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| <b>(51) International Patent Classification <sup>6</sup> :</b><br><b>A61L 2/00, A23L 3/00, B65B 55/00,<br/>G03C 1/73</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 96/06643</b><br><b>(43) International Publication Date:</b> 7 March 1996 (07.03.96)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
| <b>(21) International Application Number:</b> PCT/US95/10572<br><b>(22) International Filing Date:</b> 16 August 1995 (16.08.95)<br><b>(30) Priority Data:</b><br>08/298,465 30 August 1994 (30.08.94) US<br><b>(71) Applicant:</b> THE UNIVERSITY OF AKRON [US/US]; 302 E.<br>Buchtel Common, Akron, OH 44325 (US).<br><b>(72) Inventor:</b> KANAKKANATT, Sebastian, V.; 2459 Audubon<br>Road, Akron, OH 44320 (US).<br><b>(74) Agents:</b> WEBER, Ray, L. et al.; Renner, Kenner, Greive,<br>Bobak, Taylor & Weber, 1610 First National Tower, Akron,<br>OH 44308 (US).                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |           | <b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH,<br>CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE,<br>KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN,<br>MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK,<br>TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE,<br>CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT,<br>SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML,<br>MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ,<br>UG).<br><br><b>Published</b><br><i>With international search report.<br/>Before the expiration of the time limit for amending the<br/>claims and to be republished in the event of the receipt of<br/>amendments.</i> |
| <b>(54) Title:</b> MULTICHROMIC POLYMERS<br><br><b>(57) Abstract</b><br><br>Several methods of using dyes within polymers and specifically in packaging materials are disclosed. These dyes respond to specific stimuli and indicate exposure to stimuli by a change or shift in the frequencies of light which they absorb. The stimuli include temperature, radiation, chemicals (e.g. H <sub>2</sub> O, CO <sub>2</sub> , NO <sub>2</sub> , ethylene, and SO <sub>2</sub> ), and tensile or compressive stress. Within packaging materials (or affixed thereto as a label, decal or tag) these dyes could indicate spoilage or the possibility of spoilage, that the product has been irradiated, or that the product has been exposed to an undesirably high or low temperature. Many of the shifts in absorption frequencies result in visible color change which a consumer could quickly identify. The tensile or compressive stress sensitive dyes could indicate whether common opposing interlocking polymeric strips used to seal plastic bags have been effectively interlocked to seal the bags. |           |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |

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## MULTICHROMIC POLYMERS

### FIELD OF THE INVENTION

5           This invention relates to the use of photochromic, chemichromic, and piezochromic dyes to indicate specific changes in the environment of the dyes, which dyes respond to specific environment by shifting their light absorption frequencies. One specific field of use  
10 is in packaging materials and bags (desirably transparent containers) where the dyes can indicate gases or volatile liquids from contamination or spoilage. Another field of use is frequency specific photochromic dyes in packaging materials which later during use undergo long term color  
15 changes to indicate whether the package has or has not been exposed to specific irradiation frequencies. Another field of use is piezochromic dyes which are incorporated into a synthetic polymer to indicate by an absorption of specific light frequencies or alternatively by developing  
20 stress whitening to indicate whether stress is present in the polymer.

### BACKGROUND

          Photochromic dyes are known to undergo reversible color changes on exposure to ultraviolet light. U.S. Patent Nos. 3,341,330, 3,355,293 and 3,346,385 teach how to form persistent images from thin layers of dyes and how to further treat them with NO<sub>2</sub>. Similar technology is known in photochromic photography (color photography).

30           Chemichromic dyes are probably best known by analytical chemists who use pH sensitive dyes to indicate pH and dyes sensitive to specific elements or oxidation states thereof to make calorimetric test methods for determining quantitatively compounds such as iron, amines  
35 and lead.

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Piezochromic dyes are compounds which upon exposure to different compressive or tensile forces alter or shift the frequencies of light which they absorb.

5

#### SUMMARY OF THE INVENTION

Disclosed are a variety of dyes which can be incorporated into polymeric materials to indicate (by changes in the relative light frequencies which they absorb) the occurrence of an event. The event can be exposure of the dye to a specific irradiation, exposure to a specific chemical, or compressive or tensile forces. These dyes are particularly useful when their shift in light frequency absorption is visibly detectable color change and when used in combination with transparent packaging materials.

