(51) International Patent Classification: G01N 33/48

(21) International Application Number: PCT/US2004/018847

(22) International Filing Date: 14 June 2004 (14.06.2004)

(25) Filing Language: English

(26) Publication Language: English


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(54) Title: PRODUCT SHELF LIFE MONITORING SYSTEMS

(57) Abstract: A product shelf life monitoring system (30) comprising a labeled substrate (11,23) that carries an active indicator sport (13) and a UV blocking layer (33).
PRODUCT SHELF LIFE MONITORING SYSTEMS

BACKGROUND OF THE INVENTION

The present invention relates to systems, and elements, components, and compositions therefor, for monitoring and indicating the elapse of a predetermined integral of ambient conditions, such as time, temperature, humidity, actinic radiation, vaporous atmosphere, and the like, to which such a system has been exposed. Typically, for example in monitoring a thermal ambient, a composition comprising an indicator system is formulated to exhibit a readily discernible property variation, such as a change of color or color density, upon the elapse of a given time-temperature integral. The system, which may often take the form of a label, is associated with a product of foodstuff, medicament, or the like the useful shelf life, i.e., the safe or potent utility, of which is known to expire substantially concurrently with the elapse of the given time-temperature integral.

Substituted diacetylenic monomers useful in the present invention have been studied and utilized in TTI systems for many years. Such utility of numerous monomers comprising at least two conjugated acetylene groups (-C≡C-C≡C-) and their unique physico-chemical properties, e.g., responsiveness to temperature change by transforming into contrastingly colored solid state polymerization reaction products, have, for instance, been described by Patel et al. U.S. Patent No.3,999,946, the entire disclosure of which is hereby incorporated herein by this specific reference thereto. The synthesis of these monomers and their implementation in useful TTI and other shelf life indicator compositions are discussed there at length by Patel et al. and continue to be valid in formulating embodiments of the present invention. Likewise, the use of these diacetylenic monomer shelf life system components and improvements thereon, including asymmetric substitutions and complexes, and improved methods of monomer synthesis, have
been described at length by Patel (U.S. 4,384,980) and Preziosi et al. (U.S. 4,788,151). Such useful descriptions and
eamples of diacetylenic monomer components that can be employed in
the present invention that appear in the aforesaid patents are hereby incorporated herein by this
specific reference thereto.

While the consistent and predictable response of these diacetylenic monomer compositions to
thermal stimuli provides a basis for highly functional and reliable TTI system products, a similar
contemporary color-generating solid state polymerization response to other ambient actinic
stimuli, such as ultraviolet radiation, significantly compromises their utility in such systems.

This detraction has been recognized long since even by Patel et al who suggested the use of
active ultraviolet light-absorbing compounds, such as benzophenones, benzotriazoles, and the
like to mitigate these results. Thus, diacetylenic monomer composition TTI products comprising
sheet elements, such as labels or marker tabs, bearing a localized deposit of active monomer
indicator composition have had laminated thereto an overlying film comprising a UV-absorbing
composition. While such a fabrication practice has provided a TTI product with significantly
reduced sensitivity to UV stimuli, the expanse of UV-blocking film usually far exceeds that
needed to cover the relatively small deposit of active TTI composition component. As a result, a
significant amount of expensive UV-absorber composition utilized in the fabrication process
serves no advantageous purpose and merely represents a wasted cost factor resource. Further, in
some TTI product applications the complete expanse of UV-blocking material prevents the
selective employment of otherwise useful areas of a TTI label.

In particular, the present invention relates to responsive compositions of shelf life systems
comprising substituted diacetylenic monomer components which exhibit a distinct color change
as a result of and generally concomitant with a solid state polymerization effected by the
ambient condition integral; typically, as in the case of a time-temperature indicator (TTI)

system, the integral of time and temperature. More particularly, through incorporation of integral
elements for isolating actinic stimuli. In some embodiments, the invention provides TTI
systems and compositions of remarkable durability, sensitivity, and responsiveness which yield
significant functional and economic improvements while greatly reducing the consumption of
highly priced components and resources.
In some useful embodiments, the present invention obviates the noted shortcomings and disadvantages of prior diacetylenic monomer composition TTI system products and provides such products which yield effective results while reducing costs and achieving savings in fabrication time and material resources.

