

Reversible photochromism: effects and applications



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1. Introduction

In this report I will be looking at the smart material property known as Reversible Photochromism. This property contains a range of chemicals that react to UV light. This report will explore a range of the effects of the compound, which will include a review of the applications of this property and the process that make them possible, by exploring the, ' Ring Process', method. This report will also include looking at general applications where Reversible Photochromism technology is being used and any future concepts, such as, smart materials/technology involving textiles, dyes and inks. Including existing products, such as, transition lenses, and how that technology can be used for greater achievements.

2. What is Photochromism?

Photochromism is the reversible alteration of a chemical variety between two forms by the absorption of electromagnetic radiation, where the two forms have different absorption spectrum.

This can be described as a reversible change of colour upon exposure to light. Where the current substance transforms into a different colour once exposed to UV light. Once the UV light is removed, the substance under goes a transformation into its original state.

Interest in Photochromism was constant but limited until the 1940-1960 periods, which saw an increase of studies, particularly in the research groups of Hirshberg and Fischer in Israel. In 1950, Hirshberg suggested the term " photochromism" [from the Greek words: phos (light) and chroma (colour)] to describe the phenomenon. This is the name used today.

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The mechanism for Photochromism in plastic crystalline materials is shown below.

(Closed Form) (Open Form)

Photochromic colours/dyes are plastisol-based inks, which are off-white when not exposed to UV radiation. It gains colour when exposed to Sun light / UV light. The colour change is “ reversible,” i. e., the colour will fade again and appear colour less or ‘ clear’ upon removal from UV light / sun light exposure. These inks are available in various colours; ranging from dark tones to bright pink.

3. How are Photochromic Lenses Made?

There is a vast range of different states Photochromism can be manipulated into. All of these states have extra compounds and particles. The most common Photochromic state is glass lenses.

Photochromic lenses are lenses that darken on exposure to ultraviolet (UV) radiation. Once the UV is removed, for example by walking indoors, the lenses will slowly return to their clear state. Photochromic lenses may be made of glass, polycarbonate, or another plastic. The glass version of this type of lenses was first developed by Corning in the 1960s. More recently, plastic versions of these lenses have been commercialised. The first of these was the Photolite lens sold in the early 1980s. But the first commercially successful plastic Photochromic lens was introduced by Transitions Optical in 1991.

The glass version of these lenses achieve their Photochromic properties through the embedding of microcrystalline silver halides (usually silver chloride), or molecules in a glass substrate. Plastic Photochromic lenses rely on organic Photochromic molecules to achieve the reversible darkening effect. The reason these lenses darken in sunlight but not indoors under artificial light, is that room light does not contain the UV found in sunlight. Transport windows also block UV so these lenses would darken less in a car. Lenses that darken in response to visible (rather than UV) light would avoid these issues, but they are not feasible for most applications. In order to respond to light, it is necessary to absorb it, thus the glass could not be made to be clear in its low-light state. This correctly implies Photochromic lenses are not entirely transparent; specifically they filter out UV light. This does not represent a problem, because the human eye does not see in the UV spectrum.

With the Photochromic material dispersed in the glass substrate, the degree of darkening depends on the thickness of glass, which poses problems with variable-thickness lenses in prescription glasses. With plastic lenses, the material is normally embedded into the surface layer of the plastic.

Typically, Photochromic lenses darken substantially in response to UV light in less than one minute, and then continue to darken very slightly. This can take 15 minutes. The lenses fade back to clear along a similar pattern. The lenses will begin to clear as soon as they are away from UV light, and will be noticeably lighter much quicker than the darkening process. However, it can take up to more than 20 minutes for the lenses to completely fade to their non-exposed state.

Because Photochromic compounds fade back to their clear state by a thermal process, the higher the temperature, the less dark Photochromic lenses will be. This thermal effect is called “ temperature dependency” and prevents these devices from achieving true sunglass darkness in very hot weather. In contrast, Photochromic lenses will get very dark in cold weather conditions; which makes them more suitable for snow skiers than sun worshippers while outside. Once inside, away from the triggering UV light, the cold lenses take longer to regain their clear colour than warm lenses.