15

#### DETAILED DESCRIPTION

Dyes known to be photochromic, chemichromic, and piezochromic may be incorporated into polymeric material where they will continue to demonstrate the specific stimuli sensitivity. Some polymers may increase or decrease the sensitivity of the dye while other polymers may cause a shift in the absorbed frequencies of light of the dye. The wavelengths of light desirably absorbed are from about 10 nm to about 1 mm which include ultraviolet, visible and infrared. More desirably, one or more frequencies of absorbed light, which shift on exposure to the stimuli, are in the visible light region which is from about 0.4  $\mu\text{m}$  to about 0.7  $\mu\text{m}$ . Exposure of the dye to its specific stimuli causes a change in the dye which causes a change in the amount of one or more frequencies of light which the dye absorbs. These shifts are usually characterized by a spectrometer which measures the amount of absorbed or reflected light from a material at numerous different frequencies. Many of these dyes after exposure to their specific stimuli undergo a large enough shift in one or more frequencies of visible light absorbed by the dye that the exposure to the stimuli can be detected by a

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person as a change in the perceived color of the dye. These dyes having visual color changes are preferred for packaging applications and for household use or consumption. Commercial applications of packaging materials might use visible, ultraviolet or infrared color changes as indicators but would require equipment to determine if the dyes had changed their absorption frequencies in only nonvisible wavelengths of light.

A preferred use of these dyes is in packaging materials to indicate the usable condition of the packaged article. Such uses include photochromic dyes which indicate whether a packaged food or medical use product has been partially or fully sterilized by an irradiation process. Photochromic dyes are dyes which undergo a change or shift in the relative amounts of light of specific frequencies which they absorb, when they are exposed to specific frequencies of irradiation. A temporary color change would indicate upon immediate inspection that the irradiation was successfully completed. A more permanent color change would indicate to the final consumer that the packaged article had, in fact, been irradiated and was safe to use.

Chemichromic dyes could function with packaged articles to indicate whether a gas or a volatile liquid was present inside the packaged article. Chemichromic dyes undergo a change, when exposed to specific chemicals (such as  $H_2O$ ,  $CO_2$ ,  $NO_2$ , ethylene,  $SO_2$ ), in the relative amount of specific frequencies of radiation absorbed. As recited above, for photochromic dyes, this can result in a visually detectable or a detectable by instrument color change. Desirably, the dyes are sensitive to undesirable products (such as moisture in moisture sensitive goods (e.g. electronics) or products of degradation or spoilage of food products (e.g.  $CO_2$ , ethylene,  $SO_2$  in food containers). Thus, one use of the dye is to detect if spoilage of the contained food product is imminent or has already occurred. A label, legend, or decal would be desirably included with the packaged article explaining where the

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dye was and how to determine if an undesirable product was contained within the package by examining the portion of the packaging containing the dye.

Thermochromic dyes which change the one or more  
5 frequencies of light which they principally absorb in response to one or more temperature changes can be used to indicate whether a polymer is currently or has in the past been exposed to a particular temperature. The color change can be a permanent shift in the one or more fre-  
10 quencies absorbed or a reversible shift that slowly or quickly reverts back to absorbing appropriate frequencies for the initial temperature. A reversible shift would be desirable to monitor a process or storage conditions and avoid prolonged exposure to elevated or reduced tempera-  
15 tures. A permanent shift would be desirable to monitor whether a product has since the packaging was installed been exposed to specific elevated or reduced temperature.

Piezochromic dyes would desirably be included in a polymeric material to indicate whether the specific  
20 polymeric material was in compressive or tensile stress. In packaging materials, these dyes would be useful as they could identify stressed (tensile or compressive) areas within the package. Holes, tears, and abraded areas could be identified by their different apparent color. Chemical  
25 compounds known as sensitizers could optionally be added to the dyes to change or adjust the amount of stress required to trigger an absorption of different light frequencies or cause a color change. Compressive stress could be applied by stacking the articles or other means.  
30 One use of absorption changes of piezochromic dyes would be to indicate whether a desired or undesired compressive stress is present in interlockingly engagable polymer strips. These strips are known to consumer and are used to seal many transparent bags. The strips may engage with  
35 themselves in some circumstances but usually one strip is used with a longitudinally positioned second strip having an appendage or channel to engage with an appendage or channel of the first strip. A problem with these strips

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is that it is difficult to visually perceive if they have been securely interlocked to seal the contents of the package. Desirably, the piezochromic dye is included in the polymer of the one or more appendages and/or channel forming material in one or both strips. In the interlocked position of one or more strips, the appendages and channel material would be in compressive or tensile stress. Desirably, the dye would indicate this stressed condition by a change in absorbed light frequencies in the appendages and/or channel material.