SUMMARY OF THE INVENTION

Some embodiments of TTI system products of the instant invention can comprise a self-adhesive substrate label having deposited or printed on its face surface an isolated area or spot of coating or ink composition comprising a selected active diacetylenic monomer compound. In practice, economics favor such a fabrication of a multiplicity of TTI label units, as in a repetitive printing operation upon a continuous web of release sheet-backed substrate moving at high speed past printing or composition application stations.

In order to provide the noted protection from anticipated vagrant exposure to actinic ultraviolet light during label use, the fabrication process has typically included a "downstream" station at which a continuous web of transparent film bearing a UV-absorbent, or UV-blocker, composition is laminated upon the printed, active monomer face of the label substrate web. To ensure thorough coverage of UV-absorbent composition upon active monomer depositions, the overlay film is normally applied coextensive with the substrate web. A subsequent, final operation in the fabrication stream may be utilized to die-cut and remove extraneous adhesive-backed substrate and overlay film, leaving the desired multiplicity of individual TTI labels on the release sheet backing support web. Along with the excess areas of UV-blocker composition remaining on each label surface, the extraneous overlay film material discarded in this final fabrication operation represents substantial waste of this composition which amounts to a significant component of product cost.

In a preferred embodiment of the present invention, a printing or coating station is situated downstream from the point of active diacetylenic monomer composition application and effects deposition of UV-blocker composition directly upon and in substantial register with the active monomer deposition to provide the latter component optimum protection from incident UV radiation. As in the past, additional printing stations may be provided in the fabrication process
for application of desired indicia, such as reference color patches, use instructions, and advertising.

The selective location, according to the invention, of UV-blocker composition only over those areas occupied by active monomer provides additional advantages beyond the direct saving in cost of otherwise wasted UV-absorbent composition. Since, in this improvement, the major extent of the label area is devoid of UV-blocker, indicia may be applied to various portions of that area at a later time and at a greater rate and diversity, and thus more economically, by means of UV-cured printing inks.

Further, and of particular significance in expanding the capabilities of the diacetylenic monomer compositions into multiple response indicator systems, portions of a label face outside the UV-blocker protected TTI site may be employed as sites for indicators, including selected diacetylenic monomer compositions, dedicated as responsive to UV-radiation, thereby incorporating into a single label indicators for both time-temperature and time-radiation integrals relevant to the shelf life of an associated product.

BRIEF DESCRIPTION OF THE DRAWINGS
Some embodiments of the present invention will be described with reference to the accompanying drawing of which:

FIG. 1 depicts in plan view the general conformation and functional response of a time-temperature indicator (TTI) system device of the prior art typically comprising an active diacetylenic monomer indicator composition and a UV-protective overlay film;

FIG. 2 depicts in elevational cross-section, taken at 2-2 in FIG.1(a), the structure of the prior art TTI system device;

FIG. 3 depicts in elevational cross-section, taken at 3-3 in FIG.4, the structure of a TTI system device embodying the present invention;

FIG. 4 depicts in plan view multiple TTI system devices embodying the present invention;
FIG. 5 presents graphic data depicting the UV-protective efficacy of a device embodying the present invention; and

FIG. 6 presents graphic data depicting the comparative UV-protective efficacy of a device embodying the present invention and one of the prior art.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

As seen in FIG. 1(a), a TTI system label 10 of the prior art typically comprises a self-adhesive substrate 11 upon which is printed a spot 13 of active diacetylenic monomer indicator composition. A threshold reference color body, such as shown in the form of a ring 15 surrounding spot 13, is printed in close proximity to the active indicator composition and is provided in a color tone closely approximating the color density which will be developed in indicator spot 13 upon accumulation of the time-temperature integral predetermined to be representative of the shelf-life beyond which the intended associated product, e.g., a foodstuff, such as fish or fowl, or a medicament, such as vaccine or medicine, is expected to lose its utility or potency. As an example of such an expired shelf-life, the indicator composition spot 17 of the label in FIG. 1(b) is shown to have polymerized under the influence of ambient temperature beyond the threshold integral period to yield a tone which is far darker than that of reference color ring 15.

