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GRAFTED PAPER AND GRAFTED CELLOPHANE COMPOSITIONS CONTAINING PHOTOCHROMIC MATERIALS

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This invention relates to photochromic cellulosic paper and photochromic regenerated cellulose. More particularly, this invention relates to grafted cellulosic paper and grafted regenerated cellulose containing, uniformly distributed throughout its mass, a photochromic material. Still more particularly, this invention relates to grafted cellulosic paper and grafted regenerated cellulose film containing, uniformly dispersed throughout its mass, a photochromic material which exhibits its photochromic properties in solution.

The development of a paper product which will exhibit photochromic activity upon contact with ultraviolet light is not new in the art. Berman, in U.S. Patent No. 2,953,454, discloses the production of photochromic paper which has, coated upon the surface thereof, minute, liquid-containing capsules possessing light-translucent walls, the liquid having dissolved therein, a photochromic material. The method of producing such a product, however, is relatively expensive and very difficult to carry out, especially in regard to obtaining a uniform, continuous covering of the paper base with the microscopic, solution-containing capsules. Additionally, since the applied capsules are very 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 these relatively commercially unattractive characteristics of the prior art photochromic articles may be overcome by incorporating the photochromic material, which is active in solution, directly into grafted cellulosic paper or grafted regenerated cellulose, thereby producing a photochromic article which has a uniform, continuous photochromic surface. We have quite unexpectedly found that these photochromic materials which are active in solution continue to function photochromically after having been incorporated into grafted cellulosic paper or grafted regenerated cellulose. It is even more surprising that the photochromic materials continue to function as such at all, since generally the solutions of photochromic materials tend to lose their activity after having been dispersed throughout a solid media, as evidenced by the Berman patent, above, wherein the solutions are useful only after having been encapsulated in a minute capsule. Additionally, we have found that photochromic materials which function in the solid state cannot be added to the grafted paper and cellophane bases in that they either lose their ability to function photochromically or do not posses the ability to be retained in the grafted base.

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

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

It is still a further object of the instant invention to present grafted paper and grafted cellophane containing, uniformly dispersed throughout their masses, a photochromic material which is photochromic in solution.

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

Photochromism

As mentioned above, 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 markedly in each individual system, there are two processes which account for most types of photochromic phenomena. The first process is the transformation of excited state electronic energy into vibrational and tortional twisting modes of the molecule. Usually, systems observed to be photochromic have very efficient routes for internal transformation of absorbed energy and are generally never fluorescent or phosphorescent. Internal transformation often takes place very rapidly, that is to say, the primary process in the photo production of a colored species often occurs in about a millimicrosecond. However, optical observation of the colored species normally takes considerably longer than this because of the very small amounts of colored material produced per unit time and the depletion of the color by the competing reverse reaction.

The second fundamental photo-electronic mechanism generally considered as producing photochromism is charge transfer. Most charge transfer phenomena in organic molecules are rapidly reversible and therefore produce no colored intermediate. However, in organic crystals, charge transfer absorption usually leads to a colored state in which the donor-acceptor crystals have been oxidized and reduced.

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 cell length, 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 and solvent sensitivity 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.

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

The photochromic materials which are incorporated into the grafted cellulosic paper and grafted 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 solution. That is to say, compounds which exhibit photochromic properties only in the solid state cannot be used in forming the novel products of our invention. Only those materials which function photochromically in solution are contemplated herein, however, any material which fits this classification may be used. Also, compounds which function in both the solid state and in solution at room temperature or below, also fall within the scope of the instant invention. Examples of compounds which fall into the category of being photochromic in solution and which therefore may be used to form the novel products of this invention are set out more fully hereinbelow.

