenol sulfate. It is washed 5 minutes in water and then soaked for 5 minutes in a solution comprising:

	Grams
1-phenyl-3-pyrazolidone	1.0
Hydroquinone	10.0
2-dimethylaminoethanol-SO_2 addition product (20 mol percent SO_2)	174.0
Sodium thiosulfate peutahydrate	2.0
Water to make 1 liter.	

The excess liquid on the surface of the resulting processing web is removed with a squeegee.

A so-called drying tape is prepared as set out in Example 1.

A piece of photographic film having a medium grain silver bromoiodide gelatino emulsion having a total thickness in dry condition of 108 microns is exposed imagewise to light. It is then rolled in contact with the described processing web for a few minutes until full development of the exposed film occurs. The film and processing web are then peeled apart.

The resulting moist film having a total thickness of 130 microns is then contacted with the described drying tape for 15 seconds. This produces a film which is substantially dry and has no poly(ethylene oxide) residue observable on the film.

EXAMPLE 3

This example illustrates drying of a photographic film using a coating and process of the invention.

A photographic film containing a medium grain silver bromoiodide gelatino emulsion layer, prehardened during manufacture, is exposed imagewise to light. It is then processed in processing solutions and apparatus as described in U.S. Pat. 3,179,517—Tregillus et al., issued Apr. 20, 1965. The film is washed in water at about 20° C. for a period of two minutes. It is removed from the water, each surface wiped to remove surface moisture, and placed on a clean, dry, smooth, polished metal surface.

A drying tape is prepared as described in Example 1, containing a coating 0.114 millimeter thick consisting of 50% by weight poly(ethylene oxide) having an average molecular weight of about 1300 to about 1600 (Carbowax 1540, produced by Union Carbide Corporation. New York, N.Y.) and 50% by weight highly crystalline poly(ethylene oxide) having an average molecular weight of about 600,000 (Polyox WSR–N–3000) is pressed onto the moist film.

Within 15 seconds at least 95% of the moisture in the film is removed. No observable poly(ethylene oxide) residue is left on the film after the drying tape is removed from the film.

EXAMPLE 4

The procedure set out in Example 3 is repeated with the exception of using a coating 0.127 millimeter thick consisting of 100% high molecular weight poly(ethylene oxide) (Polyox WSR–N–4000, produced by Union Carbide Corporation, New York, N.Y.) having a melting point of about 65° C. on the paper support.

Substantially the same results are obtained as in Example 3.

EXAMPLE 5

The procedure set out in Example 3 is repeated with the exception of using a coating 0.152 millimeter thick consisting of 50% by weight poly(ethylene oxide) having an average molecular weight of 6000 to 7500 (Carbowax 6000) and 50% by weight poly(ethylene oxide) having an average molecular weight of about 600,000 (Polyox WSR–N–3000) on the paper support.

Substantially the same results are obtained as in Example 3.

EXAMPLE 6

The procedure set out in Example 3 is repeated with the exception of using a coating 0.152 millimeter thick consisting of 50% by weight poly(ethylene oxide) having an average molecular weight of 380 to 420 (Carbowax 400, produced by Union Carbide Corporation, New York, N.Y.) and 50% by weight poly(ethylene oxide) having an average molecular weight of about 600,000 (Polyox WSR–N–3000) on the paper support.

Substantially the same results are obtained as in Example 3.

EXAMPLE 7

The procedure set out in Example 3 is repeated with the exception of using a coating 0.152 millimeter thick consisting of 50% by weight poly(ethylene oxide) having an average molecular weight of 570 to 630 (Carbowax 600, produced by Union Carbide Corporation, New York, N.Y.) and 50% by weight poly(ethylene oxide) having an average molecular weight of about 600,000 (Polyox WSR–N–3000) on the paper support.

Substantially the same results are obtained as in Example 3.

EXAMPLE 8

The procedure set out in Example 3 is repeated with the exception of using a coating 0.114 millimeter thick consisting of 100% by weight highly crystalline poly (ethylene oxide) having an average molecular weight of about 600,000 (Polyox WSR–N–3000) on the paper support.