The TTI label product may generally bear additional indicia 12 presenting identifying or instructional text and the like. Further, in order to mitigate the effect of incident UV-light on active indicator composition 13, a sheet of transparent film 18, a section only of which is shown in FIG. 1(a), bearing a UV-absorbent blocker composition has often been coextensively laminated to the face of label substrate 11.

FIG. 2 depicts in greater detail a typical construction of the prior art TTI label of FIG. 1. Such a label 20 comprises a release sheet 21 support for label substrate 11 of stable paper or film, e.g., biaxially oriented polypropylene, and its pressure-sensitive self-adhesive coating 23. The selected area, or spot, 13 of active diacetylenic monomer indicator composition is deposited on
substrate 11, preferably as an ink or lacquer in a screen, gravure, or other printing operation. A body of reference color, such as a registered ring 15, is printed upon composition 13 to provide a means of ready comparison with polymerization color density level during progression of the target shelf-life. After application of additional desired indicia (not shown), UV-blocking overlay film 18 is laminated, preferably by means of an integral self-adhesive layer (not shown), upon the resulting composite label device.

In contrast to the foregoing structure of the prior art, the TTI system label 30 of the present invention is fabricated in a manner to yield the device depicted in FIG. 3. While similar release sheet support web 21 and self-adhesive label substrate 11, 23 materials may be employed to carry the active indicator spot 13 of diacetylenic monomer composition, the present invention departs from past practice by applying a UV-blocking component layer 33, preferably as a printed UV-absorbent transparent lacquer ink composition, directly over active monomer component 13. The area of applied layer 33 may be in precise register with that of active spot 13; however, the simpler application may preferably be such that layer 33 extends to some degree beyond the area of monomer 13 to thus obviate concern of excessive and costly register control parameters. Such application provides the additional benefit of encompassing the monomer deposition with UV-blocker to minimize lateral exposure to vagrant radiation. In this manner, the UV-sensitive monomer component of the TTI system label is accorded optimum protective coverage with UV-blocker composition 33 while requiring only a minimum amount of such composition and avoiding in great measure the previously encountered costly waste.

A color contrast comparison reference component 15 may be printed in turn with other desired indicia according to prior practice, but with the advantageous exception that improved and highly preferred UV-setting compositions and inks may now be employed without concern of deleteriously affecting the active monomer indicator composition with processing UV light. The utility of reference component ring 15 remains as with prior TTI labels in that, as seen in FIG. 4, the color density change progression of indicator 13 may be observed at any time through visible-transparent UV-blocker film 33 revealed at the annular opening in reference ring 15. As an optional component to provide protection from physical abrasion or abuse, substantially inert, transparent film 38 may be applied over the label product in the manner previously employed with a UV-blocker overlay film 18.
In addition to a capability for subsequent application of printed indicia 42, such as point-of-sale information, in label areas now unobstructed by UV-blocker, a further advantageous embodiment afforded by the invention may be seen in FIG. 4 which generally depicts a multiplicity of TTI system labels 40 as typically arranged in series during continuous printed fabrication on a section of carrier web 21. Areas of label substrate 11 not otherwise occupied by active TTI components, and being devoid of UV-blocking composition, are now available to support active components of a responsive system, represented generally at 44, for indicating an integral of time and UV-light exposure, that is, one constituting an indicator of shelf life vis-à-vis ultraviolet light to which an associated foodstuff or other product may, along with excessive heating, be susceptible. The limited and localized disposition of UV-absorbent composition achieved in systems of the present invention has enabled such expanded and complementary indicator utility.

Representative implementations of the present invention may be seen more specifically in the following examples.

Example I

An active TTI system indicator composition comprising a commonly used substituted diacetylenic monomer is prepared by first ball milling about 9.0 parts by weight of 2,4-hexadiyn-1,6-bis(ethyurea) and 25 parts n-butanol for about 16 hours to obtain a fine particle dispersion which is then mixed with a lacquer solution of about 8.3 parts of ethyl cellulose and 60 parts n-butanol. The mixture is then thinned to a desired printing ink consistency with up to about 85 parts of n-butanol.