A variation of using piezochromic dyes in the stressed portion of interlocking polymer strips is to mold or machine the strips to create dimensional variation in one or more areas in the interlocking strips. These portions of the polymer strips, due to their having one or more areas of increased dimension as compared to adjacent areas (of the appendage or channel), or their having one or more areas of decreased dimension relative to adjacent areas serve as a stress concentrator within the appendage or channel. The dye in areas of stress concentration would thus be able to change its relative light absorption frequencies at a lower total tensile or compressive stress enhancing its sensitivity. With stress whitening polymers the areas of stress concentration may whiten without any dye present indicating that the interlocking strips are interlocked sealing the container and the polymer used in one or more parts of the strip is under compressive or tensile stress.

The above photochromic, chemichromic thermochromic, and piezochromic dyes may undergo temporary or permanent change (shift) in the relative amounts of specific frequencies of light absorbed. For applications where the polymer is to be reused without remolding it, the color changes would be desirably temporary or reversible. In applications where the polymer is used one time before being recycled, desirably the color change is permanent. Specific applications may require reversible, temporary, permanent, and semipermanent changes. The use

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of temperature changes and/or exposure to chemicals are viable ways of reversing color changes. Thus a polymeric food container could be designed to reverse any color change during the wash or dry cycle within a dishwasher  
5 where it would be exposed to elevated temperature and chemicals.

The polymer containing the dye can be processed by a variety of well known polymer processing techniques. These include extrusion, calendering, injection molding,  
10 transfer molding, compression molding, solution casting and variations thereof. The dyes may be adsorbed onto or absorbed into polymers. The dyes may be part of a polymer dispersion such as latex, paint, ink, etc. which is coated onto a polymer and dried.

15 Food products are a preferred material to be contained in the packaging materials of this application. Food includes fruits, vegetables, meats (beef, pork, poultry, fish etc.), cereals, grains, dairy products (cheese butter, milk, sour cream, ice cream) and mixtures  
20 or combinations of the above materials and partially or fully cooked versions thereof.

The packaging material anticipated includes natural and synthetic polymers such as paper; waxes; thermoplastic polymers including polyolefins such as poly-  
25 ethylene, poly-(vinylidene chloride), polystyrene, foamed polystyrene; thermoset polymers; thermoplastic elastomers; liquid crystal polymers such as Xydar from Amoco, and aromatic liquid crystal polyesters such as 2-naphthalene-carboxylic acid, 6-(acetyloxy)-, polymer with 4-  
30 (acetyloxy)benzoic acid sold as Vectra™ by Hoechst Celanese Corp.; etc. Preferred packaging materials include at least one transparent component. The packaging material is also known as bags, wraps, films, pads, trays, papers and molded containers or spacers. If desired the  
35 dye may be affixed or incorporated into packaging material or the package product may include the dye as a label, decal, legend or coating.

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The dye may be the following which are chemichromic and/or photochromic:

benzoindolinospiropyran with one or more substituents selected from alkyls of 1 to 5 carbon atoms optionally with one or more other substituent groups either as part of the alkyl or separately present selected from hydroxyl, hydroxyalkyl, amino, carboxyl, aceto, carboxylate, aryloxy, alkylamino, or mercapto;

polyalkylbenzoindolino spiro naphthoxazines with or without one or more substituents as given above for spiropyrans;

triarylmethane leuco dyes such as malachite green leucocyanide, malachite green leucohydroxide, malachite green leucobisulfite and similar leuco dyes from crystal violet, brilliant green, auramine, etc; and

metal dithizonates with mercury, platinum, or palladium as the metal atom with or without substituents as described above for spiropyrans.

The following are additional chemichromic dyes: dyes indicating acidic pH, dyes indicating basic pH, other indicating dyes and triarylmethane dyes.

