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PHOTOCHROMIC CELLULOSIC PAPER, SYNTHETIC PAPER AND REGENERATED CELLULOSE

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This invention relates to photochromic cellulosic paper, photochromic synthetic paper and photochromic regenerated cellulose. More particularly, this invention relates to cellulosic paper, synthetic paper or regenerated cellulose film containing uniformly distributed throughout its mass, a photochromic material. Still more particularly, this invention relates to cellulosic paper, synthetic paper or regenerated cellulose film containing uniformly distributed throughout its mass, a photochromic compound which exhibits its photochromic properties in the solid state.

The production of photochromic paper per se is not new in the art. Berman, in U.S. Patent No. 2,953,454, discloses a method for the production of photochromic paper wherein the paper is coated with minute, liquid-containing capsules having light-translucent walls, said liquid having dissolved therein a photochromic material. The method disclosed by Berman, however, is relatively expensive and very difficult to conduct, especially in regard to obtaining a uniform, continuous covering of the paper with the microscopic, solution-containing capsules. Additionally, since these capsules are pressure sensitive and the photochromic material is only active in solution, the treated paper must be carefully stored and handled lest its usefulness will be destroyed by rupture of the capsules upon the slightest contact.

We have found that the relatively commercially unattractive characteristics of the prior art photochromic articles may be overcome by incorporating a photochromic material which is active in the solid state into the cellulosic paper, synthetic paper or regenerated cellulose thereby producing a photochromic article which has a uniform, continuous photochromic surface. We have unexpectedly and surprisingly found that these solid state photochromic materials continue to function as such, and as effectively, after having been dispersed throughout the two types of paper or regenerated cellulose. This result is even more surprising in view of the fact that generally, solid state photochromic materials lose their activity upon being dispersed throughout other solid binders. For example, TiO_2 activated with an iron oxide, a photochromic substance, functions in the pure solid state, however, upon incorporation into a solid glass binder, it ceases to possess its color changing ability. Additionally, we have found that photochromic materials which function only in solution cannot be added to the cellulosic paper, synthetic paper or regenerated cellulose without losing their ability to function photochromically.

It is an object of the instant invention to present photochromic cellulosic paper, photochromic synthetic paper and photochromic regenerated cellulose.

It is a further object of the instant invention to present cellulosic paper, synthetic paper and regenerated cellulose films having uniformly dispersed throughout their masses, a photochromic material.

It is still a further object of the instant invention to present cellulosic or synthetic paper and regenerated cellulose, containing, uniformly dispersed throughout their masses, a photochromic compound which is photochromic in the solid state.

These and further objects of the instant invention will become more apparent to one skilled in the art upon reading the more detailed description set forth hereinbelow.

PHOTOCHROMISM

Molecules or complexes which undergo reversible photo-induced color changes are termed photochromic systems. That is to say, in the absence of activating radiation, the system has a single stable electronic configuration with a characteristic absorption spectrum. When the system is contacted with ultraviolet irradiation the absorption spectrum for the system changes drastically, but when the irradiation source, is removed, the system reverts to its original state.

Photochromism has been observed in inorganic and organic compounds both in solution and solid state. Although the exact mechanism of color change varies in each individual system, in many inorganic systems it can be related to one of two possible reaction schemes.

The first process is the alteration of the force field around the nucleus of a coordination compound by photo-initiated dissociation, ligand exchange, or isomerization. This alteration can lead to a marked change in the light absorption properties of a molecule.

The second fundamental photo-electronic mechanism generally considered as producing photochromism is electron delocalization. This mechanism is rapidly reversible in organic molecules and therefore usually produces no colored intermediate. However, in inorganic crystals, photoinitiated electron delocalization from an impurity can lead to a colored state in which the electron is either trapped by a crystal defect to form a color center or otherwise reacts with the crystal host to leave the system in a colored state.

There are three major factors which govern the behavior of a photochromic system.

(A) *Absorption of incident radiation*

According to the quantum theory, each absorbed quantum creates one activated molecule and only absorbed radiation can produce a chemical change. Variables which control the number of photons absorbed include the concentration and extinction coefficient of the photochrome, the screening coefficients of other components of the system, and the wavelengths of the incident radiation.

(B) *Quantum yield*

All excited molecules will not undergo transformation to the colored form, so that the quantum yield will generally be less than unity. Various deactivating processes which compete for the excited molecules include fluorescence, phosphorescence, permanent chemical change and thermal release.

(C) *The reverse reaction*

In both the forward and reverse reactions, the concentration of the colored form is dependent on the intensity of the radiation, the kinetics of the reverse reactions, and temperature of the reactions. The kinetics for the reverse reaction will normally be controlling, however some reverse reactions are thermally sensitive and are accelerated by irradiation or heating.

By the terms "photochromic compound," "photochromic substance" or "photochromic material," as used in the instant disclosure, is meant compounds, substances or materials which change their transmission or reflectance upon being subjected to ultraviolet or visible irradiation and subsequently revert to their original color state upon subjection thereof to a different wavelength or radiation, or removal of the initial ultraviolet source.

The ability of various materials to change color and to then revert back to their original color is not a new phenomena. In fact, such compounds have been widely

used in various ways, as described above. Generally, these compounds change their color when exposed to ordinary sunlight and revert back to their original color upon removal thereof from the rays of the sun. Various other materials, however, change color only when subjected to a certain degree of irradiation, and as such, sunlight will not affect them. High intensity radiation, such as 10–25 cal./cm.^{2}/sec. or more is necessary in regard to these compounds, while sunlight (0.2 cal./cm.^{2}/sec.) will affect the former.