A UV-blocker ink composition of printable consistency is prepared by thoroughly mixing about 3.5 parts by weight of 2-2' dihydroxy-4-methoxybenzophenone, 2.5 parts Orsol Yellow dyes, and 2.1 parts ZnO into a lacquer base prepared with about 18.4 parts nitrocellulose, 5.0 parts 2-ethylhexyl-2-cyano-3,3-diphenyl acrylate, and 1 part silicone-based flow adjunct in a solvent mixture of about 45 parts ethyl-3-ethoxy propionate, 5.7 parts isopropanol, 11.4 parts ethyl acetate, and 5.4 parts diacetone alcohol.
The above indicator ink composition is printed as a series of spot images of about 6 mm diameter on a first length of continuous strip substrate web of white-pigmented biaxially oriented polypropylene in a Gallus R250 (Gallus, Inc., Philadelphia, PA) rotary screen printing press utilizing a 39%, 180 μm screen. A second length of substrate web is likewise printed with indicator composition, and at a subsequent press station the buff-colored indicator spots are overprinted in similar manner with the above UV-blocker ink as substantially registered images of about 8 mm diameter. Samples are taken from the two printings for comparative testing in the following manner.

Sample sections (A and B) are taken from the first length of printed strip web without UV-blocker overprint. Sample (A) is sealed within an opaque foil envelope for use as a control and sample (B) is retained for use as is. A third sample (C) is taken from the second length of printed web having UV-blocker overprint for use as is. These samples and controls are exposed together to mid-day sunlight (at about 22°C and 25% relative humidity) with measurements of indicator spot color density being taken at regular intervals with a commercial reflection densitometer (X-Rite 404) operating in the cyan mode until a predetermined threshold color density of a sample is observed.

Results of these tests are shown in FIG. 5 as traces of the relative color density change data. As anticipated, data 53 of the enclosed control sample (A) showed no color density change. Data 55 of the unprotected sample (B) indicator spots showed an increase in color density at a regular rate to a final dark blue-black during the nearly 3 hour test period, thus confirming the susceptibility of the active indicator composition to the polymerizing influence, at least in part, of ultraviolet light. Data 57 of indicator sample (C) comprising UV-blocker overprint according to the invention, on the other hand, showed substantially no change in color density during the test period, thereby indicating the high efficacy of the overprint embodiment. The offset of these latter data from those of control sample (A) are attributable to the color initially imparted by UV-blocker composition dyes.

Example II

The comparative efficacy of the present invention and the prior art with respect to exposure over a more limited wavelength range of ultraviolet light, such as would normally be encountered in
artificial lighting of refrigerated foodstuff display counters, is tested in the following manner. Samples (D and E) of plain and UV-blocker overprinted active indicator composition are prepared in the manner of Example I with the exception of utilizing as the active substituted diacetylenic monomer component a co-crystallized 2:1 mixture of 2,4-hexadiyn-1,6-bis(ethylurea) and 2,4-hexadiyn-1,6-bis(propylurea). A comparative sample (F) according to the prior art is prepared by laminating a commercial UV-blocker film over a portion of sample (D) plain active indicator composition web material.

The prepared samples are exposed to about 2800 lux under a fluorescent light fixture in a constant ambient of about 4°C to substantially simulate storage in a commercial food market display case. As in Example I, regular measurements are made of active indicator composition color density and the relative color density change data are plotted to provide the results shown in FIG. 6. The substantially regular increase in UV-initiated color density in plain sample (D) is represented in the data of trace 63 and is seen to reach a maximum during the 9 day test period.

The limited increase in color density of the prior art sample during the same period in overlay-protected sample (F) is shown in the data of trace 65, while trace 67 data from sample (E) shows the lesser rate of UV-initiated color increase achieved by the greater efficacy of the present invention arrangement.

Other TTI system label devices are prepared according to the present invention utilizing various monomer components described in the above-noted patent specifications to achieve a range of time-temperature integral endpoints representative of numerous foodstuff and medicament shelf lives. In each instance, in addition to the readily calculable savings in reduced materials waste, the devices responded with improved efficacy as compared with prior art products.

The UV-blocker ink composition described in Example I is but one example of another aspect of the invention which provides transparent printable “ink” compositions containing a UV blocker which are suitable for printing in one or more desired patterns, for example as spot images, onto a continuous strip substrate, overlaid on spots of indicator ink composition, to protect the indicator from the action of UV light.
For example, as described above with reference to Fig. 3, the UV blocker composition can be overprinted in enlarged areas 33 on indicator spots 13 supported on a suitable substrate 11. Desirably, the inventive printable UV blocker composition is sufficiently clear or transparent to permit a functional color change in the underlying ink spot to be clearly perceived. Desirably also the UV blocker composition of the invention yields a film product which is reasonably or completely free of blooming which may obscure or discolor deposited spots of the composition.