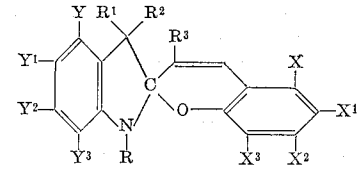
One class of compounds which may be employed to form our novel products are the spiropyrans, some of which include 1',3',3'-trimethyl-6-nitro-spiro(2H-1-benzopyran-2,2'-indoline), 1',3',3'-trimethyl-8-nitro-spiro(2H-1-benzopyran-2,2'-indoline), 1',3',3'-trimethyl-6-nitro-8-methoxy-spiro(2H-1-benzopyran-2,2'-indoline), 1',3',3'-trimethyl - 6-methoxy-8-nitro-spiro(2H-1-benzopyran-2,2'-indoline), 1',3',3'-trimethyl-5-nitro-8-methoxy-spiro(2H-1-benzopyran - 2,2'-indoline), 1',3',3'-trimethyl-6-chloro-8-nitro-spiro(2H-1-benzopyran - 2,2' - indole), 3'-phenyl-6-nitro - spiro(2'H,1' - benzopyran-2,2'[2H,1-benzopyran]) and the like.

These photochromic spiropyran compounds and methods for the preparation thereof, are disclosed, for example, in U.S. Patents 2,953,454 and 3,022,318 and these patents are hereby incorporated into the instant specification by reference.

A second class of the benzospiropyran compounds, similar in structure to those above but containing a greater

degree of substitution, which are useful in our invention are those having the formula

(I)



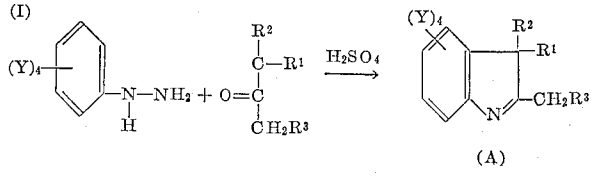
wherein R, R^1 and R^2 represent the same or different alkyl radicals having 1 to 20 carbon atoms, inclusive, and R^1 and R^2 taken together form a saturated carbocyclic ring, R^3 is hydrogen or an alkyl radical having 1 to 20 carbon atoms, inclusive, X, X^1, X^2, X^3, Y, Y^1, Y^2 and Y^3 represent hydrogen, an alkoxy radical having 1 to 4 carbon atoms, inclusive, a nitro radical or a halogen radical, and the pairs Y and Y^1, Y^1 and Y^2, Y^2 and Y^3, X and X^1, X^1 and X^2 or X^2 and X^3, when taken together, form a conjugated aromatic ring, no more than three of said X, X^1, X^2 and X^3 and no more than three of said Y, Y^1, Y^2 and Y^3, being hydrogen.

These compounds are soluble in the various aliphatic alcohols, e.g., ethanol; ethyl acetate; the aromatic hydrocarbons, e.g. benzene, toluene and, as such, may be used in the practice of the present invention, as solutions in these materials.

Examples of the compounds which correspond to Formula I, and therefore may be used in producing the products of the present invention, include 1',3',3'-trimethyl-5',6-dinitro-spiro(2H-1-benzopyran-2,2'-indoline), 1',3',3'-trimethyl - 5',6-dinitro-8-methoxyspiro(2H-1-benzopyran-2,2'-indoline), 1',3',3'-trimethyl-5',8-dinitro-6-methoxy-spiro(2H-1-benzopyran-2,2'-indoline), 1',3',3'-tributyl-8-chloro - 6' - butoxyspiro(2H-1-benzopyran-2,2'-indoline), 1' - octyl-3'-methoxy-3'-ethyl-3-propyl-4',7-diethoxyspiro-(2H-1-benzopyran-2,2'-indoline), 1',3',3'-tristearyl-3-butyl - 5,6 - benzo-6'-fluorospiro(2H-1-benzopyran-2,2'-indoline), 1',3',3' - trimethyl-6-nitro-6',7'-benzospiro(2H-1-benzopyran-2,2'-indoline), 1',3',3'-triethyl-7-bromo-4',7'-dimethoxyspiro(2H - 1 - benzopyran - 2,2'-indoline), 1'-methyl - 3' - cyclohexyl - 5,8-dichloro-5'-methoxy-7'-iodo-spiro(2H-1-benzopyran-2,2'-indoline), and the like.

