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PHOTOGRAPHIC PAPER WITH POLYOLEFIN COATING

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ABSTRACT OF THE DISCLOSURE

Improved photographic papers having a polyolefin coated paper base are disclosed. It has been found that photosensitive emulsions perform better when they are coated directly upon a layer of cellulose ester such as celluose acetate. Improved adhesion of such a 2-layer coating to polyolefin coated paper results when a layer of chlorinated polyolefin is utilized as a "sub" between the polyolefin coating (on the paper) and the cellulose ester coating (under the emulsion).

This invention relates to improved photographic papers in which the paper base is coated with a polyolefin such as polyethylene or polypropylene.

Polyolefin coated paper has been used as a base for photographic papers for several years. Generally the preferred polyolefin for coating such paper is polyethylene. Examples of such coated materials are shown in U.S. Pat. 3,165,432 and U.S. Pat. 3,230,135. Such coated papers exhibit valuable properties for photographic applications because of their excellent low rate of moisture absorption (during processing, for example) and good surface qualities. On the other hand, photographic emulsions that are primarily based on gelatin or gelatin-related materials and contain radiation-sensitive materials dispersed therethrough generally have properties that are best displayed when the emulsions are physically coated over a layer of material that consists essentially of one or more plasticized lower fatty acid esters of cellulose (wherein the lower fatty acid chains contain from 1 to 4 carbon atoms), such as cellulose acetate, cellulose butyrate, cellulose acetate butyrate and the like. Thus, a product in which the features of these two groups of coatings are combined would be a valuable photographic sensitized paper product.

However, heretofore, efforts to simply coat the desired layers of (a) cellulose ester, (b) appropriate "sub," if desired and (c) the photographic emulsion directly onto polyolefin-coated paper stock were not successful because of the drastic lack of adhesion of the cellulose ester to the polyolefin coated paper stock. For example, the dry adhesion of a conventional, commercially available cellulose acetate coating onto paper having a thin extruded coating of medium density polyethylene is essentially zero.

It has now been discovered that the "wet" and "dry" adhesion problem between a layer of cellulose ester and polyolefin-coated paper can be solved by applying a thin layer of a chlorinated polyolefin directly between these two layers of materials, the chlorinated polyolefin layer thereby becoming a valuable sub to result in a remarkably improved adhesion of the cellulose ester layer to the polyolefin-coated paper base. The resulting product of the present invention, then, is a multilayered product having as its base polyolefin coated paper and having coated thereon the following layers:

(a) on the polyolefin coating, a thin layer of chlorinated polyolefin,

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(b) over the chlorinated polyolefin "subbing" layer, a layer of lower (i.e. 2–4 carbon atoms) fatty acid ester of cellulose, and

(c) over the layer of cellulose ester, at least one layer of photosensitive emulsion. (If desired a conventional sub, such as a very thin gel-nitrate layer can be applied and used between the cellulose ester layer and the photosensitive emulsion).

The "chlorinated polyolefin" material that has been found to perform so well in the practice of the present invention includes chlorinated polyethylene, chlorinated polypropylene and the like in which the material contains from about 25 to about 50 weight percent of chlorine, has a melt viscosity of from about 10,000 to about 25,000 poises, and has a tensile strength of from about 500 to about 2500 pounds per square inch. Such materials are readily soluble in organic non-polar solvents such as toluene to levels of 25 weight percent or more. As a matter of fact, the casting and curing of 25 weight percent solutions of the chlorinated polyolefin in toluene represents a preferred method of applying the layer of chlorinated polyolefin onto the polyolefin-coated paper stock in the practice of this invention. Curing of the cast layer can preferably be accomplished by simply heating the treated material (coated paper overcoated with a solution of one or more chlorinated polyolefins, as set out above, dissolved in a nonpolar, organic solvent) at a temperature somewhat higher than 40° C. until the organic solvent has been evaporated.