4. The Chemical Compounds of Reversible Photochromism

Photochromism can be manipulated into different states, liquids; gels, dyes and water like substance, and solids; thin plastic like films and pigment powders. The most common form of Photochromism is liquid dye. This dye is a clear substance that can be penetrated and manipulated into different forms. Dyes reversibly alter their colour upon exposure to ultraviolet sources. These chameleon-like dyes respond to natural solar irradiation as well as artificial sources such as 365 nanometer “ black light.” When sunlight or ultraviolet (UV) radiation is applied, the Photochromic dye becomes excited and the molecular structure is changed allowing a colour to appear. When the stimulus (sunlight/UV radiation) is removed, the dye will return to a state of rest, which is its colourless form. Photochromic molecules are not reactive in their crystalline state and need to be dissolved in a solvent or polymer to function.

A common feature of the Photochromic is a colourless isomer that contains a carbon-oxygen bond which dissociates with UV activation.

The colourless isomer contains two localized pi systems that absorb only in the UV part of the spectrum. Hence, the molecule appears colourless. After the carbon-oxygen bond dissociates, the two pi systems change into a single delocalised pi system which absorbs in the visible part of the spectrum, causing colour formulation.

The life of Photochromic material depends on the amount of Photochromic compound used, the stabilisers used and the material in which it is used. Generally, it is suggested that 0.1 gram per square foot be used to provide an adequate reservoir of Photochromic compound. The use of ultraviolet absorbers will also extend the life of the Photochromic, but will reduce the colour intensity.

There are effectively two changes occurring simultaneously; a chemical change arises when the molecule is exposed to UV light that enables conjugation to take place throughout the molecule; a structural change also occurs to enable the overlap of molecules. Therefore, spatially, the molecules must be able to flatten out to allow this conjugation to take place.

It is a fully reversible reaction so that when the light source is removed, the molecule returns to its uncoloured state. Heat can also help drive the reaction back to the uncoloured form, so in very hot conditions, there is always competition between light and heat to determine the given colour observed. In general, a colour change is still observed, albeit weaker than at room temperature. Similarly, in cold conditions in the presence of sunlight, an intense colour is observed as there is little or no competition from the back reaction.

Such dyes incorporated within a sol-gel matrix can have several practical applications, such as optical switches (if the reversal is very fast) and optical storage for computer memory (if the reverse colour change is not possible at room temperature). Sol-gel

Materials mixed with Photochromic dyes have also been investigated as fibre optic delay generators (Meer 1990), fibre optic shutters, and in Photomasking and Photoresist materials (Hawker 1993). Sol-gel based coatings may also be used for ophthalmic lenses such as scratch resistant coatings on sunglasses.

The colouring changing process is described as the, ' ring opening/ring-closing process' (Brown 1971)

This is where the molecules lie ' flat' in there closed form before UV radiation. In this state the substance is colourless. Once UV light is exposed to the substance, the molecules react by ' twisting', creating an open form. This open form causes the Photochromic dye to turn into a colour. Once the UV light is removed, the molecules ' twist' back to their ' flat' state, reversing back to the colourless substance. Depending on the intensity of the UV light and heat, the speed of which the reverse effect may vary. This process can be repeated many times; however the colour will become less and eventually dim. New Photochromic dyes are now being introduced to slow the fading effect and eventually stop it.

Scientists can create different colours of Photochromic dyes by mixing Photochromic pigment powder. In their pure state, Photochromic dyes are powdered crystals that must be dissolved in the inks to which they are

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added. Some manufacturers microencapsulate the Photochromic dye in their own system, as with leucodye microcapsules. Microencapsulating Photochromic systems enables them to be used in inks that cannot dissolve them, such as water-based systems. Even on cloudy days, Photochromic dyes exhibit bright colour changes when taken outdoors. (Just as with lenses) The colour you see may differ slightly on very hot days or if a UV lamp, rather than sunlight, is used to excite the materials.