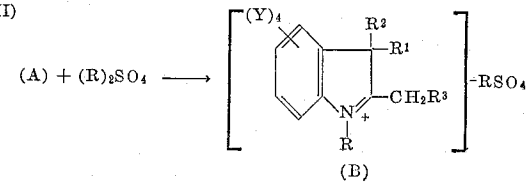
The compounds of Formula I may be produced by any known procedure. A preferred method however, is that set forth and claimed in copending application, Serial No. 239,334, filed November 21, 1962, wherein the compounds and the method of producing them are generically and specifically disclosed and claimed. Basically, said procedure comprises reacting an appropriately substituted hydrazine with a ketone having at least three carbon atoms, in the presence of a strong acid. The acid is then neutralized by adding alkali and the product (Compound A) is quaternized by reacting it with an alkyl sulfate or other alkyl-containing quaternizing agent. This step forms Compound B which is then reacted with an equimolar amount of a basic material to produce an indole tribase. The tribase is thereafter reacted with an appropriately substituted salicylaldehyde to yield the desired benzospiropyran, i.e.,

(I)



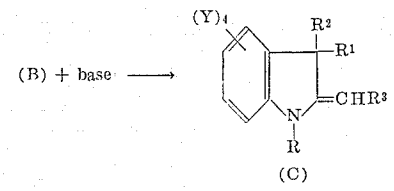
(A)

(II)

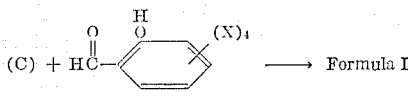


(B)

(III)

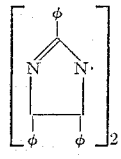


(IV)



Other materials which exhibit photochromic behavior in solution which may be used in the production of our novel products, but which are not in the least all inclusive, include

(1) 2,3-diphenyl-1-indenone oxide
(2) Mercury bisdithiazone
(3) Lophine oxidation product, i.e.



wherein φ is a phenyl radical,

(4) α-Naphthylaminocamphor
(5) m-Phenylenebisaminocamphor
(6) Tetrahydro-α-naphthylaminocamphor
(7) 10,10′-dihydroxydiphenanthryl-9,9′-amine
(8) Pararosaniline cyanide
(9) Benzaurine cyanide
(10) Rosanaline sulfite
(11) Hexamethyl tris(p-aminophenyl)carbinol
(12) p,p′-Benzylidene bis-N,N-dimethylaniline, and the like.

The following table sets forth the color change of a majority of the above photochromic compounds in addition to the solvents useful for each.

TABLE I

Compound*	Solvent	Color Change
1	Ethyl alcohol	Colorless to pink.
2	Benzene	Orange to blue.
3	Ethyl alcohol	Colorless to purple.
4	Methyl or ethyl alcohol	Colorless to green.
5	Chloroform	Do.
6	do	Do.
7	Benzene	Pink to yellow.
8	Ethyl alcohol	Colorless to red.
9	Water	Do.
10	Water and sulfur dioxide	Do.
11	do	Colorless to violet.
12	do	Colorless to green.

*As identified above.

The grafted cellulosic paper base

Any cellulosic paper material may be used to prepare the grafted paper which is used to prepare the novel photochromic products of the present invention. The cellulosic paper per se 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 and 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 such as those formed from nylon and related polyamide fibers, polyethylene glycol terephthalate and related polyester fibers, polymers of acrylonitrile such as copolymers containing at least 75% by weight, of acrylontrile, alone or with other vinyl monomers.

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 melamineformaldehyde 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.