The "cellulose ester" material that can be utilized in the practice of this invention can be any (or a mixture) of those cellulose ester materials that are conventionally useful as photographic film base materials. For example, they can be cellulose acetates, cellulose butyrates, cellulose propionates, cellulose acetate butyrates, and the like that have intrinsic viscosities of at least about 0.8 (and preferably at least about 1.3) measured in acetone or $MeCl_2/MeOH$ (9:1) and contain at most about 3.75 weight percent (and preferably at most about 2.5 weight percent) hydroxyl. They should also preferably be substantially transparent. The "cellulose ester" layer may or may not, but will preferably also contain a significant amount (5 weight percent or more, for example) of one or more plasticizers. Such plasticizer(s) are all of those that can ordinarily be used in cellulose ester film base materials. This includes such well known materials as triphenylphosphate and the like. The amount of chlorinated polyolefin that can be utilized as the "subbing" layer in the practice of this invention should be at least about 0.5 grams per square meter (and preferably from about 0.75 to about 5.0 grams per square meter) of polyolefin surface coated thereby, and the material should be fairly uniformly spread over the polyolefin.

EXAMPLE I

Onto each surface of photographic paper stock weighing about 27 pounds per thousand square feet were extruded a thin layer (about 2 mils) of medium density polyethylene. Onto one surface of the resulting PE-coated paper was applied a layer of a 25 percent solution of chlorinated (about 35 weight percent chlorine, melt viscosity=15,000) polyethylene (CPE) in toluene, at a rate of 0.98 grams of CPE per square meter (based on dry weight). This material was then "cured" by warming it to about 100° C., for 20 minutes and then overcoated with a cellulose acetate dope made up by dissolving cellulose acetate (0.9% hydroxyl, 43.5% acetyl, I.V.=2.14) in a 9 to 1 weight ratio mixture of methylene chloride and methanol at the 10 weight percent cellulose acetate level. The thickness of the resulting cellulose acetate coating or layer (after subsequent air-drying of the dope

layer at about 30° C. for 15 minutes followed by oven drying at 100° C. for 15 additional minutes to remove practically all of the organic solvents) was about 1.5 mils.

This product was found to have a "peel strength," measured on a conventional tensile tester (tradenamed "Inston") of 147 grams/inch. By comparison, a composite material that was treated in a manner identical to that of Example I, except that no CPE was utilized, had a "peel strength" value of zero.

Any desired photographic emulsion can be coated on the cellulose ester layer in any of a number of well-known methods as desired to yield the final photographic paper product of the present invention. It should be noted that the valuable high "adhesion" that is made possible via the practice described above of this invention is retained in photographic paper products even during and after the usual "wet" chemical processing of these paper products.

This 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.

What is claimed is:

1. A polyolefin coated paper article containing on at least one surface thereof a multiple-layered coating consisting essentially of

(a) immediately adjacent the polyolefin coating on said surface, a first layer of solid chlorinated polyolefin; said first layer containing at least about 0.5 grams of said chlorinated polyolefin per square yard of said surface;

(b) a second layer of at least one lower fatty acid ester of cellulose; said second layer being immediately adjacent said first layer; and

(c) overlying said second layer, a photosensitive emulsion.

2. A polyolefin coated paper article as in claim **1**, wherein said polyolefin is polyethylene.

3. A polyethylene coated paper article as in claim **2**, wherein said chlorinated polyolefin is selected from the group consisting of chlorinated polyethylene and chlorinated polyethylene and chlorinated polypropylene, has a melt viscosity of from about 10,000 to about 25,000 poises, and contains from about 25 to about 50 weight percent of chlorine.

4. A polyethylene coated paper article as in claim **3**, wherein said ester of cellulose is selected from the group consisting of cellulose acetates, cellulose butyrates, cellulose propionates and cellulose acetate butyrates having intrinsic viscosities of at least about 1.3 and containing at most about 2.5 weight percent hydroxyl.

5. A polyethylene coated article as in claim **4**, wherein said ester of cellulose is cellulose acetate containing at least about 42 weight percent acetyl.

6. A polyethylene coated article as in claim **5**, wherein said chlorinated polyolefin is chlorinated polyethylene.

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