Preferred dyes are:

1',3'-dihydro-1',3'3'-trimethyl-6-nitrospiro (2H-1-benzopyran-2,2'-(2H)-indole), crystal violet, cresolphthalein, bromocresol green, methyl red, thymol phthaline, malachite green, alizarin red, phloxine B.

Thermochromic dyes are made by reacting the below thermochromic dye intermediate with organic acids, alcohols, or esters. The shifts in light absorption frequency can be adjusted to specific temperatures by the choice of the one or more organic acids, alcohols, or esters or combinations thereof chosen. The acids can be monoacids, diacids and less desirably polyacids. The alcohols can be monohydric, dihydric and less preferably polyols. The alcohols can include carboxylic acid functionality therein. The esters can have monoester, diester, or polyester functionality along with alcohol or carboxylic acid functionality. The desirable acids,

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alcohols, and esters are organic and have from about 3 to 35 carbon atoms per molecule and more desirably from 10 to 18 carbon atoms per molecule. They can contain linear aliphatic, cyclic, branched, and aromatic groups therein. Desirably they are free of heteroatoms other than carbon, hydrogen, and oxygen.

The dye intermediates useful for this purpose along with their visually detectable color are:

Thermochromic dyes based on the following thermochromic dye intermediates:

Blue: crystal violet lactone or 3,3-bis(4-dimethylaminophenyl)-6-dimethyl amino phthalide.

Green: Malachite green: spiro(isobenzofuran-1 (3H), 9'-(9H) xanthen)-3-one, 2'-(bisphenylmethyl) amino-6-(diethylamino).

Black: 2-anilino-3-methyl-6-diethyl-amino fluoran.

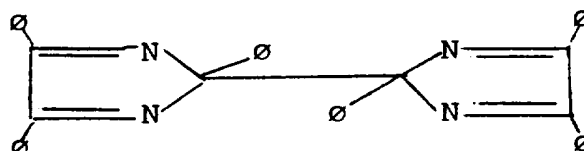
Yellow (orange): 3-(4-dimethylamino) phenyl-3-(di (4-octyl) phenylamino) 1-(3H)-isobenzofuranone.

Pink (Magenta): rosaniline (3,3-bis(4-amino-phenyl)-6-aminophthalide.

Red: 3,3-bis(1-butyl-2-methylindol-3-yl) phthalide.

Piezochromic dyes include:

a. Triaryl imidazole dimers of Bis-2,4,5-triaryl imidazoles having one or more substituents groups selected from aryl groups such as phenyl, p-tolyl, p-chlorophenyl, p-anisyl



Preferred are: 2, 2', 4, 4' 5, 5'-hexaphenyl bisimidazole;

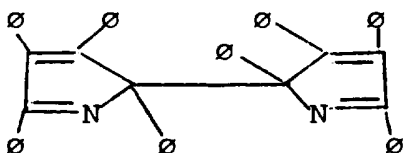
2, 2', 4, 4' 5, 5'-hexa-p-tolyl bisimidazole;

2, 2', 4, 4' 5, 5'-hexa-p-chlorophenyl

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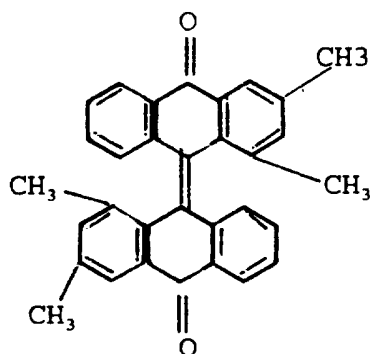
bisimidazole;  
 2, 2'-di-*p*-chlorophenyl-4, 4', 5, 5'-  
 tetraphenyl bisimidazole;  
 2, 2'-di-*p*-Anisyl-4, 4', 5, 5'-tetraphenyl  
 bisimidazole; and  
 2, 2'-di-*p*-tolyl-4, 4', 5, 5'-tetraphenyl  
 bisimidazole;

b. Bistetraaryl pyrrole



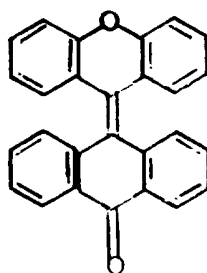
Preferred is: Bistetra phenyl pyrrole

c. Bianthrone: Δ 10, 10'-bianthrone



Preferred is: 2, 4, 2', 4'-tetramethyl bianthrone

d. Xanthylidene anthrone



e. Dixanthylene

f. Helianthrone

g. Mesonaphthobianthrone

The amount of the above described dyes to be  
 used in polymeric compositions is desirably from 0.001 to  
 5 wt. % based on the portion of the polymeric composition  
 containing the dye. More desirably the amount is from

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0.01 to 5 wt. % and preferably from 0.1 to 1 wt. %. If the polymeric composition includes a non-reactive diluent or solvent that will be removed, the wt. % dye is to be calculated based on the composition less the diluent or solvent.