In the normal manufacture of paper, 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 paper-making. During the beating operation the cellulosic fibers fibrillate, the fibrillation manifesting itself by a fraying or shedding 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 regenerated cellulose base

This invention contemplates, as the regenerated cellulose base from which the grafted cellophane etc. bases are prepared, 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 consist-

ing of, for example, nitrocellulose, resins, plasticizers and waxes.

The cellophane or other material represented by the generic disclosure above, from which the grafted material is prepared, may be produced by any known method, the specific method of preparation thereof, as in the case of the cellulosic paper base, 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 viscosity 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 period 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 warn 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.

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 grafted cellulosic paper and regenerated cellulose bases

The cellulosic paper and regenerated cellulose, formed by any of the methods disclosed above, are grafted with a vinyl monomer, by any known procedure, to form the base material used in the production of the novel products of the instant invention. That is to say, the cellulosic paper base or regenerated cellulose may be grafted with a vinyl monomer by any grafting procedure, such as irradiation polymerization, solution polymerization, emulsion polymerization, etc.

In irradiation polymerization, the base material, after having been swelled by contacting it with water for several hours, is contacted with the vinyl monomer to be grafted thereon. Generally, the vinyl monomer is in the form of a solution containing at least 2–3% of water and the actual grafting is best conducted in a non-oxygen atmosphere. To achieve this condition, nitrogen gas, for example, is continually bubbled through the monomer solution and over the wet substrate. The irradiation, when in the form of X-ray, amounts to at least about 250 k.e.v. and may be as high as 3 m.e.v. When electrons are used for the grafting, 3 m.e.v. electrons, may be used. Regardless of the type of ionizing radiation used (X-rays, γ-rays or electrons), a dosage of 0.05 to 1.0 M rad will be required, depending upon the oxygen concentration of the atmosphere and monomer solution. A dose of 1 rad signifies the absorpiton of 100 ergs of energy per gram of paper or substrate employed. The monomer pick-up, or weight gain of the paper or regenerated cellulose, may range up to about 400% or even higher, based on the dry weight of the cellulosic paper or regenerated cellulose. More specific details of such a method of grafting the substrates may be found, for example, in U.S. Patent Nos. 2,940,869, 2,955,953, and 2,956,899 and these references are hereby incorporated into the instant specification by reference.

Other methods of grafting cellulosic paper and cellophane are set forth in U.S. Patents 2,764,504, 2,865,872 and 2,919,059, which patents are also incorporated herein by reference. These patents teach various procedures for grafting wherein different catalyst systems and different reaction conditions are employed for grafting a plurality of base materials with a plurality of graftable monomers.

A preferred method for grafting the cellulosic paper base or cellophane film, preferred because of its ease of manipulation and execution, comprises contacting the cellulosic paper or cellophane in an aqueous medium, at a pH of not greater than 3.5 and in the presence of a ceric salt. More complete details in regard to this ceric ion grafting procedure may be found in U.S. Patents 2,922,768 and 2,929,743, which references are also hereby incorporated herein by reference.