Substantially the same results are obtained as in Example 3.

EXAMPLE 9

The procedure set out in Example 3 is repeated with the exception of using a coating 0.140 millimeter thick consisting of 25% by weight poly(ethylene oxide) having an average molecular weight of 570 to 630 (Carbowax 600) and 75% by weight high molecular weight, highly crystalline poly(ethylene oxide) (Polyox WSR–N–3000) on the paper support.

Within 5 seconds at least 90% of the moisture in the film is removed. No observable residue is left on the film.

EXAMPLE 10

This example illustrates the use of sugars, such as sucrose, in the practice of the invention.

The procedure set out in Example 3 is repeated with the exception of using a coating 0.203 millimeter thick consisting of 50% by weight ordinary table sugar, i.e. sucrose, and 50% by weight high molecular weight, highly crystalline poly(ethylene oxide) (Polyox WSR–N–3000) on the paper support.

Within 5 seconds at least 90% of the moisture in the film is removed.

EXAMPLE 11

This example illustrates the use of sugars in the practice of the invention.

The procedure set out in Example 3 is repeated using a coating 0.229 millimeter thick consisting of 10% by weight poly(ethylene oxide) having an average molecular weight of about 6000 to 7500 (Carbowax 6000), 45% by weight high molecular weight highly crystalline poly (ethylene oxide) (Polyox WSR–750, produced by Union Carbide Corporation, New York, N.Y.) and 45% by weight ordinary table sugar, i.e. sucrose, on the paper support.

About 90% of the moisture in the film is removed within about 5 seconds.

EXAMPLE 12

The procedure set out in Example 3 is repeated using a coating 0.127 millimeter thick consisting of 6% by weight poly(ethylene oxide) having an average molecular weight of 6000 to 7500 with 94% by weight poly(ethylene oxide) having an average molecular weight of about 300,000 (Polyox WSR–N–750) on the paper support.

Substantially the same results are obtained as in Example 3.

EXAMPLE 13

The procedure set out in Example 3 is repeated using a coating 0.107 millimeter thick consisting of 100% by weight poly(ethylene oxide) having an average molecular weight of about 4,000,000 (Polyox WSR–301, produced by Union Carbide Corporation, New York, N.Y.) on the paper support.

At least 90% of the moisture in the film is removed within 30 seconds.

EXAMPLE 14

The procedure set out in Example 3 is repeated using a coating 0.127 millimeter thick consisting of 10% by weight poly(ethylene oxide) having an average molecular weight of about 6000 to 7500 (Carbowax 6000) and 90% by weight poly(ethylene oxide) having an average molecular weight of about 200,000 (Polyvox WSR–35, produced by Union Carbide Corporation, New York, N.Y.) on the paper support.

At least 90% of the moisture in the film is removed within 5 seconds.

EXAMPLE 15

The procedure set out in Example 3 is repeated using a coating 0.178 millimeter thick consisting of 100% poly (ethylene oxide) having an average molecular weight of about 200,000 (Polyox WSR–35) on the paper support.

At least 90% of the moisture in the film is removed within 5 seconds.

EXAMPLE 16

This example illustrates the use of an inorganic desiccant in a coating according to the invention.

The procedure set out in Example 3 is repeated with the exception of using a coating consisting of 10% by weight poly(ethylene oxide) having an average molecular weight of about 6000 to 7500 (Carbowax 6000), 85% by weight poly(ethylene oxide) having a molecular weight of about 600,000 (Polyox WSR–N–3000) and 5% by weight crystalline alumino silicate molecular sieve material on the paper support.

At least 90% of the moisture in the film is removed within 5 seconds. Also, increased moisture capacity as well as decreased adhesion between the film and drying tape are observed in comparison to coatings not containing the molecular sieve material.

EXAMPLE 17

This example illustrates the use of a semi-permeable membrane between a material from which diffusible liquid is to be removed and a polymeric coating in the practice of the invention.