Pursuant to this aspect, the invention provides a transparent, printable UV blocker composition comprising effective quantities of each of an organic UV blocking agent, an inorganic UV blocking agent, a film-forming agent and a volatile carrier for the foregoing ingredients. If desired, the film-forming agent may be formulated with the volatile carrier as a lacquer base into which the organic and inorganic UV blockers are mixed. Commercially available lacquer bases may be employed, if desired.

A useful, optional ingredient that may also be included is a transparent dye selected to absorb undesired visible wavelengths that may adversely impact the time-temperature indicator. A further useful optional ingredient is a silicone-based flow agent which may be used to improve wetting of the UV blocker composition on the substrate and indicator composition.

Other flow agents, for example fluorine-based flow agents may be employed for this purpose, if desired.

The organic UV blocking agent can comprise any suitable such agent which is soluble in or can be transparently dispersed in an organic solvent useful as or in the volatile carrier, as will be known to, or will become known to those skilled in the art, in light of this disclosure and the development of the art in the future. If desired, the organic UV blocking agent can comprise multiple components and optionally, these multiple components may be mixed with different phases of the composition, which phases are subsequently mixed together to provide the inventive UV blocker composition. For example, one component may be incorporated in the lacquer base, if separately formulated, and another component may be mixed into the lacquer along with the inorganic UV blocker, if desired.
Some suitable organic UV blockers, or filters for use in useful embodiments of the
invention include, for example, 2-2' dihydroxy-4-methoxybenzophenone, triazine derivatives,
hydroxyphenyltriazine compounds, benzotriazole compounds, amides containing a vinyl group,
cinamic acid derivatives, sulfonated benzimidazoles, Fischer base derivatives, diphenylmalonic
acid dinitriles, oxalyl amides, camphor derivatives, diphenyl acrylates, para-aminobenzoic acid
(PABA) and derivatives thereof, salicylates, benzophenones and other organic UV blockers
known to or that become known to the art, for example as disclosed in Luther U.S. Patent
6,746,666, the entire disclosure of which is hereby incorporated herein by this specific reference
thereof.

Some suitable inorganic UV blockers that can be employed in the compositions of the
invention are insoluble in the volatile carrier and include zinc oxide, titanium dioxide, mixtures
of zinc oxide and titanium dioxide, other effective metal oxides and equivalents of or
alternatives to zinc oxide or titanium dioxide as is known, or becomes known to those skilled in
the art. Desirably, the zinc, titanium or other inorganic metal oxide is finely divided and capable
of forming a transparent suspension in the volatile carrier, for which purpose the zinc or titanium
or other inorganic metal oxide may be coated to render it hydrophobic, as is known in the art.
To this end the inorganic metal oxide may be “micronized” with substantially all its particles
having a particle size of less than about 1 micron, for example about 200 nanometers.

Any suitable film-forming polymer can be employed, including, not only nitrocellulose
but also alternatives to nitrocellulose, for example vinyl and acrylic co- and terpolymers, such as
copolymers of vinyl acetate with crotonic acid and vinyl tert-butylbenzoate; copolymers of
acrylic acid and ethyl acrylate with N-tert-butylacylamide; copolymers of N-octylacylamide,
methyl methacrylate, hydroxypropyl methacrylate acrylactic acid and tert-butylaminoethyl
methacrylate copolymer; or a terpolymer of acrylic acid, ethyl acrylate and tert-butyl acrylate.

The volatile carrier can comprise a volatile organic solvent system such as is employed
in Example 1 or, as alternatives to the solvent system described therein, any suitable solvent may
be employed as the volatile carrier, as will be apparent to those skilled in the art. Suitable
solvents systems include individual solvents or mixtures selected from the group consisting of
heptane, acetate, amyl acetate, butyl acetate, butyl cellosolve acetate, cellosolve acetate, methul
cellosolve acetate, acetone, methyl ethyl ketone, methyl isobutyl ketone, butyl cellosolve, cellosolve, methyl cellosolve, ethyl alcohol, isopropyl alcohol, butyl alcohol, toluene, and xylene. Other suitable solvent systems will be apparent to those skilled in the art.