Examples of monomers which may be used to graft the cellulosic paper or regenerated cellulose include acrylic and methacrylic esters such as the methyl, ethyl, propyl, butyl, isobutyl, amyl, hexyl, cyclohexyl, octyl, decyl esters of acrylic and methacrylic acid, as well as the nitro alcohol esters such as 3-nitro-2-butanol, 2-nitro-3-hexanol, 2-methyl-2-nitro-1-butanol, of acrylic acid and the acrylic and methacrylic type acid esters of polyhydric alcohols such as ethylene glycol, glycerol, pentaerythritol, diethylene glycol and the like. Additionally, dimethylaminoethylmethylacrylate, styrene, substituted styrenes such as ring-substituted and side chain-substituted styrenes, e.g. α-chlorostyrene, α-methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, 2,4-dimethylstyrene, 2,4,5-trimethylstyrene, p-ethylstyrene and the like. Also, acrylic acid per se, and its homologs such as methacrylic acid, α-methacrylic acid, α-chloroacrylic acid, and the anhydrides, amides and nitriles of acrylic and methacrylic acid. Additionally one may use butadiene, isoprene, chloroprene, etc. More specifically, one may use allyl acetate, allyl propionate, allyl chloroacetate, allyl caproate, allyl linoleate, allyl benzoate, methallyl acetate, the allyl ester of isobutyric acid, allyl acrylate, diallyl carbonate, diallyl oxalate, diallyl phthalate, diallyl maleate, triallyl cyanurate and the like. Still further, one may make use of the vinyl or vinylidene esters such as vinyl acetate, vinyl chloride, vinylidene chloride, vinyl propionate, vinyl butyrate, and the like. Vinyl ethers may also be used such as vinylethylether, vinylpropylether, vinylisobutylether and the like or other vinyl compounds such as divinylsulfone, divinylsulfide, vinyl pyridine and the like. Additionally, one may make use of the unsaturated polymerizable amides such as acrylamide, methacrylamide, ethacrylamide, methylene bisacrylamide and the like, or the nitriles such as acrylonitrile, methacrylonitrile, ethacrylonitrile, alpha-chloro-acrylonitrile and the like. Whenever desirable, these polymerizable monomers may be used either singly or in combination with one another.

It should be stressed at that this point that the above disclosed methods of paper-making, cellophane-making, paper-grafting and cellophane grafting do not, per se, form part of the instant invention and are merely set forth herein as exemplary of known procedures which can be

used to prepare the grafted materials useful in forming the novel products of the present invention.

The photochromic material addition

The photochromic materials set forth hereinabove, i.e., any photochromic material which exhibits its photochromic properties in solution, may be added at any time during or after the grafting procedure. The preferred point of incorporation is after the grafting of the paper has been completed. However, if during grafting, conditions are such that no material degradation or destruction of the photochromic characteristics of the photochromic material will occur, the grafting and addition of the photochromic material may be carried out simultaneously. For example, if the grafting is carried out under acidic conditions, such as in the ceric ion grafting procedure, or very high temperatures are necessary, or if other chemicals are present which would react with the photochromic material to negate its color-changing ability, such as with the benzospiropyrans under acidic conditions, the grafting of the paper or cellophane must be completed before the photochromic material is incorporated therein. Therefore, in order to achieve the best results in regard to a highly functional product, it is generally preferred that complete grafting be effected before addition of the photochromic material.

In order to incorporate the solution-state photochromic material into the grafted cellulosic paper or grafted regenerated cellulose the paper or regenerated cellulose is soaked in a solution of the photochromic material and the photochromic material is absorbed thereby. The amount of the photochromic material absorbed or impregnated into the paper or regenerated cellulose depends materially on the degree of grafting which has been accomplished previously. Generally, the more grafting which was accomplished, i.e., the greater the pick-up of monomer onto the base paper or cellophane, the more photochromic material impregnated. The paper or regenerated cellulose is permitted to soak up the solution of the photochromic material for a length of time ranging from about 5 seconds to about 50 hours, the greater time being used to insure greater impregnation or absorption of the photochromic material. After sufficient photochromic solution has been taken up, the paper or regenerated cellulose is dried by any applicable method and is ready for the use contemplated by the consumer.

The amount of photochromic material added to the cellulosic paper, or regenerated cellulose according to the above defined procedures, is not critical. It is however, generally necessary to insure the addition of enough photochromic additive so as to assure a visual change in color. That is to say, the cellulosic 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 still produce a color change when it comes into contact with the reduced quantity of ultraviolet light. We have generally found that amounts ranging from about 0.1% to about 15%, by weight, based on the dry weight of the grafted cellulosic paper or grafted regenerated cellulose, are sufficient to obtain a satisfactory visible color change, however, it is possible and not outside the scope of the present invention, to add more photochromic material in amounts even up to about 75%, by weight, or higher.