5. Organic Photochromism

Fritzsche reported in 1867 the bleaching of an orange-coloured solution of tetracene in the daylight and the regeneration of the colour in the dark. Later, Meer found a change of colour of the potassium salt of dinitroethane in the solid state (yellow in the dark; red in the daylight). Another early example was published by Phipson, who noted that a painted gate post appeared black all day and white all night (due to a zinc pigment). Research and experiments into organic photochromism has enabled the photochromic process to be used on plastic and other materials. However, organic photochromism is controversial, as this goes beyond the domain of variable optical transmission and includes a number of reversible physical phenomena such as optical memories and switches, variable electrical current, ion transport through membranes, variable wet ability, etc. For this purpose, organic photochromic compounds are often incorporated in polymers and liquid crystalline materials.

6. The Chemical Process of Organic Photochromism

Organic Photochromic materials consist of a polymer matrix of optical quality having a refractive state and at least one dye that imparts Photochromic

properties to the matrix. A dye must be selected from a group consisting of spiropyrans and chromenes. This compound is then put under intense radiation to form Organic Photochromism. This then can be placed in specialist lenses and materials.

7. Organic Photochromism in Cosmetics

In general cosmetic materials, Organic Photochromism is being used in cosmetic and related formulations.

Colouration has been employed as a cosmetic device for many centuries (Farrer-Halls, 2007) Materials and methods for achieving predictable and safe cosmetic colouration are being continually explored and improved as evidenced by the large and expanding worldwide cosmetic business.

Materials which change colour under the influence of light, i. e.

photochromics, can be designed on the molecular level to interact with light to maintain, or even evolve a particular colouration. These materials can be designed to maintain a particular cosmetic look as the ambient lighting changes or as the user moves from place to place. It may be advantageous for the Photochromic response to be reversible. The influence of water can be anticipated and pH balance must be incorporated into the overall system design. It would be advantageous to design a class of materials for which ambient office light, or highly directed light such as in a tanning booth, or even laser light, could be utilised, each creating and imparting a particular predictable cosmetic look. There are, of course, many organic Photochromic materials. However, by necessity, to have a strong absorption feature in the visible part of the spectrum which could be the basis for an effective cosmetic colouration system, the molecular structure often contains a

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delocalised pi electron system (Farrer-Halls, 2007) Molecules having bonding features associated with such electronic structure, e. g. polycyclic aromatic hydrocarbons, coal tar products, azo dyes, quinoline, and like molecules with or without fused heterocycles, are often carcinogenic and so less desirable or unacceptable as candidates for use as cosmetics as Gill Farrer-Halls (2007, pg2) claims in her book, ' Naturals and Organics in Cosmetics' " Many types of organic molecules penetrate the skin barrier and so pose increased toxicity risk." This is a major problem because it would require more complicated testing and evaluation to establish the risk of such materials.

Inorganic materials are well known which, because of their insolubility in water and their relatively large particle size, do not penetrate the stratum comeum to any major extent. For example, rouge, being iron oxide, and titanium-dioxide are two widely used oxides with well established safety history (Farrer-Halls, 2007) In fact, most metal oxides, with the possible exception of those used close to the eyes, are more likely ingested, and therefore dangerous if the particles are breathed. There is, therefore, a negligible risk if the oxides are immobilised in a cosmetic formulation.

" The objective of the design is to identify metal oxides, metal bronzes, and protein based Photochromic systems (materials) which combine novel cosmetic properties with sun blocking." (Farrer-Halls, 2007 pg5) Organic Photochromic systems have novel applications in cosmetics because the colouration they supply can be accented and softened and otherwise manipulated by the application of light, allowing greater control and range of effect than for a single colour application. Conventional colouration, i. e. rouge, can only be manipulated by mechanical means, i. e. rubbing and <https://assignbuster.com/reversible-photochromism-effects-and-applications/>

spreading. In addition to using these materials for their pleasing colouration effects, they can also be used as an actinometer/dosimeter that a person can use to gauge his/her exposure to bright sunlight or in other tanning/burning settings.