Desirably, the transparent dye is selected to absorb near-ultraviolet blue or blue-green wavelengths for which purpose a yellow or orange dye may be employed. Desirably the dye is soluble in the volatile carrier and suitable dyes, including for example Orosol yellow dyes are known to those skilled in the art. Preferably, such a yellow or orange dye, if employed is used at low saturation, for example at an intensity of not more than 10%, desirably not more than 5%, however, situations of 2% or less may be employed, if desired.

If desired, the UV blocking ink composition may include one or more plasticizers to provide film flexibility and to reduce film shrinkage that may occur on drying. Suitable plasticizers include isopropyl alcohol fatty acid esters, C8 alcohol fatty acid esters, organic succinates, phthalates and adipates, and other plasticizers as known to those skilled in the art.

The various ingredients of the UV blocker compositions can be employed in relative amounts or proportions effective for their intended purposes as may be determined without undue experimentation. Some useful ranges of percentages by weight based upon the total weight of the UV blocker composition include:

a range of from about 0.5 to about 35 percent, or of from about 3 to about 20 percent, or desirably from about 7 to about 15 percent of a combined proportion of the UV blocking agents;

from about 2 to about 40 percent, or of from about 10 to about 30 percent, or desirably from about 15 to about 25 percent of a film forming agent; and

from about 20 to about 95 percent, or of from about 40 to about 85 percent, or desirably from about 60 to about 75 percent of a volatile carrier.

If a soluble dye is employed, a range of from about 0.1 to about 10 percent, desirably from about 1 to about 5 percent, for example about 2 to 3 percent may be employed. The flow agent, if employed can be used in conventional proportions for example of from about 0.1 to about 5 percent, e.g. about 1 percent.
Useful ranges of organic UV blocker include from about 1 to about 10 percent, or about 2 to about 5 percent of a non-lacquer component and from about 0 to about 12 percent of an optional component incorporated in the lacquer composition. Total organic UV blocker can range from about 2 to about 15 percent or from about 4 to about 10 percent.

One useful range of the inorganic UV blocker is from about 0.5 to about 8 percent or from about 1.5 to about 5 percent. The proportion of inorganic to organic UV blocker can usefully be from about 1:10 to about 1:1 or from about 1:5 to about 1:3.

Desirably, the UV blocker composition is completely free of any opaque insoluble pigment particles or is sufficiently free of insoluble pigment particles that the useful transparency of the UV blocker film is not impaired.

It will be understood that, many other UV blocker compositions which can be used to fulfill the objectives of the invention will be, or will become, apparent to those skilled in the art, or can be devised without undue experimentation in light of this disclosure.

The includes methods of making and using UV blocker compositions which follow the teaching of Examples 1 and 2 hereinabove but employ the ingredients and/or proportions described in the immediately preceding paragraphs. In particular the invention includes the print-like application of the described UV blocker compositions as protective overlays on time-temperature indicator spots or patches.

The product shelf life monitoring system can be employed in an desired manner for indicating a useful shelf life or other useful purpose and may be employed in an active manner with bar-coded products. To this end, a transparent shelf life monitoring system according to the invention is overlaid on a bar code label or the like so as to render the bar code initially usable. However, the progressive formation of color of the time-temperature indicator component of the monitoring system can ultimately obscure the bar code, signaling the expiration of the product shelf life. Such a use of a shelf life monitoring system is disclosed in U.S. Patent No. 6,5443,925, the entire disclosure of which is incorporated herein by this specific reference thereto.
The term “UV blocker” is used herein to include compounds or compositions which block, absorb, attenuate or otherwise obstruct the passage of ultraviolet light.