In summary, the present invention is directed to the product produced from any grafted cellulosic paper or grafted regenerated cellulose to which has been added any of the photochromic materials mentioned hereinabove. The only governing feature of the photochromic material addition is that the material should not be added during or prior to any substrate formation or treatment stage at which a material, chemical, or condition is used which will tend to reduce or neutralize the color changing ability of the photochromic material or wash or filter it from the substrate. More particularly, the photochromic material should be added subsequent to any step wherein reactive materials are present and where any filtering or washing steps which will tend to remove the material are used.

It is possible to lengthen the life of the grafted cellulosic paper, or grafted 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 benzophenone; 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 base material, may be used.

The products of the present invention are not merely coatings of the photochromic materials on the paper base 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, in the interstices between interwoven fibers or absorbed into the fibers, and as such, they will not fall off, be destroyed or rendered ineffective when the photochromic paper or regenerated cellulose is being handled by the consumer.

The novel photochromic cellulosic paper, and photochromic 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 or oscillographs; decorative materials, e.g., package wrappings, advertising articles; photocopy methods, e.g., production of permanent positives, 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

A sheet of paper, 7" x 11", produced from wood pulp and formed in a Nash hand sheet machine, is covered with a solution of 10 parts of ethyl acrylate in 90 parts of water containing 0.1 part of azobisisobutyroamide hydrochloride. The paper is grafted with the ethyl acrylate according to the procedure set forth in U.S. Patent 2,764,504. The paper picks up 147% of the ethyl acrylate, by weight, based on the dry weight of the paper sheet.

The resultant sheet is contacted with an acetone solution of 1',3',3'-trimethyl-6-nitrospiro(2H-1-benzopyran-2,2'-indoline) for 19 hours and is then dried. The sheet is pink in color and changes to a deep purple when contacted with ultraviolet light of 360 mμ wavelength. The paper reverts to its pink color upon removal of the ultraviolet light source.

Examples 2–5

Four sheets of tissue paper, grafted with the specific monomers mentioned in Table II and prepared according to the process disclosed in U.S. Patent 2,922,768, are soaked in an acetone solution of 1',3',3'-trimethyl-6-nitrospiro(2H-1-benzopyran-2,2'-indoline) for periods ranging from 15 minutes to 20 hours, and dried. The results of the incorporation of the photochromic material are set forth in Table II, below.

TABLE II

Ex.	Paper Form	Monomer Grafted	Percent Grafted	Time of Contact, min.	Color Change
2	Tissue	Methyl Methacrylate	105	15	White to pink.
				60	Do.
				[1] 20	White to very dark pink.
3	do	do	51.8	15	White to pink.
				60	Do.
				[1] 20	Do.
4	do	Methyl Methacrylate:dimethylaminoethyl methacrylate (9:1).	68.6	15	Do.
				60	Do.
				[1] 20	Do.
5	Filter	do	33	15	Do.
				60	Do.
				[1] 20	Do.

[1] Hours.

Example 6

Cellophane, grafted with ethyl acrylate, produced by irradiation with a demountable cathode ray tube with 25 kev. electrons at 10 michoamps, according to the process disclosed in U.S. Patent 2,955,953, 68% pick-up, is soaked in a methyl ethyl ketone solution of 1',3',3'-trimethyl-6-nitro-8-methoxyspiro - (2H-1 - benzopyran-2,2'-indoline) for 3 hours. The cellophane film is dried and contacted with sunlight for 5 minutes. The light blue sheet darkens to a deep blue and reverts to light blue when placed in darkness. The paper contains about 12%, by weight, of the photochromic material.

Examples 7–12

Cellophane is grafted, according to the process of Example 6, with the specific monomers set forth in Table II and is soaked in an acetone solution of 1',3',3'-trimethyl - 5 - nitro-8-methoxy-spiro(2H-1-benzopyran-2,2'-indoline) and dried. The results achieved when the resultant cellophane sheet is contacted with ultraviolet light are set forth in Table III.