The concept is based upon the use of the intrinsic Photochromic properties of certain solid transition metal oxides for cosmetic and sun blocking effects. The solid metal oxides suitable for use in this invention are those which undergo Photo induced and thermo enhanced loss of gas phase O₂ to produce mixed valence oxides and include WO₃, V₂O₅, TiO₂ and MoO₃ (Farrer-Halls, 2007) A particular oxide can be operationally established for any possible choice of oxide by exposing a possible candidate oxide to blue-green or shorter wavelength light under vacuum and observing whether a colour change occurs. In some cases, the oxide is doped with an alkali metal ion or proton to enhance the colour change.

As described above, tungsten and molybdenum oxide, and oxides of other metals, and bronzes derived from such oxides, constitute a broad class of materials having potential application as Organic Photochromic sun block/cosmetics. These materials are well known in the context of Photochromic optical data storage media and they offer an excellent match with the very properties needed for cosmetic applications. This relates to the adaptation of the class of tungsten and molybdenum oxide-photochromics to sun blocking/dosimetry, energy storage, and cosmetic colouration (Farrer-Halls, 2007)

8. Photochromic Textiles

Photochromism in textiles seems to be a long and complicated process.

However it is rather a simple method to produce dyes and inks that can be transformed into fibre to create textiles that react to UV light. Generally the colour-change inducing light has a wavelength in the visible or near visible range. Other factors which may affect the colour of these pigments have been cited by Glyn Phillips (1997 pg 4) include, ' temperature, moisture, electricity, and gases.' Photochromic pigments have previously been applied to textiles by coating processes. Such coated textiles have aesthetic qualities associated with the Photochromic pigments. However, these textiles are not sufficiently colour-fast and their aesthetic qualities are easily destroyed by soiling. Mentioned previously, each time the colour changes due to the reaction of UV light, the colour intensity drops to eventually no apparent change will take place.

It has now been discovered that Photochromic pigments can be blended into resinous fibers, yarns or non-woven textiles without substantial loss of Photochromic properties. ' The dye used can be introduced into this process from a master pigment batch obtained by mixing chromogenic pigments with a low melting polymer.' (Phillips, 1997 pg. 5) In the process, the dye is blended with resin (the " primary resin") and the mixture is processed into textiles by spinning and drawing or by the spin-bond process. The textiles manufactured by this process are advantageous over the prior method coated products in that the resultant Photochromic pigment-containing textiles are more durable (e. g., more colour-fast), more brightly pigmented,

easily laundered after staining (e. g., by soil, solvents or oil) and readily woven directly into the desired fashion.

Generally, conventional methods of blending polymers and dyes and of extruding synthetic fibers or non-woven textiles are used in this process. ' Blending can be done in a fusion type metric mixer, a volumetric type mixer or a weight type mixer.' (Phillips, 1997 pg 7) The processes that may be used to manufacture the fibers or non-woven textiles include spinning and drawing processes, continuous spin-draw processes and spun-bond processes for the manufacture of non-woven textiles. However, these processes are modified in accordance with the concept/product such that the Photochromic dye is not subjected to a temperature in excess of about 250° C.

Preferably, the Photochromic dye is introduced into the polymer mixing process in a " master batch" of polymer-encapsulated dye pellets. Such Photochromic dye pellets have been described, ' Generally, the amount of pigment in the masterbatch is from 1 to 10%, preferably from about 2 to 7%.' (Phillips, 1997 pg 8) The use of dye pellets in place of directly adding dye facilitates uniform mixing and enhances the the overall process.

For use in the production of synthetic fibers or non-woven textiles containing Photochromic pigments, the " master batch" is mixed with a " primary" resin, which may or may not be the same as the carrier resin in the " master batch". ' The amount of " masterbatch" blended with the " primary" resin ranges from 1: 2 to 1: 100. The resins used as the primary resin are those with a melting point between about 105° C. and about 215° C.' (Phillips 1997

pg 8) Useful resins include, polypropylene, polyethylene, polyolefins copolymers and terpolymers. Additional fillers and pigments, such as talc, silica, titanium dioxide, calcium carbonate, and conventional organic pigments, may be added either to the “ master batch” or during the final fiber or non-woven textile manufacture process.