THE PHOTOCHROMIC ADDITIVES

The photochromic additives which are incorporated into cellulosic paper, synthetic paper or regenerated cellulose to form the novel products of the present invention are not critical in regard to the specific chemical class of compounds used, except that the compounds must be photochromic in the solid state. That is to say, compounds which are solid but only exhibit photochromic properties in solution cannot be employed to form the products which constitute the subject matter of the present invention. Only those materials which are solid and which function photochromically, as such, are contemplated herein. However, a material which functions photochromically both in the solid state and in solution falls within the scope of the present invention. By "solid" as used in the present specification, is meant those compounds which are solid, as opposed to liquid, at room temperature and reversibly change color at that temperature when contacted with ultraviolet light. Examples of compounds which fall into this category and therefore may be used to form the novel products of the present invention are set out more fully hereinbelow.

One class of photochromic materials which are useful in producing the products of the present invention are composed of inorganic metal oxides. The materials generally consist of a primary or host inorganic metal oxide "doped" with a lesser or contaminating amount of another guest inorganic metal oxide. The materials which are contemplated as useful in the novel compositions of our invention are the following: TiO_2 doped with Fe_2O_3, FeO, Cr_2O_3, CuO, NiO, MnO_2 or Mn_2O_3; Nb_2O_5 doped with Fe_2O_3, FeO, Cr_2O_3, CuO, V_2O_5, MnO_2 or Mn_2O_5; Al_2O_3 doped with Cr_2O_3 or V_2O_5; ZnO doped with CuO or V_2O_5; SnO_2 doped with CuO; or ZrO_2 doped with CuO or NiO. In regard to the TiO_2, the rutile form of the compound is sufficient, however, the anatase form containing at least 5% of the rutile material is preferred. These photochromic materials contain from about 0.01 to 5.0 mole percent of the doping guest oxide, preferably 0.1 to 2.0 mole percent, based on the number of moles of the host oxide.

These doped oxides are well known in the art and generally may be prepared by any applicable method. Various methods which may be used include those set out in the following articles. Williamson, Nature (London), 140, 238 (1937); McTaggert et al., J. Appl. Chem., 5, 643 (1955); Frydryck, Doctoral Thesis, Free University of Berlin (1961), and the method set forth hereinbelow. By the word "doped" or "doping" as used herein in regard to all the oxides, is meant the result obtained from or the method of forming the photochromic oxides as set forth in the above-enumerated articles.

A second class of photochromic materials that may be employed in forming the products of the present invention comprises materials composed of TiO_2 with a combination of two doping (guest) metal oxides. These materials composed of guest oxides, in admixture with TiO_2, exhibit a more pronounced effect in the color intensity of the products than either doping metal (guest) oxide used alone. For example, TiO_2 doped with Fe_2O_3 or FeO and NiO or TiO_2 doped with Fe_2O_3 or FeO and CuO, result in a more intense color change than TiO_2 doped with Fe_2O_3, FeO, NiO or CuO, alone. That is to say, a synergistic effect is observed wherein the results obtained utilizing a mixture of guest oxides is better than that obtained from either guest oxide alone or the mere additive results of both together. Here, again, the rutile form of the host compound is satisfactory, but the anatase form containing at least 5% of the rutile material is preferred. When a combination of the different doping oxides are used, amounts ranging from 100:1 to 10:1, preferably 25:1 to 5:1, of the iron oxide to the nickel or copper oxide are satisfactory, the total amount of the mixed oxides still however, being within the range (in mole percent) specified above.

These materials composed of host and guest oxides, either, as such, or with combinations or doping guest oxides, may be prepared, among other methods, by slurrying a solution of the doping metal oxide salt, the guest metal oxide itself, or mixtures thereof, with the host metal oxide. The slurry is evaporated and ground, then calcined at a temperature between 400° and 1100° C. to give the active composition. In the case of TiO_2, the host crystalline compound desired can be previously prepared, or starting the preparation with anatase, the desired final proportion of rutile can be controlled by the length of time the admixture is calcined above the phase transition temperature (ca. 800° C.). The final active photochromic materials are not merely mechanical or physical blends, but are crystalline materials consisting of a host material matrix wherein is contained substitutionally or interstitially, the doping guest metal oxide.

A third class of photochromic inorganic oxide materials which may be used to form the products of the present invention are TiO_2 reacted with MoO_3 or WO_3. These materials are produced in mole ratios of about 1 to 15 mole percent of TiO_2 to about 25 to 1 mole percent of MoO_3 or WO_3. The preferred mole ratios range from about 1:4 to about 12:1, respectively. The TiO_2 component may be in either the rutile, anatase, or mixed phase form, and in place of TiO_2 other metal oxide components may be used, such as, for example, ZnO, ZrO_2, SnO_2 and GeO_2 in the same mole ratio given above for TiO_2.

These two phase materials constituting the third class of photochromic materials are prepared as described and claimed in copending application, Serial No. 239,159, filed November 21, 1962. In a typical procedure, the materials are prepared by dissolving the MoO_3 or WO_3 in an aqueous basic solution and adding to this solution an acidified aqueous slurry or solution of the primary metal oxide component. After heating at up to 100° C. for several hours or longer, the desired active material is formed in a very high yield, separated from the solvent, washed free of acid, and dried.

Superficially taken, it would appear that the third class of materials are merely mechanical or physical mixtures of the two oxide components. However, these latter chemically prepared coprecipitated materials are of extremely greater photo-sensitivity in comparison to a mixture of their individual metal oxides. Additionally, X-ray evidence clearly indicates that the crystalline matrix of the MoO_3 or the WO_3 has been completely altered. Although not wishing to be bound by any particular theory, it is possible that this phenomena can be explained as follows. Since the photochromic color in these compounds is deep blue, the most likely theoretical alternative as to the nature of this photochromic reaction is that a net electron delocalization to Mo or W takes place either by an inter- or intra-phase photoinitiated electron transfer from the second component of the active material.