The above described dyes dispersed in a polymer are useful to indicate either that a particular chemical material is present at one or more specific concentration; that a product has been exposed to one or more particular radiation frequencies; or that a polymer is under compressive or tensile stress; or combinations thereof. The change in the relative absorption of one or more light frequencies indicates whether the stimuli (chemical, radiation, or stress) is present or has occurred.

The following examples illustrate the use of dyes in polymers and their use to detect different stimuli.

#### Example 1

One-tenth of a gram of 6-nitro-1', 3', 3'-trimethylbenzoindolinospiropyran or 6-nitro BIPS is mixed with 100 g of polystyrene commonly known as general purpose polystyrene (GPPS). The mixture is placed in the hopper of a laboratory model injection molding machine. Several 1" x 1" x 0.1" chips were molded at 400°F. (205°C). The chips, on cooling, did not have any appreciable coloration. They were clear. These chips were exposed to U.V. light of wavelength 336 nm for 2 sec., 1 min. and 5 min. intervals. The chip exposed for 2 sec. only changed to light purple, which returned to the original shade in 15 minutes. The chip exposed to 1 min. was deeper purple, but it did not return to the original shade for several hours. The chip that was exposed for 5 mins. or more did not return to the original color although the intensity decreased during a period of several days. Although the mechanism of color persistence of overexposed chips is not fully understood, it is explained as follows. On exposure for a few seconds, the first layers of the polymeric chip become partially translucent

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due to the decreased solubility of the colored form of the photochromic dye in the polymeric substrate allowing only more penetrating, shorter wavelengths of the U.V. light. However, on reaching the inner layers of the polymeric substrate, this effects the coloration. These layers being heat shielded by the outer layers are protected from thermal reversal of the coloration. This can further be promoted by traces of acidic or hydrophilic material incorporated in the photochromic dye or the plastic substrate.

These chips were then suspended in an environmental chamber containing NO<sub>2</sub> for 5 minutes. Then they turned yellow and were immersed in hot water for a few seconds. The chips turned red. The intensity of the yellow shade varied; the deeper yellow was obtained from the samples which had longer exposure to U.V. light.

Then some yellow chips were again suspended in the environmental chamber purged with ammonia gas. The chips turned orange to red. The depth and shade of the color depended on the heat and exposure history of the chips.

Both the yellow and red colors on the chips were permanent colors under normal conditions. Thus, three colors were sequentially obtained from a clear chip: from clear to purple, from purple to yellow, and finally from yellow to red.

#### Example 2

Example 1 was repeated using high impact polystyrene (HIPS). This has a hazy white color to begin with, and the final results gave color change from white to purple, from purple to yellow, and from yellow to red under experimental conditions described in example 1.

#### Example 3

One-tenth of a gram of 8-Methoxy-6-nitro BIPS was intimately mixed with PVC plastisol along with a few drops of toluene. The mixture was used to mold circular patties, 2" in diameter and 0.2" in thickness. This was done using aluminum weighing dishes. The plastisol

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mixture was taken and heated in an oven at about 205°C for about two minutes. The patties were flexible and blue in color when hot but returned to white color on cooling. When the patty was exposed to U.V. light for a second, it  
5 turned deep blue. The color returned in 60 minutes. When the exposure time was increased to five minutes, the return time was extended to several hours, but the coloration was blue. When the exposure to U.V. continued for 90 minutes, the yellow color so formed was permanent.  
10 When the U.V. exposure was performed in an atmosphere of an acid vapour such as HCl, the blue coloration that occurred was permanent under ordinary conditions. Thus two colors were obtained from the starting white color without any sequential treatment. That means from white  
15 to blue and from white to yellow. The mechanism of the acid environment which prevents the molecular arrangement of the colored form to revert to that of the colorless form is well known. The mechanism of yellow coloration on prolonged exposure to U.V. is attributed to the breakdown  
20 of chromophore into nonphotochromic entities.