The procedure set out in Example 3 is repeated with the exception that a strip of moisture permeable cellophane about 30 centimeters long, about 8.25 centimeters wide and about 0.1 mm. thick is soaked in water and, after removing surface moisture, applied between the moist film and drying tape before the drying tape and moist film are pressed together. Also, a coating consisting of 56% by weight poly(ethylene oxide) having a molecular weight of about 1300 to about 1600 (Carbowax 1540) and 18% by weight poly(ethylene oxide) having a molecular weight of 600,000 (Polyox WSR–N–3000) is used on the paper support. Some of this mixture is absorbed into the paper support. The polymer content in and on the paper support is 4.9 grams per square foot.

About 84% of the moisture is removed from the film within 60 seconds.

EXAMPLE 18

This example illustrates the use of a semi-permeable membrane in the practice of the invention.

A drying tape is impregnated with a highly crystalline poly(ethylene oxide) having a molecular weight of about 600,000 (Polyox WSR–N–3000) by soaking a paper support in an aqueous solution consisting of 2 grams of the poly(ethylene oxide) per liter of water. The resulting support is allowed to dry under room conditions producing a paper support containing 18.7 grams of the poly (ethylene oxide) per square foot. Use of this drying tape as set out in Example 3 with a semi-permeable layer of cellophane between the moist film and drying tape as set out in Example 17 removes at least 90% of the moisture from the film within 60 seconds.

EXAMPLE 19

The procedure set out in Example 18 is repeated with the exception that an overcoat consisting of a mixture of 70% by weight poly(ethylene oxide) having a molecular weight of 570 to 630 (Carbowax 600, produced by Union Carbide Corporation, New York, N.Y.) is applied to the drying tape to produce a total poly(ethylene oxide) content in and on the drying tape of 27.0 grams per square foot.

Substantially the same results are obtained as in Example 18. In this example, without the cellophane between the drying tape and the moist film, a noticeable residue remains on the film after removal of moisture.

EXAMPLE 20

This is a comparative example comprising use of a polymeric coating of the invention for drying a gelatino emulsion in production of a photographic film to air drying an identical emulsion.

A high contrast photographic silver chlorobromide gelatino emulsion is coated on a polyethylene terephthalate support at the rate of 351 miligrams of silver per square foot and 347 milligrams of gelatin per square foot. The emulsion is chill set and divided into two equal parts, (A) and (B).

Part (A) is contacted with a drying tape consisting of a paper support containing about 7.5 grams per square foot of a mixture of 10% by weight poly(ethylene oxide) having a molecular weight of about 6000 to 7500 (Carbowax 6000) and 90% by weight poly(ethylene oxide) having a mloecular weight of about 600,000 (Polyox WSR–N–3000) in and/or on the support. The coating on the support is about 0.064 millimeter thick. After 15 seconds, the drying tape is removed. The gelatino emulsion is dry to the touch.

Part (B) is air dried using forced air drying at about room temperature. The time required to dry the film is about 5 minutes.

After drying, both (A) and (B) are exposed 5 seconds to a standard step wedge, developed in Kodak D–85 Developer, fixed in Kodak F–5 Fixer, washed in water, and air dried. Part (A) has a 0.52 log E speed loss compared to Part (B) and the surface appears slightly reticulated.

EXAMPLE 21

A solution of 10% by weight highly crystalline poly(ethylene oxide) having a molecular weight of about 600,000 (Polyox WSR–N–3000) in acetontitrile is coated on a paper support at the rate of 6.0 grams per square foot and allowed to dry at room temperature. Some of the poly(ethylene oxide) is absorbed into the paper. An aqueous 6% by weight gelatin solution is coated on a polyethylene terephthalate support at the rate of 498 milligrams of gelatin per square foot. The resulting coating is contacted for 15 seconds with a drying tape as described in Example 20. After removing the drying tape, the gelatin coating is dry.