Further examples of solid state photochromic additives which may be used to form the novel products of the present invention include:

(1) 2,3-diphenyl-1-indenone oxide
(2) p-bromo-N-(5-bromosalicylidene)aniline
(3) N-(5-bromosalicylidene)-1-naphthylamine

(4) N-4-hydroxybenzylideneaniline
(5) p-bromo-N-4-hydroxybenzylideneaniline
(6) N-4-hydroxybenzylidene-1,2,4-xylidine
(7) N-(3-methoxysalicylidene)-1,2,5-xylidine
(8) N-o-nitrobenzylidene-p-anisidine
(9) m-chloro-N-o-nitrobenzylideneaniline
(10) o-chloro-N-o-nitrobenzylideneaniline
(11) N-o-nitrobenzylidene-1,2,4-xylidine
(12) m-salicylideneaminobenzoic acid
(13) p-salicylideneaminobenzoic acid
(14) o-salicylideneaminocinnamic acid
(15) ethyl p-salicylideneaminobenzoate
(16) N-salicylideneaniline
(17) N-salicylidene-o-anisidine
(18) N-salicylidene-p-anisidine
(19) m-bromo-N-salicylideneaniline
(20) o-bromo-N-salicylideneaniline
(21) p-bromo-N-salicylideneaniline
(22) o-chloro-N-salicylideneaniline
(23) N-salicylidene-2-naphthylamine
(24) N-salicylidene-m-toluidine
(25) N-salicylidene-p-toluidine
(26) N-salicylidene-1,3,4-xylidene
(27) N-(6-nitroveratrylidene)-p-anisidine
(28) N-o-nitrobenzylidene-4-biphenylamine
(29) N-o-nitrobenzylidene-o-anisidine
(30) N-o-nitrobenzylidene-1-naphthylamine
(31) N-o-nitrobenzylidene-2-naphthylamine
(32) o-nitro-N-o-nitrobenzylideneaniline
(33) m-nitro-N-o-nitrobenzylideneaniline
(34) p-nitro-N-o-nitrobenzylideneaniline
(35) N-o-nitrobenzylidene-p-phenetidine
(36) anisaldehyde phenylhydrazone
(37) benzaldehyde phenylhydrazone
(38) 1-phenyl-1-penten-3-one phenylhydrazone
(39) 1-phenyl-1-hexen-3-one phenylhydrazone
(40) cinnamaldehyde phenylhydrazone
(41) diethyl dimethyloxalacetate phenylhydrazone
(42) 5-methyl-1-(3,4-methylenedioxyphenyl)-1-hexen-3-one phenylhydrazone
(43) p-tolualdehyde phenylhydrazone
(44) benzaldehyde m-tolylhydrazone
(45) cinnamaldehyde m-tolylhydrazone
(46) p-isopropylbenzaldehyde m-tolylhydrazone
(47) piperonal m-tolylhydrazone
(48) benzaldehyde p-tolylhydrazone
(49) cinnamaldehyde p-tolylhydrazone
(50) p-isopropylbenzaldehyde p-tolylhydrazone
(51) furfural p-tolylhydrazone
(52) piperonal p-tolylhydrazone
(53) anisaldehyde (m-chlorophenyl)hydrazone
(54) cinnamaldehyde (m-chlorophenyl)hydrazone
(55) p-isopropylbenzaldehyde (m-chlorophenyl) hydrazone
(56) piperonal (m-chlorophenyl)hydrazone
(57) p-tolualdehyde (m-chlorophenyl)hydrazone
(58) benzaldehyde (p-chlorophenyl)hydrazone
(59) cinnamaldehyde (p-chlorophenyl)hydrazone
(60) p-isopropylbenzaldehyde (p-chlorophenyl) hydrazone
(61) p-tolualdehyde (p-chlorophenyl)hydrazone
(62) benzaldehyde (p-bromophenyl)hydrazone
(63) cinnamaldehyde (p-bromophenyl)hydrazone
(64) p-isopropylbenzaldehyde (p-bromophenyl) hydrazone
(65) salicylaldehyde (p-bromophenyl)hydrazone
(66) benzaldehyde (p-methoxyphenyl)hydrazone
(67) cinnamaldehyde (p-methoxyphenyl)hydrazone
(68) p-isopropylbenzaldehyde (p-methoxyphenyl) hydrazone
(69) piperonal (p-methoxyphenyl)hydrazone
(70) vanillin (p-methoxyphenyl)hydrazone
(71) anisaldehyde 3,4-xylylhydrazone
(72) benzaldehyde 3,4-xylylhydrazone
(73) p-isopropylbenzaldehyde 3,4-xylylhydrazone