#### Example 4

One-tenth of a gram of finely divided phthalimide was incorporated in polypropylene homopolymer of melt index 18 by injection molding 1" x 1" x 0.1"  
25 chips. A 1% solution of 6-Nitro BIPS in toluene was made, and it was adsorbed on the phthalimide in the polymer chip which was immersed in the above solution for several minutes. A red color was formed on exposure to U.V. light which was permanent under normal conditions as well as on  
30 exposure to visible light. Certain photochromic compounds show negative photochromism and positive thermochromism. A negative photochromism is exhibited by 6-Nitro BIPS under certain conditions: for example, coloration occurred in the absence of light which is erased on exposure to  
35 visible light. This is partially explained as a positive thermochromic effect in the dark and a negative photochromic effect in the visible light. The presence of phthalimide in the system prevented the photo erasure.

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Example 5

High impact polystyrene (1" x 1" x 0.1") chips containing 0.1% nitro BIPS and 0.01% Rhodamine B lactam were made by injection molding as in example 1. The chip  
5 was exposed to U.V. light, it turned bluish purple. On treating it with SO<sub>2</sub> gas in an environmental chamber for two minutes, the bluish chip turned yellow, and this yellow color was permanent. On heating the chip gently to effect reaction with Rhodamine B lactam, the final perma-  
10 nent red color was obtained.

While in accordance with the patent statutes the best mode and preferred embodiment has been set forth, the scope of the invention is not limited thereto, but rather by the scope of the attached claims.

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WHAT IS CLAIMED IS:

1. A method of using packaging materials for monitoring undesirable products or reaction products within a packaged material, comprising:
  - a) affixing to or incorporating into the packaging material one or more chemichromic organic dye;
  - b) preparing a package with said packaging material; and
  - 10 c) the dye absorbing one or more radiation frequencies indicating the presence of said undesirable products or reaction products.
2. A method according to Claim 1, wherein said  
15 chemichromic organic dyes include one or more of benzo-indolino-spiropyrans, polyalkylnaphthoxazines, fulgides, triaryl methane leuco-cyanides, triaryl methane leucohydroxides or triaryl methane leucobisulfites.
- 20 3. A method according to Claim 2, wherein said undesirable products are CO<sub>2</sub>, ethylene, NO<sub>2</sub>, H<sub>2</sub>O, an acid, a base, or sulfidic compounds.
4. A method according to Claim 3, wherein said  
25 one or more radiation frequencies absorbed by said dye are visible light radiations facilitating the determination of the presence of said one or more products or reaction products by visual inspection.
- 30 5. A method according to Claim 4, wherein said packaging material is a transparent bag or a transparent wrapping material.
6. A method of using packaging material to  
35 indicate its exposure to one or more types of irradiation, comprising:
  - a) affixing to or incorporating into the packaging material one or more photochromic dyes;

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b) preparing a package with said packaging material; and

c) the dye absorbing one or more radiation frequencies indicating exposure or lack of exposure to  
5 irradiation.

7. A method according to Claim 6, wherein said one or more photochromic dyes are one or more of benzo-indolino-spiropyrans, polyalkylnaphthoxazines, fulgides,  
10 triaryl methane leuco-cyanides, triaryl methane leucohydroxides or triaryl methane leucobisulfites.

8. A method according to Claim 7, wherein the radiation frequencies absorbed are visible light frequencies facilitating the detection of said irradiation by a  
15 visually perceptible color change.

9. A method of indicating in a synthetic polymer when said polymer is in stress, comprising:

20 a) incorporating one or more piezochromic organic dyes into one or more portions of said synthetic polymer;

b) optionally adjusting the sensitivity of said one or more organic dyes by adding a sensitizer to the dye  
25 or the polymer; and

c) the dye in the stressed area within one or more portions of said polymer changing the relative amount of absorption of one or more frequencies of light indicating the stress.  
30

10. A method according to Claim 9, wherein the one or more frequencies of light absorbed are visible light frequencies and the change in absorption can be detected by a human visually.  
35

11. A method according to Claim 9, wherein the synthetic polymer is in the form of one or more strips which are interlockingly engaged with itself or with

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another strip.

12. A polymeric composition comprising either  
a thermochromic, photochromic, chemichromic, or  
5 piezochromic dye dispersed in a molded, extruded, or  
shaped by calendering polymeric article.