TABLE III

Ex.	Substrate	Monomer Grafted	Percent Grafted	Time of Contact, min.	Color Change
7	Cellophane	None		60	None.
8	do	Acrylamide:ethyl acrylate (3:1).	92	60	White to red.
9	do	Ethyl acrylate:vinyl chloride (5:1).	126	60	Do.
10	do	Ethyl acrylate:acrylonitrile (2:1).	150	60	Do.
11	do	Acrylamide	11	60	White to purple.
12	do	do	64	60	White to dark purple.

Table IV, points out the effectiveness of color change of grafted cellulosic paper and grafted regenerated cellulose containing representative solution state photochromic materials set forth as applicable in producing the articles of the present invention.

TABLE IV

Ex.	Base	Grafted With	Percent Pickup	Activated With	Color Change
13	Paper	Ethyl acrylate	78	A	White to blue.
14	do	do	111	B	Do.
15	Cellophane	Methyl Methacrylate	67	C	Do.
16	do	n-Butyl acrylate	127	D	Do.
17	Tissue paper	Ethyl acrylate-acrylonitrile (6:1).	92	E	Do.
18	do	Ethyl Acrylate	297	1*	White to deep pink.
19	Cellophane	do	146	2	Slightly orange to dark blue.
20	do	Ethyl Methacrylate	41	6	White to green.
21	do	Acrylamide	102	8	White to red.
22	Paper sheet	Styrene	197	11	White to purple.

*=As designated by numbers 1 to 12 in the specification above under "photochromic materials"; incorporated as set fourth in Example 1 with the appropriate solvent therefore.
A=1',3',3'-trimethyl-6-methoxy-8-nitrospiro(2H-1-benzopyran-2,2'-indoline).
B=1',3',3'-trimethyl-5',6-dinitrospiro(2H-1-benzopyran-2,2'-indoline).
C=1',3',3'-trimethyl-5',6-dinitro-8-methoxyspiro(2H-1-benzopyran-2,2'-indoline).
D=1',3',3'-tributyl-8-chloro-6'-butoxyspiro(2H-1-benzopyran-2,2'-indoline).
E=1',3',3'-trimethyl-5',8-dinitro-6-ethoxyspiro(2H-1-benzopyran-2,2'-indoline).

We claim:

1. A base material selected from the group consisting of grafted, fibrous, cellulosic paper, and grafted, non-fibrous, regenerated cellulose film having intimately and uniformly dispersed throughout the body thereof at least about 0.1%, by weight, based on the weight of the base, of a photochromic material which functions photochromically in solution.

2. A grafted, nonfibrous, regenerated cellulose film having intimately and uniformly dispersed throughout the body thereof at least about 0.1%, by weight, based on the weight of the film, a photochromic material which functions photochromically in solution.

3. Grafter, fibrous, cellulosic paper having intimately and uniformly dispersed throughout the body thereof at least about 0.1%, by weight, based on the weight of the paper, of a photochromic material which functions photochromically in solution.

4. A transparent, non-fibrous, grafted, regenerated cellulose film having intimately and uniformly dispersed throughout the body thereof at least about 0.1%, by weight, based on the film, of a photochromic material which functions photochromically in solution.

5. A base material according to claim 1 wherein the photochromic material is 1',3',3'-trimethyl-6-nitrospiro (2H-1-benzopyran-2,2'-indoline).

6. A base material according to claim 1 wherein the photochromic material is 1',3',3'-trimethyl-6-nitro-8-methoxyspiro(2H-1-benzopyran-2,2'-indoline).

7. A base material according to claim 1 wherein the photochromic material is 1',3',3'-trimethyl-5',6-dinitrospiro(2H-1-benzopyran-2,2'-indoline).

8. A base material according to claim 1 wherein the photochromic material is 2,3-diphenyl-1-indenone oxide.

9. A base material according to claim 1 wherein the photochromic material is tetrahydro-α-naphthylaminocamphor.

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