(74) piperonal 3,4-xylylhydrazone
(75) salicylaldehyde 3,4-xylylhydrazone
(76) p-tolualdehyde 3,4-xylylhydrazone
(77) benzaldehyde 3,5-xylylhydrazone
(78) cinnamaldehyde 3,5-xylylhydrazone
(79) anthranilaldehyde 2-naphthylhydrazone
(80) benzaldehyde 2-naphthylhydrazone
(81) cinnamaldehyde 2-naphthylhydrazone
(82) p-isopropylbenzaldehyde 2-naphthylhydrazone
(83) 2,4-dihydroxybenzaldehyde 2-naphthylhydrazone
(84) p-dimethylaminobenzaldehyde 2-naphthylhydrazone
(85) furfural 2-naphthylhydrazone
(86) m-hydroxybenzaldehyde 2-naphthylhydrazone
(87) p-hydroxybenzaldehyde 2-naphthylhydrazone
(88) m-anisaldehyde 2-naphthylhydrazone
(89) o-anisaldehyde 2-naphthylhydrazone
(90) piperonal 2-naphthylhydrazone
(91) m-tolualdehyde 2-naphthylhydrazone
(92) o-tolualdehyde 2-naphthylhydrazone
(93) p-tolualdehyde 2-naphthylhydrazone
(94) vanillin 2-naphthylhydrazone
(95) veratraldehyde 2-naphthylhydrazone
(96) 1-(p-methoxyphenyl)-1-penten-3-one semicarbazone
(97) 1-(p-methoxyphenyl)-5-methyl-1-hexen-3-one semicarbazone
(98) 1-phenyl-1-penten-3-one semicarbazone
(99) cinnamaldehyde thiosemicarbazone
(100) 4-(4-hydroxyphenyl)-3-methyl-3-buten-2-one thiosemicarbazone
(101) 4-(4-hydroxyphenyl)-3-methyl-3-buten-2-one phenylsemicarbazone
(102) 1-(o-hydroxyphenyl)-1-penten-3-one phenylsemicarbazone
(103) 1-(p-isopropylphenyl)-1-penten-3-one thiosemicarbazone
(104) 1-(p-isopropylphenyl)-1-penten-3-one phenylsemicarbazone
(105) 1-(p-isopropylphenyl)-1-hexen-3-one thiosemicarbazone
(106) 1-(p-isopropylphenyl)-1-hexen-3-one phenylsemicarbazone
(107) o-methoxycinnamaldehyde thiosemicarbazone
(108) p-methoxycinnamaldehyde semicarbazone
(109) 4-(o-methoxyphenyl)-3-methyl-3-buten-2-one thiosemicarbazone
(110) 3-(p-methoxybenzylidene)-2-pentanone thiosemicarbazone
(111) 3-(p-methoxybenzylidene)-2-pentanone phenylsemicarbazone
(112) 1-(p-methoxyphenyl)-5-methyl-1-hexen-3-one semicarbazone
(113) 1-(o-methoxyphenyl)-4-methyl-1-penten-3-one thiosemicarbazone
(114) t-methyl-1-[1(4H)-naphthylidene]-2-pentanone semicarbazone
(115) 1-[1(4H)-naphthylidene]-2-pentanone semicarbazone
(116) 5-methyl-1-(1-naphthyl)-1-hexen-3-one semicarbazone
(117) 1-(1-naphthyl)-1-hexen-3-one semicarbazone
(118) 3-nitrochalcone semicarbazone
(119) 2-nitrochalcone semicarbazone
(120) 1-phenyl-1-penten-3-one semicarbazone
(121) 1-(3,4-methylenedioxyphenyl)-1-penten-3-one thiosemicarbazone
(122) 1-(3,4-methylenedioxyphenyl)-1-penten-3-one phenylsemicarbazone
(123) 5-methyl-1-(3,4-methylenedioxyphenyl)-1-hexen-3-one semicarbazone
(124) 5-methyl-1-(3,4-methylenedioxyphenyl)-1-hexen-3-one thiosemicarbazone
(125) 4-methyl-1-(3,4-methylenedioxyphenyl)-1-penten-3-one thiosemicarbazone

(126) 4-methyl-1-(3,4-methylenedioxyphenyl)-1-penten-3-one phenylsemicarbazone
(127) 1-phenyl-1-hepten-3-one semicarbazone
(128) 4-phenyl-3-buten-2-one thiosemicarbazone
(129) 4-phenyl-3-buten-2-one phenylsemicarbazone
(130) 2-(2,4-dinitrobenzyl)pyridine
(131) N-(3-pyridyl)sydnone and the like.

THE CELLULOSIC PAPER BASE

According to the present invention, any cellulosic paper material may be used to form the photochromic products of the present invention. The cellulosic paper may be made from all types of fiber stocks, including those of poor quality, such as oak, poplar, and yellow birch, and those of extremely short fiber length, as well as those of long fiber length and of good quality derivation, such as from spruce and hemlock. A wide variety of fibrous cellulosic material used in the preparation of paper, board, molded resin fillers, and the like may be used, such as kraft pulp, rag pulp, soda, sulfate, ground-wood, sulfite pulp and alpha pulp. Similarly, other forms of paper-forming fibrous cellulose such as cotton linters, and the like may be employed. These materials may be used alone or in admixture with fibers from other sources, such as jute, hemp, sisal, strings, chopped canvas, and other material, either cellulosic or non-cellulosic.

It is further stressed that the cellulosic base paper may also be obtained from bleached or unbleached kraft, bleached or unbleached sulfite, or bleached or unbleached semi-chemical pulps. In addition, the paper may be made from mixtures of cellulosic paper-forming pulps with up to 10% and preferably containing 1 to 5% of other fibers, such as glass fibers or a minor amount of any of the synthetic fibers mentioned hereinbelow.

For most purposes it is preferred that the starting cellulosic paper be unsized and generally free of added resins. However, for some purposes, it may be desirable to employ as the starting paper base sheet, a porous, high wet strength, paper such as may be obtained by incorporation into the paper base sheet 0.5 to 5% by weight, based on the weight of the fibers, of a thermosetting aminoplast resin, such as a urea-formaldehyde resin, a melamine-formaldehyde resin or methylolated ureido polymers, such as those obtained by the reaction of formaldehyde with polymers and copolymers of N-vinyl-oxyethyl-N,N'-ethyleneurea. Such wet strength cellulosic papers are obtained in the conventional way by the use of one of the resins just cited applied to the pulp suspensions followed by sheeting and baking at temperatures of 210° to 400° F. for periods of about one-half or an hour to five or ten minutes, respectively.