13. A polymeric composition according to Claim  
12, wherein said article was formed by compression mold-  
10 ing, injection molding, extruding, blow-molding,  
calendering or transfer molding.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/10572

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : A61L 2/00; A23L 3/00; B65B 55/00; G03C 1/73

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 426/323, 331, 415, 544, 545; 523/ 100; 430/138, 338; 524/106, 356

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS; Piezochromic, chemichromic and packag?, dye# and packag?

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                         | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | JP, A, 8,210,564 (FUJI TOKUSHO SHIGYO KK) 07 December 1993, abstract                                                                                       | 1, 6                  |
| X         | US, A, 5,208,132 (KAMADA ET AL) 04 May 1993. See column 2, line 57 to column 4, line 6, column 6, lines 20-39, column 7, line 40 to column 8, line 2.      | 1-4, 6-8, 12, 13      |
| X         | US, A, 5,206,118 (SIDNEY ET AL) 27 April 1993, See column 3, lines 55-66 and columns 11-12.                                                                | 1, 6                  |
| Y         |                                                                                                                                                            | 1-8                   |
| X         | US, A, 5,289,547 (LIGAS ET AL) 22 February 1994, See column 6, line 38 to column 8, line 40, column 10, lines 6-65, column 2, line 68 to column 3, line 1. | 1-8, 12, 13           |



Further documents are listed in the continuation of Box C.



See patent family annex.

|                                                                                                                                                                         |                                                                                                                                                                                                                                                  |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| * Special categories of cited documents:                                                                                                                                | *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention                                              |
| *A* document defining the general state of the art which is not considered to be of particular relevance                                                                | *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone                                                                     |
| *E* earlier document published on or after the international filing date                                                                                                | *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | *G* document member of the same patent family                                                                                                                                                                                                    |
| *O* document referring to an oral disclosure, use, exhibition or other means                                                                                            |                                                                                                                                                                                                                                                  |
| *P* document published prior to the international filing date but later than the priority date claimed                                                                  |                                                                                                                                                                                                                                                  |

Date of the actual completion of the international search

18 OCTOBER 1995

Date of mailing of the international search report

03 JAN 1996

Name and mailing address of the ISA/US  
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/10572

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                          | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------|-----------------------|
| Y         | US, A, 4,842,981 (SANDERS ET AL) 27 June 1989, See column 6, lines 18-49.                                   | 2-5, 7, 8             |
| Y         | US, A, 4,758,547 (ITABASHI ET AL) 19 July 1988, See columns 6-9 .                                           | 2-5, 7, 8             |
| X         | US, A, 5,320,784 (MIYASHITA) 14 June 1994, See column 1, lines 20-35.                                       | 9-13                  |
| X         | US, A, 4,913,999 (TAMAGAWA ET AL) 03 April 1990, See column 10, line 63 to column 11, line 2.               | 9-13                  |
| X         | US, A, 4,171,980 (CEINTREY) 23 October 1979, See abstract and column 10, lines 28-35.                       | 12, 13                |
| Y         | US, A, 4,885,224 (YAMAMOTO ET AL) 05 December 1989, See column 13, lines 65-68.                             | 12, 13                |
| Y         | US, A, 4,830,947 (OKA) 16 May 1989, See column 9, lines 23-30                                               | 12, 13                |
| A, P      | US, A, 5,371,058 (WITTIG, JR. ET AL) 06 December 1994, See column 3, lines 42-46 and column 4, lines 56-64. | 12, 13                |

**INTERNATIONAL SEARCH REPORT**International application No.  
PCT/US95/10572**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

- I. Claims 1-5 drawn to a method of using chemichromic dyes, classified in class 426, subclass 321.+.
- II. Claims 6-8 drawn to a method of using photochromic dyes, classified in class 430, subclass 338+.
- III. Claims 9-11 drawn to a method of using piezochromic dyes, classified in class 430, subclass 138.
- IV. Claims 12-13, drawn to a polymeric composition classified in class 524 subclass 86+.

The listed invention lack unity of invention under PCT Rules 13.1 and 13.2 because there are different reaction mechanisms of dyes in Group I and II.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/10572

## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

426/323, 331, 415, 544, 545; 523/ 100; 430/138, 338; 524/104, 106, 110, 356