EXAMPLE 22

A multilayer photographic film containing gelatino silver halide emulsion, red, green and blue sensitive layers (Kodak Ektachrome-X film) is soaked in water for several minutes until the emulsion layers are swollen, i.e. from a total support and emulsion thickness in a dry condition of 152 microns to a total thicknes of 242 microns. The surface moisture is removed by wiping. The resulting moist film is contacted with a drying tape consisting of a paper support having a coating 0.064 millimeter thick consisting of 7.5 grams per square foot of a mixture of 10% by weight poly(ethylene oxide) having a molecular weight of about 6000 to 7500 (Carbowax 6000) and 90% by weight poly (ethylene oxide) having a molecular weight of about 600,000 (Polyox WSR–N–3000). Within 60 seconds, at least 90% of the moisture is removed from the moist film, i.e. the total thickness of the support and emulsion layers is 157 microns. No noticeable residue remains on the film.

EXAMPLE 23

The procedure set out in Example 22 is repeated with the exception that a coating 0.051 millimeter thick consisting of 10% by weight poly(ethylene oxide) having an average molecular weight of 6000 to 7500 (Carbowax 6000) and 90% by weight of a copolymer of acrylamide with 2-acetoacetoxyethyl methacrylate containing 90% by weight acrylamide is on the paper support. Substantially the same results are obtained as in Example 22.

EXAMPLE 24

Several lines of blue ink are placed with a conventional ink pen on a piece of conventional writing paper. A drying tape as described in Example 22 is contacted with the paper by pressing the drying tape over the portion of the paper containing the ink lines while the ink is still moist. The drying tape effects drying of the ink within less than 5 seconds without leaving noticeable residue on the writing paper or distorting the lines.

EXAMPLE 25

This example illustrates use of a multilayer polymeric coating in the practice in the practice of the invention.

The procedure set out in Example 3 is repeated with the exception that an initial coating consisting of 10% by weight poly(ethylene oxide) having a molecular weight of about 6000 to 7500 (Carbowax 6000), 75% by weight poly(ethylene oxide) having a molecular weight of about 600,000 (Polyox WSR–N–3000) and 15% by weight crystalline alumino silicate molecular sieve material is applied to the paper support and allowed to dry followed by application of an overcoat, about the same thickness as the initial coating, consisting of 10% by weight poly(ethylene oxide) having a molecular weight of about 6000 to 7500 (Carbowax 6000) and 90% by weight poly(ethylene oxide) having a molecular weight of about 600,000 (Polyox WSR–N–3000).

At least 90% of the moisture in the moist film is removed within 15 seconds.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A flexible, liquid permeable drying element comprising a support having on at least one surface a thin, adherent liquid permeable coating consisting essentially of a poly(ethylene oxide) having an average molecular weight of at least about 100.000 or said poly(ethylene oxide) having dispersed therein about 10% to 50% by weight of a poly(ethylene oxide) having an average molecular weight of about 190 to about 20,000.

2. A drying element as in claim 1 wherein said coating has the property of removing at least about 60% by weight of water from a wet gelatin layer coated on a support upon contacting said layer for a period of no more than 60 seconds with said drying element.

3. A drying element as in claim 1 wherein the high molecular weight poly(ethylene oxide) has an average molecular weight of about 100,000 to about 5,000,000.

4. A drying element as in claim 1 wherein said coating is about 0.001 millimeter to about 1.0 millimeter thick.

5. A flexible, liquid permeable drying element comprising a paper support having a coating consisting essentially of a mixture of about 10% to 50% by weight poly (ethylene oxide) having an average molecular weight of about 6,000 to 7,500 with about 90% by weight poly (ethylene oxide) having an average molecular weight of about 100,000 to about 5,000,000.

6. A flexible, liquid permeable drying element comprising a support having coated on at least one surface at least one thin, adherent, liquid permeable coating consisting essentially of a poly(ethylene oxide) having an average molecular weight of at least about 100,000 or said poly(ethylene oxide) having dispersed therein about 10% to 50% by weight of a poly(ethylene oxide) having an average molecular weight of about 190 to about 20,000 said coating further containing an alumino silicate molecular sieve material.

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