The method of making the cellulosic paper base is not critical and any paper-making process may be employed to form the paper bases used in the present invention. In the normal manufacture of paper, for example, cellulosic fibers such as those derived from wood pulp are beaten in water to disperse the fibers therein and to reduce them to a length and fineness suitable for use in papermaking. During the beating operation the cellulosic fibers fibrillate, the fibrillation manifesting itself by a fraying or shredding of the surfaces and ends of the fibers to produce minute tendrils or fibrils which serve to interlock the fibers together when they are deposited on the forming screen of a paper-making machine to make a sheet therefrom and dried. The interlocking of these fibrils projecting from the deposited fibers imparts coherency and strength to the paper. In other words, the strength in the paper is attained through the interlocking of large numbers of fiber branches or fibrils during sheet formation.

The photochromic material may be added to the cellulosic paper anytime during the production thereof or even after the paper has been sheeted. Therefore, it is within the scope of the present invention, to prepare a beater pulp of papermaking cellulose fibers of any convenient consistency, for example, between about 0.5% to 5%. To this can be added any of the photochromic materials, described hereinabove. The suspension is agitated gently to distribute the emulsion particles uniformly therethrough and the aqueous suspension of fibers is then sheeted, preferably at a pH between 4.5 and 6, to form a wet water-laid web containing the photochromic additive. The web is then dried on steamheated rolls, in accordance with conventional practice.

More specifically, in mills where various pigments are added at the beater, the photochromic material may be added therewith or at any point more than about one minute from the wire. In such mills the photochromic material may be added at any time but sufficiently far from the wire to permit deposition of the added photochromic composition in the fibers before the sheeting step begins.

In mills where the paper pulp suspension is given heavy refining, the photochromic material may be added to the beater, to the refiner effluent or to the screen effluent sufficiently ahead of the wire so that deposition becomes substantially complete before the sheeting step.

Thus, the application of the photochromic material may be easily adapted to most types of paper or mill conditions. Therefore, the photochromic material may be added to the paper pulp prior to sheet formation or may be applied to the sheet at a convenient point after sheet formation, even at the size press or calendar stacks, for example.

The paper obtained consists essentially of cellulose fiber having the photochromic material uniformly dispersed throughout its mass. The paper changes color upon contact with ultraviolet light and reverts to its original color upon removal of the light.

If the photochromic material is to be incorporated into a sheet of pre-formed cellulosic paper, it is only necessary to first wet the sheet on a screen, for example, and contact the wet web with the photochromic material, preferably for a period of time sufficient to enable substantially complete, thorough and uniform incorporation of the material into the paper fibers. The paper sheet is then dried to produce the desired photochromic cellulosic paper sheet.

THE SYNTHETIC PAPER BASE

As mentioned hereinabove, it is also within the scope of the present invention to utilize fibrous or nonfibrous synthetic paper bases formed from synthetic paper-forming polymers to produce the novel products of the present invention. In this regard, such materials as nylon and related polyamide polymers, polyethylene glycol terephthalate, and related polyester resins, polymers of acrylonitrile, such as copolymers containing at least 75%, by weight, of acrylonitrile with other comonomers such as vinyl acetate, vinyl chlorode, vinyl pyridine, and esters of acrylic or methacrylic acid may be employed in the present invention.

By the term "synthetic paper," as used herein and throughout the instant specification is meant, those paper sheets produced from synthetic polymeric materials such as those set forth hereinabove, more specific examples of which are shown in e.g., U.S. Patent No. 2,810,646, along with methods for the production thereof, which patent is hereby incorporated into the instant disclosure by reference.

It can therefore be seen that synthetic paper comprising randomly intermingled discontinuous fibers which are at least in part composed of highly fibrillated, synthetic, non-cellulosic fibers of paper-making length may be used to form the novel products of the present invention. More particularly, synthetic paper comprising randomly intermingled discontinuous fibers which are at least in part composed of fibrillated wet-spun thermoplastic products of a polymerized mass of polymerized acrylonitrile may be used.

As in regard to the cellulosic paper bases, the photochromic materials which are added to the synthetic paper base, may be incorporated therein at any time during the manufacture of the synthetic paper sheet. Any method may be used to produce these synthetic sheets including, for example, the so-called "hot method" wherein a thermoplastic organic polymer is melted and extruded through spinnerettes into cooler air. A filament is formed when the polymer has cooled below its melting point. The photochromic material may conveniently be added, therefore, to the polymer at such times as when the polymer is melted or before.

A second method used to produce the synthetic paper bases useful in the production of the products of the present invention is the "air dry" method. In this method a polymer is dissolved in a suitable volatile solvent and the solution is again extruded through spinnerettes into air. A filament develops upon volatilization of the solvent. It can readily be seen that in this process the photochromic material may be added to the solution of the polymer or anytime before extrusion.

The "wet spinning" method may also be used especially since this method is the most widely used commercially. According to this method, the polymer is dissolved in a suitable solvent, and the solution is extruded through spinnerettes into a liquid in which the solvent dissolves but in which the polymer is insoluble. A filament develops when the solvent is leached from the polymer by the body of liquid into which the dissolved polymer is extruded. Here again the photochromic material may be added to the polymer at any time before extrusion thereof.

The filaments produced by any of the three methods disclosed above are then formed into synthetic paper by a process comprising three basic steps.

First, the filament of convenient length and denier are refined in aqueous suspension until they have fibrillated and formed felting properties.

Second, the fibrillated filaments, alone or with other felting fibers, in water, are sheeted to form a water-laid web.

Third, the web is heated to dry the same and to develop the bonding properties developed by step one.

Conveniently, and perhaps preferably, the photochromic material, if not added during the filament production, may be added during steps one or two of the sheet making process.

The refining step is performed in the same manner disclosed above in regard to the cellulosic papermaking process. That is, the filaments are beaten by ordinary methods, i.e. with Niagara and Hollander beaters, Hydropulpers and the like. The only difficulty which arises in the addition of the photochromic material at this stage or before, is that there exists the danger that the material will be washed away or shaken from the filaments during the beating operation. It is for this reason that the photochromic material is preferably added at step two, i.e. the web-forming.