It is anticipated that other embodiments and variations of the present invention will become readily apparent to the skilled artisan in the light of the foregoing description and examples, and such embodiments and variations are intended to likewise be included within the scope of the invention as set out in the appended claims.
What is claimed is:

1. A product shelf life monitoring system comprising a substrate surface bearing upon a limited portion of its area an active indicator composition responsive in a visible change under incident thermal and ultraviolet light energy to at least one of which an associated product is susceptible, said system comprising visibly transparent means disposed between said indicator composition and the source of said incident ultraviolet light to intercept and ameliorate the effects of said incident ultraviolet light upon said indicator composition

   characterized in that

   said ultraviolet light intercepting means comprises a layer of visible-transparent, ultraviolet light-absorbent composition closely proximate and at least substantially co-extensive with said indicator composition and situated within said limited area portion of said substrate surface.

2. A system according to claim 1 wherein said associated product is a foodstuff.

3. A system according to claim 1 wherein said associated product is a medicament.

4. A system according to claim 1 wherein said active indicator composition comprises an ink printed upon said substrate and said ultraviolet light absorbent composition comprises an ink overprinted upon said substrate above said indicator composition.

5. A system according to claim 1 wherein said ultraviolet light absorbent composition is overprinted upon said indicator composition.

6. A system according to claim 1 wherein said active indicator composition comprises a substituted diacetylenic monomer comprising at least two conjugated acetylene groups.

7. A system according to claim 6 wherein said active indicator composition monomer is selected from the group consisting of symmetrically and asymmetrically substituted mono- and bis-urethane and urea derivatives.
8. A system according to claim 5 wherein said ultraviolet light absorbent composition comprises an active component selected from the group consisting of benzophenones and benzotriazoles others.

9. A product shelf life monitoring system according to claim 1 characterized in that said substrate surface bears upon a portion of its area situated outside said limited area portion a secondary active indicator composition responsive in a visible change under incident ultraviolet light energy to which an associated product is susceptible.

10. A product shelf life monitoring system according to claim 9 wherein said secondary active indicator composition comprises a substituted diacetylenic monomer comprising at least two conjugated acetylene groups.

11. A transparent, printable UV blocker composition comprising effective quantities of each of an organic UV blocking agent, an inorganic UV blocking agent, a film-forming agent and a volatile carrier for the foregoing ingredients.

12. A UV blocker composition according to claim 11 comprising a transparent dye, optionally being a yellow or an orange dye.

13. A UV blocker composition according to claim 11 comprising a flow agent, optionally, a silicone-based flow agent.

14. A method of protecting a time-temperature indicator area from ultraviolet light comprising applying a UV blocker composition according to claim 11 to the time-temperature indicator area and permitting the UV blocker composition to form a protective film over the time temperature area.
1. A product shelf life monitoring system comprising a substrate surface bearing upon a limited portion of its area an active indicator composition responsive with a visible change to incident thermal and ultraviolet light energy to at least one of which an associated product is susceptible, said system comprising visibly transparent means disposed between said indicator composition and the source of said incident ultraviolet light to intercept and ameliorate the effects of said incident ultraviolet light upon said indicator composition characterized in that said ultraviolet light intercepting means comprises a layer of visible-transparent, ultraviolet light-absorbent composition situated only within said limited area portion of said substrate surface closely proximate to and substantially co-extensive with said indicator composition or having only a limited additional extent beyond the area of the indicator composition sufficient to minimize lateral exposure to vagrant radiation.

2. A system according to claim 1 characterized in that the major extent of the substrate surface is devoid of said ultraviolet light intercepting means.

3. A system according to claim 2 characterized in that said associated product is a foodstuff, a medicament, a vaccine or a medicine.

4. A system according to claim 2 characterized in that said active indicator composition comprises an ink printed upon said substrate and said ultraviolet light absorbent composition comprises an ink overprinted upon said substrate above said indicator composition.

5. A system according to claim 1, 2, 3 or 4 characterized in that said ultraviolet light absorbent composition is overprinted upon said indicator composition.

6. A system according to claim 1, 2, 3 or 4 characterized in that said active indicator composition comprises a substituted diacylenic monomer comprising at least two conjugated acetylene groups.
7. A system according to claim 6 characterized in that said active indicator composition monomer is selected from the group consisting of symmetrically and asymmetrically substituted mono- and bis-urethane and urea derivatives.

8. A system according to claim 5 characterized in that said ultraviolet light absorbent composition comprises an active component selected from the group consisting of benzophenones and benzotriazoles others.