9. General Applications

General applications of Photochromism can be divided into two categories:

- a) Those directly related to the change in absorption or emission spectra such as variable transmission optical materials, optical information storage, cosmetics, authentication systems, and flow field visualisation.
- b) Those related to other physical or chemical property changes such as refractive index, electric conductivity, phase transitions, solubility, viscosity, and surface wet ability.

Photochromic can now be used in many areas of design. As photochromism has a wide range of solid states, from textiles to glass, (but only one function) most products which use this process are novel. Here are some examples;

On garments to create novel products and promotional items like T-shirts

On fabric/garment to print company logo / brand name to prevent duplication

On garment which are used for party wear

Thermometers and temperature indicators

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Security printing

Food industry to indicate temperature of packaged food

Photochromic substances can be found in inks, paints, papers and textiles.

This property is a boon for scientists doing research on intelligent textiles and smart materials where they are making use of this property to store data on the surface of textile fabrics and polymer sheets. (Whereas the same property of some reactive dyes; is a bane for textile processors. The change in shade after dyeing creates unwanted problems in dyeing)

An optical recording medium contains, on a base, one or more dyes and a polymer which forms liquid-crystalline phases. The information is written into the equally oriented liquid-crystalline polymer layer, for example by means of a laser. During this procedure, the polymer heats up locally to above a phase transition temperature. By cooling, the resulting change is frozen in the glass state. The information can be erased by applying an electric field and/or heating. The recording material permits high-contrast storage and possesses high sensitivity, good resolution and excellent stability.

There are other chromatic properties called electrochromatism and thermochromatism of dyes that are affected by electric field and heat respectively.

10. Future Products

The first Photochromic eye lens is being developed by scientists in Singapore, the Institute of Bioengineering and Nanotechnology (IBN), the world's first bioengineering and nanotechnology research institute. This lens
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is another world first. The IBN has developed a Photochromic contact lens that will darken upon exposure to sunlight to protect the eyes against harmful ultraviolet radiation and glare. The lenses will conveniently adapt to changes in light and provide optimal indoor and outdoor vision. The IBN scientists also claim that this will help treat eye diseases by incorporating medication into the lens which can deliver medication effectively rather than eye drops. Another future product is Photochromic windows at home and workplaces. These windows will change colour when exposed to UV light from the sun, which will in return make home/workplace cooler and a more comfortable place to be in.

Reversible Photochromic textiles have been around for 20 years, (mainly on novel garments) designers and scientists are trying to convert this technology into safety equipment and garments. The only drawback to this concept is that to make the product work during the night, when these safety garments are more needed. Photochromic relies on UV light to work effectively. Unless car head-lights radiate UV, this won't work, and car head-lights giving off UV light is a whole and completely different matter.

As mentioned above in general applications, scientist can record and store data using Photochromic dyes. This data can be stored onto any material surface, but at the moment only being used on textiles. This technology has a huge amount of potential. Imagine the data on a personal USB device being stored onto a piece of fabric that the user can roll up into a pocket. The technology can be manipulated to give data back to the user through many objects. The user could watch/read the news on the users' glasses;

receive emails and correspondence and perhaps even text messages. The only drawback is responding to them.

11. Conclusion

Photochromic technology has an immense amount of potential to create new products and in some cases a whole new lifestyle. Scientists can now manipulate Photochromic technology into most applications. Controlling the colour result of Reversible Photochromic is in itself a great achievement. Instead of a dull tone of grey, the colour can be anything from bright green to pink. Making Photochromic available in different materials, from glass to liquid, including textiles, makes this technology unique. Experimentation in novel-products, such as, T -Shirts that change colour when exposed to sun light, has enabled scientists to understand the chemical compounds and how to manipulate them to suit a concept. Now Photochromic technology is being used in more sophisticated ways, such as, the eye contact lens and storing data. This break through in new technology can have fantastic results for future generations. It will affect the way people work and learn.