In the web formation step, the fibrillated filaments are sheeted to form a web by the same procedures employed in cellulosic paper-making methods. The web may have any desired caliper so as to result in the formation of a tissue, a paper, a paper board or a building board as is known in the art, and may be subjected to suction to facilitate drying and may be passed through dandy rolls, calendar rolls and the like in the same manner as cellulosic webs.

Again, as in regard to the cellulosic paper bases, various other materials may be added during the sheeting process, such as, for example, cellulosic fibers, glass fibers, asbestos fibers, silk fibers and other nonfibrillated filaments, wet-strength imparting resins or sizing materials such as anionic or soap sizes, rosin size, wax sizes, softening agents, impregnating agents, coating materials and the like.

Additional, and more complete descriptions of fiber making procedures can be found in U.S. Patents Nos. 2,558,735, 2,595,847, 2,613,195, 2,611,929 and 2,644,803, which patents are also incorporated by reference into the instant specification.

The photochromic material employed may also be incorporated into the synthetic paper bases after complete production thereof, by wetting the synthetic paper base and contacting it with the photochromic additive much in the same manner as set forth hereinabove in regard to the cellulosic paper bases.

THE REGENERATED CELLULOSE BASE

Although the following discussion will be directed principally to cellophane as a base, this invention contemplates, as the base into which the photochromic material is incorporated, any smooth, substantially non-porous, non-fibrous sheet, especially cellulosic film, precipitated from an aqueous cellulosic dispersion or solution or from solution in an organic solvent (one or more organic liquids). This includes sheets of regenerated cellulose whether precipitated from viscose (solutions of cellulose xanthate), cuprammonium, or other aqueous solutions or dispersions of cellulose. It also includes sheets of cellulose ethers and esters precipitated from aqueous solutions or dispersions such as glycol cellulose, cellulose glycolic acid, alkyl cellulose (preferably methyl or ethyl cellulose), cellulose phthalic acid, and other similar cellulosic products.

Regenerated cellulose, in the form of cellophane, generally exists as a hydrophyllic film produced from purified wood pulp derived from spruce, pine, fur or hemlock trees. It consists of a plasticized base film of regenerated cellulose, which is generally later coated with a nitrocellulose lacquer. The base film is essentially grease proof and can be made water vapor proof and even waterproof by adding various coating formulations thereto. The ultimate characteristics desired in the cellophane generally govern the selection of film coated thereon. However, most of the coatings are of the lacquer type consisting of, for example, nitrocellulose, resins, plasticizers and waxes.

The cellophane or other material represented by the generic disclosure above, employed in the present invention may be produced by any known method, the specific method of preparation thereof, as in the case of the paper bases, not constituting part of the present invention. Generally, cellophane is produced by mixing wood chips, wood pulp or other cellulosic material with an aqueous caustic solution of 18% to 20% concentration. The cellulose is steeped in this solution for from about 20 to 60 minutes, depending upon the quality of the pulp used, and the resultant alkali cellulose is pressed to remove excess liquor. The pressing reduces the weight of the cellulose down to approximately three times that of the pulp employed. The alkali cellulose is then shredded and aged one or more days depending upon the final viscisity desired. The alkali cellulose is next xanthated by treatment with carbon disulfide in large horizontal barattes. The color of the mass changes from white through yellow to orange and the resultant sodium cellulose xanthate is dissolved in a caustic solution thereby forming viscose. This xanthate material is filtered, deaerated and ripened for a periood of at least one day. At this point various additives may be mixed with the viscose in order to prevent incrustation thereof on the extruders and to impart other desired properties thereto.

The viscose is next extruded, in the form of sheets and the like, directly from the ripening tank into a coagulating bath containing sulfuric acid and sodium sulfate in order to coagulate the viscose into a film and to regenerate the cellulose xanthate to cellulose. The film next proceeds through two tanks containing sulfuric acid and sodium sulfate of lower concentrations than in the coagulating bath and then through tanks containing hot water, wherein hydrogen sulfite and carbon disulfite are driven

off and salt and acid is washed from the cellulose film. The film is next removed to a dilute caustic bath wherein it is desulfurized and is then passed through two tanks containing warm water. A series of five tanks are then used to bleach and wash the film by removing the last traces of any remaining sulfur compounds.

It is at this point or any point further on in the cellophane making process that the photochromic material mentioned above may be incorporated. The qualification in regard to the addition of the photochromic materials is critical in the sense that they may not be added at any point in the cellophane making process whereat compounds or chemicals are present, or are to be added, which will interfere with, or negate, the color-changing property of the photochromic material or wash out or filter it out. Although it is not explicity mentioned hereinabove in regard to the paper bases, the same limitations as to interference by chemicals or compounds apply to papermaking procedures.

The last two tanks of the washing cycle in the cellophane process contain softening solutions such as aqueous ethylene glycol or aqueous glycerol. At this point in the washing cycle, water-soluble resin treatments may also be employed for coating the base film. The added resin is partially cured in the dryer and finally cured in the coating step. Sizes may also be added at this point in the system. The cellophane film is then passed through a dryer (where excess moisture is removed) and either wound into rolls or sent directly to coating machines.

The products of the present invention are not merely coatings of the solid photochromic materials on the paper bases or regenerated cellulose. The photochromic materials are actually uniformly dispersed or distributed throughout the mass of these substrates. They appear to be positioned in the fibers and in the interstices between interwoven fibers, and as such, they generally will not fall off when the papers or regenerated cellulose are being handled.