9. A product shelf life monitoring system according to claim 1, 2, 3 or 4 characterized in that said substrate surface bears upon a portion of its area situated outside said limited area portion a secondary active indicator composition responsive in a visible change under incident ultraviolet light energy to which an associated product is susceptible.

10. A product shelf life monitoring system according to claim 9 characterized in that said secondary active indicator composition comprises a substituted diacetylenic monomer comprising at least two conjugated acetylene groups.

11. A product shelf life monitoring system according to claim 1, 2, 3 or 4 characterized in that the layer of said ultraviolet light-absorbent composition is substantially in registration with the indicator composition.

12. A transparent, printable UV blocker composition characterized by comprising effective quantities of each of an organic UV blocking agent, an inorganic UV blocking agent, a film-forming agent and a volatile carrier for the foregoing ingredients.

13. A UV blocker composition according to claim 12 characterized by comprising a transparent dye, optionally being a yellow or an orange dye.

14. A UV blocker composition according to claim 12 or 13 characterized by comprising a flow agent, optionally, a silicone-based flow agent.

15. A method of protecting a time-temperature indicator area of a shelf-life monitoring system from ultraviolet light characterized by comprising applying a UV blocker composition according to claim 11 essentially only to the time-temperature indicator area and
permitting the UV blocker composition to form a protective film over the time temperature area.

16. A method according to claim 15 characterized by comprising applying printed indicia to portions of the shelf life monitoring system outside the indicator area employing UV-cured printing inks and applying UV to cure the inks.
STATEMENT UNDER ARTICLE 19(i)

US2004/0253733, as noted in the search report (category “E”) was published after applicant’s filing date and is therefore not available as a reference.

Applicant’s invention as now defined in amended claim 1 is clearly distinguished from Preziosi et al. US 4,789,637. Applicant claims in amended claim 1 use in shelf life monitoring system of an economical limited area of UV blocker (“ultraviolet light intercepting means” in claim 1) having an extent confined essentially to that of the indicator composition or having only a limited additional extent beyond the area of the indicator composition. Although production changes may be needed to manufacture such indicators in continuous web form, e.g. as labels, the high cost of a continuous web of UV-blocker material is avoided. Employment of the word “only” in claim 1 makes clear that the UV blocker material does not extend outside the defined area.

The known use of an overlying film of UV blocker is acknowledged in applicant’s specification e.g. at page 2, lines 12-15.

Preziosi et al. discloses complexing acetylenic compounds with HCl or HBr, and activating the complexes with ultraviolet radiation to effect 1,4 polymerization yielding a product which is color-sensitive to moisture. For example, halo-urea derivatives of acetylenic di-ureas may change to orange, red or yellow after UV treatment then change to blue when contacted with water making them potentially useful in moisture indicators. The search report does not point to any disclosure in Preziosi of use of a UV-blocker layer to protect a shelf-life indicator composition from the effects of ultraviolet radiation yet alone the specific economical limited area configuration of UV blocker defined in Claim 1.

Frankenbach et al. US 6,495,058 relates to wrinkle control compositions intended for spraying on fabrics. No relevance is seen to applicant’s claim for a shelf-life monitoring system employing an active indicator composition and a limited area UV-blocker layer to protect same.

The method of UV protection of claim 14 and the UV blocker composition of claim 11 are similarly distinguished from the cited art while the various dependent claims are further distinguished for the features they recite.
FIG. 5

FIG. 6
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

**IPC(7)**: G01N 33/48  
**US CL**: 422/58  
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.**: 422/58, 61, 56; 436/1; 164, 166, 169

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) none

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category *</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X.E</td>
<td>US 2004/0253733 A (PRUSIK et al) 16 December 2004, see claims 1-10</td>
<td>1-14</td>
</tr>
<tr>
<td>X</td>
<td>US 4,789,637 A (PREZIOSI et al) 06 December 1988, see the entire document</td>
<td>1-7 and 9-14</td>
</tr>
<tr>
<td>X</td>
<td>US 6,649,058 (FRANKENBACH et al) 17 December 2002, see the entire document</td>
<td>1-5 and 5-14</td>
</tr>
</tbody>
</table>

* Further documents are listed in the continuation of Box C.  

See patent family annex.

Date of the actual completion of the international search: **25 July 2005 (25.07.2005)**

Date of mailing of the international search report: **11 Aug 2005**

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