The amount of photochromic material added to the cellulosic paper, synthetic paper or regenerated cellulose according to the above defined procedures, is not critical. It is however, generally necessary to add enough photochromic additive so as to produce a visual change in color. That is to say, the cellulosic paper, synthetic paper or regenerated cellulose itself may have the ability to block out some of the ultraviolet light with which the photochromic component is to come into contact and therefore enough photochromic material must be present so as to allow for this reduced quantity of ultraviolet light with which it comes into contact and still produce a color change. We have generally found that amounts ranging from about 0.1% to about 15%, by weight, based on the dry weight of the cellulosic paper, synthetic paper or regenerated cellulose, are sufficient to obtain a satisfactory visible color change.

In summary, the process used for the production of the paper bases or regenerated cellulose does not form part of the present invention. The present invention is directed to the product produced by any paper or cellophane making process to which has been added the photochromic materials mentioned hereinabove at almost any point during the substrate-making process. The only governing feature of the photochromic material addition step is that the material should not be added during or prior to any step in the process at which a material, chemical, etc., is present which will react with the photochromic material and tend to reduce or neutralize its color changing ability, or to wash or filter it out. Therefore, the photochromic material should be added subsequent to any step wherein reactive materials are present and any filtering or washing steps which will tend to remove the material.

It is possible to lengthen the life of the cellulosic paper, synthetic paper or regenerated cellulose compositions by incorporating various amounts of ultraviolet light absorbers into them or by coating them with a material containing an ultraviolet light absorber. When additives such as these are added, any conventional compound known to function as an ultraviolet light absorber may be employed. Examples of such compounds are the 2-hydroxy benzophenones, e.g., 2,4-di-hydroxy benzophenones; the 2(2-hydroxyphenyl)benzotriazoles, e.g., 2(2-hydroxy-4-methoxyphenyl)benzotriazole and the like. In this manner, the photochromic life of the photochromic material is lengthened by preventing an extraneous amount of ultraviolet light from coming into contact therewith. When absorbers of this type are added, amounts up to about 20% by weight based on the weight of the substrate may be used.

The novel cellulosic paper, synthetic paper and regenerated cellulose products of the instant invention may be used for such items as memory devices, e.g., temporary photographic proofs, temporary data storage, temporary high speed direct recording paper for oscillographs; decorative materials, e.g., package wrappings, advertising articles; photocopy methods, e.g., production of permanent positive temporary negatives, temporary positives and the like.

The following examples are set forth for purposes of illustration only and are not to be construed as limitations on the present invention except as set forth in the appended claims. All parts and percentages are by weight unless otherwise specified.

Example 1

To an aqueous slurry of wood pulp, containing 1% of a sulfite rosin size and 2% alum, is added 10%, by weight, of TiO_2 activated by 0.2% Fe_2O_3, based on the weight of the dry pulp. The pH of the slurry is adjusted to approximately 7.0 and the slurry is agitated for 10 minutes. The resultant suspension is formed into white hand sheets at 50 lb. basis weight (25" x 40"/500 ream) on a Nash hand sheet machine and dried at 240° F. The sheets produced are conditioned at 60° F. and 50% relative humidity for 24 hours. They are then contacted with ultraviolet light for 10 minutes. The white sheets turn a deep tan.

Example 2

An aqueous suspension, of about 0.7% consistency, of bleached Northern Craft Pulp beaten to a Canadian Standard freeness of 450–500 ml. is formed. The pH of the system is adjusted to about 7.0 and 5%, based on the dry weight of the fibers, of TiO_2 activated with 0.2% Fe_2O_3 and 0.02% CuO, by weight, is added. The pH of the suspension is readjusted to 7.0 and the suspension is gently stirred for 5 minutes. The suspension is formed into white hand sheets in a manner set forth above in Example 1. The sheets turn a deep tan upon contact with ultraviolet light.

Example 3

An 18% aqueous caustic solution of wood pulp is produced by mixing the wood pulp with NaOH solution. The wood pulp is steeped for about 35 minutes and the resultant alkali cellulose is pressed, shredded and aged for 3 days. Carbon disulfide is added to the alkali cellulose in a large vat to produce sodium cellulose xanthate which is then dissolved in a caustic solution. The xanthate material is filtered, deaerated and ripened for 2 days. The resultant viscose is agitated and then extruded in the form of sheets into a coagulating and regenerating bath of sulfuric acid and sodium sulfate. The film is then washed with dilute sulfuric acid and sodium sulfate and then with dilute caustic. To this film is then added 15% by weight, based on the weight of the dry pulp, of $TiO_2 \cdot 12WO_3$ (produced by reacting one mole of TiO_2 with 12 moles of WO_3). Warm water is then contacted with the film which is then washed with a softening solution comprising aqueous ethylene glycol. The film is then passed through a dryer and dried at 165° F. The

resultant cellophane turns a deep blue-green upon contact with ultraviolet light.

Example 4

Wet spun, 3-denier polyacrylonitrile textile filaments are hand chopped to about ¼" to 1" lengths and slurried with water to a 1% consistency. The resultant slurry is beaten in a one pound Valley laboratory beater with ten pounds on the bedplate arm.

To the resultant beaten slurry is then added 8% by weight, based on the dry weight of the polyacrylonitrile, of 2,3-diphenyl-1-indenone oxide. Samples of the suspension are then withdrawn and are formed into synthetic paper sheets on a Nash handsheet machine. The sheets are dried on a drum dried at 240° F. for about 60 seconds.

Upon contact of the dry sheets with ultraviolet light, they turn from white to a deep pink.

TABLE I

Ex.	Base	Activated With—	Color Change	Time Activation, Sec.
5	Cellulosic Paper	TiO_2·12MoO_3	White to deep blue	60
6	Cellophane	ZnO·6WO_3	Faint yellow to deep blue-green	30
7	Cellulosic Paper	TiO_2+FeO	Off-white to tan	60
8	do	TiO_2+Cr_2O_3	Off-white to light tan	1,800
9	do	TiO_2+CuO	do	120
10	do	TiO_2+NiO	do	120
11	Synthetic Paper	TiO_2+MnO_2	do	100
12	do	TiO_2+Mn_2O_5	do	100
13	do	TiO_2+Fe_2O_3	Off-white to deep tan	100
14	do	TiO_2+FeO+NiO	do	60
15	do	TiO_2+FeO+CuO	Off-white to brown	60
16	Cellophane	Nb_2O_5+Fe_2O_5	Off-white to grey	60
17	do	Nb_2O_5+FeO	do	1,200
18	do	Nb_2O_5+Cr_2O_3	do	1,200
19	do	Nb_2O_5+CuO	do	2,400
20	do	Nb_2O_5+V_2O_5	do	1,400
21	do	Nb_2O_5+MnO_2	do	2,400
22	do	Nb_2O_5+Mn_2O_5	do	1,500
23	do	Al_2O_3+Cr_2O_3	do	1,500
24	do	Al_2O_3+V_2O_5	Off-white to grey	3,600
25	Cellulosic Paper	ZnO_2+CuO	do	3,600
26	do	ZnO_2+V_2O_5	do	2,700
27	do	SnO_2+CuO	do	2,700
28	do	ZrO_2+CuO	Off-white to deep tan	2,700
29	do	ZrO_2+NiO	Off-white to grey	2,700
30	Cellophane	TiO_2·WO_3	do	2,700
31	do	TiO_2·WO_3	Faint yellow to blue-green	2,700
32	do	ZnO·MoO_3	Faint yellow to deep blue green	60
33	do	ZrO_2·MoO_3	{White to light blue White to blue	300 60
34	do	ZrO_2·WO_3	{White to light blue White to blue	300 60
35	Synthetic Paper	SnO_2·MoO_3	Faint yellow to light blue-green	300
36	do	SnO_2·WO_3	White to light blue	60
37	do	GeO_2·WO_3	White to blue	60
38	do	GeO_2·MoO_3	Faint yellow to light blue-green	300
39	Cellulosic Paper	[1]	do	60
40	do	19	White to light blue	60
41	do	23	White to blue	60
42	do	26	Pale yellow to deep yellow	300
43	do	32	do	60
44	do	43	Yellow to orange	120–180
45	Cellophane	47	do	120–180
46	do	44	Pale yellow to deep yellow	120–180
47	do	49	Yellow to deep yellow	120–180
48	do	55	Yellow to red	<60
49	do	60	White to pink	300
50	do	64	Colorless to orange	<60
51	do	70	Pale yellow to deep yellow	<60
52	Synthetic Paper	78	Slight yellow to orange	300
53	do	93	Yellow to red	60
54	do	85	Pale yellow to deep yellow	60
55	do	90	Yellow to brown	60
56	do	105	Pale yellow to deep pink	120–180
57	do	110	Pale yellow to pink	120–180
58	Cellophane	121	Pink to red	120–180
59	do	126	White to yellow	120–180
60	do	130	Colorless to orange	120–180
61	do	131	White to yellow	120–180
			Colorless to yellow	120–180
			Colorless to deep blue	120–180
			Colorless to blue	<60
				60

[1] Examples 39 to 60 employed photochromic additives as designated by numbers 1 to 130 in the specification in amounts as set forth in Examlpe 1.

Table I, above, discloses the effectiveness of color change of cellulosic paper, synthetic paper and cellophane containing representative numbers of the various solid state photochromic materials set forth as applicable in producing the articles of the present invention. In the examples the oxide materials were incorporated into the specific base in equal amounts, as disclosed in Example 1, i.e. Examples 5 to 38 followed Example 1 in photochromic material concentration. In Examples 39 to 60, the procedure set forth in Example 4 was followed in regard to the concentration employed of the solid state photochromic material.

We claim:

1. A water-laid web comprising water-fibrillated, randomly intermingled, interlocked, filaments of paper-making length of a material selected from the group consisting of a fibrous, cellulosic material and a fibrous, thermoplastic, acrylonitrile-containing, polymeric material, said web having uniformly distributed throughout the interstices thereof, at least 0.1%, by weight, based on the weight of the web, of a photochromic material which is a solid at room temperature and which functions photochromically as a solid.

2. The base material of claim 1 wherein the photochromic material is TiO_2 activated with Fe_2O_3.

3. The base material of claim 1 wherein the photochromic material is 2,3-diphenyl-1-indenone oxide.

4. The base material of claim 1 wherein the photochromic material is piperonal m-tolylhydrazone.

5. The base material of claim 1 wherein the photochromic material is benzaldehyde m-tolylhydrazone.

6. The base material of claim 1 wherein the photochromic material is cinnamaldehyde 3,5-xylylhydrazone.

7. The base material of claim 1 wherein the photochromic material is p-tolualdehyde 2-naphthylhydrazone.

8. The base material of claim 1 wherein the photochromic material is 3-(p-methoxybenzylidene)-2-pentanone thiosemicarbazone.

9. The base material of claim 1 wherein the photochromic material is 2-(2,4-dinitrobenzyl)pyridine.

10. A web according to claim 1 wherein said material is a fibrous, cellulosic material.

11. The cellulosic paper of claim 10 wherein the photochromic material is TiO_2 activated with Fe_2O_3.

12. A web according to claim 1 wherein said material is a fibrous, thermoplastic, polymeric material.

13. The synthetic paper of claim 12 wherein the photochromic material is TiO_2 activated with Fe_2O_3.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,314,795 April 18, 1967

George Henry Dorion et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 54, for "chlorode" read -- chloride --; column 10, line 56, for "viscisity" read -- viscosity --; columns 13 and 14, in TABLE I, third column, line 9 thereof, for "$TiO_2+Fe_2O_3$" read -- $TiO_2+Fe_2O_3+NiO$ --.

Signed and sealed this 14th day of November 1967.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents